Iron Carbides and Sodium-Sulphur Promotion in Fischer-Tropsch Synthesis Catalysts

Pasi Petteri Paalanen

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Iron Carbides and Sodium-Sulphur Promotion in Fischer-Tropsch Synthesis Catalysts

Ijzercarbiden en Natrium-Zwavel Promotie in Fischer-
Tropsch Synthese Katalysatoren

(met een samenvatting in het Nederlands)

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An
early worm
is caught by
the bird

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Chapter 1

A General Introduction

Heterogeneous catalysis is an industrially important field enabling a vast range of chemical reactions which otherwise would not easily take place. These catalysis reactions are utilized to produce most materials in a modern society. Many of the production processes begin with crude oil derived hydrocarbons as the feedstock. As the crude oil resources will deplete in the foreseeable future, other hydrocarbon sources are needed. Fischer-Tropsch Synthesis (FTS) reaction catalytically converts CO and H₂ input gases into hydrocarbons over d-block transition metals, thus offering a possible future alternative source of hydrocarbons. Despite the FTS reaction already first being observed at the beginning of the 20th century, plenty remains to be learned on this intriguing reaction. This PhD Dissertation concentrates on *the effect of chemical promotion Na-S on the Fe carbides in Fe-based catalysis of the FTS reaction*. The Fe carbides are the catalytically active phases for the FTS reaction in the Fe-based catalyst materials. This Chapter introduces general concepts of the industrial Fischer-Tropsch Process (FTP) in which the FTS reaction is employed as part of the overall process. The aim is to relate and explain the FTS reaction's importance in a broader context. With the overall FTP, an input carbon containing feedstock is converted into refined hydrocarbon products. The history, main process steps, environmental viability and some aspects for further development of the FTP are highlighted. Finally, the scope and outline of this PhD Dissertation are presented.

This PhD chapter is based on: *Pasi P. Paalanen and Bert M. Weckhuysen, "Fischer-Tropsch Synthesis over Iron-based Catalysts: A Review", ChemCatChem, accepted.*

1.1 HETEROGENEOUS CATALYSIS

A catalyst can be defined as a chemical compound that can aid and accelerate thermodynamically feasible chemical reactions to take place. The essence of catalysis phenomenon is to lower the required activation energy for a chemical reaction, allowing it to proceed more easily than would be the case without the catalyst material (**Figure 1.1**).¹

The major branches of the broad field of catalysis can be divided into two: heterogeneous and homogeneous catalysis. In heterogeneous catalysis the employed catalyst materials and reactants exist in distinctly different phases, e.g. as in the case of gas phase reactants being catalyzed by a solid catalyst material. With homogeneous catalysis, the catalysts do their catalyzing work in the same phase as the reactants, e.g. with both the catalyst material and the reactants indistinctively residing in a liquid phase. Essentially, for the existence of Life on Earth, enzymes perform the necessary homogenous catalysis tasks in all of the living beings.¹

A vast majority of the modern industrial processes rely on heterogeneous catalysis.

Figure 1.1

A schematic representation on the difference on the activation energies and reaction steps between uncatalysed (E , red) and catalyzed (E_c , green) chemical reactions. *With catalyzed chemical reactions:* reactants for the chemical process (A) adsorb on the catalyst (B). The catalyst material lowers the activation energy for the chemical reaction between the adsorbed reactants so that $E_c < E$ and the chemical reaction can proceed readily to form adsorbed reaction products (C) on the catalyst surface. The adsorbed products further desorb from the catalyst to give the chemical products of the overall reaction (D). Figure adapted from reference [1].

To name few examples: NH_3 synthesis with Fe-based catalyst materials via the Haber-Bosch Process is the backbone in producing fertilizers for agriculture. Each modern car nowadays is equipped with catalyzators removing pollutants, such as NO_x and CO, from the engine exhaust fumes. Crude oil refineries catalytically process the input crude into ready-to-use transportation fuels for the cars and airplanes, as well as to many other petrochemical products. Furthermore, chemical building blocks used as input materials for further chemical production processes, such as preparing plastics, are derived from crude oil via catalytic refinery processes.¹

The general requirements and design aspects for an industrially useful heterogeneous catalyst material can be listed, as after Le Page et al.:²

Activity - High activity in converting the reactants to reaction products, or the catalyst is able to enable the desired chemical reaction at lower reaction temperatures than without a catalyst.

Selectivity - High selectivity for the reactants to be converted only, or as much as possible, to the desired reaction products.

Stability - The catalyst should change very little during the reaction it is catalyzing. In practice, the catalyst materials degrade in time under the reaction conditions, eventually losing their catalytic capabilities.

Morphology - The external morphological features, such as the shape and size of the catalyst particle, have to suit the reaction and reactor in which it is used. Various shapes of catalyst materials as e.g. rings, beads or spherical powders, are employed in industry for matching the requirements for the reaction and the catalysis reactors they are used in.

Mechanical strength - As is especially true for the heterogeneous catalyst materials, they should maintain their shape and form without degradation in the reaction they are employed in.

Thermal characteristics - Depending on the requirements of the catalyzed reaction, the catalysts thermal properties should match the reaction. For example, for ensuring a uniform catalyst reactor bed temperature in the reactor.

Regenerability - The catalyst materials, in practice, are not indefinitely stable and eventually deactivate. The catalysts should be regenerable to their (near-)original state, making the catalyst replacement as infrequent as possible.

Reproducibility - The preparation of the catalyst materials should be reproducible from preparation batch to batch. The catalyst materials should also be reproducibly scalable from lab to the industrial scale.

Originality - For patenting and making the development of the catalyst materials economically sensible: the catalyst materials should be sufficiently original or

improved from the previously devised catalyst materials.

Cost – The preparation of the catalyst material should be feasible on an industrial scale. This in order of having an economically competitive overall industrial process utilizing the catalyst.

Naturally, developing such catalyst materials satisfying all the required properties is not a very straightforward process. Fundamental research on understanding and further improving catalyst materials is still needed in many of the areas in which heterogeneous catalysis is applied.

One such area is the catalysis of Fischer-Tropsch Synthesis (FTS) reaction, a reaction that converts catalytically the input $\text{H}_2\text{:CO}$ gas mixture (i.e. syngas) into a mixture of hydrocarbons. The FTS reaction possibly offers in its part one of the future solutions for replacing the crude oil from Earth's crust as the hydrocarbon source for industrial processes. The first observations on catalytic conversion of CO and H_2 reactants to hydrocarbons over d-block transition metals date back to the early 20th century. Despite of all the time that has passed and the dedicated research that has been done since the first observations, a lot remains to be learned on the complex topic of the heterogeneously catalyzed FTS reaction.

Thus, to begin with, we shall embark on a short introduction on the general industrial application of the FTS reaction, from both historic and contemporary perspectives. In its industrial application, the FTS reaction is one part of the complete Fischer-Tropsch Process (FTP) where an input carbon containing feedstock is step-wise converted into refined hydrocarbon products. The main aim of the section is to give an overview on how the catalyzed FTS reaction as part of the overall industrial FTP relates to the wider society, including discussion on its environmental and economic realities.

At the end of this Chapter, the scope and outline for the following research chapters in this PhD Dissertation are laid out.

1.2 FISCHER-TROPSCH SYNTHESIS IN INDUSTRY

1.2.1 A Short History of the Industrial Application

One of the earliest observations on the catalyzed formation of liquid hydrocarbons over d-block transition metals under a flow of $\text{H}_2\text{:CO}$ gas mixture are by Mittasch and Schneider in their work conducted for Badische Anilin & Soda Fabrik (BASF) around 1916.^{3,4} In their patent the authors describe conversion of >5 bar gas mixture of $\text{H}_2\text{:CO}$ to various saturated and unsaturated hydrocarbons and their oxygenated derivatives. As catalysts, various d-block transition metals (e.g. Cr, Co, Mn, Mo and Os) or their

compounds were used. It was also noted, that impregnation of their transition metal catalyst materials with a basic compound in the form of an alkali metal hydroxide or carbonate (e.g. KOH or K_2CO_3) was advantageous for the hydrocarbon conversion.³

In the beginning of the 1920's, further research on the conversion of a $H_2:CO$ gas mixture to hydrocarbons over alkalized Fe, and Co and Ni transition metals was performed by Fischer and Tropsch while working at the Kaiser Wilhelm Institut für Kohlenforschung at Mülheim an der Ruhr.⁴⁻⁶ Despite the inability of Fischer and Tropsch to reproduce some of the claims in the earlier work by Mittasch and Schneider,⁶ the work by Fischer and Tropsch led to the basis on the industrial application of the transition metal catalyzed $H_2:CO$ conversion into hydrocarbons. Thus, the reaction became known as the Fischer-Tropsch Synthesis (FTS).^{4,5,7}

The first application of the FTS reaction as a part of an industrial process took place in Germany, with a demonstration plant in Mülheim commissioned in 1932. Further facilities were constructed by the beginning of the World War II with a total of nine Fischer-Tropsch facilities operational by the year 1939. The incentive for employing the FTS reaction as a part of an industrial process came for the wartime Germany from a necessity. With limited access to a crude oil supply during the War, large available German coal reserves could be transformed into liquid hydrocarbon fuels in part with utilizing the FTS reaction on an industrial scale. At 1944, 7 % of fuels consumed in Germany were produced with using the FTS reaction in the process. Majority of the coal-to-liquids conversion was done via coal hydrogenation, i.e. with the Bergius Process, accounting for 40 % of the consumed fuels.⁸

After the World War II, the Allies acquired the German FTS reaction technology. Consequently, the researchers at the United States Bureau of Mines conducted a significant amount of seminal research in the post-war years on the FTS reaction.^{5,9}

In 1950 in South Africa, Suid Afrikaanse Steenkool en Olie (Sasol) company was formed with the aim of converting the locally available coal into hydrocarbons, in a bid to decrease South Africa's dependency on imported crude oil. The Sasol 1 Fischer-Tropsch facility was commissioned in 1955 using American and German technology. Initial operational issues ensued with the American (Kellogg) technology and Sasol established its own research department in 1957 to solve the issues.⁸ A significant amount of FTS knowledge available in the open literature has come from the Sasol research ever since.

However, mostly due to the availability of cheap crude oil, interest in utilizing the FTS reaction industrially somewhat waned in the rest of the World between the 1950's post-war period up to 1970's oil crisis. Thus, no significant industrial investment took place beyond the Sasol 1 Fischer-Tropsch facility within the period.^{5,9,10}

The first large scale, modern industrial utilization of the FTS reaction in an industrial

process took place in South Africa by Sasol. Incentive for the renewed industrial application of the FTS reaction in South Africa came from both the supply scarcity of crude oil due to the global 1970's oil crisis, and the international sanctions on South Africa due to Apartheid policies up to until around 1993.^{5,9,11-13} The Sasol 2 and Sasol 3 facilities (nowadays collectively called Sasol Synfuels) were commissioned in 1980-1982 to accompany the smaller Sasol 1 facility from 1955.^{5,9,11} Also, the Sasol 1 has gone through several upgrades from the 1970's up to the latest expansion project between 2009-2015, which is expected to double the facility's production capacity.^{8,14}

Besides Sasol and conversion of coal to hydrocarbons, the South African government initiated the Moss gas project in 1984 in order to search for off-shore natural gas. By 1992, a facility converting natural gas into hydrocarbons employing the FTS reaction was commissioned.⁸ This facility is now operated by the Petroleum Oil and Gas Corporation of South Africa (PetroSA), after a merger of the South African state owned petroleum assets in 2002.⁸

Outside South Africa, the initiative for development of industrial Fischer-Tropsch facilities came from increased discoveries of natural gas reserves.⁸ In the cases where natural gas reserves are far from the hydrocarbon markets, liquefaction of the gas to a more energy dense form e.g. with the use of the FTS reaction in the process, can make the transportation of the produced, dense hydrocarbon products to the market region economically viable.^{5,8} Thus, the fundamental driving force for the industrial FTS reaction development utilizing natural gas sites is the price difference between the process feed natural gas in comparison to the FTS produced and further refined hydrocarbons.⁵

Following the discoveries and utilization of natural gas fields, the Dutch Royal Shell commissioned Fischer-Tropsch facilities in both Bintulu (Malaysia) in 1993 and the Shell Pearl in Ras Laffan (Qatar) in 2011. Both facilities convert natural gas into hydrocarbons with employing the FTS reaction in the process. Explosion of the air separation unit at Bintulu facility at the end of 1997 caused the facility to shut down until 2000.⁸ The explosion was due to fine particles from forest fires accumulating into an air separation unit in the facility.¹⁵ Sasol and Qatar Petroleum (QP) commissioned the Oryx natural gas conversion facility using the FTS reaction, in Ras Laffan (Qatar) in 2006. The Oryx facility initially encountered issues with the fragmentation of the used Co-based FTS catalyst material, which caused clogging downstream from the FTS reactor. By 2008, the Oryx facility's production was ramped up $\approx 70\%$ of the design capacity.⁸

The latest industrial scale facility utilizing the FTS reaction in the process to convert natural gas has been commissioned by Chevron and Nigerian National Petroleum Corporation (NNPC) in Escravos (Nigeria) in 2014.⁵ Though, at least up to 2017, the

Table 1.1

Current operational industrial scale facilities utilizing the Fischer-Tropsch Synthesis (FTS) reaction in the process for producing hydrocarbons. Details are from references:[5][8].

Operator	Site	Feedstock	Capacity ^{a)} (bbl/day)	Commission Year	Initial investment incentive
Sasol	Sasol 1 (Sasolburg, South Africa)	Initially coal, currently natural gas	7 000 – 5 500	1955 ^{b)}	- To decrease dependency on crude oil imports
Sasol	Sasol Synfuels (formerly Sasol 2 & 3) (Secunda, South Africa)	Coal, later also natural gas	120 000	1980-1982	- 1970's oil crisis - Sanctions against Apartheid
PetroSA	- (formerly Moss gas) (Mossel Bay, South Africa)	Natural gas	22 500	1992	
Shell	- (Bintulu, Malaysia)	Natural gas	14 700	1993	
Sasol & QP	Oryx (Ras Laffan, Qatar)	Natural gas	(34 000) ^{c)}	2006	- Conversion of natural gas to higher value products
Shell	Pearl (Ras Laffan, Qatar)	Natural gas	140 000	2011	
Chevron & NNPC	- (Escravos, Nigeria)	Natural gas	(34 000) ^{d)}	2014	

a) Estimated Fischer-Tropsch Process (FTP) design capacity at 2013 in crude oil equivalents.

b) Since the initial commissioning in 1955, significant upgrades have taken place.^{8,14}

c) At least up to 2008, the production was constrained to 24 000 bbl/day.

d) At least up to 2017, the site has experienced production problems.^{16,17}

Chevron-NNPC Escravos Fischer-Tropsch facility has experienced production issues and the plant is under continued optimization of the processes.^{16,17}

To summarize the discussion so far, the driving force for industrial scale application of the FTS reaction in the process for producing hydrocarbon products has mainly either been:

- i) to decrease dependency on the availability of the hydrocarbons from crude oil (Germany 1930-1945, South Africa 1955-1993), or
- ii) economic incentive in valorizing natural gas to higher valued, more energy dense, liquid hydrocarbons (chemical companies from around 1990's onwards).

The currently operational industrial scale Fischer-Tropsch facilities, their initial investment incentive and FTP design capacities at 2013 are summarized in **Table 1.1**.

From the 2010's onwards, new directions for the industrial utilization of the FTS reaction are emerging as current companies (e.g. Velocys, formerly Oxford Catalysts, CompactGTL, Greyrock Energy) pursuing "scaling down" of the Fischer-Tropsch facilities mature.⁵ Small-scale Fischer-Tropsch facilities may be better suited in utilizing carbon from biomass and/or municipal waste, as the FTS reaction feedstock. The first commercial small-scale FTS facility in the United States for converting municipal waste into liquid hydrocarbons via the FTS reaction is expected to be commissioned within 2020.¹⁸ The new facility employs cost effective FTS technology developed by BP and Johnson Matthey (JM). Also, stranded and small natural gas sources e.g. on off-shore oil platforms, where natural gas is normally flared, may be utilized towards hydrocarbon production with small-scale Fischer-Tropsch facilities in the future. A specific future opportunity for small-scale Fischer-Tropsch facilities could be to address the ever-growing problem with recycling municipal plastic waste,¹⁹⁻²¹ via the $H_2:CO$ gas mixture,^{21,22} into hydrocarbons usable in industrial processes. Significant benefits for the small-scale Fischer-Tropsch facilities are the decreased capital investment, thus decreased risk in investment, and the ability to adapt to the local availability of the carbon feedstock.^{5,23}

1.2.2 From Feedstock to Hydrocarbons in an Industrial Process

In the previous section, the commissioning of several Fischer-Tropsch facilities was discussed. However, by no means is the FTS reaction the only catalytic process taking place in these manufacturing complexes, when the raw feedstock conversion into hydrocarbon products takes place.

The complete Fischer-Tropsch Process (FTP) utilizing the FTS reaction as one of the chemical process steps, from the input feedstock into refined chemical products, can be simplified to general steps of (**Figure 1.2**):⁸

- i) **Feedstock-to-Syngas** - conversion of carbon containing feedstock into a mixture of $H_2:CO$ (i.e. to synthesis gas or syngas),
- ii) **Syngas-to-Syncrude** - conversion of the produced $H_2:CO$ mixture into a mixture of hydrocarbons and hydrocarbon oxygenate derivatives (i.e. to synthetic crude or syncrude) using the catalyzed FTS reaction,
- iii) **Syncrude-to-Products** – processing, separating and upgrading (i.e. refining) the desired hydrocarbons or oxygenates from the syncrude depending on their desired use (i.e. transportation fuels or feedstock for chemical industry).

Figure 1.2

The overall Fischer-Tropsch Process (FTP) for converting carbon containing feedstocks into various product hydrocarbons utilizing the Fischer-Tropsch Synthesis (FTS) reaction in the process.

The overall FTP is similar to crude oil refining with the exception of the syncrude being “made up” from a carbon containing feedstock via syngas with the FTS reaction, instead of using crude oil from Earth’s crust. In the following sections, primary contributions from each process step to the total industrial FTP are briefly considered in order to highlight some of their important aspects. The fundamentals of the FTS reaction catalysis will be discussed more in depth in the later research chapters.

Feedstock-to-Syngas. The overall FTP, from the input feedstock to refined hydrocarbon products, can be named after the feedstock: Biomass-to-Liquids (BTL), Coal-to-Liquids (CTL), Gas-to-Liquids (GTL) and Waste-to-Liquids (WTL), or collectively Anything-to-Liquids (XTL). Syngas can be produced from a solid, carbon containing material (BTL, CTL, WTL) by heating the feedstock material under O_2 and H_2O without burning the material (i.e. gasification) or via reforming (e.g. with Steam Methane Reforming, SMR) natural gas as in the case of GTL.⁵

The CO_2 footprint (i.e. the measure of greenhouse gas emissions in CO_2 equivalents) of the total FTP is in part depended on the syngas production and the type of the used feedstock.⁵ The FTS reaction can be idealized as (**Reaction 1.1**),

where the hydrocarbons are polymerized as $-(CH_2)-$ units and O atom from CO is removed as H_2O . This ideal synthesis consumes input elements in ratio of 4:1 H:C (i.e. in molecular ratio 2:1 $H_2:CO$).

In **Table 1.2**, the nominal and effective H:C ratios and CO_2 footprints are given for the different FTP feedstocks. The effective H:C ratio is the actual ratio of elemental H:C

Table 1.2

Estimated CO₂ footprint for the total Fischer-Tropsch Process (FTP) as depending only on the process input feedstock. The table is modified from reference [5].

Feedstock	Elemental Analysis (wt-%)					H:C (elemental ratio)		CO ₂ footprint due to feed ^{a)} (CO ₂ :Hydrocarbons kg:kg)
	C	H	N	S	O	Nominal	Effective	
Natural gas ^{b)}	74.9	25.1	0	<0.1	0	4.00	4.00	0.00
Waste ^{c)}	53.3	8.2	4.9	0.1	33.5	1.83	0.65	3.96
Coal ^{d)}	75.7	5.0	1.2	1.0	17.1	0.80	0.40	4.80
Biomass ^{e)}	50.1	6.1	0.9	0.1	42.8	1.45	0.12	5.75

a) Based in ideal Fischer-Tropsch Synthesis (FTS) reaction i.e. $\text{CO} + 2 \text{H}_2 \rightarrow -(\text{CH}_2)- + \text{H}_2\text{O}$. CO₂ footprint estimated from carbon efficiency using CO₂ equivalent.

b) Dry natural gas with all the hydrocarbons removed.

c) Municipal waste.

d) Mean values over various coal types.

e) Switchgrass.

available for hydrocarbon formation in the FTS reaction after all of the heteroatoms (N, O, S) in the feedstock are hydrogenated and subsequently removed during a syngas cleaning step.^{5,24} As can be seen from the **Table 1.2**, the CO₂ footprints are in the order GTL < WTL < CTL < BTL. The increase in the CO₂ footprint due to input feedstock fundamentally comes from the necessity of adding more H to the system for satisfying the required FTS reaction stoichiometry. That is, from satisfying the effective elemental H:C ratio of ≈ 4 , for the hydrocarbon synthesis via the FTS reaction.^{5,24}

To further highlight the use of different raw carbon feedstocks, only GTL can actually be a net producer of H₂O as per 1 mole of CO consumed 1 mole of H₂O is produced in the FTS reaction without need for extra added H.⁵ BTL, CTL and WTL will require input of H atoms in a one way or another, e.g. from commonly used Water-gas Shift (WGS) reaction converting $\text{H}_2\text{O} + \text{CO} \rightarrow \text{H}_2 + \text{CO}_2$ or possibly from H₂O electrolysis, for satisfying the need for the effective input H:C ratio of ≈ 4 . This in practice means input of fresh water, thus making the non-GTL processes rather water intensive.⁵ For industrial Fischer-Tropsch facilities, the benchmark in total FTP water management is the zero fresh water input Shell Pearl GTL facility. In the facility, the acidic and corrosive water produced in the FTS reactor units is purified and reused for the needs of the facility and even for some irrigation of the plant surroundings.^{5,25}

Although, despite the very simplified and idealized discussion presented here on the different feedstocks for the FTP, the point is: BTL and WTL processes via the FTS reaction are often mentioned as sustainable pathways for hydrocarbon production, but their low effective H:C ratio makes them more demanding feedstocks than GTL for the purpose. To make up the H:C deficiency, the added H will need to come from an

environmentally sustainable process for the BTL and WTL processes to be able to compete against the GTL in environmental viability and in minimal CO₂ footprint. Furthermore, biomass and waste need to be gathered to the Fischer-Tropsch facility in a sufficient quantity implying added transportation costs, decreasing the availability of the feedstocks with added environmental penalty.⁵

Naturally, the Feedstock-to-Syngas step is not the only step affecting the Fischer-Tropsch facility's CO₂ footprint. Although, the step can have an significant impact on the total footprint.^{5,26} Each process step, from feedstock to refined hydrocarbon products should be optimized by the Green Chemistry principles: *avoiding waste, maximizing atom economy, increasing energy efficiency and designing less hazardous chemical syntheses*.⁵ In other words, from each process input CO molecule maximum amount elemental C should end up to the hydrocarbon products with minimum energy used, and waste products formed.

The carbon efficiencies for the total FTP from feedstock into hydrocarbon products are $\approx 75\%$ for GTL,⁵ and $\approx 28\text{--}34\%$ for CTL.^{5,24} For comparison, in crude oil refineries the carbon efficiency is estimated to be about 89% .⁵ The production of purified syngas accounts for around $30\text{--}50\%$ of the capital costs for GTL- and $60\text{--}70\%$ for CTL-based processes.^{8,27} The expensive syngas should be turned into hydrocarbon products as efficiently as possible also from the viewpoint of economic viability of a Fischer-Tropsch facility.

Syngas-to-Syncrude. Within the step, the FTS reaction is used for converting the prepared H₂:CO syngas mixture into syncrude with various hydrocarbons. Two important parameters for the step are i) the used catalyst material and ii) the used reaction conditions. The aim with both is to steer the hydrocarbon synthesis towards the desired products with maximum C efficiency. General requirements for an industrially good FTS reaction catalyst material are:⁵

- i) **Activity towards FTS** – the less of catalyst material is required for converting the input CO to product hydrocarbons, the lower the associated costs are. Alternatively, the catalyst can also be negligibly cheap.
- ii) **Selectivity** – the FTS reaction inherently produces a slate of various hydrocarbons. The narrower the selectivity range towards the desired products is, the better. This potentially allows the whole FTP to be simplified (e.g. less gas looping, less separation and purification processes).
- iii) **Stability** – the longer the catalyst stays active with a stable selectivity towards the desired hydrocarbons, the less of the catalyst material is needed. This, in turn lowers the associated costs. Also, an important point is the *mechanical stability* of catalyst and not just the *catalytic stability*. No active catalyst

Table 1.3

General compositions of industrially produced syncrude compositions for Fischer-Tropsch Synthesis (FTS) reaction types applied in industry. The table is modified from reference [5].

Hydrocarbon Chain Length	Hydrocarbon Type	Syncrude Composition (wt-%) ^{a)}		
		Fe-HTFT	Fe-LTFT	Co-LTFT
C ₁	Methane	12.7	4.3	5.6
C ₂ -C ₄	Olefin	26.8	7.0	3.5
	Paraffin	7.5	2.8	2.8
C ₅ -C ₁₀	Olefin	25.8	7.7	7.8
	Paraffin	4.3	3.3	12.0
C ₁₁ -C ₂₂	Olefin	4.8	5.7	1.1
	Paraffin	0.9	13.5	20.8
>C ₂₂	Olefin	1.6	0.7	0.0
	Paraffin	0.4	49.2	44.6
>C ₅	Aromatic	3.2	0.0	0.0
	Oxygenate	2.3	1.6	0.2
C ₁ -C ₅	Alcohol	4.5	3.9	1.4
(Aqueous products)	Carbonyl	3.9	0.0	0.0
	Carboxylic acid	1.3	0.3	0.2

Olefin = at least one unsaturated C-C bond, paraffin = all C-C bonds are saturated.

a) Excluding CO₂.

material should leach downstream from the catalytic FTS reactor as its pieces will cause issues and also need to be separated from the hydrocarbon products.

Beyond the intrinsic properties of the used catalyst material, the reaction conditions (e.g. reaction temperature, input feed H₂:CO ratio and pressure) affect how the catalyst behaves and which hydrocarbon products are formed. In the currently operational Fischer-Tropsch facilities, either Low-temperature Fischer-Tropsch (200-250°C, LTFT) or High-temperature Fischer-Tropsch (320-375°C, HTFT) have been used with reaction pressures of 15-60 bar.⁵

So far, only Fe and Co have been employed as the active transition metals in the FTS reaction catalysts applied in the industrial Fischer-Tropsch facilities. Fe-based catalyst materials have been used on both LTFT and HTFT, while Co has only been used for LTFT. **Table 1.3** summarizes the generic compositions for the industrially produced syncrude compositions obtained from the used FTS reaction types.⁵ The hydrocarbons formed in the FTS reaction are primarily straight-chained, but also minor amounts of methyl-branched hydrocarbons can be observed. Low amounts of oxygenated hydrocarbons and at high temperature, aromatics, may also form in the FTS reaction.²⁸

The most significant differences from **Table 1.3** are: Fe-HTFT produces ≈53 weight

percent (wt-%) of C₂-C₁₀ olefins (unsaturated hydrocarbons) in comparison to ≈11-15 wt-% from the Fe- or Co-LTFT. Furthermore, Fe-HTFT produced syncrude contains ≈1 wt-% >C₁₁ paraffins (saturated hydrocarbons) against ≈63-65 wt-% obtainable from the Fe- or Co-LTFT reactions. This means, Fe-HTFT is best suited for short-chained olefin-rich syncrude while the low temperature Fe- or Co-LTFT favors long-chained, paraffin-rich syncrude. Ideally, no low economic value CH₄ should be produced and its production should be suppressed. Especially with GTL, the production of CH₄ is merely reversing the first FTP step of Feedstock-to-Syngas with no added value.

In terms of catalyst stabilities, Fe-based FTS catalyst materials can be stable up to ≈4 months for LTFT and ≈1.5 months for HTFT while Co-based LTFT catalysts can be used for up to a couple of years. Co-based catalyst material used at the Shell Bintulu facility, may have lasted with acceptable stability for 8 years without a catalyst regeneration step.⁵ Especially for the Fe-based catalyst materials, the stability aspects have room for further improvement. A major issue for the Fe-based FTS catalysts, especially in the HTFT application, is the fragmentation of the catalyst material into fine powders.^{5,9,27-30}

Syncrude-to-Products. The final step for a Fischer-Tropsch facility and for the total FTP, is to process the syncrude into final hydrocarbon products. This is the step where the most of the value addition to the FTP occurs with only ≈10 % of the facility's capital costs.⁸ Similar chemical processes can be applied to syncrude refining as are applied to crude oil refining e.g. fractional distillation, hydrocracking, hydrotreating and oligomerization. The most significant differences in syncrude in comparison to crude oil are, that syncrude can contain:⁸

- i) multiple product phases: gaseous, organic liquid and aqueous. Organic solids can also be part of the product mixture in case of the LTFT,
- ii) higher concentration of oxygenates, olefins and linear products, and
- iii) metal carboxylates.

Crude oil does not contain significant amounts of olefins and syncrude, unlike crude oil, does not contain N or S impurities. These impurities are removed during the Feedstock-to-Syngas process step, when syngas is purified, as discussed earlier. All of the listed differences essentially make crude oil and syncrude refining facilities incompatible with each other and all of the Fischer-Tropsch facilities listed in **Table 1.1** refine their syncrude on site.⁸

In the past, products from a Fischer-Tropsch facility were steered towards assuring energy security, i.e. by producing fuels in German (1939-1945), and in South African facilities until about 1993. The post-1993 Fischer-Tropsch facilities aim for production

of hydrocarbons with high added value used as is or as chemical building blocks in production other chemical compounds. These developments mainly follow from the global political and economic events.^{5,8,31}

The final item worth attention is that the so-called paraffinic fuels derived from the syncrude produce less tail pipe emissions and burn cleaner than the corresponding crude oil derived fuels. As the S and N heteroatoms are cleaned during the Feedstock-to-Syngas step, the FTP produced fuels burn NO_x and SO_x free and release less particulate matter. In addition, the FTP derived fuels have several other favorable liquid fuel properties.^{26,32-34}

1.2.3 Opportunities and Challenges for the Fischer-Tropsch Process

From the discussed historical developments as well as from the aspects on the industrial application of the FTP, there are some reasons in favor and against continued investment and research on the field, as well as some opportunities for improvement.⁵ Some of them can be summarized as follows:

Arguments in favor:

Strategic – diversification from reliance on crude oil availability either due to political incentive (short-term), or due to eventual depletion and scarcity of the non-renewable crude oil supplies from Earth's crust (long-term).

Economic – valorization of input feedstock to value-added hydrocarbon products of high-quality paraffinic fuels and various hydrocarbons for chemical industries.

Syngas-to-Syncrude directly – the FTS reaction employed in FTP is a direct step from syngas to syncrude while most of the alternative hydrocarbon synthesis routes go via an intermediate chemical species.³⁵ Potentially, direct routes for the Syngas-to-Syncrude process step can be less complex to realize in comparison to going via an intermediate chemical species.

Arguments against:

Complexity – the more parts in the complex FTP need to function together, the more likely there are problems. Several Fischer-Tropsch facilities have experienced start-up and operational problems, the Chevron-NNPC Escravos GTL plant being the latest.^{16,17}

High capital costs – a Fischer-Tropsch facility is a multi-billion US\$ investment. High capital costs make failures expensive and limit the amount of parties that would be interested and capable of developing and utilizing the complete FTP on industrial scale.

Price of crude oil – the economic viability of the total FTP is determined by the

price differences and processing costs between FTP feedstocks (i.e. coal, biomass, natural gas and waste) against crude oil as the feedstock for traditional crude oil refineries. Average break even crude oil price estimates for FTP against crude oil refining per barrel are: for GTL ≈ 30 US\$, for CTL ≈ 65 US\$ and for BTL ≈ 100 US\$ (in 2011 terms).³¹ As crude oil prices may fluctuate wildly, it can be demanding to predict the competitiveness of a Fischer-Tropsch facility.

Opportunities for improvement:

Engineering – simplify and reduce the complexity of the Fischer-Tropsch facilities by streamlining the FTP and instead of re-using old technologies, innovation to create new solutions.

Fundamental research – even after 100 years, the FTS reaction at the heart of the FTP is still relatively poorly understood. This lack of fundamental understanding has led to initial production problems in several Fischer-Tropsch facilities. Continued research in the fundamental understanding of the FTS reaction is still needed.

Syncrude flexibility – via the FTS reaction, the produced syncrude can be steered towards desired hydrocarbons. Ideally, the syncrude synthesis should be as specific hydrocarbon product selective as possible, with minimum amount of CH_4 produced, leaving room for catalyst material development.

Fe catalyst stability – Fe-based catalyst is usable for LTFT $\lesssim 4$ months, and for HTFT ≈ 1.5 months, while Co-based LTFT catalyst can be used for a few years. Thus, especially improving Fe-based catalyst materials' stability is of interest.

Small-scale facilities – can offer a possible solution for high risk/high capital investment problem. Smaller-scale Fischer-Tropsch facilities are far cheaper to construct with less penalty from failure. With less capital investment needed, more parties have the possibility to invest. Thus, the potential for disruptive innovations is increased. Potentially less technical complexity and the possibility for tailoring to the availability and amount of the feedstock and, if needed: scaling-up can be done with small units operating in parallel.

All in all, GTL-based Fischer-Tropsch facilities are at the moment the most competitive primarily due to i) cheap and abundant natural gas as feedstock, and ii) high ratio of effective H:C (**Table 1.2**). The high effective H:C ratio decreases complexity in the syngas production step, decreasing associated costs.²⁷ The future of BTL and WTL might lie in the small-scale facility integrations into the local waste management systems turning “waste into money”. Otherwise, the feedstock quantities might be too small for large industrial scale facilities. CTL remains as the less attractive and more

expensive FTP option. If natural gas for GTL is not available, CTL will probably continue to-be employed when the strategic diversification from crude oil availability is the most important aspect, as its role has been historically.

In terms of fundamental FTS catalyst material research, important aspects for improvement are to: i) improve the overall stability of the Fe-based catalyst materials, ii) increase understanding on how to steer selectivities of the FTS catalyst materials towards desired hydrocarbon products without wasted C atoms, and iii) how to minimize/eliminate the CH₄ from the product slate.

As an alternative to the FTS reaction, the leading competing method for converting syngas to hydrocarbons in future industrial processes are the methanol intermediate based Methanol-to-Hydrocarbons (MTH) reactions.³⁶⁻³⁹ Of these, Methanol-to-Olefins (MTO) facilities are currently being implemented beyond demonstration scale for commercial hydrocarbon production.⁴⁰

On the lab-scale, an interesting new method type for hydrocarbon synthesis using a bifunctional catalyst bed, dubbed as OX-ZEO (Oxide-Zeolite), has recently been demonstrated.^{41,42} The OX-ZEO method can be used to directly synthesize short-chained hydrocarbons from input H₂:CO gas.^{41,42} Whether the FTP with the FTS reaction or something else will be the future choice for hydrocarbon production, remains to be seen.

1.3 SCOPE AND OUTLINE OF THIS PHD DISSERTATION

Within this PhD Dissertation, we aim to further advance the understanding on the FTS reaction when Fe-based catalyst materials are used on its heterogeneous catalysis. More specifically, the main aim of this work is to probe: *the effect of chemical promotion Na-S on the Fe carbides in Fe-based catalysis of the FTS reaction*. Fe carbides are the catalyst's active phases in the Fe-based FTS reaction. The PhD Dissertation is arranged as follows.

Chapter 2 – An overview of the literature on the Fe-based FTS reaction catalysis is presented. The FTS reaction related topics, such as generic Fe-based catalyst compositions, various chemical reaction pathways, and means to alter the product hydrocarbon selectivity, are reviewed. As the specific topics of this Dissertation: i) the application of alkali(Na, K)-S promotion for modifying the FTS reaction hydrocarbon product selectivity is discussed in a reasonably detailed manner within the Chapter. In addition, ii) the nomenclature and identification of various Fe carbides observed in the FTS reaction, a traditionally confusing topic in the Fe-based FTS literature, is reviewed in detail. The Fe carbides relevant for the FTS research field are identified from literature as ϵ -Fe₃C, η -Fe₂C, χ -Fe₅C₂ (the Hägg carbide), θ -Fe₃C (cementite) and θ -Fe₇C₃

(the Eckström-Adcock carbide). Each of these FTS-relevant Fe carbides is assigned with their precise crystal structures and Mössbauer Absorption Spectroscopy (MAS) hyperfine field parameters, in a unified manner, for use in the later Chapters.

Chapter 3 – The Fe carbides identified in **Chapter 2** are prepared on Fe(-Na-S)/ α -Al₂O₃ FTS reaction catalyst materials, with and without Na-S promotion, via CO carburization. Both, ex-situ X-ray Powder Diffractometry (XRPD) with Rietveld Quantitative Phase Analysis (R-QPA) and ex-situ MAS are employed for verifying the unified Fe carbide nomenclature as established in **Chapter 2**. Furthermore, any effects arising from the Na-S promotion on the Fe carbide formation and/or properties are probed. Thermogravimetric Analysis with Mass Spectrometry (TGA-MS) is applied for determining the inactive carbon deposition on the prepared catalyst materials due to the employed CO carburizations. Transmission Electron Microscopy (TEM) is used to follow the catalyst materials' morphology.

Chapter 4 – The Fe(-Na-S)/ α -Al₂O₃ catalyst materials with the preformed Fe carbides prepared in **Chapter 3**, are further tested for their 72 h FTS reaction (340°C, 10 bar, 2:1 H₂:CO) catalysis performance. R-QPA is applied on the ex-situ collected XRPD patterns for quantifying the effects of the Na-S promotion on the Fe carbides *after* their utilization under 10 bar H₂:CO atmosphere in the FTS reaction. The results are compared to the Fe carbide properties from **Chapter 3** *before* the FTS reaction. Especially, with utilizing the R-QPA method, the often overlooked property of the Fe carbide lattice parameters and their changes are followed in detail. The Fe carbides are assigned into subtypes after their defining lattice parameters. Additionally, TEM is used to follow the catalysts' morphology changes after the FTS reaction.

Chapter 5 – Fe(-Na-S)/ α -Al₂O₃ catalysts materials, with and without Na-S promotion, are prepared for study. These catalysts are either reduced with H₂ or applied directly after a catalyst calcining step in 72 h FTS reactions (340°C, 3, 10 and 20 bar, 1:1 H₂:CO). R-QPA is used to quantify the differences in the ex-situ collected XRPD patterns. This quantification is particularly, in the terms of Fe carbide lattice parameters versus the different combinations of i) reaction pressure, ii) Na-S promotion and iii) calcined versus H₂ pre-reduced catalyst materials. The catalysts' FTS reaction performance i.e. activity and selectivity, is further correlated to the Fe carbide subtypes assigned in **Chapter 4**.

Chapter 6 – With the use of combined XRPD/Raman Spectroscopy approach, the Fe(-Na-S)/ α -Al₂O₃ catalyst materials with the preformed Fe carbides from **Chapter 3** are characterized *in-situ* during 72 h FTS reaction (340°C, 10 bar, 2:1 H₂:CO). R-QPA is applied for quantifying the Fe phases from the quasi- and in-situ collected XRPD patterns, while Raman Spectroscopy is simultaneously used to study the accompanying carbon species evolution. The Raman spectra of the formed carbon species are

compared to those measured ex-situ for carbon reference materials in order to identify the formed carbon species during the FTS reaction catalysis.

Chapter 7 – The overall summary of the work performed as well as the main findings in this PhD Dissertation are given. Furthermore, some interesting future research directions are highlighted which may inspire new research directions in Fe-based FTS reaction catalysis.

1.4 REFERENCES

- [1] Le Page, J. F., Cosyns, J., Courty, P., Freund, E., Franck, J. P., Jacquin, Y., Juguin, B., Marcilly, C., Martino, G., Miquel, J., Montarnal, R., Sugier, A. and van Landeghem, H., "General" in *Applied Heterogeneous Catalysis: Design, Manufacture, Use of Solid Catalysts* (ed. Le Page, J. F.), 1–15 (Éditions Technip, Paris, 1987).
- [2] Le Page, J. F., Cosyns, J., Courty, P., Freund, E., Franck, J. P., Jacquin, Y., Juguin, B., Marcilly, C., Martino, G., Miquel, J., Montarnal, R., Sugier, A. and van Landeghem, H., "Developing Industrial Catalysts" in *Applied Heterogeneous Catalysis: Design, Manufacture, Use of Solid Catalysts* (ed. Le Page, J. F.), 67–74 (Éditions Technip, Paris, 1987).
- [3] Mittasch, A. and Schneider, C., "Producing Compounds Containing Carbon and Hydrogen", Patent US1201850A (1916).
- [4] Blekkan, E. A., "Fischer-Tropsch Synthesis Over Cobalt Catalysts: State of the Art and Examples from Natural Gas and Biomass Conversion to Fuels" in *Kokkola Material Week* (Metal Kokkola, Kokkola, 2013).
- [5] Maitlis, P. M. and de Klerk, A., "Greener Fischer-Tropsch Processes for Fuels and Feedstocks", (Wiley-VCH, Weinheim, 2013). DOI:10.1002/9783527656837
- [6] Xiang, Y. and Kruse, N., "Tuning the catalytic CO hydrogenation to straight- and long-chain aldehydes/alcohols and olefins/paraffins", *Nat. Commun.* **7**, 13058–13064 (2016).
- [7] Fischer, F. and Tropsch, H., "Verfahren zur Gewinnung mehrgliedriger Paraffinkohlenwasserstoffe aus Kohlenoxyden und Wasserstoff auf katalytischem Wege", Patent DE484337C (1929).
- [8] de Klerk, A., "Fischer-Tropsch Refining", (Wiley-VCH, Weinheim, 2011). DOI:10.1002/9783527635603
- [9] van de Loosdrecht, J., Botes, G. F., Ciobica, I. M., Ferreira, A. C., Gibson, P., Moodley, D. J., Saib, A. M., Visagie, J. L., Weststrate, C. J. and Niemantsverdriet, J. W., "Fischer-Tropsch Synthesis: Catalysts and Chemistry" in *Comprehensive Inorganic Chemistry II* (eds. Reedijk, J. & Poeppelemeier, K.), 525–557 (Elsevier, Amsterdam, 2013). DOI:10.1016/B978-0-08-097774-4.00729-4
- [10] Mitchell, T., "The Resources of Economics - Making the 1973 Oil Crisis", *J. Cult. Econ.* **3**, 189–204 (2010).
- [11] Murphy, C., "To Cope With Embargoes, S. Africa Converts Coal Into Oil", *Washington Post* (1979). Available at: https://www.washingtonpost.com/archive/politics/1979/04/27/to-cope-with-embargoes-s-africa-converts-coal-into-oil/cd39adab-5084-4e46-a28f-79de2896f75e/?utm_term=.291aeeccf9cef (Accessed: January 2018).
- [12] Levy, P. I., "Sanctions on South Africa: What Did They Do?", *Am. Econ. Rev.* **89**, 415–420 (1999).
- [13] Crawford, N. C., "Oil Sanctions Against Apartheid" in *How Sanctions Work* (eds. Crawford, N. C. & Klotz, A.), 103–126 (Palgrave Macmillan UK, London, 1999). DOI:10.1057/9781403915917
- [14] Chemicals-Technology, "Sasol Wax Expansion Project", (2017). Available at: <http://www.chemicals->

- technology.com/projects/sasol-wax-expansion-project/ (Accessed: January 2018).
- [15] Khelaly, M. El, "Shell restarts damaged Bintulu GTL plant", *Oil & Gas Journal* (2000). Available at: <http://www.ogj.com/articles/2000/06/shell-restarts-damaged-bintulu-gtl-plant.html> (Accessed: January 2018).
 - [16] Chevron, "Nigeria", (2016). Available at: <https://www.chevron.com/worldwide/nigeria> (Accessed: January 2018).
 - [17] Wood-McKenzie, "Escravos GTL - Asset Report", (2017). Available at: <https://www.woodmac.com/reports/upstream-oil-and-gas-escravos-gtl-19005114> (Accessed: January 2018).
 - [18] Green Car Congress, "BP and Johnson Matthey License Fischer-Tropsch Technology to Waste-to-Biofuels Producer Fulcrum BioEnergy for Biojet", *Green Car Congress* (2018). Available at: <https://www.greencarcongress.com/2018/09/20180928-bp.html> (Accessed: April 2019).
 - [19] Schlanger, Z., "The World Will Finally Have to Confront Its Massive Plastic Problem Now that China Won't Handle It", *Quartz* (2018). Available at: <https://qz.com/1310240> (Accessed: June 2018).
 - [20] Doyle, A., "Plastics mines? Europe struggles as pollution piles up", *Reuters* (2018). Available at: <https://uk.reuters.com/article/uk-environment-plastics-insight/plastics-mines-europe-struggles-as-pollution-piles-up-idUKKBN1IC0FS> (Accessed: May 2018).
 - [21] Brems, A., Dewil, R., Baeyens, J. and Zhang, R., "Gasification of plastic waste as waste-to-energy or waste-to-syngas recovery route", *Nat. Sci.* **05**, 695–704 (2013).
 - [22] Hirn, G., "Generating syngas from plastic wastes", (BINE Information Service, Eggenstein-Leopoldshafen Germany, 2016). Available at: <http://www.bine.info/en/topics/renewable-energy-sources/biomass/publikation/synthesegas-aus-kunststoffabfaellen-erzeugen/> (Accessed: May 2018).
 - [23] Williams, M., "Smaller Scale Fischer-Tropsch Enables Biomass-to-Liquids" in *Gasification & Syngas Technologies Council* (Velocys, 2014).
 - [24] de Klerk, A., "Indirect Liquefaction Carbon Efficiency" in *Synthetic Liquids Production and Refining* (eds. de Klerk, A. & King, D.) **1084**, 215–235 (American Chemical Society, Washington, DC, 2011).
 - [25] Shell Global, "Pearl GTL - Overview", (2017). Available at: <https://www.shell.com/about-us/major-projects/pearl-gtl/pearl-gtl-an-overview.html> (Accessed: January 2018).
 - [26] Dry, M. E., "Fischer–Tropsch reactions and the environment", *Appl. Catal. A Gen.* **189**, 185–190 (1999).
 - [27] Dry, M. E., "The Fischer–Tropsch process: 1950–2000", *Catal. Today* **71**, 227–241 (2002).
 - [28] Dry, M. E., "The Fischer-Tropsch Synthesis" in *Catalysis - Science and Technology* (eds. Anderson, J. R. & Boudart, M.) **1**, 159–256 (Springer-Verlag, Berlin, 1981).
 - [29] Shultz, J. F., Hall, W. K., Seligman, B. and Anderson, R. B., "Studies of the Fischer-Tropsch Synthesis. XIV. Hägg Carbide as Catalysts", *J. Am. Chem. Soc.* **77**, 213–221 (1955).
 - [30] Steynberg, A. P., Espinoza, R. L., Jager, B. and Vosloo, A. C., "High temperature Fischer–Tropsch synthesis in commercial practice", *Appl. Catal. A Gen.* **186**, 41–54 (1999).
 - [31] Höök, M., Fantazzini, D., Angelantoni, A. and Snowden, S., "Hydrocarbon liquefaction: viability as a peak oil mitigation strategy", *Philos. Trans. R. Soc. A Math. Phys. Eng. Sci.* **372**, 20120319–20120355 (2013).
 - [32] Shell Global, "Shell GTL Fuel - Product Benefits", (2017). Available at: <https://www.shell.com/business-customers/commercial-fuels/shell-gtl-fuel/product-benefits.html> (Accessed: January 2018).
 - [33] Paraffinic Fuels for Europe (ASFE), "Air Quality of Paraffinic Fuels", (2017). Available at: <http://www.synthetic-fuels.eu/paraffinic-fuels/air-quality> (Accessed: January 2018).

- [34] Dry, M. E., "High quality diesel via the Fischer-Tropsch process - a review", *J. Chem. Technol. Biotechnol.* **77**, 43–50 (2001).
- [35] Torres Galvis, H. M. and de Jong, K. P., "Catalysts for Production of Lower Olefins from Synthesis Gas: A Review", *ACS Catal.* **3**, 2130–2149 (2013).
- [36] Keil, F. J., "Methanol-to-hydrocarbons: process technology", *Microporous Mesoporous Mater.* **29**, 49–66 (1999).
- [37] Stöcker, M., "Methanol-to-hydrocarbons: catalytic materials and their behavior", *Microporous Mesoporous Mater.* **29**, 3–48 (1999).
- [38] Yarulina, I., Chowdhury, A. D., Meirer, F., Weckhuysen, B. M. and Gascon, J., "Recent trends and fundamental insights in the methanol-to-hydrocarbons process", *Nat. Catal.* **1**, 398–411 (2018).
- [39] Olsbye, U., Svelle, S., Bjørgen, M., Beato, P., Janssens, T. V. W., Joensen, F., Bordiga, S. and Lillerud, K. P., "Conversion of Methanol to Hydrocarbons: How Zeolite Cavity and Pore Size Controls Product Selectivity", *Angew. Chem., Int. Ed.* **51**, 5810–5831 (2012).
- [40] Tian, P., Wei, Y., Ye, M. and Liu, Z., "Methanol to Olefins (MTO): From Fundamentals to Commercialization", *ACS Catal.* **5**, 1922–1938 (2015).
- [41] Jiao, F., Li, J., Pan, X., Xiao, J., Li, H., Ma, H., Wei, M., Pan, Y., Zhou, Z., Li, M., Miao, S., Li, J., Zhu, Y., Xiao, D., He, T., Yang, J., Qi, F., Fu, Q. and Bao, X., "Selective conversion of syngas to light olefins", *Science* **351**, 1065–1068 (2016).
- [42] de Jong, K. P., "Surprised by selectivity", *Science* **351**, 1030–1031 (2016).

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Chapter 2

Fischer-Tropsch Synthesis over Iron-based Catalysts: A Review

Fischer-Tropsch Synthesis (FTS) reaction, the synthesis of hydrocarbons over a transition metal from a $\text{H}_2\text{:CO}$ gas mixture, is reviewed. This review concentrates on Fe-based FTS reaction catalysis. The overall chemical reactions taking place over the course of application of the FTS reaction are reviewed. Furthermore, the reaction pathways for the C originating from the input CO under FTS reaction conditions are defined. The process conditions and catalyst compositions for steering the C pathways and the FTS hydrocarbon product selectivities are overviewed. As the specific topics of this PhD Dissertation: the alkali-S chemical promotion is discussed in detail and the confusing Fe carbide nomenclature used within the FTS reaction literature is clarified. This clarification is done by assigning the Fe carbide crystal structures with their corresponding Mössbauer Absorption Spectroscopy (MAS) hyperfine fields, in a unified and precise manner, on the basis of the available literature. Furthermore, the expected formation conditions of the identified Fe carbides encountered in the FTS research field, namely $\epsilon\text{-Fe}_3\text{C}$, $\eta\text{-Fe}_2\text{C}$, $\chi\text{-Fe}_5\text{C}_2$, $\theta\text{-Fe}_3\text{C}$ and $\theta\text{-Fe}_7\text{C}_3$, are reviewed. The literature review performed in this Chapter establishes the necessary background for understanding the following experimental research Chapters of this PhD Dissertation.

This PhD chapter is based on: *Pasi P. Paalanen and Bert M. Weckhuysen, "Fischer-Tropsch Synthesis over Iron-based Catalysts: A Review", ChemCatChem, accepted.*

2.1 INTRODUCTION

Within this Chapter, the fundamentals of the Fischer-Tropsch Synthesis (FTS) reaction are introduced with emphasis on the Fe-based catalyst material chemistry. Especially, i) the use of alkali-S promotion and ii) the identification of the Fe-based catalysts' FTS reaction active phases i.e. Fe carbides, are both discussed with more detail. Occasionally, few comparisons to Co-based FTS reaction chemistry are made. In the following sections:

Catalyst Compositions the components making up a FTS reaction catalyst material are introduced in general terms,

Reactions, Fe Phase Changes and Catalyst Deactivation discusses the overall reactions related to the FTS reaction and their effect on the working catalyst,

Hydrocarbon and C Pathway Selectivity introduces possible ways for altering the selectivity of the reactions taking place in the FTS reaction, by varying the process conditions and alkali, S or combined alkali-S chemical promotion.

Fe carbides in the Fischer-Tropsch Synthesis Reaction section discusses the identification of the Fe carbides (Fe_xC , $x = 2-3$) which are the active phases in the Fe-based FTS reaction. A common nomenclature is established between Fe carbide crystal structures and available Mössbauer Absorption Spectroscopy (MAS) hyperfine field assignments from literature. This is done in order to clarify and unify the often unclear and ambivalent Fe carbide phase nomenclature. The established nomenclature is applied to identify the general formation conditions for each of the identified Fe carbides.

Aim for the current Chapter is not to give a comprehensive review on the Fe-based FTS reaction up-to-date. Rather, the aim is to give a solid base for understanding the following research Chapters and each Chapter's relevance in the FTS research field. This especially with regard to the topics of Na-S chemical promotion and different Fe carbides in the Fe-based FTS reaction.

2.2 CATALYST COMPOSITIONS

A FTS reaction catalyst material is commonly composed of, at least one, transition metal and a chemical promoter and either an inert structural promoter or a support material.

A wide range of transition metals can catalyze the FTS reaction. They include Ru, Fe, Ni, Co, Rh, Pd, Pt, Ir, Os and Mo.¹⁻³ In practice, Ru, Fe, Co and Ni are the most suitable

ones with respect to their activity and selectivity towards the FTS reaction.^{1,4-6} Ru is active and can be well-suited for the FTS reaction, but is very expensive, and is not readily available in large quantities. Thus, Ru is less applied in commercial FTS reaction catalysis.^{3,4,6} Ni has the tendency to produce larger amounts of undesired CH₄ than Fe or Co do, and Ni is also susceptible for formation of volatile Ni carbonyls under its FTS reaction conditions.^{1,5,7-9} A Ni-based, Ni-MnO-Al₂O₃-kieselguhr catalyst was one of the first FTS reaction catalysts tested in Germany, around 1933, in a demonstration scale FTS facility. However, difficulties with the Ni as the active metal lead to research efforts towards the more suitable Fe- and Co-based FTS reaction catalyst materials.^{7,9} The Fe and Co have been, and are still, the most suitable active transition metals for catalyzing the FTS reaction, and the only ones applied on a large scale in industry.^{3,10}

Besides the catalytically active transition metal, chemical promoters can also be added to a FTS reaction catalyst. These promoters are most often basic alkali, or sometimes earth-alkaline, compounds which are added in order to modify the catalyst's hydrocarbon product selectivities.^{2,3,11-14} The chemical promoters enhance the electronic properties of the FTS reaction active transition metal.¹⁵ Combining the basic chemical promoter with S has shown further favorable properties towards the FTS reaction,¹⁶⁻²¹ giving an additional dimension for modifying the properties of the active transition metal in the FTS catalyst materials.

Addition of possibly alloying metals to Fe- or Co-based catalyst materials, such as e.g. Mn, Ni or Pt, can also modify the catalyst's FTS reaction properties.^{7,22-24} Especially in older FTS literature, also Cu was added to the Fe-based catalyst's composition in order to aid with the Fe oxide phases reduction.^{3,4,10}

The most common catalyst preparation methods for the Fe-based FTS reaction catalyst materials have been, either i) precipitating the catalyst from a precursor solution, or ii) fusing the catalyst from input materials at high temperatures, cooling down and breaking the formed ingot.^{3,25} The catalyst materials prepared via these routes are commonly known as the bulk or unsupported catalysts. For the bulk catalyst materials, structural promoters as inert oxides of, e.g. Si, Al or Mg, can be added for mainly to prevent loss of the active metal area and to improve the catalyst's stability under the FTS reaction conditions.^{3,14}

Impregnation methods are commonly used to prepare supported Fe-based FTS reaction catalyst materials. Usually, ≤ 20 weight percent (wt-%) of elemental Fe is impregnated on a support material with the use of a precursor solution containing the desired chemical promoters and the solvated Fe-ions.^{20,22,25} The major advantage from the impregnation of support materials in comparison to the bulk preparation methods is that the active Fe is in a highly dispersed form. This allows its efficient utilization in the FTS reaction catalysis.²⁵ Some of the support materials which have been applied for

FTS reaction catalyst materials are e.g. α -Al₂O₃, γ -Al₂O₃, β -SiC, SiO₂ and carbon nanofibers (CNF).^{20,25–27}

2.3 REACTIONS, FE PHASE CHANGES AND CATALYST DEACTIVATION

2.3.1 Reactions

The main chemical reaction in the FTS is the conversion of the input H₂:CO gas mixture into various hydrocarbons and the side-product H₂O,^{4,28}

where **Reaction 2.1** refers to formation of paraffins (i.e. saturated hydrocarbons) and **Reaction 2.2** refers to formation of olefins (i.e. unsaturated hydrocarbons). The olefins formed as the FTS reaction's primary products may re-adsorb on the catalyst material and be hydrogenated into paraffins via secondary reactions.^{28,29}

As both of the hydrocarbon forming reactions are exothermic (**Reaction 2.1** and **Reaction 2.2**), attention needs to be paid on the isothermal operation of the FTS reactor bed.^{3,10} Exposing the H₂:CO mixture directly to the FTS reaction catalyst material with too high starting temperature results in non-isothermal bed operation and undesired heating of the catalyst bed.³⁰

Both CO and H₂ adsorb dissociatively under the FTS reaction conditions giving C, O and H atoms adsorbed on the Fe phases' surface. H and C atoms then recombine to form -CH₂- units which polymerize to hydrocarbon chains, via the so-called "surface carbide mechanism".^{4,28,31} Preferably, the O atoms from the CO dissociation recombine with H atoms and desorb as a H₂O molecule. If H₂ is unavailable, as can be the case with low H₂:CO ratio syngas,³² the adsorbed O atom from the CO dissociation may react with an another CO molecule and be removed as CO₂, instead of H₂O.^{3,31,33} Several mechanisms for the FTS reaction have been proposed to explain the variety of hydrocarbon products and their derivatives.^{3,4,31,34} However, within this Dissertation their existence is acknowledged, but only the surface carbide mechanism is considered to be active.

The formation of oxygenate derivatives of hydrocarbons (mainly alcohols) can be taken as a side-reaction, as their contribution to the overall FTS reaction products is usually low.^{3,10,35} Saturated alcohols form in the FTS reaction according to equation:²⁸

Besides the **Reaction 2.3** for exothermic formation of alcohol oxygenates, also some water soluble carboxylic acids and aldehydes may form in the FTS reaction.^{3,10,35} The generic reaction equations for the carboxylic acid and aldehyde formation are omitted here, but can be found e.g. as presented by Dry.³ Mechanism for the formation of the hydrocarbon oxygenate derivatives possibly involves a non-dissociative CO adsorption/insertion step in contrast to the main FTS reactions forming hydrocarbons via CO dissociation.^{3,4,31,34}

The Water-gas shift (WGS) reaction is used industrially in the production of H₂.^{36,37} It follows the reaction equation:

The WGS reaction is not usually active for Co-based FTS reaction catalyst materials but can be active under the FTS reaction conditions if a Fe-based catalyst is used (**Reaction 2.4**).^{4,6,11,12,28,38} With increasing reaction temperature, the WGS reaction equilibrium shifts towards the formation of the reactants CO and H₂O (i.e. is an exothermic reaction). If the reaction is kinetically limited i.e. CO + H₂O partial pressures are above the equilibrium expectations, the total forward reaction may benefit from an increased reaction temperature.^{37,39} In the presence of sufficient amounts of CO₂ and H₂, the reverse WGS reaction can also take place forming CO and H₂O.^{33,35,40–42} If a low H₂:CO ratio reactant feed is used; the WGS reaction may become the FTS reaction rate-determining step. In this case all of the available H₂ for the FTS reaction hydrocarbon products is coming from the WGS reaction.¹¹

In the industrial application of the WGS reaction, a Cu/ZnO/Al₂O₃ catalyst material is used for ~210–240°C and a Fe₃O₄/Cr₂O₃ catalyst for ~310–450°C reaction temperatures.^{36,37,39} For both high and low WGS reaction temperatures, the reaction proceeds with an oxidic active phase unable for CO dissociation.^{36,37} This is unlike in the FTS reaction where CO is dissociatively adsorbed by Fe carbides. That is, the WGS reaction active phase with Fe-based FTS reaction catalysts is Fe₃O₄, not a FTS active Fe_xC Fe carbide phase(s), this despite the presence of Fe phases carburizing CO.

The Boudouard reaction is an unwanted reaction pathway under the FTS reaction conditions causing formation of inactive carbon species (“coke”) on the catalyst:⁴³

The Boudouard reaction (i.e. CO disproportionation) deposits adsorbed carbon species on the catalyst, while releasing CO₂ (**Reaction 2.5**). When raising the FTS reaction temperature from Low-temperature Fischer-Tropsch (LTFT) at ~225°C to

High-temperature Fischer-Tropsch (HTFT) conditions at $\approx 345^\circ\text{C}$, the rate of carbon deposition becomes significant for Fe-based FTS catalyst materials at $\geq 300^\circ\text{C}$.^{3,14,44,45} The Boudouard reaction becomes a major reaction consuming CO, if the CO is exposed to Fe at temperatures $\geq 400^\circ\text{C}$.^{46,47}

Small amounts of added H_2 , or H_2O converted to H_2 via the WGS reaction, can increase the carbon deposition rate from the Boudouard reaction.^{3,44,48,49} Presumably, H_2 removes the adsorbed and catalyst surface sites blocking O atoms from the CO dissociation as H_2O more efficiently than CO does as CO_2 . The improved O removal probably increases the rate at which CO molecules can adsorb and dissociate on the surfaces of (near-)zerovalent Fe phases (i.e. $\alpha\text{-Fe}$ or Fe_xC).^{33,50} However, the increased carbon deposition only takes place with small amounts of added H_2 to input CO. If higher $\text{H}_2\text{:CO}$ ratios ($\geq 5\text{:}1$) with above $\approx 15\text{-}20$ bar reaction pressure are used, the carbon deposition can be decreased during the FTS reaction in relation to the hydrocarbon formation.^{3,51}

Noteworthy emphasis is that both the Boudouard reaction (**Reaction 2.5**), and the main FTS reactions (**Reaction 2.1** and **Reaction 2.2**), result in an adsorbed elemental C intermediates on the Fe_xC surface. The adsorbed C atoms can either react to form hydrocarbon products or inactive carbon deposits on the catalyst.^{3,4,34} The generic types of inactive carbon formed are either encapsulating carbon over the Fe phases if only CO is present or filamentous carbon if both CO and H_2 are available.⁵²⁻⁵⁴

2.3.2 Fe Phase Changes

Several possible Fe phase changes take place on a Fe-based catalyst material when moving from the as-synthesized catalyst to catalyst under FTS reaction conditions and, possibly, to a deactivated catalyst material. The generic Fe phase changes for a Fe-based catalyst follow relation:^{3,4,35}

The initial, as-synthesized, FTS reaction catalyst material is commonly in a form of a Fe oxide, mainly either as $\alpha\text{-Fe}_2\text{O}_3$ (hematite), $\gamma\text{-Fe}_2\text{O}_3$ (maghemite) or Fe_3O_4 (magnetite).⁴ The Fe oxides are not active for the hydrocarbon forming FTS reactions (**Reaction 2.1** and **Reaction 2.2**),⁵⁵⁻⁵⁷ and are commonly reduced to $\alpha\text{-Fe}$ (metallic Fe) prior to starting the FTS reaction. Upon exposure to $\text{H}_2\text{:CO}$ in the FTS reaction, the $\alpha\text{-Fe}$ then readily reacts to form various Fe carbide phases (Fe_xC , $x = 2\text{-}3$).^{34,58-62} Alternatively, the Fe oxides can also be exposed directly to the FTS reaction conditions, i.e. to a $\text{H}_2\text{:CO}$ atmosphere. In this occasion the FTS active Fe carbides form

simultaneously with the Fe oxide reduction to α -Fe.^{29,47,63–67}

The reaction equations for reducing Fe oxides to metallic α -Fe with either H_2 or CO are:^{4,28,68}

Fe oxide reduction with H_2 leads to formation of pure metallic α -Fe (**Reaction 2.6**). In general, a H_2 reduction temperature of $\geq 350^\circ C$ is required, with adequate reaction time, for reducing Fe_xO_y to α -Fe.⁶⁸ The most stable Fe_xC phase (namely θ - Fe_3C) decomposes between 500 – $600^\circ C$ into α -Fe and carbon species.^{30,69–71} Thus, only α -Fe is observed as the CO reduction product $\geq 500^\circ C$ (**Reaction 2.7**).^{68,71} With CO (or H_2 :CO) reduction temperatures of $\leq 500^\circ C$, Fe_xC phases are stable and can form, i.e. the Fe oxides are reduced to α -Fe and simultaneously carburized (**Reaction 2.8**).^{58,69,71}

Furthermore, the H_2 reduction pathway for the Fe oxides is dependent on the used temperature.⁶⁸

With H_2 reduction temperatures above $570^\circ C$ (**Reaction 2.10**), an intermediate Fe_xO (wüstite) phase appears, which is absent if the reduction is done $\leq 570^\circ C$ (**Reaction 2.9**).⁶⁸ Experimentally, however, the Fe_xO phase can be stabilized also at lower temperatures $\leq 570^\circ C$ by strong interaction between the Fe oxide with other oxides (e.g. SiO_2) or by addition of alkali (e.g. K).^{68,72} The Fe_xO phase is an intermediate also if the reduction is done with CO instead of H_2 , with reduction temperature $\geq 570^\circ C$.⁶⁸

At sufficiently high reduction temperatures, Fe_3O_4 may go through an undesired solid-state reaction with the support or the structural promoter inert oxide.^{6,73} As an example, the formation of $FeAl_2O_4$ (Fe aluminate) with a Fe/γ - Al_2O_3 catalyst material at temperatures around 450 – $470^\circ C$, can take place.⁷⁴ Such solid-state reactions are undesirable as the Fe in the $FeAl_2O_3$ compound stays in the oxidized, inactive ionic state for the FTS reaction.^{6,73}

The FTS reaction active Fe_xC phases form in the presence of CO from reduced α -Fe (**Reaction 2.11**):

where $x = 2-3$ and $z = 2x-3$. If H_2 is also present during the carburization reaction, then the O from CO dissociation may also be removed as H_2O instead of CO_2 , as was discussed earlier.

2.3.3 Catalyst Deactivation

The primary pathways for Fe-based catalyst deactivation in the FTS reaction are:³

- i) **Fe phase changes** – conversion of the FTS reaction active Fe_xC into inactive Fe_3O_4 ,
- ii) **Sintering** – loss of active Fe_xC surface area due to increasing Fe particle size,
- iii) **Fouling** – deposition of inactive carbon on the catalyst material, and
- iv) **Chemical poisoning** – deposition of chemical compounds of e.g. S, Cl, Br, Pb or Sn, on the Fe_xC surface.

The conversion of Fe_xC phases into Fe_3O_4 takes place if either of the $H_2O:H_2$ or $CO_2:CO$ ratios are above critical molar ratios.^{3,36,37,57,63,75-77} In general, H_2O is more potent Fe oxidant than CO_2 .^{36,63,77}

When moving along a fixed bed reactor towards the FTS reactor outlet,^{65,78} or towards the inner core of the Fe-based catalyst material particle,⁵⁷ the reducing $H_2:CO$ mixture progressively converts to H_2O and CO_2 . Due to the increasing H_2O and CO_2 concentrations, the oxidation potential towards forming Fe_3O_4 from Fe_xC increases.^{3,57,75,76} Up to around 100-200 μm depth from the particle surface, the Fe-based catalyst particle might remain under reductive environment at FTS reaction conditions. For depths beyond >200-400 μm from the FTS reaction catalyst particle surface, the environment may become oxidative and Fe_xC oxidation to Fe_3O_4 can take over.⁵⁷

Fe_3O_4 is active for the WGS but not for the FTS reaction.^{3,36,37} With sufficient reaction temperature (>310°C), the catalyst may become a bifunctional catalyst where the Fe_xC catalyst part reoxidized to Fe_3O_4 works as a WGS and the Fe_xC part as a FTS reaction catalyst. At lower (<310°C) temperatures the Fe_3O_4 phase is a less efficient WGS reaction catalyst.^{36,37}

The loss of active Fe surface area via Fe particle growth, i.e. sintering, can cause loss in the number of available active Fe surface sites. This in turn causes lost activity towards the FTS reaction. Deposition of the inactive carbon, i.e. fouling, takes place in the presence of CO or $H_2:CO$, causing gradually lost FTS reaction activity as the active Fe sites become harder to access for the reactants.³ Excessive inactive carbon deposition via the Boudouard reaction (**Reaction 2.5**) and/or carbon filament growth

Figure 2.1

A simplified summary of reaction pathways for C atoms from input CO in a Fe-based Fischer-Tropsch Synthesis (FTS) reaction catalyst particle. The input CO + H₂ gives originally a reductive environment (*Red*). For C from CO dissociation the pathways to react are: (1) with α-Fe to form Fe_xC, (2) with H to form hydrocarbons, (3) with C to form inactive carbon. Without CO dissociation: C pathway (4) may reduce Fe_xO_y to α-Fe while releasing H₂O or CO₂. Removal of O atoms from CO as H₂O or CO₂ gradually leads to an oxidative environment (*Ox*) towards the core of the catalyst particle, and the outlet of a fixed bed reactor. If the reaction active Fe_xC is oxidized to Fe₃O₄, pathway (5) may convert H₂O + CO to CO₂ + H₂ via the Water-gas Shift (WGS) reaction.

causes fragmentation of the, especially bulk, Fe-based catalyst materials into a fine powder.^{3,6,10,76,79} The carbon deposition relates to sintering in a twofold manner: i) initially the availability of the FTS reaction active Fe sites may increase due to the catalyst fragmentation into smaller Fe particles exposing new active Fe sites. However, ii) after a longer Time-on-Stream (ToS) the Fe tends to sinter into larger Fe particles, in total resulting in loss of available Fe_xC surface area.^{4,80}

The fragmentation of the Fe-based FTS reaction catalyst materials is a major issue for their industrial application. The catalyst fragments cause clogging downstream from the FTS reactor and the fragments also need to be separated from the liquid/wax hydrocarbon products.^{3,6,10,79} If a Fe-based FTS reaction catalyst material is deactivated by carbon deposition, it can be regenerated with H₂ reduction >350°C by hydrogenating and removing the carbon deposits.³ However, if the catalyst has fragmented, the resulting fine Fe powder still needs to be dealt with to avoid the related issues.^{3,6,10,79} In this case, the simple H₂ regeneration is insufficient method for increasing the Fe catalyst's life-time.

Deposition of chemical compounds on the Fe phases can decrease their reactivity

under FTS reaction conditions. Commonly, the addition of electropositive compounds as chemical promoters (e.g. compounds of K or Na) can have a beneficial effect on the hydrocarbon forming FTS reaction.^{3,11-13} While deposition of electronegative compounds, most commonly S containing compounds, have a deactivating effect decreasing CO conversion and thus the catalyst's FTS reaction activity.^{3,19,81-83}

Work function describes the minimum energy that is required to remove an electron from a chemical compound's highest occupied energy level (the Fermi level).⁸⁴ In general, lower the work function, the easier for a chemical phase is to donate electrons towards an adsorbate causing it to react. Within context of current discussion, the electronegative compounds increase the α -Fe/ Fe_xC surface's work function, thereby lowering its reactivity and ability to adsorb and dissociate H_2 and CO.⁸⁵⁻⁸⁸ Deactivation of Fe with S containing compounds is not only via the mentioned electronic effects but also geometric effects i.e. Fe_xC surface site dependent effects, can play a role.^{86,87,89} These electron donation and geometric effects are discussed more later on.

To conclude the current section and to summarize the main discussion points, the C atoms from input CO has five pathways to react under FTS reaction conditions when a Fe-based catalyst material is used (**Figure 2.1**):

1) with α -Fe to form Fe_xC phases	(Reaction 2.11)
2) with H to form hydrocarbons	(Reactions 2.1 and 2.2)
3) with C to form inactive carbon	(Reaction 2.5)
4) as CO to form CO_2 via Fe_xO_y reduction	(Reaction 2.8)
5) as CO to form CO_2 via WGS reaction	(Reaction 2.4)

The O from CO dissociation is removed as H_2O or CO_2 , possibly gradually transforming the FTS reaction atmosphere, from reductive/carburizing H_2 :CO towards oxidative H_2O - and/or CO_2 -rich conditions. Under the oxidative atmosphere, FTS reaction active Fe_xC may reoxidize to Fe_3O_4 , a phase which can catalyze the WGS reaction. The reverse WGS reaction in turn may convert the CO_2 back to CO. Ideally, to keep up with the earlier mentioned Green Chemistry principles with minimum waste of elemental C (**Chapter 1**): only the pathway 2) should be active with all the O atoms preferably removed as H_2O . This in order to achieve the ideal FTS reaction carbon efficiency from the input H_2 :CO.³²

2.4 HYDROCARBON AND C PATHWAY SELECTIVITY

By varying the FTS reaction process conditions and the catalyst composition, the FTS hydrocarbon product selectivity can be steered towards the desired hydrocarbons. The

changes can also affect the relative C pathways (**Figure 2.1**) by modifying the pathway selectivity towards or away from the FTS reaction producing the hydrocarbons.

In the following sections, we will discuss the effects of the applied FTS reaction process conditions and the alkali-S chemical promotion, mainly as when applied in Fe-based FTS reaction. Within the scope of this Chapter, the FTS reaction hydrocarbon selectivity discussion is limited to the CH₄ formation, to so-called α -value and to FTS hydrocarbon products' olefinicity. Processes such as chain-branching and oxygenate formation are not discussed here.²⁸ We shall start by introducing the Anderson-Schulz-Flory (ASF) distribution that governs the hydrocarbon chain length fractions obtainable from the FTS reaction.

2.4.1 Anderson-Schulz-Flory Distribution

In the ASF distribution model, the earlier discussed -CH₂- entities on the FTS reaction catalyst's active metal surface may either polymerize to longer hydrocarbon chains or terminate the chain growth and desorb as the primary products. The ASF distribution in its logarithmic form can be expressed as (**Equation 2.1**):⁷³

$$\ln\left(\frac{S_n}{n}\right) = n \ln \alpha + \ln \frac{(1 - \alpha)^2}{\alpha} \quad \text{ASF Distribution} \quad (\text{Eq. 2.1})$$

where S_n is the hydrocarbon selectivity with n carbon atoms. The probability for the hydrocarbon chain growth is represented by the parameter α . A higher α -value gives longer chained hydrocarbons while a lower α -value gives increasing amounts of CH₄ and short-chained hydrocarbons from the FTS reaction. Plotting the $\ln(S_n/n)$ versus n , should give a linear correlation in which the term $\ln(\alpha)$ is equal to the slope of the fitted line and the value of the parameter α can be solved.

In practice, deviations from the predicted linearity are commonly observed. The slope of the $\ln(S_n/n)$ versus n plot may change with higher chain length ($\geq C_{10}$) hydrocarbon selectivities,^{28,29,90} and averaged α -values from separate linear fits may be needed for linearly approximating the data.²⁹ Alternatively, more complex carbon chain length distribution models can be used.^{28,90} A single α -value obtained from the fit within the region $\leq C_{10}$ is generally lower than the $\geq C_{10}$ α -values, especially for Fe-based catalyst materials.^{28,29,90}

Within the $\leq C_{10}$ region, the C₁ and C₂ selectivities also commonly deviate from the expected linearity. The C₁ selectivity (i.e. mainly CH₄) can be higher, and the C₂ selectivity is commonly lower than predicted by the ASF distribution. The deviating C₁ selectivity might be e.g. due to hotspots in the FTS reactor bed or preferable reaction sites on the catalyst towards methanation instead of hydrocarbon chain growth, among

other possible reasons. The C₂ deviation is commonly attributed to the secondary reactivity of C₂H₄ (ethene) which can readsorb on the active metal surface and polymerize, participating on the hydrocarbon chain growth.^{3,28,90}

Nevertheless, despite the deviations, the ASF distribution (**Equation 2.1**) via the α -value is a simple method for approximating the hydrocarbon chain length selectivities between various catalyst materials applied in the FTS reaction.

2.4.2 Effect of Process Conditions

Pinpointing the causality effects of FTS reaction process conditions on the formed hydrocarbon products can be a challenging task, due to the intertwined nature of the FTS reaction processes.^{3,91} The main FTS reaction process parameters for controlling the formed hydrocarbon products and the C reaction pathways are i) reaction temperature, ii) input H₂:CO ratio and iii) the used gas space velocity. The effect of total reaction pressure is less straightforward for a Fe-based FTS reaction catalyst material. CO conversion level directly by itself does not significantly affect the hydrocarbon selectivities.^{11,91}

2.4.2.1 Reaction Temperature

The FTS reaction temperature has the effect of decreasing the α -value.^{3,29,91,92} The reaction temperature's effect is more complex and unclear with respect to the olefin formation. With increasing reaction temperature, the olefin content in total may not change or decreases,^{3,29,91,93} or even might increase for some of the Fe-based catalyst materials promoted with K.²⁹ Conversion of α -olefins into internal olefins increases with increasing reaction temperature.^{29,91}

On Fe-based catalyst materials, also conversion of CO via the WGS reaction,^{36,37,39} and via the Boudouard reaction increases with increasing reaction temperature.^{3,14,44,45} This increases the total CO conversion, but away from the FTS reaction hydrocarbon products. The inactive carbon deposition from the Boudouard reaction increases roughly 50 % for every 10°C increase in the reactor bed temperature.³ How the FTS reaction hydrocarbon production C pathways change in relative terms in comparison to the competing WGS and inactive carbon formation C pathways, against increasing temperature, is not clear at the time being.

2.4.2.2 Input H₂:CO Ratio

Increasing the FTS reaction input feed H₂:CO ratio increases the hydrogenation ability of the applied catalyst material. The increased hydrogenation ability decreases the α -value via increased probability for the hydrocarbon chain termination and also, the olefin content decreases as any unsaturated C-C bonds are more likely to be hydrogenated.^{3,29,91} Short-chained α -olefins are affected more than longer internal

olefins, as the short α -olefins are more susceptible towards secondary hydrogenation reactions.^{29,91} Also, increasing input feed $H_2:CO$ ratio, in general decreases the inactive carbon deposition rate.^{3,6,51} This, while keeping in mind the earlier mentioned exception of small amount ($\approx 1\%$) of H_2 in CO increasing the inactive carbon deposition in comparison to pure CO input reactant.^{3,44,48,49}

Despite the input feed $H_2:CO$ ratio effect being rather clear – more input H_2 in relation to CO results in more hydrogenation – noteworthy emphasis is that the actual $H_2:CO$ ratio over the different catalyst sites and bed positions may vary. Conversion of $H_2:CO$ in ratio of $\approx 2:1$ (i.e. ideal FTS),^{6,91} WGS activity in forward or reverse directions,^{6,33,35,40–42,91} and the possibility of incorporating H and/or C to inactive carbon species,^{14,44,52–54} can all modify the local ratio of $H_2:CO$ (and H_2O and CO_2 content, as discussed earlier) along the catalyst particle or the reactor bed. The locally altered $H_2:CO$ ratios can affect the hydrocarbon selectivities.^{3,6,57}

2.4.2.3 Gas Space Velocity

Increasing the reactor gas space velocity has the effect of increasing FTS reaction's hydrocarbon products' olefin content, especially in the short-chained α -olefins fraction. As the space velocity increases, the probability for olefin readsorption decreases, decreasing the probability for the secondary hydrogenation reactions.^{3,29,91} The α -value remains unchanged with the changing space velocity.^{3,91} CO conversion decreases, while the FTS and WGS reaction rates, especially with Na and K promoted catalyst materials, increase with increasing space velocity.^{11,38} As the FTS reaction hydrocarbon production rate increases faster than the WGS reaction rate,^{11,38} relatively more CO is converted towards the desired hydrocarbon products at higher space velocities than is consumed by the WGS reaction.

2.4.2.4 Reaction Pressure

The effect of the total FTS reaction $H_2:CO$ pressure on the hydrocarbon product selectivity is more complex than the effects of the other aforementioned FTS reaction process parameters. While for a Co-based FTS catalyst the CH_4 selectivity decreases with increasing $H_2:CO$ pressure within range ≈ 5 -25 bar, no significant change in the CH_4 selectivity with changing reaction pressure is observed for a Fe-based catalyst material.⁹⁴ This holds when the reactor outlet $H_2:CO$ ratio (i.e. $\approx$ reactor $H_2:CO$ ratio) is kept constant.⁹⁴ With increasing $H_2:CO$ total pressure within the range ≈ 15 -25 bar, Todić et al. observed a somewhat increased α -value and decreased olefin content, but also the outlet $H_2:CO$ ratio dropped, in this way affecting the hydrocarbon selectivities.⁹¹ In experiments at Sasol with Fe-based catalyst materials, both an increase in the α -value and an increase in the olefin content, as well as no change in either of the hydrocarbon selectivity variables with increasing $H_2:CO$ reaction pressure, have been observed.³ An

increase in the total $H_2:CO$ pressure increases the Fe-based catalyst material's activity for the FTS reaction.⁹⁴ This in turn can affect the actual reactor $H_2:CO$ ratio as well as the partial pressures of H_2O and CO_2 via increased CO conversion, altering the hydrocarbon selectivities, as discussed previously. In overall, the effect of total reaction pressure on the Fe-based FTS hydrocarbon selectivities depend on the individual partial pressures of H_2 , CO , H_2O and CO_2 present in the FTS reactor.^{3,6,9,91} Their relation further depends on the used reaction temperature.^{6,9}

With regard to the inactive carbon deposition, as previously briefly mentioned earlier, with the total reaction pressure of ≥ 15 bar with $H_2:CO$ ratio ≥ 5 , the inactive carbon formation can be suppressed.^{3,51} This, while improving the C pathway selectivity towards the FTS reaction hydrocarbon products.^{3,51} With lower input $H_2:CO$ ratios of ≤ 1 , the carbon deposition increases with increasing reaction pressure.⁵¹ According to Todic et al., the WGS reaction extent decreases with increasing total FTS reaction pressure.⁹¹

2.4.3 Effect of Alkali-S Promotion

Modifying the catalyst composition by adding chemical promoters can alter the FTS reaction's hydrocarbon product and C pathway selectivities towards the desired reaction products.

The addition of combined alkali-S (alkali as Na or K) as chemical promoters for Fe-based FTS catalyst materials has the following effects: i) a decreased CH_4 selectivity to a lower value than predicted by the ASF-distribution when alkali and S are present in an optimal ratio,^{19,20} ii) a lesser increase in the hydrocarbon chain length (α -value) in comparison to if only alkali is added,^{16,18,95} iii) an increased hydrocarbon selectivity towards olefins,^{16,17,19,20} and iv) an overall increased CO conversion.^{20,81,95,96} Suppression of the CO_2 selectivity, without detrimentally affecting the hydrocarbon production, by addition of sufficient amount of S to a K containing Fe-based FTS reaction catalyst material has also been claimed.⁹⁷

First, we shall discuss the general principles of the effect of individual alkali (as Na or K) and S on the adsorption of H_2 and CO over a transition metal surface. The discussion is then continued towards the experimentally observed effects of alkali, S and alkali-S promotion on the FTS reaction hydrocarbon and C pathway selectivities.

2.4.3.1 General H_2 and CO Adsorption Principles

The simplified effects of chemical promoters added as electropositive (e.g. Na or K) or –negative (e.g. S) adsorbates on a transition metal (e.g. Fe) are (**Figure 2.2**):

- i) Electropositive adsorbates donate electrons towards the transition metal

Figure 2.2

A schematic summary on the general effects of chemical promoter addition on H_2 and CO adsorption over the (near-)zerovalent Fe surfaces (e.g. $\alpha\text{-Fe}$ or Fe_xC). **With added electropositive alkali (as Na or K):** a) (i) increased Fe surface electron density increases electron back-donation towards antibonding orbitals of Fe surface adsorbed intermediate H_2^- and CO^- states, (ii) formed alkali-Fe surface dipole moment stabilizes the intermediate H_2^- and CO^- states via electrostatic interaction, and also (iii) formation of formates and/or carbonates is observed. With alkali, both effects (i) and (ii) *increase* dissociative adsorption of H_2 and CO . **With added electronegative S:** b) (i) electron back-donation from Fe surface is weakened, and (ii) intermediate H_2^- and CO^- states are destabilized. With S, the effects (i) and (ii) *decrease* dissociative adsorption of H_2 and CO .

surface, decreasing the measurable surface work function; while the electronegative adsorbates do the opposite.^{84,86,98}

- ii) To modify the electrostatic potential near the transition metal surface, due to dipole moment formed between the - partly or fully ionized - chemical promoter adsorbate and the transition metal surface.^{84,98}
- iii) To possibly offer direct adsorption or reaction sites for reactants (e.g. H_2 or CO).^{87,98-100}

Under FTS reaction relevant conditions on Fe_xC surface, both H_2 and CO adsorb dissociatively due to the electron back-donation from the Fe d-orbitals to the antibonding C-O π^* and H-H σ^* molecular orbitals.^{85-88,98-100} The dissociation of the adsorbed H_2 and CO on Fe_xC surface is affected by i) the availability of electrons in the Fe d-orbitals for the back-donation and ii) stability of the Fe_xC surface adsorbed, intermediate states of the H_2 and CO molecules.^{85,88,98,99}

Addition of alkali in moderation increases the Fe d-orbital electron density and availability, i.e. decreases the surface work function; while the S addition does the

opposite.^{85-88,98-100} Via the electrostatic interaction between the formed promoter-surface dipole moment and the reactant adsorbates: electropositive alkali stabilizes the H_2^- and CO^- intermediate states on the Fe_xC surface, while the electronegative S destabilizes them.^{85,88,98,99} In total then, alkali as an individual chemical promoter in Fe-based catalyst material increases the dissociative adsorption of H_2 and CO. While added S promoters, individually, work vice versa decreasing the dissociative adsorption of H_2 and CO. The dissociative H_2 and CO adsorption promoting effects by electropositive alkali K and inhibiting effects by electronegative C, O and S over a surface of metallic state Fe have been experimentally observed e.g. by Benziger and Madix.⁸⁷

Furthermore, with added alkali, carbonate or formate species are commonly observed upon CO adsorption, species which are absent without alkali promotion.^{26,98,101-104} Also, direct interaction between the alkali and the metallic state Fe surface adsorbed H_2 and CO has been suspected, possibly aiding in the molecules' dissociation.^{87,105}

Upon addition of alkali (as K), the desorption temperatures for adsorption products of H_2 and CO are increased with the expense of lower temperature desorption.^{87,99,100} That is, added alkali increases the overall binding strength of H_2 and CO adsorption/desorption products. Within the FTS reaction relevant temperatures ($\lesssim 340^\circ\text{C}$), the H_2 adsorption products are more strongly bound than the CO products with addition of alkali K.⁸⁷ Addition of electronegative adsorbates (e.g. S or O) has the opposite effect of lowering the desorption temperatures for the adsorbed products of CO and H_2 .^{87,99}

The measured adsorption energy change for an alkali K promoted Fe metal surface is higher for CO ($\approx +3.0$ kcal/mol) than for H_2 ($\approx +1.5$ kcal/mol).¹⁰⁰ Worth noting is that in a commonly cited study in the realm of FTS reaction research by Dry et al.,¹⁰⁶ the heat of H_2 chemisorption was found to decrease due to the addition of K promotion. That is, added K would inhibit the H_2 adsorption, in contradiction to the present discussion. However, as noted by Benziger and Madix,⁸⁷ the results by Dry et al. were likely obtained on an oxide rather than a Fe metal (or carbide) surface and the observed H_2 inhibition effect was more likely due to the presence of O atoms rather than K.⁸⁷

Besides the added chemical promoter electropositivity and -negativity arguments on the H_2 and CO adsorption, as mainly discussed above, also the alkali or S adsorbate Fe surfaces' binding geometry can play a role.⁸⁷ Despite O atom adsorbates being more electronegative and C atom adsorbates having similar electronegativity as S has, the S atom adsorbates on metallic Fe surface showed more pronounced inhibition effect on CO and H_2 adsorption than either O or C did. The effect was thought to be due to different binding geometries which the O and C take versus the S adsorbates on the metallic Fe surface.⁸⁷ The different binding of O and S elements might be a very relevant

factor when a combined Na-S promotion is applied in the FTS reaction, as will be discussed later.

2.4.3.2 Alkali in the Fischer-Tropsch Synthesis Reaction

The most common chemical promoter added to a Fe-based FTS catalyst material is alkali as an electropositive chemical species of K or Na.^{2,3,11,13,95,107} Other alkali and alkaline-earth elements have also been screened for the FTS reaction promotion but K and Na remain the most suitable, in both terms of the FTS reaction activity and selectivity.^{9,11-13}

The addition of alkali by itself to a Fe-based catalyst material has the effect on the FTS reaction hydrocarbon selectivity of increasing i) the α -value and ii) the hydrocarbon product slate olefin content.^{3,9,11,29,50,93,107} The alkali hydrocarbon selectivity effect is commonly attributed to an overall decrease in the catalyst's hydrogenation ability i.e. on the Fe_xC surface H:C ratio. The decreased H:C ratio results in decrease in the hydrocarbon chain termination and in olefin hydrogenation via primary or secondary pathways.^{3,9,29,50,107}

The lowered H:C surface ratio with alkali addition can be explained as i) adsorption energy is increased more for CO (+3.0 kJ/mol) than for H_2 (+1.5 kJ/mol).¹⁰⁰ Thus, CO is more preferably adsorbed than H_2 when H_2 and CO compete for the alkali promoted Fe_xC surface adsorption sites. Additionally, ii) alkali increases the elemental binding strength of H more than that of C on metallic Fe(/ Fe_xC) surface, as has been observed via the increased desorption temperatures of the H_2 and CO adsorption products.⁸⁷ The increased binding strength of H to the Fe_xC surface results in depletion of weakly bound H available for the FTS reaction.¹⁰⁸ Therefore, both of the mentioned alkali addition effects in total effectively decrease the Fe_xC H:C surface ratio available for hydrocarbon forming FTS reactions.

Increasing alkali promotion has the intrinsic tendency to increase the inactive carbon deposition C pathway via the Boudouard reaction, along the in overall increased CO conversion and dissociation.^{3,14,46} Although, a sufficiently low level of added alkali may nevertheless decrease the carbon deposition rate in comparison to a respective unpromoted Fe-based catalyst material.³ This effect with still observable alkali promotion effects in the FTS hydrocarbon selectivity.³ The alkali also increases the WGS reaction rate,^{50,107,109} consuming CO towards the WGS reaction products. This simultaneously decreases the C pathway selectivity towards the FTS reaction hydrocarbon production.^{11,12} Alkali promotes the WGS reaction even without a presence of a transition metal.^{103,104} That is, as undesired effects from the alkali addition: C pathway selectivity towards FTS reaction hydrocarbon products decreases due to CO being consumed towards the WGS and/or inactive carbon depositing

Boudouard reactions.

Nevertheless, in the case of low input $H_2:CO$ ratio, the WGS reaction may become the rate determining step for the FTS reaction as the hydrocarbon production becomes dependent on the H_2 from the WGS reaction.^{11,38} In this case, the CO consuming and alkali promoted the WGS reaction becomes a possibly useful property for the applied FTS reaction catalyst material.²⁸

2.4.3.3 S in the Fischer-Tropsch Synthesis Reaction

The effect of S individually in heterogeneous catalysis is a complex phenomenon.^{86,89} Too much of added S compounds result in a catalyst poisoning.^{81,82,86,110} However, small amounts of added S may have beneficial FTS reaction catalysis effects. S containing impurities in the CO gas can also gradually enrich on the catalyst, thus altering its behaviour.⁴⁶ From a review article by Madon and Shaw, some of the possible effects of the S addition in FTS reaction are:⁸⁶

- 1) avoiding reactor hotspots via decreased CO conversion,
- 2) selective S adsorption on different reaction sites i.e. selectively affecting reaction pathways,
- 3) S itself may become an active site for reactions,
- 4) S functions as an electron acceptor i.e. is an electronegative adsorbate on the transition metals and depletes the metals from electrons, as also was discussed previously.

As mentioned earlier, the FTS reaction is in total an exothermic reaction and any hotspots created by the released heat to the reactor bed may cause the bed temperature to increase locally. This results in decreased α -value, which most easily can be seen as increased CH_4 selectivity, and/or inactive carbon deposition via the Boudouard reaction (**Reaction 2.5**). If a FTS reactor bed is operated non-isothermally, S poisoning decreases CO conversion eliminating the hotspots, which can result in increased α -value (decreased CH_4) and decreased carbon deposition. That is, the listed point 1) is relatively easy to understand.

Dalla Betta, Piken and Shelef observed decreased catalyst activities with added S, as well as decreased CH_4 and increased C_{2+} selectivities and also discussed signs of possible non-isothermal reactor bed operation in their data.¹¹¹ Similar effects where S addition likely affects the initial reactor bed operating temperature, can be observed in the studies by van Dijk et al. and Zhou et al. with Fe-based FTS reaction at 350°C.^{112,113} In the study by van Dijk et al., the added S prevented an initial spike of high FTS catalysis activity in comparison to the non-sulphated catalyst. The added S likely prevented any

excessive reactor bed heating at the initiation of the FTS reaction, limiting the fast catalyst deactivation from excessive formation of inactive carbon species.¹¹² Same comments apply to the study by Zhou et al. who exposed their pre-reduced Fe-based FTS reaction catalyst material to H₂:CO directly at 350°C.¹¹³ This is an initial reaction temperature too high for ensuring isothermal bed operation without excessive reactor bed heating.³⁰ The likely role of the sufficient S addition in their study has been to poison the catalyst and to decrease the CO conversion, and thus to dampen the initial non-isothermal FTS reactor bed operation. This would explain the observed decrease in the carbon deposition with S addition in the study.¹¹³

Definitely pinpointing the effect of the listed points 2), 3) and 4) and their possible combinations in relation to Fe-based FTS reaction catalysis effects is a complex task. In addition, unfortunately, a variety of the S poisoning studies with FTS reaction have been conducted with alkali containing Fe-based catalyst materials. Thus, mixing both the FTS reaction promotion effects by alkali-S combination and possible poisoning by excessive S addition. This further complicates the task of assigning causality on the S effects in the FTS reaction, in relation to the listed points.

In several studies, positive S promotion effects in the Fe-based FTS reaction have been observed. However, in these studies alkali promoted catalysts promoted, intentionally or inadvertently, with synthesis precursors or precipitation agents containing the alkali promoters, have commonly been used.^{81,82,95,114–118} Washing of the prepared catalyst materials with deionized water in order to remove the alkali,^{81,117} or possible S-ions,^{117,119} is insufficient in order to have an alkali- or a S-free FTS reaction catalyst material free of promotion or poisoning effects.

From a S poisoning study by Bromfield and Coville,¹¹⁷ it can be pointed out that Na₂S was used as the S precursor and Na₂CO₃ as the catalyst precipitation agent. Despite the subsequent washing to remove the Na atoms from the precipitated Fe catalyst material, with low levels of added S, the catalytic FTS reaction results resemble of what would be expected for the Na-S promotion. That is, increased catalytic activity and increased olefin content.¹¹⁷ It seems unlikely that the Na atoms were removed with catalyst washing and the combined Na-S rather than S-only promotion explains the positive S addition effects in their study. Presumably, the work led to a later Sasol patent on Na-S promotion with Fe-based FTS reaction catalyst materials.¹⁸

Furthermore, in a study by Shultz et al., the initial S addition on K containing catalysts resulted in an initial promotion effect by K-S but this was followed by S poisoning effects when too much of S was added.⁸² In the study, with low level of COS added as the S bearing gas compound, slight increase in hydrocarbon products olefinicity could be observed. Despite the increased reaction temperature, there was no increase in CH₄ selectivity. Both effects can be explained by K-S promotion. Further

addition of COS increased the CH₄ selectivity (and seemingly decreased the α -value), this despite the simultaneously decreased reaction temperature which should decrease the CH₄ selectivity. And also simultaneously with the increasing S addition, the olefin selectivity decreased for the catalyst.⁸² The S poisoning effects of decreased olefin content and increased CH₄ formation can also be observed when different experimental runs with the same reaction temperature are compared in the study.⁸² Similar observations have been made by Botes et al., i.e. excessive S addition on alkali containing Fe-based catalysts increases CH₄ selectivity in the FTS reaction.¹⁹

In the simplest way, the “promotion effects” of increasing CH₄ selectivity and decreasing olefin content by S poisoning of alkali containing catalyst material can be explained as S being electronegative adsorbate (i.e. with the listed point 4)). That is, functioning in an opposite way to the alkali addition (**Figure 2.2**).⁸⁶ The S addition thus likely increases the overall H:C surface ratio resulting in increased hydrocarbon hydrogenation and chain termination reactions.

It is unclear how the S effects which are not directly related to the S elements electronegativity, i.e. the points 2) and 3), affect the observed selectivities in the Fe-based FTS reaction. Generally, the adsorbate S might selectively block some geometric reaction sites, such as the active steps. This might affect different the reaction rates and pathways to different degrees in the FTS reaction.^{86,89} Some evidence has been observed on the effect of site-blocking for some model catalytic systems.⁸⁹ However, how the data obtained from ultra-high vacuum model experiments compares to a more dynamic Fe-based FTS catalyst materials behavior at higher reaction pressures, is not clear.⁸⁹

As excessive addition of S eventually covers the active Fe_xC surface decreasing its FTS reaction activity,^{82,114,115,117,118} and CO dissociation capability,^{46,120} it's unlikely that S itself performs as an active site for the FTS reaction. However, some cautious doubt can be expressed as observations of the S compounds possibly assisting in dehydrogenation reactions with Fe-based catalyst materials have been made.¹²¹

In contrast to the cited *alkali-containing* Fe-based catalyst material studies on the S effects in the FTS reaction, when catalyst precursors *free of alkali* have been used, the catalyst is directly poisoned by a low level of S addition. S poisoning effects of decreasing: i) α -value,⁸³ ii) olefin content versus paraffins,^{83,112} and iii) overall CO conversion,^{81,83} have been observed. Interestingly in the study by Xu et al. with alkali-free Fe-based catalyst material in the FTS reaction: the CH₄ selectivity remained virtually unaffected despite the increasing S content and decreasing α -value.⁸³ This seems to be in contrast to the Fe-based, alkali containing catalyst materials for which the CH₄ selectivity increases with excessive addition of S.^{19,82}

In terms of the various C pathways, the effect of the added S might be simply to

decrease the overall CO and H₂ dissociation, without altering the relation between the C pathway selectivities. Although the overall carbon deposition decreases with added S,^{46,120,122} so does the CO conversion.⁸³ That is, whether S truly suppresses carbon deposition without decreasing the FTS reaction hydrocarbon production as a promotion effect, as is sometimes discussed, needs to be compared in relative terms to the CO converted to FTS reaction hydrocarbon products. Such studies do not seem to exist at the moment. On Fe-based WGS reaction catalysts, S behaves as a poison.^{37,39} Thus, unlike the alkali, S does not promote the WGS reaction. In overall, further studies would be of interest on determining - with alkali-free Fe-based catalyst materials - the effect of individually added S on the relative C pathway selectivities in FTS reaction catalysis. Moreover, in these studies, the results should be normalized to the overall CO conversion over the observation period.

2.4.3.4 Alkali-S in the Fischer-Tropsch Synthesis Reaction

In the light of individual alkali and S promotion properties with regard to the FTS reaction hydrocarbon selectivities: *the combined alkali-S promotion effect resembles both*. The increased olefin selectivity and CO conversion are “alkali-like”, while the decreased α -value in comparison to alkali-only addition is “sulfur-like”. The unique effect of decreased CH₄ selectivity to a lower value than expected from the ASF-distribution is solely an combined alkali-S effect.¹⁹ Together these effects enable increased yields towards short-chained C₂-C₄ olefins.

The unique disruption of the lowered CH₄ selectivity has been proposed to be due to a changed binding geometry of the chemical promoter compound when the S is added as a counter-ion for the alkali promoter.¹²³ Commonly, the alkali is thought to be in an oxidized form under the FTS reaction conditions, although the exact chemical compound is uncertain.^{98,106} Benziger and Madix have observed oxidation of K atoms by O from CO dissociation in their metallic Fe surface studies, in support of the thought for K oxidation.⁸⁷

The added S to Na promotion likely replaces the O as the alkali's counter-ion resulting in a Na-S compound instead of a Na-O compound under the FTS reaction conditions.¹²³ From a combination of experimental data and theoretical calculations applying Density Functional Theory (DFT), Xie et al. concluded that the counter-ion change from O to S i) increases the Na electron donation towards Fe as S is less electronegative than O, as well as ii) changes the Na-S promoter compound binding geometry on the Fe_xC surface. The combined effect decreases the availability of H for the hydrogenation reactions, resulting in especially suppressed CH₄ formation.¹²³

As mentioned before, Benziger and Madix have discussed the individual difference between O (and C) and S adsorbates on the metallic Fe surface.⁸⁷ Their experimental

Figure 2.3

A schematic summary on the effects of chemical promoters on (near-)zerovalent Fe surfaces (e.g. α -Fe or Fe_xC). The effects of a) alkali (as Na or K), b) S and c) alkali-S in molar ratio of 2:1 in Fe-based Fischer-Tropsch Synthesis (FTS) reaction, on FTS hydrocarbon product and C pathway selectivities and on overall CO conversion. **Green** – increased, **Red** – decreased, and ? – an unknown change in the property in comparison to an unpromoted catalyst material. The combined c) alkali-S promotion increases CO_2 selectivity, likely indicating increased Water-gas Shift (WGS) and/or Boudouard reaction C pathway selectivities.

results and discussion are in support of the different binding modes for O and S. The S adsorbates bind on the metallic Fe surface in a manner which more effectively inhibits the adsorptive dissociation of H_2 and CO than do O adsorbates, despite O being more electronegative and Fe surface electron depleting than S.⁸⁷ The experimental results from Benziger and Madix thus make similar suggestions as do the results by Xie et al.. How the chemical promoter alkali-S, in comparison to alkali-O adsorbate compound, covers the Fe_xC surface, can have an effect on the observed FTS reaction promotion effects.

Combined alkali-S promotion affects the C reaction pathways for the dissociated CO by: increasing the overall CO conversion,^{20,81,95,96} and might also increase, at least the initial, carbon deposition rate.^{21,95,96} Although, in the cited studies regarding the carbon deposition, the vast differences in the CO conversion levels have not been accounted for between the different catalysts and promotion levels. The source for inactive carbon deposited on the catalysts is CO. For low CO conversion carbon deposition is necessarily low and vice versa. For meaningful comparison of carbon deposition between various alkali-S promoted catalysts: the carbon deposition needs to be normalized to the total (i.e. integral of) CO conversion over the measurement period. Otherwise, the carbon deposition results can be misleading and the conclusions misguided.

Table 2.1

The effects of various Fischer-Tropsch Synthesis (FTS) reaction process parameters and alkali, S and alkali-S chemical promoters on the C reaction pathways and on the FTS hydrocarbon selectivity in the Fe-based FTS reaction.

Parameter	Hydrocarbon Selectivity			CO Conversion	C Pathway Selectivity		
	CH ₄	α -value	Olefins		FTS	WGS	Carbon Deposition
Temperature	↑	↓	~	↑	~	↑	↑
H ₂ :CO	↑	↓	↓	~	~	~	↓
Space Velocity	~	↔	↑	↓	↑ ^{a)}	↓	~
Total Pressure	~	~	~	↑	~	↓	↑ ^{b)}
Alkali	↓	↑	↑	↑	↓	↑	↑ ^{c)}
S	~ ^{d)}	↓	↓	↓	~	~	~ ^{e)}
Alkali-S ($\approx$ 2:1)	↓ ^{f)}	↑ ^{g)}	↑	↑	~	~ ^{h)}	↑ ^{h,i)}

Symbols: ↑ or ↓ - increasing or decreasing FTS reaction property against increasing parameter.

↔ - no effect.

~ - complex or unclear effect.

Alkali: Na or K atoms as added promoters.

a) FTS rate increases faster than the Water-gas Shift (WGS) reaction rate with increasing space velocity.

b) With ≥ 15 bar total reaction pressure and $5 \geq \text{H}_2:\text{CO}$ ratio carbon deposition can be suppressed.

c) Low addition levels of alkali may not increase the carbon deposition rate and might even lower it.

d) Excessive S addition increases the CH₄ selectivity, if alkali is present.

e) Commonly, a decrease is observed, likely, due to the overall decrease in CO conversion.

f) Selectivity of CH₄ can be suppressed to a value below the Anderson-Schulz-Flory (ASF) distribution expectations.

g) The α -value is increased less than with only alkali addition.

h) CO₂ selectivity with alkali-S promotion increases.

i) At least, the initial carbon deposition rate at the start of the FTS reaction might increase.

Nevertheless, as significant CO₂ selectivity in the FTS reaction has been observed in the presence of alkali-S promotion with the Fe-based catalyst materials:^{20,21,95,96} either increased WGS and/or carbon depositing Boudouard reactions, both releasing CO₂, can be suspected to be active. Increased CO₂ selectivity with the presence of alkali-S promotion would be akin to the earlier discussed alkali-only addition of increasing WGS and carbon deposition reactions, therefore, being an “alkali-like” property. Moreover, after experiments at Sasol, Botes et al. suggest that CO conversion selectivity towards FTS reaction hydrocarbon production decreases with the added alkali-S promotion. However, the precise data was not given.¹⁹

In precisely quantified terms, how the alkali-S promotion affects the WGS reaction or the inactive carbon depositing Boudouard reaction, in relation to the FTS reaction hydrocarbon production, is unclear for the time being. More research on the effect of alkali-S promotion on the C pathway selectivities is warranted.

Figure 2.3 gives a schematic summary on the effects of alkali (Na or K), S and

combined alkali-S and their effect on the FTS hydrocarbon and C pathway selectivities. **Table 2.1** further summarizes the effects of all of the discussed FTS reaction process parameters together with the effects of the alkali, S and alkali-S chemical promoters in the Fe-based FTS reaction.

2.4.4 Comparison of Fe and Co as Fischer-Tropsch Synthesis Active Transition Metals

In the following, the Fe and Co transition metals are shortly compared regarding their general FTS reaction catalysis capabilities. Co is more i) active per gram of metal for hydrocarbon production,^{6,94} and ii) selective towards paraffin formation than Fe is.^{3,28} Co responds strongly to increased reaction temperature, producing mostly CH₄ if the reaction temperature is increased from LTFT conditions (200-250°C).^{6,94} In general, Fe can operate over a wider range of FTS reaction conditions with an useful reaction hydrocarbon selectivity than Co can.⁹⁴ Finally, Co-based catalysts generally do not show WGS reaction activity unlike the Fe-based catalyst materials do.^{28,73,94} Regarding the application of alkali-S promotion, both Fe-based,¹⁶ and Co-based FTS catalyst materials,¹⁷ seem to react in a same similar manner.

2.5 FE CARBIDES IN THE FISCHER-TROPSCH SYNTHESIS REACTION

The most common Fe carbide observed in the FTS reaction related research is the χ -Fe₅C₂ phase, which is also known as the Hägg carbide. The so-called “ ϵ -carbides” (or (pseudo-)hexagonal) Fe carbides are also often observed and labelled as ϵ' -Fe_{2.2}C, Fe₂C, ϵ -Fe₂C or ϵ -Fe₃C in the literature. Less common Fe carbides encountered under FTS reaction conditions are θ -Fe₃C (cementite) and Fe₇C₃ (the Eckström-Adcock carbide). The Fe₇C₃ phase is a somewhat rare, but an interesting special case. The mentioned Fe carbides, while excluding the Fe₇C₃ phase, are also commonly formed as unwanted precipitates during tempering (i.e. heat treating) of martensitic steels.

Within this section, we concentrate the discussion on the proper identification and formation conditions of the different Fe carbides observable in the FTS reaction research. Especially, the nomenclature and identification of the “ ϵ -carbides” in the literature is rather confusing, while the χ -Fe₅C₂ and θ -Fe₃C phases are more consistently identified. Identification and formation conditions of the Fe₇C₃ phase are also somewhat unclear as the phase is less encountered in overall.

Thus, the aims within this section are to identify from the literature i) the expected lattice parameters (space group, unit cell) and their proper crystal structures for the Fe carbides. Furthermore, also ii) to determine the corresponding Mössbauer hyperfine field parameters for each of the identified Fe carbide crystal structure. This is done in

Figure 2.4

The unit cell of the hexagonal ϵ -Fe₃C $P6_322$ (182). The Fe lattice is purely hexagonal and the C atoms occupy third of the octahedral Fe lattice interstitial spaces in a random, distorted manner.

order to establish a unified nomenclature between the precise crystal structures and Mössbauer Absorption Spectroscopy (MAS) characterization technique. And lastly, the expected formation conditions from the literature for each of the identified Fe carbide are shortly reviewed using the established, unified Fe carbide nomenclature. The identified unit cells for each of the Fe carbides are visualized within this Chapter with the use of VESTA software.¹²⁴

2.5.1 “ ϵ -carbides” (ϵ -Fe₃C and η -Fe₂C)

The so-called “ ϵ -carbides” or Fe carbides with (pseudo-)hexagonal Fe lattices have traditionally been the most difficult Fe carbides to identify due to an unfortunate confusion with the labelling and identification of the ϵ' -Fe_{2.2}C, (ϵ' -)Fe₂C and ϵ -Fe₃C phases. It is often unclear to which actual crystal lattice/structure the used nomenclature, as per author, refers to.

The ϵ -Fe₃C phase has been identified by Nagakura.⁶⁹ In their Electron Diffraction (ED) study on Fe thin films, the author solved the diffracting Fe carbide structure to have a space group of hexagonal $P6_322$ (182). This Fe lattice is hexagonally ordered and the C atoms occupy one third of the octahedral interstitial Fe spaces in a disordered manner (**Figure 2.4**). The disordered C packing was observed from the broadening of the superstructural diffraction peaks, which for the Fe carbides originate from the interstitial C atoms. By decomposing the formed ϵ -Fe₃C phase by heating it under vacuum back to α -Fe and graphite, its stoichiometry was estimated to be around Fe_{2.8}C.⁶⁹

As commented by Nagakura,⁶⁹ the studied ϵ -Fe₃C phase had the same lattice parameters, when ignoring the weak superstructural C diffraction, as a Fe carbide labelled as “Fe₂C” with hexagonal Fe lattice observed earlier by Hofer, Cohn and Peebles.⁶² That is, the earlier “hexagonal Fe₂C” and Nagakura’s ϵ -Fe₃C were the exact same carbide.

The stoichiometry for the Hofer’s Fe₂C was determined by a comparison to - what at the time was thought to be - isomorphism with a “Hägg carbide Fe₂C”. Experimental

C:Fe ratio for the carbide was further determined by *total sample weight* increase upon carburization.⁶² Both, in retrospective, are inaccurate assumptions for determining a carbide stoichiometry. Later, after more accurate structural solutions were provided for the Hägg carbide,¹²⁵ the original assumptions in the identification of the “hexagonal Fe₂C” and its stoichiometry were acknowledged by the researchers at the time to be inaccurate.¹²⁶ No evidence of a Fe carbide as “hexagonal Fe₂C” exists as after Hofer, Cohn and Peebles.⁶² Unfortunately, the acknowledgement of the mistaken original labelling went unnoticed and several later studies cite a “hexagonal Fe₂C” carbide originating from the study by Hofer, Cohn and Peebles.^{22,67,127} This has resulted in unfortunate confusion in the characterization of the actual Fe carbide phases in the FTS reaction.

Furthermore, unfortunately, in a French written study by Dirand and Afqir,¹²⁸ the “Fe₂C” carbide with the data from the study of Hofer, Cohn and Peebles was solved to have a space group of hexagonal $P6_3/mmc$ (194). This was done with the use of newly available computerized diffraction pattern indexing (i.e. space group solving) software. Dirand and Afqir also acknowledged the existence of the ϵ -Fe₃C phase indexed as $P6_322$ (182) after Nagakura, but unfortunately did not acknowledge that the carbides were the same. The reason why the same carbide was solvable with different space groups is due to the originally used diffraction techniques to collect the data. The electron diffraction pattern by Nagakura contains *the diffraction originating from both Fe and C* in the crystal lattice. The X-ray Powder Diffractometry (XRPD) data collected by Hofer, Cohn and Peebles is not sensitive to the low atomic number element C and essentially only *the diffraction from Fe* was observable. Thus, the $P6_322$ (182) is the full, proper space group with Fe and C diffraction while the $P6_3/mmc$ (194) is an incomplete space group only for the Fe diffraction, for the same hexagonal ϵ -Fe₃C phase observed by both Nagakura and Hofer, Cohn and Peebles.^{62,69}

The International Centre for Diffraction Data Powder Diffraction File-4+ (ICDD-PDF-4+) database lists the Dirand and Afqir’s solution based on Hofer, Cohn and Peebles’s unit cell as a Fe carbide with space group $P6_3/mmc$ (194) with database number 00-036-1249 (or 36-1249 in pre-2016 databases). As discussed above, Nagakura’s crystal structure solution with space group $P6_322$ (182) and database number 04-008-9572 (or 89-3689) should be used instead. Dirand and Afqir’s $P6_3/mmc$ (194) incomplete lattice solution should not be used in order to avoid any unnecessary confusion for the future identification of the ϵ -Fe₃C phase.

Nagakura’s ϵ -Fe₃C is not the only Fe carbide phase observed with a (pseudo-)hexagonal Fe lattice. In a spent FTS reaction catalyst material, Barton and Gale observed a similar hexagonal Fe carbide to what Hofer, Cohn and Peebles observed earlier (i.e. the ϵ -Fe₃C phase properly identified by Nagakura). However, the Fe carbide differed from the previous observations by i) having split X-ray diffraction peaks,

suggesting that a distortion from the hexagonal Fe lattice was present, and by ii) having significantly different unit cell parameters.¹²⁹ As XRPD was used, Barton and Gale could not conclusively solve the observed Fe carbide structure or the space group due to the missing superstructural diffraction from the interstitial C atoms. Barton and Gale assumed a stoichiometry of Fe₂C after the study by Hofer, Cohn and Peebles for their carbide.

Barton and Gale, however, calculated from their XRPD data that instead of having a purely hexagonal Fe lattice with lattice parameter $\gamma = 120^\circ$, their observed Fe carbide crystal lattice had a distortion from the Fe lattice hexagonality where $\gamma = 120.92^\circ$. This angle distortion accounting for the observed peak splitting in the X-ray diffraction patterns. As possible space group solutions for the crystal lattice, Barton and Gale gave trigonal $P\bar{3}m1$ (164), hexagonal $P6_3/mmc$ (194) and orthorhombic $Pbcn$ (60).¹²⁹

From tempering studies on martensitic steel, Hirotsu and Nagakura solved a Fe carbide crystal structure on the basis of its electron diffraction patterns,¹³¹ which resembled the earlier hexagonal ϵ -carbide (i.e. the ϵ -Fe₃C phase) observed by Hofer, Cohn and Peebles and Nagakura.^{62,69} However, the Fe carbide was different to Hofer, Cohn and Peeble's observations as the Fe lattice was not purely hexagonal but rather a pseudo-hexagonal one with the Fe lattice distorted from hexagonality. Hirotsu and Nagakura labelled their Fe carbide as η -Fe₂C with an orthorhombic space group $Pnnm$ (58) (**Figure 2.5**).¹³¹ The C atoms in η -Fe₂C structure occupy half of the octahedral interstitial spaces in the Fe lattice, in a regular manner.¹³¹ Hirotsu and Nagakura have proposed orthorhombic unit cell dimensions, after their η -Fe₂C phase, for the Fe carbide observed by Barton and Gale.¹³⁰

The crystal structures of the ϵ -Fe₃C and η -Fe₂C phases, with the unit cell by Hirotsu and Nagakura corresponding to the Barton and Gale's Fe carbide, are depicted in the **Figure 2.6**. Their hexagonal (in ϵ -Fe₃C) and distorted hexagonal (in η -Fe₂C) Fe lattice planes are in plane with the paper. The carbides indeed have very similar hexagonal Fe planes with differences of, that for i) η -Fe₂C $\gamma = 120.47^\circ$ instead of $\gamma = 120.0^\circ$ as for the purely hexagonal

Figure 2.5

The unit cell of the orthorhombic η -Fe₂C $Pnnm$ (58). The Fe lattice is distorted from hexagonality and the C atoms occupy half of the octahedral Fe lattice interstitial spaces in an ordered manner.

Figure 2.6

The crystal lattices of a) the hexagonal $\epsilon\text{-Fe}_3\text{C}$ $P6_322$ (182) viewed along the c -axis, b) the orthorhombic $\eta\text{-Fe}_2\text{C}$ $Pnnm$ (58) viewed along the b -axis, so that the (distorted-)hexagonal Fe planes are in plane with the paper. The $\eta\text{-Fe}_2\text{C}$ unit cell is after Hirotsu and Nagakura corresponding the Fe carbide by Barton and Gale.¹³⁰ **Blue, dashed line** – the respective unit cells for each crystal lattice, **Black, solid line** – In plane Fe atom positions used for measuring the lattice angle parameter γ . For the $\epsilon\text{-Fe}_3\text{C}$ $\gamma = 120.0^\circ$ i.e. the Fe lattice is hexagonal, while for $\eta\text{-Fe}_2\text{C}$ $\gamma = 120.47^\circ$ i.e. the Fe lattice is distorted from hexagonality. In the $\eta\text{-Fe}_2\text{C}$ lattice the interstitial Fe spaces are occupied by C to a higher degree than in the $\epsilon\text{-Fe}_3\text{C}$ lattice.

lattice of $\epsilon\text{-Fe}_3\text{C}$ and ii) there are no empty octahedral interstitial Fe lattice spaces in the lattice of $\eta\text{-Fe}_2\text{C}$. The crystal structures of $\epsilon\text{-Fe}_3\text{C}$ and $\eta\text{-Fe}_2\text{C}$ are similar and closely related.

That is, the orthorhombic structure of the $\eta\text{-Fe}_2\text{C}$ phase with the orthorhombic unit cell dimensions proposed by Hirotsu and Nakagura is a proper solution for the Fe carbide observed by Barton and Gale. It is the crystal structure for what is occasionally labelled in the literature as a pseudo-hexagonal ($\epsilon'\text{-Fe}_{2.2}\text{C}$ or Fe_2C) Fe carbide phase.^{60,132} The crystal structure for the $\eta\text{-Fe}_2\text{C}$ phase by Hirotsu and Nakagura is listed with database number 04-013-9510 in the ICDD-PDF-4+ 2016 database.

To summarize the discussion so far, the labelling of a Fe carbide in the FTS reaction as (ϵ)- Fe_2C phase is improper and should not be used further as there is no evidence that such a Fe carbide exists. What can be grouped as the “ ϵ -carbides” are two different carbides: $\epsilon\text{-Fe}_3\text{C}$ with hexagonal space group $P6_322$ (182) where the Fe lattice is purely hexagonal and C atoms occupy third of the octahedral Fe interstitial spaces in a random, disordered manner; $\eta\text{-Fe}_2\text{C}$ with orthorhombic space group $Pnnm$ (58) where the Fe lattice is distorted from the hexagonal symmetry and C atoms occupy half of the octahedral Fe interstitial spaces in a regular, ordered manner. A “pseudo-hexagonal Fe

carbide" either labelled as a Fe_2C or ε' - $\text{Fe}_{2.2}\text{C}$, should not be used to describe a Fe carbide with distorted Fe lattice but rather the orthorhombic η - Fe_2C should be used instead. The crystal lattice of the η - Fe_2C phase contains the distorted (pseudo-)hexagonal Fe lattice.

2.5.2 The Hägg Carbide (χ - Fe_5C_2)

The most commonly observed Fe carbide in the FTS reaction is the χ - Fe_5C_2 phase, which is mostly properly and consistently identified. The first observations of the Hägg carbide are from 1934,¹³³ and the carbide's crystal structure was later solved to be monoclinic, with a stoichiometry Fe_5C_2 .¹²⁵ Retief has further improved the accuracy of the structural solution over the years for the known χ - Fe_5C_2 phase with a monoclinic space group $C2/c$ (15) (**Figure 2.7**).¹³⁴ Du Plessis et al. have argued that the proper space group for the χ - Fe_5C_2 phase is not a monoclinic $C2/c$ (15) but a triclinic $P\bar{1}$ (2).¹³⁵ However, Leineweber et al. have explained the observations by du Plessis et al. being due to anisotropic microstrain broadening and the monoclinic $C2/c$ (15) space group should be regarded as the correct one for the Hägg carbide χ - Fe_5C_2 .¹³⁶ The crystal structure solved by Retief is a proper solution for the Hägg carbide χ - Fe_5C_2 and is listed in the ICDD-PDF-4+ 2016 database with number 00-051-0997. The crystal structure solutions provided by Leineweber et al. are also accurate for the Hägg carbide.¹³⁶

2.5.3 Cementite (θ - Fe_3C)

As being the most thermally stable Fe carbide,^{58,137} cementite θ - Fe_3C is - akin to χ - Fe_5C_2 - a well-studied and consistently identified Fe carbide phase. Already the early studies have identified the cementite θ - Fe_3C crystal structure

Figure 2.7

The unit cell of the monoclinic χ - Fe_5C_2 $C2/c$ (15) (the Hägg carbide).

Figure 2.8

The unit cell of the orthorhombic θ - Fe_3C $Pnma$ (62) (cementite).

with an orthorhombic space group *Pnma* (62).¹³⁸ Later, Wood et al. have applied Neutron Powder Diffraction (NPD) to further improve the cementite θ -Fe₃C structure solution. These experiments provide to date the most accurate crystal structural solutions for the θ -Fe₃C phase, at various temperatures.⁷⁰ The crystal structure of θ -Fe₃C by Wood et al., at room temperature, is available in the Crystallography Open Database (COD) with the database number 9014027 (**Figure 2.8**).¹³⁹

Figure 2.9
The unit cell of the orthorhombic θ -Fe₇C₃ *Pnma* (62) (the Eckström-Adcock carbide).

2.5.4 The Eckström-Adcock Carbide (θ -Fe₇C₃)

The Eckström-Adcock carbide is rather rarely observed in the FTS reaction but has been known to exist since the initial observations of a new carbide by Eckström and Adcock.¹⁴⁰ It may form during the FTS reaction after extended times under industrial high-pressure reaction conditions.³

The initial identification of the carbide observed by Eckström and Adcock was done as a hexagonal Fe₇C₃ with a space group *P6₃mc* (186) by Herbstein and Snyman.¹⁴¹ However, in later studies Fruchart et al. proposed the crystal structure of Fe₇C₃ to be an orthorhombic *Pnma* (62).¹⁴² In a single crystal ED study by Audier, Bowen and Jones, the orthorhombic space group was agreed over the hexagonal one.¹⁴³ The observed diffraction intensities were more accurately predicted by using an orthorhombic rather than a hexagonal crystal lattice for the Fe₇C₃ phase.¹⁴³ Therefore, the preferred crystal structure for the Eckström-Adcock carbide Fe₇C₃ has an orthorhombic space group *Pnma* (62) by Fruchart et al. (**Figure 2.9**).¹⁴² The orthorhombic crystal structure for the Fe₇C₃ phase is available in the ICDD-PDF-4+ database with the database number 04-002-8165.

To make the distinction and to avoid any confusion between the Fe₇C₃ crystal lattices, the orthorhombic Fe₇C₃ *Pnma* (62) is arbitrarily labelled as θ -Fe₇C₃ akin to same space group θ -Fe₃C. The use of various Greek prefix letters,¹⁴⁴ to name the Fe carbides is rather arbitrary and not systematic.

The crystal lattice details for the discussed Fe carbides observable in the FTS reaction research i.e. ε -Fe₃C, η -Fe₂C, χ -Fe₅C₂, θ -Fe₃C and θ -Fe₇C₃ are listed in the

Table 2.2

The crystal lattice details of the Fe carbides encountered in Fe-based Fischer-Tropsch (FTS) reaction with author references for the most accurate crystal structure solutions up-to-date. All lattice parameters are at room temperature. It is advised that the nomenclature of ϵ' -Fe_{2.2}C or (ϵ -)Fe₂C should not be used for describing any of the Fe carbides.

Fe Carbide Phase	Space Group	Lattice Parameters		Database Number	Author
		(Å)	(°)		
ϵ -Fe ₃ C	Hexagonal, P6 ₃ 22 (182)	a=4.767	α =90	04-008-9572	Nagakura (1959) [69]
		b=4.767	β =90		
		c=4.354	γ =120		
η -Fe ₂ C	Orthorhombic, Pnnm (58)	a=4.704	α =90	04-013-9510	Hirotsu (1972) [131]
		b=4.318	β =90		
		c=2.830	γ =90		
η -Fe ₂ C ^{a)}	Orthorhombic, Pnnm (58)	a=4.862	α =90	-	Hirotsu (1974) [130]
		b=4.360	β =90		
		c=2.755	γ =90		
χ -Fe ₅ C ₂	Monoclinic, C2/c (15)	a=11.588	α =90	00-051-0997	Retief (1999) [134]
		b=4.579	β =97.746		
		c=5.059	γ =90		
θ -Fe ₃ C	Orthorhombic, Pnma (62)	a=5.081	α =90	9014027 ^{b)}	Wood (2004) [70]
		b=6.754	β =90		
		c=4.515	γ =90		
θ -Fe ₇ C ₃	Orthorhombic, Pnma (62)	a=4.540	α =90	04-002-8165	Fruchart (1965) ^{c)} [142]
		b=6.879	β =90		
		c=11.942	γ =90		

a) Lattice parameters are translated according to Hirotsu and Nagakura,¹³⁰ to correspond the distorted Fe carbide observed by Barton and Gale.¹²⁹

b) Crystallography Open Database number.

c) The original article written in French by Fruchart et al. is not readily available but some discussion on the crystal structure can be found in publication by Audier, Bowen and Jones.¹⁴³

Table 2.2. The crystal structure solutions are available from the listed authors in **Table 2.2** and from the ICDD-PDF-4+ and COD databases. As a next step, the established nomenclature for the Fe carbides is expanded to the MAS literature. This is done for connecting the Fe carbide crystal lattices to observed hyperfine fields, which are used to fingerprint the various Fe carbides with MAS.

2.5.5 Fe Carbide Hyperfine Fields

Just as was the case with their X-ray and electron diffraction data based crystal lattice solutions, the literature data with various Fe carbides identified in FTS research with MAS can be challenging to follow due to the unclear nomenclature, as per author.

As based on the solved crystal structures for the Fe carbides, by the authors listed

in **Table 2.2**, the total count and the site ratios for the crystallographically non-equivalent Fe positions can be determined. Each non-equivalent Fe position should ideally give a distinct MAS hyperfine field component with fields' spectral contribution ratios following the non-equivalent Fe site ratios.¹⁴⁵ Determining the non-equivalent Fe positions from the crystal structures gives the ideal Fe site ratios as: i) the ϵ -Fe₃C and η -Fe₂C phases have one equivalent Fe position in their respective crystal structures (i.e. all Fe sites are ideally equivalent), ii) the χ -Fe₅C₂ phase has three non-equivalent Fe positions in ratio of 2:2:1, iii) the θ -Fe₃C phase has two non-equivalent Fe positions in ratio 2:1 and iv) the θ -Fe₇C₃ phase has five non-equivalent Fe positions in ratio 2:2:1:1:1. In the following, we shall assign the room-temperature hyperfine fields from experimental MAS data in literature, for each of the non-equivalent Fe positions for the Fe carbides listed in **Table 2.2**.

Le Caër et al. have discussed the MAS hyperfine field assignment of the “ ϵ -carbides” on the basis of experimental data gathered from literature.⁶¹ As Le Caër et al. note, the “ ϵ -carbides” can be grouped around two hyperfine field values of 24.5 ± 0.8 T and 17.2 ± 0.3 T (at room temperature). Furthermore, increasing the amount of interstitial C atoms in the Fe lattice decreases the measured hyperfine field.^{61,146–148} Thus, the field 24.5 ± 0.8 T belongs to a “ ϵ -carbide” with a low C content and the field 17.2 ± 0.3 T for a “ ϵ -carbide” with a higher C content. Recalling from the earlier discussion on the crystal structures of the Fe carbides: for the ϵ -Fe₃C phase third of the interstitial Fe lattice sites are occupied by C atoms while for the η -Fe₂C phase half of the interstitial sites are occupied by C. That is, the η -Fe₂C phase has the higher C content in its crystal structure. Therefore, the hyperfine field 24.5 ± 0.8 T is assigned for the one equivalent Fe site in the ϵ -Fe₃C crystal structure and 17.2 ± 0.3 T for the one Fe site in the η -Fe₂C phase. Occasionally, also an additional minor intensity hyperfine field ≈ 13.0 T has been assigned for “ ϵ -carbides”.^{61,149,150} However, whether this is correct and from where the low ≈ 13.0 T hyperfine field arises from, is uncertain. The two assigned hyperfine fields are the primary ones for the ϵ -Fe₃C and η -Fe₂C phases for correctly identifying the carbides.

The experimentally assigned, averaged hyperfine fields from the cited studies, for the Hägg carbide χ -Fe₅C₂ are the fields 21.4 ± 0.3 T, 18.1 ± 0.4 T and 10.9 ± 0.9 T with respective spectral contribution ratio of $\approx 2:2:1$.^{60,77,150,151} The spectral contribution ratio is in agreement with the expected non-equivalent Fe site ratios for the χ -Fe₅C₂ phase. In addition to the commonly assigned hyperfine fields, Barinov, Protasov and Surikov have proposed an additional field of ≈ 16.0 T to account for a possible anisotropy in the χ -Fe₅C₂ crystal structure.¹⁵¹ The proposal by Barinov, Protasov and Surikov perhaps could account for the earlier discussed anisotropy phenomena observed by Leineweber et al. for the χ -Fe₅C₂ phase.¹³⁶ However, whether or not such

Table 2.3

Mössbauer Absorption Spectroscopy (MAS) hyperfine field assignments based on the experimental literature data. The hyperfine fields are compared to the theoretically calculated values for the Fe carbides observable in the Fischer-Tropsch Synthesis (FTS) reaction research.

Fe Carbide Phase	Space Group	Non-equivalent Fe Positions ^{a)}		Hyperfine Field (at room temperature)	
		Tot. Count	Rel. Ratio	Experimental ^{b)}	Theoretical ^{c)}
				(T)	(T)
Hexagonal,					
ϵ -Fe ₃ C	P6 ₃ 22 (182)	1	1	24.5±0.8	N/A
Orthorhombic,					
η -Fe ₂ C	Pnnm (58)	1	1	17.2±0.3	18.0 ^{d)}
Monoclinic,					
χ -Fe ₅ C ₂	C2/c (15)	3	2	21.4±0.3	23.7
			2	18.1±0.4	20.9
			1	10.9±0.9	14.0
Orthorhombic,					
θ -Fe ₃ C	Pnma (62)	2	(2)	20.8±0.3	24.4
			(1)	20.0±0.3	23.7
			Avg. ^{e)}	20.8±0.5	
Orthorhombic,					
θ -Fe ₇ C ₃	Pnma (62)	5	(2)	22.9±0.1	22.9
			(2)	-	22.9
			(1)	18.5±0.1	18.7
			(1)	16.3±0.1	17.4
			(1)	(21.0) ^{f)}	19.9

a) Determined on the basis of the crystal structures from authors in **Table 2.2**. The nominal relative ratios in parentheses () could not be conclusively assigned.

b) Mean hyperfine fields from the experimental literature data with their Standard Deviations (STDs).

c) Theoretical calculations by Liu et al. from reference [148]. No calculations were performed for the structure corresponding to Nagakura's ϵ -Fe₃C phase.⁶⁹

d) Based on the unit cell of η -Fe₂C (#04-013-9510) from reference [131].

e) Commonly, a single (averaged) hyperfine field is used for the θ -Fe₃C phase in the experimental literature data.

f) The assignment of hyperfine field 21.0 T for the θ -Fe₇C₃ phase is uncertain.

anisotropy is present, the three assigned hyperfine fields are sufficient for identifying the χ -Fe₅C₂ phase.

The experimentally assigned, averaged hyperfine fields for cementite θ -Fe₃C can be obtained from studies by Bi et al. and Kniep et al. and have values of 20.8±0.3 T and 20.0±0.3 T.^{152,153} However, as the values are very close to each other, commonly only one average hyperfine field value of 20.8±0.5 T is used for the MAS fitting of θ -Fe₃C.^{60,127,154,155} Neither Bi et al. nor Kniep et al. report the MAS-based relative spectral contribution areas for the θ -Fe₃C assigned hyperfine fields. Thus, how the crystallographically expected 2:1 non-equivalent Fe site ratio is assigned to the

hyperfine fields, is unclear for the time being for the θ -Fe₃C phase.

The assignment of the hyperfine fields from the experimental literature data for the θ -Fe₇C₃ phase is problematic as the carbide is less often observed than the other carbides, and therefore less studied. For the orthorhombic crystal lattice of the θ -Fe₇C₃ phase, five non-equivalent Fe sites are expected with corresponding hyperfine fields. However, only three fields have been experimentally assigned so far in the literature. Averaging the hyperfine fields from the studies of Bi et al. and Yamada et al. gives field assignments as 22.9 ± 0.1 T, 18.5 ± 0.1 T and 16.3 ± 0.1 T.^{152,155} Bi et al. have also assigned a fourth field for their (θ -)Fe₇C₃ phase as 21.0 T which might belong to the θ -Fe₃C impurity from the sample synthesis.¹⁵²

In a theoretical MAS study, Liu et al. have predicted the hyperfine fields of 22.9 T, 22.9 T, 19.9 T, 18.7 T and 17.4 T for the orthorhombic θ -Fe₇C₃ phase.¹⁴⁸ The assignments by Liu et al. are relatively close to the experimental assignments by Bi et al.¹⁵² That is, if the hyperfine field 21.0 T is assumed belonging to the θ -Fe₇C₃ phase rather than an impurity θ -Fe₃C phase and if the same field of 22.9 T is indeed assignable for two non-equivalent Fe positions. Bi et al. considered the Fe₇C₃ phase to only have three non-equivalent Fe sites,¹⁵² as based on the hexagonal Fe₇C₃ structure by Herbstein and Snyman.¹⁴¹ However, as discussed earlier, the hexagonal crystal lattice for the Fe₇C₃ phase is not a fully satisfactory crystal structure solution as based on the diffraction studies. The orthorhombic θ -Fe₇C₃ crystal structure should be used instead.¹⁴³ None of the cited studies assigns spectral contribution ratios for the assigned hyperfine fields for the θ -Fe₇C₃ phase. Therefore, the hyperfine fields corresponding to the specific non-equivalent Fe sites cannot be definitively identified from the literature for the θ -Fe₇C₃ phase at the moment.

To conclude, the MAS hyperfine field assignments for the θ -Fe₇C₃ phase are uncertain at the moment. However, as based on both experimental and theoretical data, the possible field assignments for the expected five sites for the orthorhombic θ -Fe₇C₃ phase are: 22.9 ± 0.1 T twice, 18.5 ± 0.1 T and 16.3 ± 0.1 T, with the field 21.0 T being uncertain. The hyperfine field spectral contribution ratios corresponding to the non-equivalent Fe site ratios are unassigned.

The assigned hyperfine fields for MAS fingerprinting of the Fe carbides encountered in the FTS reaction research, as based on the experimental literature data, are summarized in the **Table 2.3**. Hyperfine fields based on theoretical calculations by Liu et al., are reproduced in the table for comparison.¹⁴⁸

2.5.6 Formation of the Fe Carbides

Fe carbides form by dissolution of C into the interstitial spaces in the α -Fe lattice. The formation of the various Fe carbides is primarily dependent on the temperature where

Figure 2.10

Collected observation regions (*solid fill*) of the Fe carbides as temperature versus treatment exposure time from experimental literature data. θ -Fe₇C₃ data points are excluded. Data points are collected according to the criteria presented in the text.

the α -Fe lattice is exposed to an available source of C. Fe in Fe carbides has a valency state close to zero, as for example in the χ -Fe₅C₂ phase.¹²³ If a Fe oxide is used as a Fe carbide precursor, it needs to be reduced prior/simultaneously to a zero Fe valency state during the Fe carbide formation.

Fe carbides can form from α -Fe by i) gas phase carburization where e.g. the CO, either from pure CO or H₂:CO, acts as the C source,^{58,60} ii) heat treating the pre-formed Fe carbides to interchange the carbide phases,^{58,69,77} and iii) tempering (i.e. heat treating) pre-formed martensite (or austenite) resulting in Fe carbide precipitation.^{137,156} The ϵ -Fe₃C, η -Fe₂C, χ -Fe₅C₂ and θ -Fe₃C phases form relatively easily from an α -Fe/martensite precursor with any of the listed methods, i.e. by varying the heat treatment or gas phase carburization temperature. The formation of the θ -Fe₇C₃ phase seems to be a more complex phenomenon, as based on the available literature. It will be discussed separately after the formation conditions of the more common Fe carbides.

The observation temperatures for the ϵ -Fe₃C, η -Fe₂C, χ -Fe₅C₂ and θ -Fe₃C phases from the literature are gathered with the following criteria: i) the reaction takes place from metallic, zero valency α -Fe, in order to decouple the Fe reduction/carburization effects, ii) reaction treatment time is reported, and iii) it is possible to re-evaluate the reported data to correspond the nomenclature defined in **Table 2.2** and **Table 2.3**. From criteria iii) follows that only MAS- and ED-based results are included to evaluate the presence of the ϵ -Fe₃C and η -Fe₂C phases. XRPD and Thermomagnetic (TM) data are

Table 2.4

The references to the experimental literature data for the Fe carbide observations, excluding the θ -Fe₇C₃ phase, and adhering to the criteria presented in the main text. The data points from the references are collected to the **Figure 2.10**.

Fe Carbide Phase	Characterization Technique	Experiment Type	Reference Numbers
ε -Fe ₃ C	ED, MAS	- Gas phase carburization - Martensite tempering	[26,59,66,69,77,127,149,150,157,158]
η -Fe ₂ C	ED, MAS	- Gas phase carburization - Martensite tempering	[26,27,150,158,59,60,66,77,92,127,130,149]
χ -Fe ₅ C ₂	ED, MAS, XRPD	- Gas phase carburization - Martensite tempering - Carbide Heat Treatment	[35,58,157,159,60,66,69,76,77,92,135,150]
θ -Fe ₃ C	ED, MAS, XRPD, TM	- Gas phase carburization - Martensite tempering - Carbide Heat Treatment	[60,69,160,161]

ED = Electron Diffraction, MAS = Mössbauer Absorption Spectroscopy, XRPD = X-ray Powder Diffractometry, TM = Thermomagnetic.

also included for evaluating the χ -Fe₅C₂ and θ -Fe₃C phases' formation behavior. The references to the studies used to collect the data points in **Figure 2.10** are collected to **Table 2.4**.

The collected data points in **Figure 2.10** refer to the experimental observations on the Fe carbides after respective Fe carbide forming treatment. Possibly coexisting phases of α -Fe, martensite or Fe oxides are excluded from the figure. From the literature-based data points in **Figure 2.10**, the expected observation temperatures and carbide-to-carbide transition temperatures for the Fe carbides with 5 h treatment time can be roughly estimated as:

$$\varepsilon\text{-Fe}_3\text{C} (100\text{-}265^\circ\text{C}) < \eta\text{-Fe}_2\text{C} (160\text{-}350^\circ\text{C}) < \chi\text{-Fe}_5\text{C}_2 (240\text{-}350^\circ\text{C}) < \theta\text{-Fe}_3\text{C} (310\text{-}600^\circ\text{C})$$

These expectations on the Fe carbide thermal stabilities and the formation temperatures compare mainly well with the expectations presented by other authors.^{58,69,128,137,156} This, while bearing in mind the unclear nomenclature in the literature regarding the “ ε -carbides” i.e. the identification of the ε -Fe₃C and η -Fe₂C phases.

A good example on the behavior of the ε -Fe₃C and η -Fe₂C phases is from a study by Boellaard, van der Kraan and Geus.²⁶ With the FTS reaction experiments at reaction temperatures between 200-275°C, either increasing the reaction time or the temperature caused Fe carbide formation to shift from the ε -Fe₃C towards η -Fe₂C phase. Already at $\approx 200^\circ\text{C}$ with ≈ 1 h reaction time, the η -Fe₂C phase is the Fe carbide to

form in larger quantities over the ϵ -Fe₃C phase. With further increasing the reaction time or temperature, the η -Fe₂C phase content increases.²⁶ In a martensite tempering study by Williamson, Nakazawa and Krauss,¹²⁷ at 200°C the ϵ -Fe₃C phase (component M2 in their study) disappears if the tempering time is increased above 1 h. At temperatures <150°C, ϵ -Fe₃C is stable and is able to withstand longer tempering times.¹²⁷ In short, the ϵ -Fe₃C phase is the least stable Fe carbide that easily transforms to the η -Fe₂C phase, with increasing treatment time or temperature. Minor quantities of the ϵ -Fe₃C phase may nevertheless be observed with temperatures up to 250-270°C.^{26,59,66,150,157}

Within the temperature range of $\approx$ 240-350°C, both of the η -Fe₂C and χ -Fe₅C₂ phases may coexist. For these carbides the reaction exposure time seems to be less influential than in the case of relative formation of the ϵ -Fe₃C and η -Fe₂C phases. For at least up to 50 h in the FTS reaction at 300°C, both the η -Fe₂C and χ -Fe₅C₂ phases can be observed, although at the higher temperatures the χ -Fe₅C₂ phase becomes the Fe carbide to form in higher quantities.⁹³ After a short 3 h FTS reaction, Niemantsverdriet et al. were able to observe low quantities of the η -Fe₂C phase even at 350°C, while the χ -Fe₅C₂ and θ -Fe₃C phases were the major Fe carbide phases.⁶⁰ Also, after a 24 h FTS reaction at 340°C, Wezendonk et al. observed a significant presence of the η -Fe₂C phase.⁷⁷

Few catalyst composition properties are known to increase the stability of the ϵ -Fe₃C or η -Fe₂C phases (i.e. “ ϵ -carbides”) in relation to the χ -Fe₅C₂ phase. Addition of i) alkali, as at least if added as Na or K,^{29,56,64,162} or ii) Si as an inert oxide,^{61,72,150} to the Fe catalyst composition can stabilize the ϵ -Fe₃C and/or η -Fe₂C phase(s). Also, iii) smaller Fe particle size tends to favor the formation of the ϵ -Fe₃C and/or η -Fe₂C phases over the χ -Fe₅C₂.^{60,150,158,159} Unfortunately, from the literature it is not possible to conclusively determine which of the “ ϵ -carbides” i.e. ϵ -Fe₃C and/or η -Fe₂C is stabilized, in relation to the mentioned catalyst composition properties.

Above the temperature of $\approx$ 300-350°C, the χ -Fe₅C₂ and θ -Fe₃C phases are the expected main Fe-carbide phases. The highest temperature stability for the χ -Fe₅C₂ phase included in this review, has been observed to be up to $\approx$ 400°C from a martensite tempering study.¹⁵⁶ Also, the χ -Fe₅C₂ phase has been observed after heat treating of preformed Fe carbides under vacuum at 400°C for short periods of time ($\approx$ 0.1 h).⁶⁹ Above 350°C, the preferred Fe carbide to form is θ -Fe₃C.^{60,69,160,161}

From martensite tempering studies, Nagakura et al. have reported formation of θ -Fe₃C after tempering martensitic steel at 267° for 1 h,¹⁵⁶ and Williamson, Nakazawa and Krauss after 250°C for 5 h.¹²⁷ Both of these temperatures seem very low for θ -Fe₃C formation when comparing to the other literature data, and are excluded from the **Figure 2.10**.

Decomposition of the θ -Fe₃C phase into α -Fe and C under vacuum heat treatment

may start already slowly at a temperature as low as 377°C and becomes rapid at >527°C as has been observed by Wood et al.⁷⁰ Nagakura in comparison observed that the θ -Fe₃C decomposition to α -Fe only started at $\approx$ 600°C under vacuum heat treatment.⁶⁹ The increase in the most thermally stable Fe carbide's (i.e. θ -Fe₃C) decomposition temperature has been explained by Podgurski et al. to be due to formed Fe carbide oxidation shell.³⁰ The shell can retard the decomposition of the θ -Fe₃C core to α -Fe and C. The Fe carbides readily form a $\approx$ 4-5 nm oxidation layer if any O is available for the oxidation reaction.¹⁶³

As mentioned, the main Fe carbide phase determining factor is the temperature. For gas phase carburization, factors such as H₂:CO ratio and reaction pressure do not seem to play a significant role when the Fe carbides are formed from a zero valency α -Fe.

For example, with the FTS reaction at 250°C with H₂:CO ratios of 1:1 (0.5 h),⁵⁹ 2:1 (1.1 h),²⁶ and 3:1 (0.66 h),¹⁵⁰ only the ϵ -Fe₃C (minor phase) and the η -Fe₂C (major phase) phases are observed along with differences in the extent of α -Fe carburization. At 270°C after 0.66 h of FTS reaction with 10:1 H₂:CO, Tau et al. observed formation of the χ -Fe₅C₂ phase in addition to the ϵ -Fe₃C and η -Fe₂C phases from α -Fe,⁶⁶ as would be expected on the basis of the reaction temperature (**Figure 2.10**). In a systematic study, Jung et al. have observed that the increasing H₂:CO ratio decreases the rate of carburization of α -Fe.¹⁵⁹ Despite the CO-rich atmosphere being favored for the increased carburization rate, small amounts of ($\approx$ 1 %) H₂ can still aid the carburization by more efficiently, than CO, removing the surface O from CO dissociation,^{33,50} as was also discussed in the previous sections. All in all, despite the changing H₂:CO ratios, the reaction temperature is still the determining factor for the Fe carbide formation. Low H₂:CO ratios increase the α -Fe carburization rate in comparison to the higher H₂:CO ratios or pure CO.

It is, however, noteworthy to mention that when carburization with H₂:CO is done with a *Fe oxide* as the starting material *instead of α -Fe*, the Fe carbide formation is dependent on the simultaneous Fe reduction behavior.^{64,67,78,164,165} This effect will be discussed more in the **Chapter 3**.

The effect of the overall reaction pressure under which the α -Fe phase is carburized from the gas phase is somewhat unclear from the literature, as systematic studies are lacking. It seems, however, that the increased pressure does not change the expected order of the Fe carbide formation, again, when *the carburization is done from the α -Fe*. Amelse et al. performed 300°C FTS reaction (H₂:CO 3:1) for 24 h at atmospheric pressure,¹⁵⁷ and Jiang et al. 300°C FTS reaction (H₂:CO 1:1) at 10 bar pressure for 50 h.⁹³ In both studies, only the η -Fe₂C and χ -Fe₅C₂ phases were observed as the Fe carbides. After 30 bar FTS reaction (H₂:CO 2:1) for 0.3 h at 170°C, Xu et al. observed only the ϵ -Fe₃C and η -Fe₂C phases as the Fe carbides.¹⁴⁹ With 23 bar FTS reaction (H₂:CO 3:2) at

235°C for 12 h, only ϵ -Fe₃C and η -Fe₂C phases were present in a study by Wang et al.,¹⁵⁸ which is a quantification result comparable to 1.03 bar FTS reaction (3.9 h, 250°C, H₂:CO 2:1) by Boellaard, van der Kraan and Geus.²⁶

In each of the mentioned studies, the Fe carbide formation follows the expectations from the reaction temperature regardless of the applied reaction pressure. As noted by Xu et al., the elevated pressure only seems to increase the rate of carburization from α -Fe (see Supplementary Figure 2, in their study).¹⁴⁹ The formed Fe carbide phases, however, are not affected.

2.5.6.1 Formation of θ -Fe₇C₃

The formation of the θ -Fe₇C₃ phase is a special case and does not follow the temperature formation regions in **Figure 2.10**. In literature, the θ -Fe₇C₃ phase is either observed to form at extreme conditions, such as at 60 kbar with >1100°C from a mixture of graphite and α -Fe,¹⁶⁶ or via laser pyrolysis of Fe(CO)₅ under C₂H₂/4.^{152,155,167}

A more interesting case for the FTS reaction related discussion in the realm of θ -Fe₇C₃ formation is observed in a study by Tajima and Hirano, where Ba promoted Fe₃O₄ was carburized with pure CO at unspecified reaction pressure.¹⁶⁸ Within the temperature range of 300-375°C, the Ba-Fe₃O₄ carburized to a mixture of the χ -Fe₅C₂ and θ -Fe₇C₃ phases.¹⁶⁸ Without Ba, only the χ -Fe₅C₂ phase was formed within the same temperature range from the unpromoted Fe₃O₄.^{168,169} In a single crystal ED study of the θ -Fe₇C₃ phase by Audier, Bowen and Jones, single crystals of the θ -Fe₇C₃ phase were formed by carburizing the α -Fe phase under 3:1 CO:CO₂ at 500°C.¹⁴³ As the carburization to, at least some amounts of, the θ -Fe₇C₃ phase took place without Ba or a Fe oxide, perhaps, the CO₂ might play a role in facilitating the formation of the θ -Fe₇C₃ phase. The θ -Fe₇C₃ phase has also been observed in catalysts extracted from industrial FTS reactors after long reaction times at high-pressure.³

A mechanical synthesis route for the θ -Fe₇C₃ phase has been attempted by Barinov, Tsurin and Surikov.¹⁷⁰ The route has more likely to have only formed the χ -Fe₅C₂ phase,¹⁵¹ rather than any observable quantities of the θ -Fe₇C₃ phase.

Regarding the θ -Fe₇C₃ phase thermal stability, heat treatment of the θ -Fe₇C₃ phase under He leads to the phase's decomposition with temperature depending on the O atom impurity content in the θ -Fe₇C₃ crystal lattice.¹⁶⁷ High O atom impurity content causes the θ -Fe₇C₃ phase to decompose to Fe oxides and α -Fe between 300-400°C. O atom free θ -Fe₇C₃ phase can survive up to $\approx$ 400-500°C before decomposing directly to α -Fe and C atoms.¹⁶⁷

To conclude, the formation of the θ -Fe₇C₃ phase does not follow the same route as for the ϵ -Fe₃C, η -Fe₂C, χ -Fe₅C₂ or θ -Fe₃C phases but might have its own formation route. Nevertheless, formation of the θ -Fe₇C₃ phase is possible under relatively mild and FTS

reaction relevant conditions, although more systematic research is warranted on its formation specifics.

2.6 SUMMARY

The main points from the discussion in this Chapter can be summarized as follows for each of the Chapter sections:

Catalyst Compositions

A FTS reaction catalyst is most commonly comprised of the active metal (commonly as either Fe or Co), possibly in combination with chemical (alkali, possibly combined with S) and structural (inert oxides of e.g. Al, Si or Mg) promoters. Instead of a structural promoter, as with precipitated or fused bulk catalyst materials, a support material (e.g. Al_2O_3 or SiO_2) can be used instead. The support material is impregnated with a FTS reaction active metal in order to obtain the metal in a highly dispersed form on the ready catalyst.

Reactions, Fe Phase Changes and Catalyst Deactivation

In Fe-based FTS reaction, C atoms from input CO have five pathways to react (**Figure 2.1**). More specifically, C from CO dissociation can react i) with α -Fe to form Fe carbides, ii) with H from dissociated H_2 to form hydrocarbons, iii) with another C to form inactive carbon. Without CO dissociation, CO may iv) reduce Fe_xO_y or v) react via the WGS reaction, with both pathways converting CO into CO_2 . The phase transformations for a Fe-based FTS reaction catalyst material go from a Fe oxide in the as-synthesized catalyst, to α -Fe in pre-reduced state, to Fe_xC phases under FTS reaction conditions. As deactivation pathways: the Fe_xC phases may reoxidize to Fe_3O_4 under FTS reaction conditions if the local $\text{H}_2\text{O}:\text{H}_2$ or $\text{CO}_2:\text{CO}$ ratios become too high. The Fe_3O_4 phase is active for the WGS but not for the FTS reaction. The formation of inactive carbon via pathway iii) causes hindered access to the active Fe_xC surface and loss of catalyst's mechanical stability via fragmentation. The process decreases catalyst's life-time in the FTS reaction.

Hydrocarbon and C Pathway Selectivity

Adjustment of the process conditions and/or the catalyst material compositions can be used as tools for modifying the Fe-based FTS reaction's hydrocarbon and C pathway selectivities (**Table 2.1**). Input $\text{H}_2:\text{CO}$ ratio, reaction temperature and reactor space velocity are the main process parameters for modifying the α -value or olefin content of the FTS produced hydrocarbons. The reaction temperature

greatly increases the inactive carbon deposition C pathway above $\approx 300^\circ\text{C}$. Increasing temperature also increases any possible WGS reaction activity via the reaction kinetics. Addition of alkali individually increases the α -value and olefin content, while individual addition of S does the opposite. Addition of combined alkali-S in the molar ratio of $\approx 2:1$: increases the α -value less than with alkali only addition, and as a unique alkali-S promotion feature, it also decreases the CH_4 selectivity to a value lower than expected from the ASF distribution. The hydrocarbon products' olefin content increases with the alkali-S addition akin to alkali-only addition. Possibly, the S replaces O as the alkali counter-ion changing the chemical promoter compound binding on the Fe_xC surface and affecting the promotion effects with alkali-S. On the C pathways: added alkali increases the inactive carbon deposition and WGS reactions, decreasing CO conversion towards FTS reaction hydrocarbon products. Effect of individual S on C pathways is unclear. Increased CO_2 selectivity suggests increased carbon formation and/or WGS reaction C pathways for alkali-S promoted catalysts, effects that are akin to alkali-only addition.

Fe carbides in the Fischer-Tropsch Synthesis Reaction

Fe carbides (Fe_xC , $x = 2-3$) are the active phases in the Fe-based FTS reaction. The Fe carbides, which may form in the FTS reaction, with their respective crystal lattice space groups, are: hexagonal $\epsilon\text{-Fe}_3\text{C}$ $P6_322$ (182), orthorhombic $\eta\text{-Fe}_2\text{C}$ $Pnnm$ (58), monoclinic $\chi\text{-Fe}_5\text{C}_2$ $C2/c$ (15) (the Hägg carbide), orthorhombic $\theta\text{-Fe}_3\text{C}$ $Pnma$ (62) (cementite) and orthorhombic $\theta\text{-Fe}_7\text{C}_3$ $Pnma$ (62) (the Eckström-Adcock carbide) (**Table 2.2**). The $\epsilon\text{-Fe}_3\text{C}$ phase has a purely hexagonal Fe lattice with C atoms occupying a third of the octahedral interstitial Fe lattice spaces in a random manner. The $\eta\text{-Fe}_2\text{C}$ phase has a distorted (pseudo-)hexagonal Fe lattice where C atoms occupy half of the octahedral interstitial Fe lattice spaces, in an ordered manner. Nomenclature of $(\epsilon\text{-})\text{Fe}_2\text{C}$ or $\epsilon'\text{-Fe}_{2.2}\text{C}$ should not be used to label the Fe “ ϵ -carbides”. The hexagonal Fe_7C_3 is should not be used to identify the $\theta\text{-Fe}_7\text{C}_3$ phase as the correct structure is orthorhombic rather than a hexagonal Fe_7C_3 . The MAS hyperfine fields are assigned in the **Table 2.3** from the literature following the established nomenclature.

The observed temperature regions for the identified Fe carbides from a zero valency $\alpha\text{-Fe}$ precursor are plotted in **Figure 2.10** by using the experimental data collected from the literature. The literature-based thermal stabilities of the Fe carbides are in order $\epsilon\text{-Fe}_3\text{C}$ ($100\text{-}265^\circ\text{C}$) < $\eta\text{-Fe}_2\text{C}$ ($160\text{-}340^\circ\text{C}$) < $\chi\text{-Fe}_5\text{C}_2$ ($240\text{-}350^\circ\text{C}$) < $\theta\text{-Fe}_3\text{C}$ ($310\text{-}600^\circ\text{C}$). The temperature range in parenthesis refers to the estimated observation temperature limits for the carbides at 5 h treatment

exposure time (**Figure 2.10**). The θ -Fe₇C₃ phase has a different formation route in comparison to the other Fe carbides and it may form under relatively mild, FTS reaction relevant conditions. Such as, if a Ba-Fe₃O₄ catalyst is carburized with CO between 300-375°C, or α -Fe is carburized with CO:CO₂ at 500°C. Other formation pathways for the θ -Fe₇C₃ phase require extreme conditions (laser pyrolysis or 60 kbar with >1100°C).

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2.8 REFERENCES

- [1] Vannice, M. A., "The catalytic synthesis of hydrocarbons from H₂/CO mixtures over the group VIII metals I. The specific activities and product distributions of supported metals", *J. Catal.* **37**, 449–461 (1975).
- [2] Mittasch, A. and Schneider, C., "Producing Compounds Containing Carbon and Hydrogen", Patent US1201850A (1916).
- [3] Dry, M. E., "The Fischer-Tropsch Synthesis" in *Catalysis - Science and Technology* (eds. Anderson, J. R. & Boudart, M.) **1**, 159–256 (Springer-Verlag, Berlin, 1981).
- [4] de Smit, E. and Weckhuysen, B. M., "The renaissance of iron-based Fischer–Tropsch synthesis: on the multifaceted catalyst deactivation behaviour", *Chem. Soc. Rev.* **37**, 2758–2781 (2008).
- [5] Dry, M. E., "High quality diesel via the Fischer-Tropsch process - a review", *J. Chem. Technol. Biotechnol.* **77**, 43–50 (2001).
- [6] Dry, M. E., "The Fischer–Tropsch process: 1950–2000", *Catal. Today* **71**, 227–241 (2002).
- [7] Enger, B. C. and Holmen, A., "Nickel and Fischer-Tropsch Synthesis", *Catal. Rev.* **54**, 437–488 (2012).
- [8] Brynestad, J., "Iron and nickel carbonyl formation in steel pipes and its prevention: literature survey", (Oak Ridge, TN (United States), 1976). DOI:10.2172/7349456 Available at: http://www.osti.gov/bridge/product.biblio.jsp?osti_id=7349456 (Accessed: September 2015).
- [9] Dry, M. E., "Chemical concepts used for engineering purposes" in *Studies in Surface Science and Catalysis - Fischer-Tropsch Technology* (eds. Steynberg, A. P. & Dry, M. E.) **152**, 196–257 (Elsevier B.V., Amsterdam, 2004).
- [10] Maitlis, P. M. and de Klerk, A., "Greener Fischer-Tropsch Processes for Fuels and Feedstocks", (Wiley-VCH, Weinheim, 2013). DOI:10.1002/9783527656837
- [11] Ngantsoue-Hoc, W., Zhang, Y., O'Brien, R. J., Luo, M. and Davis, B. H., "Fischer–Tropsch synthesis: activity and selectivity for Group I alkali promoted iron-based catalysts", *Appl. Catal. A Gen.* **236**, 77–89 (2002).
- [12] Luo, M. and Davis, B. H., "Fischer–Tropsch synthesis: Group II alkali-earth metal promoted catalysts", *Appl. Catal. A Gen.* **246**, 171–181 (2003).
- [13] Dry, M. E. and Oosthuizen, G. J., "The correlation between catalyst surface basicity and hydrocarbon

- selectivity in the Fischer-Tropsch synthesis*", *J. Catal.* **11**, 18–24 (1968).
- [14] Dry, M. E., Shingles, T. and van H. Botha, C. S., "Factors influencing the formation of carbon on iron Fischer-Tropsch catalysts I. The influence of promoters", *J. Catal.* **17**, 341–346 (1970).
- [15] Hutchings, G. J., "Promotion in Heterogeneous Catalysis: A Topic Requiring a New Approach?", *Catal. Lett.* **75**, 1–12 (2001).
- [16] Johnson, J. Y., "Improvements in the Manufacture and Production of Unsaturated Hydrocarbons of Low Boiling Point", Patent GB322284A (1929).
- [17] Myddleton, W. W., "Improvements Relating to the Catalytic Synthesis of Hydrocarbon Oils from Gaseous Mixtures of Carbon Monoxide and Hydrogen", Patent GB509325A (1939).
- [18] Crous, R., Bromfield, T. C. and Booyens, S., "Olefin Selective FT Catalyst Composition and Preparation Thereof", Patent WO2010066386A1 (2010).
- [19] Botes, G. F., Bromfield, T. C., Coetzer, R. L. J., Crous, R., Gibson, P. and Ferreira, A. C., "Development of a chemical selective iron Fischer Tropsch catalyst", *Catal. Today* **275**, 40–48 (2016).
- [20] Torres Galvis, H. M., Bitter, J. H., Khare, C. B., Ruitenbeek, M., Dugulan, A. I. and de Jong, K. P., "Supported Iron Nanoparticles as Catalysts for Sustainable Production of Lower Olefins", *Science* **335**, 835–838 (2012).
- [21] Xie, J., Torres Galvis, H. M., Koeken, A. C. J., Kirilin, A., Dugulan, A. I., Ruitenbeek, M. and de Jong, K. P., "Size and Promoter Effects on Stability of Carbon-Nanofiber-Supported Iron-Based Fischer–Tropsch Catalysts", *ACS Catal.* **6**, 4017–4024 (2016).
- [22] Butt, J. B., "Carbide phases on iron-based Fischer-Tropsch synthesis catalysts part I: Characterization studies", *Catal. Lett.* **7**, 61–82 (1990).
- [23] Butt, J. B., "Carbide phases on iron-based Fischer-Tropsch synthesis catalysts part II: Some reaction studies", *Catal. Lett.* **7**, 83–106 (1990).
- [24] Falkenhagen, J. P., Maisonneuve, L., Paalanen, P. P., Coste, N., Malicki, N. and Weckhuysen, B. M., "Cobalt-Iron-Manganese Catalysts for the Conversion of End-of-Life-Tire-Derived Syngas into Light Terminal Olefins", *Chem. Eur. J.* **24**, 4597–4606 (2018).
- [25] Torres Galvis, H. M. and de Jong, K. P., "Catalysts for Production of Lower Olefins from Synthesis Gas: A Review", *ACS Catal.* **3**, 2130–2149 (2013).
- [26] Boellaard, E., van der Kraan, A. M. and Geus, J. W., "Behaviour of a cyanide-derived Fe/Al₂O₃ catalyst during Fischer-Tropsch synthesis", *Appl. Catal. A Gen.* **147**, 229–245 (1996).
- [27] Amelse, J. A., Butt, J. B. and Schwartz, L. H., "Carburization of supported iron synthesis catalysts", *J. Phys. Chem.* **82**, 558–563 (1978).
- [28] van der Laan, G. P. and Beenackers, A. A. C. M., "Kinetics and Selectivity of the Fischer–Tropsch Synthesis: A Literature Review", *Catal. Rev.* **41**, 255–318 (1999).
- [29] Dictor, R. and Bell, A. T., "Fischer-Tropsch synthesis over reduced and unreduced iron oxide catalysts", *J. Catal.* **97**, 121–136 (1986).
- [30] Podgurski, H. H., Kummer, J. T., DeWitt, T. W. and Emmett, P. H., "Preparation, Stability and Adsorptive Properties of the Carbides of Iron", *J. Am. Chem. Soc.* **72**, 5382–5388 (1950).
- [31] Davis, B. H., "Fischer–Tropsch Synthesis: Reaction mechanisms for iron catalysts", *Catal. Today* **141**, 25–33 (2009).
- [32] de Klerk, A., "Indirect Liquefaction Carbon Efficiency" in *Synthetic Liquids Production and Refining* (eds. de Klerk, A. & King, D.) **1084**, 215–235 (American Chemical Society, Washington, DC, 2011).
- [33] Krishnamoorthy, S., Li, A. and Iglesia, E., "Pathways for CO₂ Formation and Conversion During Fischer–Tropsch Synthesis on Iron-Based Catalysts", *Catal. Lett.* **80**, 77–86 (2002).

- [34] Niemantsverdriet, J. W. and van der Kraan, A. M., "On the time-dependent behavior of iron catalysts in Fischer-Tropsch synthesis", *J. Catal.* **72**, 385–388 (1981).
- [35] Riedel, T., Schulz, H., Schaub, G., Jun, K.-W., Hwang, J.-S. and Lee, K.-W., "Fischer-Tropsch on Iron with H_2/CO and H_2/CO_2 as Synthesis Gases: The Episodes of Formation of the Fischer-Tropsch Regime and Construction of the Catalyst", *Top. Catal.* **26**, 41–54 (2003).
- [36] Rhodes, C., Hutchings, G. J. and Ward, A. M., "Water-gas shift reaction: finding the mechanistic boundary", *Catal. Today* **23**, 43–58 (1995).
- [37] Ratnasamy, C. and Wagner, J. P., "Water Gas Shift Catalysis", *Catal. Rev.* **51**, 325–440 (2009).
- [38] Raje, A. P., O'Brien, R. J. and Davis, B. H., "Effect of Potassium Promotion on Iron-Based Catalysts for Fischer-Tropsch Synthesis", *J. Catal.* **180**, 36–43 (1998).
- [39] Chianese, S., Loipersböck, J., Malits, M., Rauch, R., Hofbauer, H., Molino, A. and Musmarra, D., "Hydrogen from the high temperature water gas shift reaction with an industrial Fe/Cr catalyst using biomass gasification tar rich synthesis gas", *Fuel Process. Technol.* **132**, 39–48 (2015).
- [40] Fischer, N., Henkel, R., Hettel, B., Iglesias, M., Schaub, G. and Claeys, M., "Hydrocarbons via CO_2 Hydrogenation Over Iron Catalysts: The Effect of Potassium on Structure and Performance", *Catal. Lett.* **146**, 509–517 (2016).
- [41] Ning, W., Koizumi, N. and Yamada, M., "Researching Fe catalyst suitable for CO_2 -containing syngas for Fischer-Tropsch synthesis", *Energy and Fuels* **23**, 4696–4700 (2009).
- [42] Martinelli, M., Visconti, C. G., Lietti, L., Forzatti, P., Bassano, C. and Deiana, P., " CO_2 reactivity on Fe–Zn–Cu–K Fischer-Tropsch synthesis catalysts with different K-loadings", *Catal. Today* **228**, 77–88 (2014).
- [43] Bartholomew, C. H., "Mechanisms of catalyst deactivation", *Appl. Catal. A Gen.* **212**, 17–60 (2001).
- [44] Dry, M. E., Shingles, T., Boshoff, L. J. and van H. Botha, C. S., "Factors influencing the formation of carbon on iron Fischer-Tropsch catalysts. II. The effect of temperature and of gases and vapors present during Fischer-Tropsch synthesis", *J. Catal.* **17**, 347–354 (1970).
- [45] Cohn, E. M., Bean, E. H., Mentser, M., Hofer, L. J. E., Pontello, A., Peebles, W. C. and Jack, K. H., "The carburization of iron oxide with carbon monoxide: Modifications of Hägg iron carbide", *J. Appl. Chem.* **5**, 418–425 (1955).
- [46] Berry, T. F., Ames, R. N. and Snow, R. B., "Influence of Impurities and Role of Iron Carbides in Deposition of Carbon from Carbon Monoxide", *J. Am. Ceram. Soc.* **39**, 308–318 (1956).
- [47] Herranz, T., Rojas, S., Pérez-Alonso, F. J., Ojeda, M., Terreros, P. and Fierro, J. L. G., "Genesis of iron carbides and their role in the synthesis of hydrocarbons from synthesis gas", *J. Catal.* **243**, 199–211 (2006).
- [48] Turkdogan, E. T. and Vinters, J. V., "Catalytic effect of iron on decomposition of carbon monoxide: I. carbon deposition in H_2 -CO Mixtures", *Metall. Trans.* **5**, 11–19 (1974).
- [49] Olsson, R. G. and Turkdogan, E. T., "Catalytic effect of iron on decomposition of carbon monoxide: II. Effect of additions of H_2 , H_2O , CO_2 , SO_2 and H_2S ", *Metall. Trans.* **5**, 21–26 (1974).
- [50] Arakawa, H. and Bell, A. T., "Effects of potassium promotion on the activity and selectivity of iron Fischer-Tropsch catalysts", *Ind. Eng. Chem. Process Des. Dev.* **22**, 97–103 (1983).
- [51] Koeken, A. C. J., Torres Galvis, H. M., Davidian, T., Ruitenbeek, M. and de Jong, K. P., "Suppression of Carbon Deposition in the Iron-Catalyzed Production of Lower Olefins from Synthesis Gas", *Angew. Chem., Int. Ed.* **51**, 7190–7193 (2012).
- [52] Alstrup, I., Tavares, M. T., Bernardo, C. A., Sørensen, O. and Rostrup-Nielsen, J. R., "Carbon formation on nickel and nickel-copper alloy catalysts", *Mater. Corros.* **49**, 367–372 (1998).
- [53] Nolan, P. E., Lynch, D. C. and Cutler, A. H., "Catalytic disproportionation of CO in the absence of

- hydrogen: Encapsulating shell carbon formation*", *Carbon* **32**, 477–483 (1994).
- [54] Mazzucco, S., Wang, Y., Tanase, M., Picher, M., Li, K., Wu, Z., Irle, S. and Sharma, R., "Direct evidence of active and inactive phases of Fe catalyst nanoparticles for carbon nanotube formation", *J. Catal.* **319**, 54–60 (2014).
- [55] Pendyala, V. R. R., Graham, U. M., Jacobs, G., Hamdeh, H. H. and Davis, B. H., "Fischer-Tropsch Synthesis: Morphology, Phase Transformation, and Carbon-Layer Growth of Iron-Based Catalysts", *ChemCatChem* **6**, 1952–1960 (2014).
- [56] Pendyala, V. R. R., Graham, U. M., Jacobs, G., Hamdeh, H. H. and Davis, B. H., "Fischer-Tropsch Synthesis: Deactivation as a Function of Potassium Promoter Loading for Precipitated Iron Catalyst", *Catal. Lett.* **144**, 1704–1716 (2014).
- [57] Shultz, J. F., Abelson, M., Stein, K. C. and Anderson, R. B., "Studies of the Fischer-Tropsch Synthesis. XVIII. Influence of Catalyst Geometry on Synthesis on Iron Catalysts", *J. Phys. Chem.* **63**, 496–500 (1959).
- [58] Hofer, L. J. E., "Nature of the carbides of iron", *U.S. Bureau of Mines Bulletin* **631** (1966). Available at: <http://www.onemine.org/document/abstract.cfm?docid=186163&title=Nature-Of-The-Carbides-Of-Iron> (Accessed: February 2014).
- [59] Pijolat, M., Perrichon, V. and Bussière, P., "Study of the carburization of an iron catalyst during the Fischer-Tropsch synthesis: Influence on its catalytic activity", *J. Catal.* **107**, 82–91 (1987).
- [60] Niemantsverdriet, J. W., van der Kraan, A. M., van Dijk, W. L. and van der Baan, H. S., "Behavior of Metallic Iron Catalysts during Fischer-Tropsch Synthesis Studied with Mössbauer Spectroscopy, X-ray Diffraction, Carbon Content Determination, and Reaction Kinetic Measurements", *J. Phys. Chem.* **84**, 3363–3370 (1980).
- [61] Le Caër, G., Dubois, J. M., Pijolat, M., Perrichon, V. and Bussière, P., "Characterization by Moessbauer Spectroscopy of Iron Carbides Formed by Fischer-Tropsch Synthesis", *J. Phys. Chem.* **86**, 4799–4808 (1982).
- [62] Hofer, L. J. E., Cohn, E. M. and Peebles, W. C., "The Modifications of the Carbide, Fe_2C ; Their Properties and Identification", *J. Am. Chem. Soc.* **71**, 189–195 (1949).
- [63] O'Brien, R. J., Xu, L., Spicer, R. L. and Davis, B. H., "Activation Study of Precipitated Iron Fischer-Tropsch Catalysts", *Energy & Fuels* **10**, 921–926 (1996).
- [64] O'Brien, R. J., Xu, L., Milburn, D. R., Li, Y.-X., Klabunde, K. J. and Davis, B. H., "Fischer-Tropsch synthesis: Impact of potassium and zirconium promoters on the activity and structure of an ultrafine iron oxide catalyst", *Top. Catal.* **2**, 1–15 (1995).
- [65] Ning, W., Koizumi, N., Chang, H., Mochizuki, T., Itoh, T. and Yamada, M., "Phase transformation of unpromoted and promoted Fe catalysts and the formation of carbonaceous compounds during Fischer-Tropsch synthesis reaction", *Appl. Catal. A Gen.* **312**, 35–44 (2006).
- [66] Tau, L. M., Borcar, S., Bianchi, D. and Bennett, C. O., "Investigation of supported iron Fischer-Tropsch synthesis catalysts by Mössbauer spectroscopy", *J. Catal.* **87**, 36–54 (1984).
- [67] de Smit, E., Cinquini, F., Beale, A. M., Safonova, O. V., van Beek, W., Sautet, P. and Weckhuysen, B. M., "Stability and Reactivity of ϵ - χ - θ Iron Carbide Catalyst Phases in Fischer-Tropsch Synthesis: Controlling μ_c ", *J. Am. Chem. Soc.* **132**, 14928–14941 (2010).
- [68] Jozwiak, W. K., Kaczmarek, E., Maniecki, T. P., Ignaczak, W. and Maniukiewicz, W., "Reduction behavior of iron oxides in hydrogen and carbon monoxide atmospheres", *Appl. Catal. A Gen.* **326**, 17–27 (2007).
- [69] Nagakura, S., "Study of Metallic Carbides by Electron Diffraction Part III. Iron Carbides", *J. Phys. Soc. Japan* **14**, 186–195 (1959).
- [70] Wood, I. G., Vočadlo, L., Knight, K. S., Dobson, D. P., Marshall, W. G., Price, G. D. and Brodholt, J.,

- "Thermal expansion and crystal structure of cementite, Fe_3C , between 4 and 600 K determined by time-of-flight neutron powder diffraction", *J. Appl. Crystallogr.* **37**, 82–90 (2004).
- [71] Jin, Y. and Datye, A. K., "Phase Transformations in Iron Fischer–Tropsch Catalysts during Temperature-Programmed Reduction", *J. Catal.* **196**, 8–17 (2000).
- [72] Mogorosi, R. P., Fischer, N., Claeys, M. and van Steen, E., "Strong-metal-support interaction by molecular design: Fe-silicate interactions in Fischer–Tropsch catalysts", *J. Catal.* **289**, 140–150 (2012).
- [73] van de Loosdrecht, J., Botes, G. F., Ciobica, I. M., Ferreira, A. C., Gibson, P., Moodley, D. J., Saib, A. M., Visagie, J. L., Weststrate, C. J. and Niemantsverdriet, J. W., "Fischer–Tropsch Synthesis: Catalysts and Chemistry" in *Comprehensive Inorganic Chemistry II* (eds. Reedijk, J. & Poeppelmeier, K.), 525–557 (Elsevier, Amsterdam, 2013). DOI:10.1016/B978-0-08-097774-4.00729-4
- [74] Ren-Yuan, T., Su, Z., Chengyu, W., Dongbai, L. and Liwu, L., "An in situ combined temperature-programmed reduction–Mössbauer spectroscopy of alumina-supported iron catalysts", *J. Catal.* **106**, 440–448 (1987).
- [75] Anderson, R. B., Hofer, L. J. E., Cohn, E. M. and Seligman, B., "Studies of the Fischer–Tropsch Synthesis. IX. Phase Changes of Iron Catalysts in the Synthesis", *J. Am. Chem. Soc.* **73**, 944–946 (1951).
- [76] Shultz, J. F., Hall, W. K., Seligman, B. and Anderson, R. B., "Studies of the Fischer–Tropsch Synthesis. XIV. Hägg Carbide as Catalysts", *J. Am. Chem. Soc.* **77**, 213–221 (1955).
- [77] Wezendonk, T. A., Sun, X., Dugulan, A. I., van Hoof, A. J. F., Hensen, E. J. M., Kapteijn, F. and Gascon, J., "Controlled formation of iron carbides and their performance in Fischer–Tropsch synthesis", *J. Catal.* **362**, 106–117 (2018).
- [78] Bukur, D. B., Okabe, K., Rosynek, M. P., Li, C. P., Wang, D. J., Rao, K. R. P. M. and Huffman, G. P., "Activation Studies with a Precipitated Iron Catalyst for Fischer–Tropsch Synthesis. I. Characterization Studies", *Journal of Catalysis* **155**, 353–365 (1995).
- [79] Steynberg, A. P., Espinoza, R. L., Jager, B. and Vosloo, A. C., "High temperature Fischer–Tropsch synthesis in commercial practice", *Appl. Catal. A Gen.* **186**, 41–54 (1999).
- [80] Sarkar, A., Seth, D., Dozier, A. K., Neathery, J. K., Hamdeh, H. H. and Davis, B. H., "Fischer–Tropsch Synthesis: Morphology, Phase Transformation and Particle Size Growth of Nano-scale Particles", *Catal. Lett.* **117**, 1–17 (2007).
- [81] Anderson, R. B., Karn, F. S. and Shultz, J. F., "Factors in sulfur poisoning of iron catalysts in Fischer–Tropsch synthesis", *J. Catal.* **4**, 56–63 (1965).
- [82] Shultz, J. F., Hofer, L. J. E., Karn, F. S. and Anderson, R. B., "Studies of the Fischer–Tropsch Synthesis; Prepoisoning of Iron Catalysts by Sulfur Compounds", *J. Phys. Chem.* **66**, 501–506 (1962).
- [83] Xu, J.-D., Chang, Z.-Y., Zhu, K.-T., Weng, X.-F., Weng, W.-Z., Zheng, Y.-P., Huang, C.-J. and Wan, H.-L., "Effect of sulfur on $\alpha\text{-Al}_2\text{O}_3$ -supported iron catalyst for Fischer–Tropsch synthesis", *Appl. Catal. A Gen.* **514**, 103–113 (2016).
- [84] San-Miguel, M. A., Oviedo, J. and Sanz, J. F., "Cluster-Substrate Interaction" in *Handbook of Nanophysics: Clusters and Fullerenes* (ed. Sattler, K. D.), 328–344 (CRC Press, Boca Raton, 2017).
- [85] Nørskov, J. K., Holloway, S. and Lang, N. D., "Microscopic model for the poisoning and promotion of adsorption rates by electronegative and electropositive atoms", *Surf. Sci.* **137**, 65–78 (1984).
- [86] Madon, R. J. and Shaw, H., "Effect of Sulfur on the Fischer–Tropsch Synthesis", *Catal. Rev.* **15**, 69–106 (1977).
- [87] Benziger, J. and Madix, R. J., "The effects of carbon, oxygen, sulfur and potassium adlayers on CO and H_2 adsorption on $\text{Fe}(100)$ ", *Surf. Sci.* **94**, 119–153 (1980).
- [88] Nørskov, J. K. and Besenbacher, F., "Theory of hydrogen interaction with metals", *J. Less Common Met.*

- 130**, 475–490 (1987).
- [89] Nørskov, J. K., Bligaard, T., Hvolbæk, B., Abild-Pedersen, F., Chorkendorff, I. and Christensen, C. H., "The nature of the active site in heterogeneous metal catalysis", *Chem. Soc. Rev.* **37**, 2163 (2008).
 - [90] Förtsch, D., Pabst, K. and Groß-Hardt, E., "The product distribution in Fischer–Tropsch synthesis: An extension of the ASF model to describe common deviations", *Chem. Eng. Sci.* **138**, 333–346 (2015).
 - [91] Todić, B., Nowicki, L., Nikacević, N. and Bukur, D. B., "Fischer–Tropsch synthesis product selectivity over an industrial iron-based catalyst: Effect of process conditions", *Catal. Today* **261**, 28–39 (2016).
 - [92] Dry, M. E., "Commercial conversion of carbon monoxide to fuels and chemicals", *J. Organomet. Chem.* **372**, 117–127 (1989).
 - [93] Jiang, F., Zhang, M., Liu, B., Xu, Y. and Liu, X., "Insights into the influence of support and potassium or sulfur promoter on iron-based Fischer–Tropsch synthesis: understanding the control of catalytic activity, selectivity to lower olefins, and catalyst deactivation", *Catal. Sci. Technol.* **7**, 1245–1265 (2017).
 - [94] Botes, G. F., Niemantsverdriet, J. W. and van de Loosdrecht, J., "A comparison of cobalt and iron based slurry phase Fischer–Tropsch synthesis", *Catal. Today* **215**, 112–120 (2013).
 - [95] Torres Galvis, H. M., Koeken, A. C. J., Bitter, J. H., Davidian, T., Ruitenbeek, M., Dugulan, A. I. and de Jong, K. P., "Effects of sodium and sulfur on catalytic performance of supported iron catalysts for the Fischer–Tropsch synthesis of lower olefins", *J. Catal.* **303**, 22–30 (2013).
 - [96] Torres Galvis, H. M., Koeken, A. C. J., Bitter, J. H., Davidian, T., Ruitenbeek, M., Dugulan, A. I. and De Jong, K. P., "Effect of precursor on the catalytic performance of supported iron catalysts for the Fischer–Tropsch synthesis of lower olefins", *Catal. Today* **215**, 95–102 (2013).
 - [97] Layng, E. T., "Synthesis of hydrocarbons with sulfur containing catalyst", Patent US2446426A (1948).
 - [98] Bonzel, H. P., "Alkali-metal-affected adsorption of molecules on metal surfaces", *Surf. Sci. Rep.* **8**, 43–125 (1988).
 - [99] Kiskinova, M., "Interaction of CO with Single Crystal Metal Surfaces" in *New Trends in CO Activation* (ed. Guzzi, L.) **64**, 37–86 (Elsevier, Amsterdam, 1991).
 - [100] Ertl, G., Lee, S. B. and Weiss, M., "The influence of potassium on the adsorption of hydrogen on iron", *Surf. Sci.* **111**, L711–L715 (1981).
 - [101] Poncet, V., "Selectivity in the Syngas Reactions" in *New Trends in CO Activation* (ed. Guzzi, L.) **64**, 117–157 (Elsevier, Amsterdam, 1991).
 - [102] Zhang, H.-B. and Schrader, G. L., "Characterization of a fused iron catalyst for Fischer-Tropsch synthesis by in situ laser Raman spectroscopy", *J. Catal.* **95**, 325–332 (1985).
 - [103] Krupay, B. W. and Amenomiya, Y., "Alkali-promoted Alumina Catalysts I. Chemisorption and oxygen exchange of carbon monoxide and carbon dioxide on potassium-promoted alumina catalysts", *J. Catal.* **67**, 362–370 (1981).
 - [104] Amenomiya, Y. and Pleizier, G., "Alkali-promoted Alumina Catalysts II. Water-Gas Shift Reaction", *J. Catal.* **76**, 345–353 (1982).
 - [105] Paul, J., "CO dissociation on potassium-promoted aluminium", *Nature* **323**, 701–703 (1986).
 - [106] Dry, M. E., Shingles, T., Boshoff, L. J. and Oosthuizen, G. J., "Heats of chemisorption on promoted iron surfaces and the role of alkali in Fischer-Tropsch synthesis", *J. Catal.* **15**, 190–199 (1969).
 - [107] Bukur, D. B., Mukesh, D. and Patel, S. A., "Promoter effects on precipitated iron catalysts for Fischer-Tropsch synthesis", *Ind. Eng. Chem. Res.* **29**, 194–204 (1990).
 - [108] Guzzi, L., "Effect of Hydrogen in Controlling CO Hydrogenation", *New Trends in CO Activation* **64**, 350–380 (1991).

- [109] Hwang, K.-R., Lee, C.-B. and Park, J.-S., "Advanced nickel metal catalyst for water–gas shift reaction", *J. Power Sources* **196**, 1349–1352 (2011).
- [110] Bartholomew, C. H., Agrawal, P. K. and Katzer, J. R., "Sulfur Poisoning of Metals" in *Advances in Catalysis* (eds. Eley, D. D., Pines, H. & Weisz, P. B.) **31**, 135–242 (Academic Press, New York, 1982).
- [111] Dalla Betta, R. A., Piken, A. G. and Shelef, M., "Heterogeneous methanation: Steady-state rate of CO hydrogenation on supported ruthenium, nickel and rhenium", *J. Catal.* **40**, 173–183 (1975).
- [112] van Dijk, W. L., Niemantsverdriet, J. W., van der Kraan, A. M. and van der Baan, H. S., "Effects of Manganese Oxide and Sulphate on the Olefin Selectivity of Iron Catalysts in the Fischer Tropsch Reaction", *Appl. Catal.* **2**, 273–288 (1982).
- [113] Zhou, X., Ji, J., Wang, D., Duan, X., Qian, G., Chen, D. and Zhou, X., "Hierarchical structured α -Al₂O₃ supported S-promoted Fe catalysts for direct conversion of syngas to lower olefins", *Chem. Commun.* **51**, 8853–8856 (2015).
- [114] Li, T., Yang, Y., Tao, Z., Wan, H., An, X., Zhang, C., Xiang, H. and Li, Y., "Effect of Sulfate on an Iron Manganese Catalyst for Fischer-Tropsch Synthesis", *J. Nat. Gas Chem.* **16**, 354–362 (2007).
- [115] Stenger, H. G. and Satterfield, C. N., "Effects of sulfur poisoning of a reduced fused magnetite catalyst in the Fischer-Tropsch synthesis", *Ind. Eng. Chem. Process Des. Dev.* **24**, 415–420 (1985).
- [116] Wu, B., Bai, L., Xiang, H., Li, Y.-W., Zhang, Z. and Zhong, B., "An active iron catalyst containing sulfur for Fischer–Tropsch synthesis", *Fuel* **83**, 205–212 (2004).
- [117] Bromfield, T. C. and Coville, N. J., "The effect of sulfide ions on a precipitated iron Fischer–Tropsch catalyst", *Appl. Catal. A Gen.* **186**, 297–307 (1999).
- [118] Karn, F. S., Schultz, J. F., Kelly, R. E. and Anderson, R. B., "Fischer-Tropsch Synthesis. Poisoning of Iron Catalysts by H₂S in Synthesis Gas", *Ind. Eng. Chem. Prod. Res. Dev.* **2**, 43–47 (1963).
- [119] Sarkar, A., Dozier, A. K., Graham, U. M., Thomas, G., O'Brien, R. J. and Davis, B. H., "Precipitated iron Fischer-Tropsch catalyst: Effect of carbidization on the morphology of iron oxyhydroxide nanoneedles", *Appl. Catal. A Gen.* **326**, 55–64 (2007).
- [120] Arabczyk, W., Moszyński, D., Narkiewicz, U., Pelka, R. and Podsiadły, M., "Poisoning of iron catalyst by sulfur", *Catal. Today* **124**, 43–48 (2007).
- [121] Sun, Y., Tao, L., You, T., Li, C. and Shan, H., "Effect of sulfation on the performance of Fe₂O₃/Al₂O₃ catalyst in catalytic dehydrogenation of propane to propylene", *Chem. Eng. J.* **244**, 145–151 (2014).
- [122] Moszyński, D., Grabke, H. J. and Schneider, A., "Effect of sulphur on the formation of graphite at the surface of carburized iron", *Surf. Interface Anal.* **34**, 380–383 (2002).
- [123] Xie, J., Yang, J., Dugulan, A. I., Holmen, A., Chen, D., De Jong, K. P. and Louwerse, M. J., "Size and Promoter Effects in Supported Iron Fischer-Tropsch Catalysts: Insights from Experiment and Theory", *ACS Catal.* **6**, 3147–3157 (2016).
- [124] Momma, K. and Izumi, F., "VESTA 3 for three-dimensional visualization of crystal, volumetric and morphology data", *J. Appl. Crystallogr.* **44**, 1272–1276 (2011).
- [125] Duggin, M. J. and Hofer, L. J. E., "Nature of χ -Iron Carbide", *Nature* **212**, 248–248 (1966).
- [126] Jack, K. H. and Wild, S., "Nature of χ -Carbide and Its Possible Occurrence in Steels", *Nature* **212**, 248–250 (1966).
- [127] Williamson, D. L., Nakazawa, K. and Krauss, G., "A study of the early stages of tempering in an Fe-1.2 Pct alloy", *Metall. Trans. A* **10**, 1351–1363 (1979).
- [128] Dirand, M. and Afqir, L., "Identification structurale precise des carbures precipites dans les aciers faiblement allies aux divers stades du revenu, mecanismes de precipitation", *Acta Metall.* **31**, 1089–1107 (1983).

- [129] Barton, G. H. and Gale, B., "The structure of a pseudo-hexagonal iron carbide", *Acta Crystallogr.* **17**, 1460–1462 (1964).
- [130] Hirotsu, Y. and Nagakura, S., "Electron Microscopy and Diffraction Study of the Carbide Precipitated at the First Stage of Tempering of Martensitic Medium Carbon Steel", *Trans. Japan Inst. Met.* **15**, 129–134 (1974).
- [131] Hirotsu, Y. and Nagakura, S., "Crystal structure and morphology of the carbide precipitated from martensitic high carbon steel during the first stage of tempering", *Acta Metall.* **20**, 645–655 (1972).
- [132] Stanfield, R. M. and Delgass, W. N., "Mössbauer spectroscopy of supported Fe-Co alloy catalysts for Fischer-Tropsch synthesis", *J. Catal.* **72**, 37–50 (1981).
- [133] Hägg, G., "Pulverphotogramme eines neuen Eisencarbides", *Zeitschrift für Krist. - Cryst. Mater.* **89**, 92–94 (1934).
- [134] Retief, J. J., "Powder diffraction data and Rietveld refinement of Hägg-carbide, χ -Fe₅C₂", *Powder Diffr.* **14**, 130–132 (1999).
- [135] du Plessis, H. E., de Villiers, J. P. R., Kruger, G. J., Steuwer, A. and Brunelli, M., "Rietveld and pair distribution function study of Hägg carbide using synchrotron X-ray diffraction", *J. Synchrotron Radiat.* **18**, 266–271 (2011).
- [136] Leineweber, A., Shang, S., Liu, Z.-K., Widenmeyer, M. and Niewa, R., "Crystal structure determination of Hägg carbide, χ -Fe₅C₂ by first-principles calculations and Rietveld refinement", *Zeitschrift für Krist.* **227**, 207–220 (2012).
- [137] Hofer, L. J. E. and Cohn, E. M., "Some Reactions in the Iron–Carbon System: Application to the Tempering of Martensite", *Nature* **167**, 977–978 (1951).
- [138] Fasiska, E. J. and Jeffrey, G. A., "On the cementite structure", *Acta Crystallogr.* **19**, 463–471 (1965).
- [139] Crystallography Open Database, "Open-access collection of crystal structures", (2018). Available at: <http://www.crystallography.net/cod/> (Accessed: February 2018).
- [140] Eckstrom, H. C. and Adcock, W. A., "A New Iron Carbide in Hydrocarbon Synthesis Catalysts", *J. Am. Chem. Soc.* **72**, 1042–1043 (1950).
- [141] Herbstein, F. H. and Snyman, J. A., "Identification of Eckstrom-Adcock Iron Carbide as Fe₇C₃", *Inorg. Chem.* **3**, 894–896 (1964).
- [142] Fruchart, R., Senateur, J. P., Bouchaud, J. P. and Michel, A., "A propos de la structure exacte du carbure de fer Fe₇C₃", *Bull. Soc. Chim. Fr.* **2**, 392 (1965).
- [143] Audier, M., Bowen, P. and Jones, W., "Transmission electron microscopic study of single crystals of Fe₇C₃", *J. Cryst. Growth* **63**, 125–134 (1983).
- [144] Kattner, U. R., "What's in a Name?", *J. Phase Equilibria Diffus.* **34**, 437–437 (2013).
- [145] Pringle, O. A. and Long, G. J., "Mössbauer Effects Studies of Hard Magnetic Materials" in *Mössbauer Spectroscopy Applied to Inorganic Chemistry* (eds. Long, G. J. & Grandjean, F.) **3**, 644 (Springer, Boston, 1989).
- [146] Dubois, J. M. and Le Caër, G., "Electron diffraction and Mossbauer studies of the ϵ phase retained in splat-quenched Fe-C and Fe-C-Si alloys", *Acta Metall.* **25**, 609–618 (1977).
- [147] Foct, J., Senateur, J. P., Dubois, J. M. and Le Caër, G., "Mössbauer Spectroscopy of Different Interstitial Compounds and Solid Solutions Containing ⁵⁷Fe", *Le J. Phys. Colloq.* **40**, 647–649 (1979).
- [148] Liu, X.-W., Zhao, S., Meng, Y., Peng, Q., Dearden, A. K., Huo, C.-F., Yang, Y., Li, Y.-W. and Wen, X.-D., "Mössbauer Spectroscopy of Iron Carbides: From Prediction to Experimental Confirmation", *Sci. Rep.* **6**, 26184 (2016).
- [149] Xu, K., Sun, B., Lin, J., Wen, W., Pei, Y., Yan, S., Qiao, M., Zhang, X. and Zong, B., "ε-Iron carbide as a low-

- temperature Fischer–Tropsch synthesis catalyst", *Nat. Commun.* **5**, 5783 (2014).
- [150] Raupp, G. B. and Delgass, W. N., "Mössbauer Investigation of Supported Fe and FeNi Catalysts II. Carbides Formed by Fischer-Tropsch Synthesis", *J. Catal.* **58**, 348–360 (1979).
- [151] Barinov, V. A., Protasov, A. V. and Surikov, V. T., "Studying mechanosynthesized Hägg carbide (χ -Fe₅C₂)", *Phys. Met. Metallogr.* **116**, 791–801 (2015).
- [152] Bi, X.-X., Ganguly, B., Huffman, G. P., Huggins, F. E., Endo, M. and Eklund, P. C., "Nanocrystalline α -Fe, Fe₃C, and Fe₇C₃ produced by CO₂ laser pyrolysis", *J. Mater. Res.* **8**, 1666–1674 (1993).
- [153] Kniep, B., Constantinescu, A., Niemeier, D. and Becker, K. D., "An In-situ Mössbauer Study of the Formation of Cementite, Fe₃C", *Zeitschrift für Anorg. und Allg. Chemie* **629**, 1795–1804 (2003).
- [154] Ron, M., Shechter, H., Hirsch, A. A. and Niedzwiedz, S., "On the Mössbauer study of cementite", *Phys. Lett.* **20**, 481–483 (1966).
- [155] Yamada, Y., Yoshida, H., Kouno, K. and Kobayashi, Y., "Iron carbide films produced by laser deposition", *J. Phys. Conf. Ser.* **217**, 012096 (2010).
- [156] Nagakura, S., Hirotsu, Y., Kusunoki, M., Suzuki, T. and Nakamura, Y., "Crystallographic study of the tempering of martensitic carbon steel by electron microscopy and diffraction", *Metall. Trans. A* **14**, 1025–1031 (1983).
- [157] Amelse, J. A., Grynkewich, G., Butt, J. B. and Schwartz, L. H., "Moessbauer spectroscopic study of passivated small particles of iron and iron carbide", *J. Phys. Chem.* **85**, 2484–2488 (1981).
- [158] Wang, P., Chen, W., Chiang, F., Dugulan, A. I., Song, Y., Pestman, R., Zhang, K., Yao, J., Feng, B., Miao, P., Xu, W. and Hensen, E. J. M., "Synthesis of stable and low-CO₂ selective ϵ -iron carbide Fischer-Tropsch catalysts", *Sci. Adv.* **4**, eaau2947 (2018).
- [159] Jung, H. and Thomson, W. J., "Dynamic X-ray diffraction study of an unsupported iron catalyst in Fischer-Tropsch synthesis", *J. Catal.* **134**, 654–667 (1992).
- [160] Cohn, E. M. and Hofer, L. J. E., "Mode of Transition from Hägg Iron Carbide to Cementite", *J. Am. Chem. Soc.* **72**, 4662–4664 (1950).
- [161] Shultz, J. F., Hall, W. K., Dubs, T. A. and Anderson, R. B., "Studies of the Fischer-Tropsch Synthesis. XV. Cementite as Catalysts", *J. Am. Chem. Soc.* **78**, 282–285 (1956).
- [162] An, X., Wu, B., Wan, H.-J., Li, T.-Z., Tao, Z.-C., Xiang, H.-W. and Li, Y.-W., "Comparative study of iron-based Fischer–Tropsch synthesis catalyst promoted with potassium or sodium", *Catal. Commun.* **8**, 1957–1962 (2007).
- [163] Janbroers, S., Louwen, J. N., Zandbergen, H. W. and Kooyman, P. J., "Insights into the nature of iron-based Fischer–Tropsch catalysts from quasi in situ TEM-EELS and XRD", *J. Catal.* **268**, 235–242 (2009).
- [164] Berry, F. J. and Smith, M. R., "A Mössbauer investigation of iron-containing catalysts prepared at low temperatures and active for carbon monoxide hydrogenation", *J. Chem. Soc. Faraday Trans. 1 Phys. Chem. Condens. Phases* **85**, 467–477 (1989).
- [165] Ribeiro, M. C., Jacobs, G., Davis, B. H., Cronauer, D. C., Kropf, A. J. and Marshall, C. L., "Fischer–Tropsch Synthesis: An In-Situ TPR-EXAFS/XANES Investigation of the Influence of Group I Alkali Promoters on the Local Atomic and Electronic Structure of Carburized Iron/Silica Catalysts", *J. Phys. Chem. C* **114**, 7895–7903 (2010).
- [166] Tsuzuki, A., Sago, S., Hirano, S.-I. and Naka, S., "High temperature and pressure preparation and properties of iron carbides Fe₇C₃ and Fe₃C", *J. Mater. Sci.* **19**, 2513–2518 (1984).
- [167] Sethuraman, A. R., "In-situ high temperature X-ray diffraction studies of nanocrystalline iron carbides", *Nanostructured Mater.* **4**, 79–92 (1994).
- [168] Tajima, S. and Hirano, S., "Synthesis and Magnetic Properties of Fe₇C₃ Particles with High Saturation

- Magnetization*", *Jpn. J. Appl. Phys.* **29**, 662–668 (1990).
- [169] Hirano, S.-I. and Tajima, S., "Synthesis and magnetic properties of Fe_5C_2 by reaction of iron oxide and carbon monoxide", *J. Mater. Sci.* **25**, 4457–4461 (1990).
- [170] Barinov, V. A., Tsurin, V. A. and Surikov, V. T., "Study of mechanically synthesized carbide Fe_7C_3 ", *Phys. Met. Metallogr.* **110**, 474–484 (2010).

Chapter 3

Identification of Iron Carbides in Fe(-Na-S)/ α -Al₂O₃ Fischer-Tropsch Synthesis Catalysts with X-ray Powder Diffractometry and Mössbauer Absorption Spectroscopy

In Fe-based Fischer-Tropsch Synthesis (FTS), the Fe carbides form under the carburizing H₂:CO reaction atmosphere providing the active phases for hydrocarbon synthesis. Identification of the Fe carbides can be challenging, as studies with the commonly applied techniques of X-ray Powder Diffractometry (XRPD) and Mössbauer Absorption Spectroscopy (MAS) apply inconsistent nomenclature for the Fe carbides in between the techniques. H₂ reduced Fe(-Na-S)/ α -Al₂O₃ catalyst materials, with and without Na-S promotion, have been carburized under CO at 240-440°C to form Fe carbides observed in the FTS reaction. Rietveld Quantitative Phase Analysis (R-QPA) was used to quantify Fe phases from the measured XRPD patterns and the results were compared with MAS. Carbon deposition and morphological changes on the catalysts were also followed. The Fe carbides formed in order of increasing temperature are ϵ -Fe₃C, η -Fe₂C, χ -Fe₅C₂ and θ -Fe₃C. Furthermore, θ -Fe₇C₃ and a distorted χ -Fe₅C₂ phase formed at 25 bar CO (340°C) from a Fe oxide precursor. Crystal structures, lattice parameters, hyperfine fields and relative C contents were assigned for the carbides. Fe carbide formation was unaffected by Na-S addition, but it had temperature dependent effects of increased Fe oxidation ($\leq 290^\circ\text{C}$), carbon deposition (340-390°C) and decreased θ -Fe₃C crystallite diameters (440°C). The results unify the Fe carbide nomenclature and specify the role of Na-S in the carburization process.

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3.1 INTRODUCTION

In Fe-based Fischer-Tropsch Synthesis (FTS) reaction, Fe phases present under the carburizing $\text{H}_2:\text{CO}$ atmosphere are Fe carbides that form via dissolution of C atoms to zerovalent $\alpha\text{-Fe}$ lattice. The Fe carbides form the reactive part for the Fe-based FTS reaction dissociating CO and H_2 . The C atoms may then further react to either form hydrocarbons with H atoms or react with other C atoms to form inactive carbon deposits on the catalyst material.

In the FTS reaction literature, the Fe carbide phases are commonly identified as (pseudo-)hexagonal or as the “ ϵ -carbides” ($\epsilon\text{'-Fe}_{2.2}\text{C}$, Fe_2C , $\epsilon\text{-Fe}_2\text{C}$ or $\epsilon\text{-Fe}_3\text{C}$),¹⁻⁹ $\chi\text{-Fe}_5\text{C}_2$ (the Hägg carbide),^{1-3,10-13} $\theta\text{-Fe}_3\text{C}$ (cementite),^{1-3,14,15} and Fe_7C_3 (the Eckström-Adcock carbide).^{1,3,16-18} While “ ϵ -carbides”, $\chi\text{-Fe}_5\text{C}_2$ and $\theta\text{-Fe}_3\text{C}$ are often observed, the Fe_7C_3 phase is less common in FTS reaction literature and seems to form under more severe, industrial FTS reaction conditions, than the rest of the carbide phases.¹⁶ From tempering studies on martensitic steel, a Fe carbide labelled as $\eta\text{-Fe}_2\text{C}$ has been observed.¹⁹ The $\eta\text{-Fe}_2\text{C}$ phase has been suggested to be closely related to the “ ϵ -carbides” encountered in the FTS reaction research field.^{2,9,20}

The most common and suitable characterization techniques applied for identifying the Fe carbide phases present in Fe-based FTS reaction catalyst materials are X-ray Powder Diffractometry (XRPD) and Mössbauer Absorption Spectroscopy (MAS). From the obtained XRPD patterns, the $\chi\text{-Fe}_5\text{C}_2$, $\theta\text{-Fe}_3\text{C}$ and Fe_7C_3 phases can readily be identified,^{1,3,17,18,21-24} while differentiation between the “ ϵ -carbides” is more challenging with XRPD. In FTS literature, when using XRPD as the characterization method, the precise crystal structures for Fe carbides identified as the “ ϵ -carbides” are often left ambiguous.^{1,3,6,21,25-29} With MAS, on the basis of the different hyperfine fields, the Fe carbides can be fingerprinted also including the Fe carbide phases which are referred to as the “ ϵ -carbides”.^{2,5,12,13,30-34} Unfortunately, the connection between the experimentally observed Fe carbides and their precise crystal structures from XRPD, in comparison to the assigned hyperfine fields from MAS, is often unclear. This being most evident in the case of the “ ϵ -carbides”. Which “ ϵ -carbides” truly exist and with what crystal structures, can be a challenging task to interpret from the literature due to the lack of unified nomenclature between the XRPD and MAS studies.

In the literature review **Chapter 2**, we have argued on the basis of our interpretation of the literature, that the Fe carbides with their crystal lattices to form in within FTS reaction research field are: $\epsilon\text{-Fe}_3\text{C}$ $P6_322$ (182), $\eta\text{-Fe}_2\text{C}$ $Pnnm$ (58), $\chi\text{-Fe}_5\text{C}_2$ $C2/c$ (15), $\theta\text{-Fe}_3\text{C}$ $Pnma$ (62) and $\theta\text{-Fe}_7\text{C}_3$ $Pnma$ (62). Of these carbides, we have discussed that the $\epsilon\text{-Fe}_3\text{C}$ and $\eta\text{-Fe}_2\text{C}$ phases are the Fe carbides cited in the literature as the “ ϵ -carbides” or (pseudo-)hexagonal Fe carbides. For each of the identified Fe carbide phases, we also

Figure 3.1

A schematic of the approach taken in this Chapter. Unpromoted and Na-S promoted Fe(-Na-S)/ α -Al₂O₃ catalyst materials are used to follow the **formation** of various Fe carbides after CO carburization treatments between 240–440°C. The formed Fe carbides are **identified** with both X-ray Powder Diffractometry (XRPD) and Mössbauer Absorption Spectroscopy (MAS) techniques, and the corresponding changes in catalyst materials **morphology** is followed with Transmission Electron Microscopy (TEM). Carbon deposition associated with changes in catalyst materials morphology is quantified with the use of Thermogravimetric Analysis combined with Mass Spectrometry (TGA-MS).

assigned hyperfine fields for MAS fingerprinting based on the established Fe carbide nomenclature.

The addition of Na-S as chemical promoters on Fe-based FTS reaction catalyst materials increases the CO conversion, α -value, hydrocarbon products' olefin content and suppresses CH₄ selectivity below expectations from the Anderson-Schulz-Flory (ASF) Distribution.^{35–38} The addition of the alkali (as Na or K) individually has been observed to stabilize the “ ϵ -carbides”,^{25,26,39,40} and to decrease the Fe catalyst reoxidation during the FTS reaction.^{39,40}

However, how the combined Na-S promotion affects the formation of the aforementioned Fe carbides is not known. Also unknown is whether the combined Na-S promotion alters the properties of the individual Fe carbides, providing possible explanations for the observed FTS reaction hydrocarbon selectivity promotion effects.

Within this Chapter, we combine both: ex-situ XRPD with Rietveld Quantitative Phase Analysis (R-QPA) and ex-situ MAS. The Fe carbide formation and properties are studied via CO carburization of supported Fe(-Na-S)/ α -Al₂O₃ FTS reaction catalyst materials, with and without Na-S promotion. This scientific approach is summarized in **Figure 3.1**. In more detail, the primary objectives of this study are i) to experimentally verify the interpretation of the literature, as proposed in **Chapter 2**, concerning the Fe carbide phases and their formation temperatures. In addition, ii) also to establish an experimental, *precise* connection between the hyperfine fields and the Fe carbide crystal structures. Furthermore, we aim iii) to follow the effect of Na-S promotion on the formation of the Fe carbides via CO carburization in terms of phase quantities, crystallite diameters and possible effects on the crystal lattice parameters. Additionally, the effect of Na-S promotion on morphological changes and carbon deposition on the CO carburized Fe(-Na-S)/ α -Al₂O₃ catalyst materials is studied. Both, Transmission Electron Microscopy (TEM) and Thermogravimetric Analysis with combined Mass Spectrometry (TGA-MS) are employed for the purpose.

3.2 EXPERIMENTAL METHODS

3.2.1 Catalyst Preparation

3.2.1.1 Catalyst Synthesis

Supported catalyst materials with a nominal 7 weight percent (wt-%) Fe loading, with and without Na-S promotion, were prepared via Incipient Wetness Impregnation (IWI) of an alpha-alumina (α -Al₂O₃) support (BASF, 7 m²/g, 212-425 μ m particle size). Ammonium Fe(III) citrate (Acros, 211840010) was used as the Fe precursor, Fe(II) sulfate heptahydrate (Sigma-Aldrich, 215422) as the S precursor and Na tribasic citrate dihydrate (Sigma-Aldrich, S4641) as the Na precursor. The elemental analysis of the ammonium Fe(III) citrate Fe precursor was performed using Inductively Coupled Plasma Optical Emission Spectrophotometry (ICP-OES) (**Table 3.1**).

The precursor solution for preparing the Na-S promoted catalyst material was readied into a glass vial by individually solvating 0.011 g of the Fe sulfate and 0.040 g of the Na citrate precursors into 0.5 ml of demineralized water. After this, 1.281 g of the Fe citrate precursor was added to the glass vial. The closed glass vial was gently heated to 40-50°C for solvating all of the Fe citrate precursor and refluxing the glass vial walls clean of the added Fe citrate. The nominal promoter loadings are 0.29 wt-% for Na and 0.04 wt-% for S in the Na-S promoted catalyst material. The unpromoted catalyst material was prepared in the same manner as the promoted one, while using 1.290 g of the Fe citrate precursor but without adding the Fe sulfate or the Na citrate precursors.

Table 3.1

Inductively Coupled Plasma Optical Emission Spectrophotometry (ICP-OES) results of elemental analysis for ammonium Fe(III) citrate precursor $x\text{Fe}(\text{C}_6\text{H}_8\text{O}_7) \cdot y\text{NH}_3$ (Acros, 211840010) and the calcined unpromoted (UP) and Na-S promoted (Na-S) catalyst materials. The measurements for the same citrate precursor were done performed both at Mikrolab Kolbe and Universiteit Utrecht (UU) GeoLab.

	Elemental Analysis (weight-ppm)						
	Co	Cr	Mn	Fe	K	Na	S
$x\text{Fe}(\text{C}_6\text{H}_8\text{O}_7) \cdot y\text{NH}_3$	16	28	44	153 600	< dl	< dl	< dl
(citrate precursor)	-	-	-	162 500	57	121	9
Fe/ α -Al ₂ O ₃ (UP)	-	-	-	65 787	-	< 132	< 91
Fe-Na-S/ α -Al ₂ O ₃ (Na-S)	-	-	-	66 315	-	2 883	400 ^{a)}

a) - Analysis error can be >10 %.

< dl - Below detection limit.

(-) - Not determined.

3.00 g of the α -Al₂O₃ support was placed into a round-bottom boiling flask along with a magnetic stirring rod. The impregnation of the α -Al₂O₃ support was performed with two sequential drying steps. First, 0.5 ml and 0.4 ml of the prepared precursor solution was dropwise added on the α -Al₂O₃ support with constant stirring using the magnetic rod. 0.2 ml of demineralized water was added to the precursor solution for washing the glass vial walls and diluting the precursor solution in order to avoid precursor recrystallization. $\approx$ 0.05 ml of the diluted precursor solution was further dropwise added on the α -Al₂O₃ support. Some dry and sticky agglomerates were formed from the impregnated support material, which were gently broken apart with a glass rod. The impregnated catalyst material was then set to oven to dry for 2 h at 120°C under static air. After drying, the singly impregnated catalyst material was further impregnated with 0.15 ml of the precursor solution. 0.1 ml of demineralized water was added to the precursor solution glass vial for washing the vial walls. The remaining precursor solution was then added on the α -Al₂O₃ support and the impregnated catalyst material was set to oven to dry overnight at 120°C under static air.

The impregnation procedure was separately repeated three times for both, the unpromoted and Na-S promoted catalyst materials. After the impregnations, the three batches of catalyst material were mixed together after their respective final drying step.

3.2.1.2 Catalyst Calcining

Catalyst material calcining was done under flowing air in an open quartz vessel by heating (10°C/min) the catalyst from room temperature to 500°C, and holding the temperature for 6 h. In order to avoid gas diffusion limitations, the catalyst materials were calcined in batches of $\approx$ 2.8 g. Each batch lost $\approx$ 21 % of its weight during the calcining step. The calcined catalyst materials were combined for each of the

unpromoted and Na-S promoted catalyst batches and re-sieved to the catalyst particle fraction of 212-425 μm in order to obtain the ready, calcined catalyst materials. The results for the elemental contents of Fe, Na and S using ICP-OES analysis on the two sets of the calcined catalyst materials are given in **Table 3.1**.

3.2.2 Catalyst Reduction and Carburization

3.2.2.1 Catalyst Reduction

The calcined catalyst materials were reduced into metallic, zerovalent $\alpha\text{-Fe}$ on the $\alpha\text{-Al}_2\text{O}_3$ support prior to carburization with CO. For each reduction or carburization treatment, a ≈ 600 mg of calcined, unpromoted or Na-S promoted catalyst material was loaded into a plug flow quartz reactor. The reactor was heated up ($10^\circ\text{C}/\text{min}$) from room temperature to 400°C under $\text{N}_2\text{:H}_2$ flow (20:12 ml/min, at atmospheric pressure) and held at 400°C for 5 h. After the 5 h reduction step, the reactor was cooled down to 200°C under the set $\text{N}_2\text{:H}_2$ flow and let to stabilize for 15 min. For the catalysts only reduced with H_2 , without any subsequent CO carburization step, the reactor was cooled down to room temperature under the $\text{N}_2\text{:H}_2$ flow and flushed with N_2 for several hours.

3.2.2.2 Catalyst Carburization

The H_2 reduced catalyst materials, either with or without Na-S promotion, were subsequently carburized with CO without removing the catalyst from the reactor after the H_2 reduction step. Under the set $\text{N}_2\text{:H}_2$ flow, the reduced catalyst was heated up ($10^\circ\text{C}/\text{min}$) from 200°C to a desired carburization temperature. Upon reaching the desired carburization temperature, the $\text{N}_2\text{:H}_2$ flow was switched to pure CO flow (20 ml/min, at atmospheric pressure). The carburization temperatures and times used were: 240°C (2 h), 290°C (3 h), 340°C (16 h), 390°C (16 h) and 440°C (16 h). After the desired carburization period, the CO flow was switched to pure N_2 and the reactor was cooled down to room temperature and flushed with N_2 for several hours.

3.2.2.3 Catalyst Carburization at 25 bar

Calcined, unpromoted and Na-S promoted catalyst materials were *carburized directly without the H_2 reduction step* at an elevated pressure. ≈ 600 mg of calcined, unpromoted or Na-S promoted, catalyst material was loaded into a plug flow quartz reactor. Under a flow of He (5 ml/min), the reactor was heated to ($10^\circ\text{C}/\text{min}$) 120°C from the room temperature. The reactor was pressurized at 120°C to 25 bar total pressure with CO:He flow (40:5 ml/min) over a period of 2 h. The reactor was then heated up ($10^\circ\text{C}/\text{min}$) to 340°C . The unpromoted catalyst material was carburized for 120 h and the Na-S promoted catalyst for 168 h at 340°C at the 25 bar total CO:He pressure. After the carburization period, the reactor was first cooled down to room temperature after

which the gas flow was switched to Ar (12 ml/min) and the pressure reduced from 25 bar to atmospheric pressure.

All of the gases used in this study (Ar, He, N₂, H₂) were grade 5.0 purity (99.999 % pure), with the exception of the CO gas which had the purity grade of 2.5 (99.5 % pure). All of the used gases were supplied by Linde Gas Benelux.

3.2.3 Catalyst Characterization

3.2.3.1 Application of Transmission Electron Microscopy

The catalyst materials were prepared on carbon polymer layered Cu grids for performing bright field TEM imaging on the catalysts. The catalyst materials were ground with a mortar and mixed to ethanol. Droplets from the prepared catalyst/ethanol mixture were dropped on the Cu grids using a syringe piston and the Cu grids were let to dry under room temperature. The TEM imaging measurements were performed using Philips Tecnai 12 (120 kV) Field Emission Gun (FEG). From the obtained TEM images, the Fe particle diameters were manually counted by their longest diameter. The obtained Fe particle counts ($N \geq 500$) were binned to 4 nm count frequencies and fitted with a lognormal distribution function. The Fe particle (number-weighted) mean diameter and Fe particle size distribution Standard Deviations (STDs) were derived from the fitted lognormal distribution.

3.2.3.2 Application of Thermogravimetric Analysis – Mass Spectrometry

The amount of carbon deposited on the carburized catalyst materials was determined with Thermogravimetric Analysis with online analysis of the exhaust gases using Mass Spectrometry (TGA-MS). Perkin Elmer 1 TGA and Pfeiffer Vacuum OmniStar MS instruments were employed in the TGA-MS measurements. The catalyst materials were first flushed with N₂ (20 ml/min) and then heated up and held at 50°C for 10 min under O₂ (10 ml/min). The carbon burn-off was performed by heating the catalysts from 50°C to 800°C with 10°C/min ramp under the O₂ flow. Carbon-free, H₂ reduced only, parent unpromoted and Na-S promoted catalyst materials were also analyzed in order to account for the catalysts' weight gain from the Fe reoxidation during the TGA measurements. Also, any possible Fe weight loading differences between the parent unpromoted and Na-S promoted catalyst materials could be accounted for this way. The carbon wt-% on the carburized catalyst materials was determined as the weight change difference between the parent, reduced only and the corresponding carburized catalyst material at the end of the TGA-MS program. The carbon wt-%s were normalized to the total CO exposure time, in order to obtain the mean carbon deposition rate during the CO carburization treatments. Total CO₂ peak areas (m/z 44) recorded with the MS were determined by integration and normalized to the initial catalyst material amounts

loaded for the TGA-MS measurements.

3.2.3.3 Application of Mössbauer Absorption Spectroscopy

Ex-situ transmission ^{57}Fe MAS was performed at room temperature (300 K) with a conventional constant-acceleration spectrometer using a $^{57}\text{Co}(\text{Rh})$ source. Velocity calibration was carried out using an $\alpha\text{-Fe}$ foil. The MAS spectra were fitted using the Mosswin 4.0 software.⁴¹ Non-equivalent Fe position ratios were determined from the fitted relation of spectral contributions for each of the Fe carbide phases' hyperfine fields.

3.2.3.4 Application of X-ray Powder Diffractometry

The XRPD patterns for the prepared catalyst materials were measured ex-situ using a Bruker D8 Discover instrument in Debye-Scherrer transmission (capillary) geometry with a Mo ($K_{\alpha 1}$ 0.709 Å) source. The use of high energy Mo radiation in capillary geometry is especially suitable for phase quantification purposes.⁴² A Göbel-mirror was used to focus a near-parallel $\approx 600 \times 15\,000\ \mu\text{m}$ (height x width) X-ray beam on a static i.e. non-rotating $1\,000\ \mu\text{m}$ (outer diameter, wall thickness $10\ \mu\text{m}$) borosilicate capillary loaded with the catalyst material. An energy dispersive LynxEye XE Position Sensitive Detector (PSD) was used, only accepting the diffracted X-ray photons originating from the Mo K_{α} emission lines. 2.5° Soller slits were used on source and detector sides.

2θ range of $6\text{--}39^\circ$ with step size 0.015° and exposure time of 30 s per step, were used for each sample measurement. Prior to each measurement, the sample capillary was manually rotated and shortly test measured in order to verify the powder diffraction conditions. No changes in diffraction intensities were observed following the capillary rotation, thus, all of the measured samples contained a sufficient amount of diffracting Fe crystallites for proper powder diffraction measurements. Throughout this Dissertation, the term X-ray Powder Diffractometry (XRPD) is used to refer to X-ray diffraction phenomena based characterization experiments that are done under powder diffraction conditions.⁴³

For each measurement, the sample capillary was focused to the incident X-ray beam for maximum diffraction intensity. Air scattering contribution to the low angle background in the diffraction pattern was reduced by installing a stainless steel plate on top of the sample capillary during the measurements.

3.2.4 Application of Rietveld Quantitative Phase Analysis

Bruker TOPAS v5.0 software was used to apply the R-QPA method on the measured XRPD diffractograms.^{44,45} The major advantage of the Rietveld method is that it can be used for diffraction patterns with overlapping peaks.^{44–46}

In the TOPAS software, a diffraction pattern convolution based approach is

applied,⁴⁷ which can be presented as:

$$F(\theta) = I(\theta) \times S(\theta) \quad \text{XRPD Pattern Convolution} \quad (3.1)$$

In the **Equation 3.1**, $F(\theta)$ is the observed diffraction pattern with diffraction angle dependency θ , $I(\theta)$ is the instrument and $S(\theta)$ is the sample contribution to the observed diffraction pattern. The instrument term $I(\theta)$ is a convolution of the instrument emission profile (W) and the geometrical and instrumental aberrations ($G(\theta)$).⁴⁷

The goal in the application of the Rietveld method is to solve a theoretical term $I(\theta) \times S(\theta)$, with the use of (non-linear) least squares fitting, which reproduces the observed term $F(\theta)$ as closely as possible. For separating the contributions originating from $I(\theta)$ and $S(\theta)$, the instrumental contribution from $I(\theta)$ needs to be solved separately.^{48,49} $I(\theta)$ can be solved by using known geometric relations and a reference material with a known defect-free crystal structure, for which the peak broadening from the term $S(\theta)$ is negligible. The separately solved $I(\theta)$ is then kept constant while refining parameters for the diffraction contribution from the $S(\theta)$ in a measured diffraction pattern. From the best fitting calculated sample contribution $S(\theta)$, quantifiable properties of the measured sample, such as phase quantification when using predetermined crystalline structures (i.e. R-QPA),⁴⁵ and the phase crystallite size-strain values,^{48,50,51} can be obtained.

Within this Dissertation, the instrumental contribution term $I(\theta)$ was solved using National Bureau of Standards - Standard Reference Material 640 (NBS-SRM) (Si, $a=5.43088$ Å).⁵² For calculating a solution for the $I(\theta)$, the Fundamental Parameters Approach (FPA) implemented in TOPAS,⁴⁹ and (Le Bail) powder pattern decomposition with the Si standard unit cell without fitting sample size-strain peak broadening,⁵³ were applied. Shifts in the natural Mo K-emission lines introduced by the used Göbel-mirror,⁴⁹ were corrected by fixing the $K_{\alpha 1}$ emission to its natural value of 0.709300 Å and refining the $K_{\alpha 2}$ line to an arbitrary value of 0.713467 Å (natural Mo $K_{\alpha 2}$ 0.713607 Å) for the best peak position fit on the used Si reference standard. Two broad, low intensity K_{α} 's were added to the emission profile to account for the asymmetry from the multiplet K-emission lines.⁴⁹ High 2θ diffraction angle peak splitting due to dense Si reference material was minimized by focusing the X-ray beam in the top part of the measurement capillary. The parameters for instrumental contribution $I(\theta)$ were refined to the best fit (lowest R-value) on the measured Si reference diffraction pattern over 2θ range 11.5 - 60° using non-linear least squares fitting (Levenberg-Marquardt).

The sample contributions $S(\theta)$ were calculated as based on known crystal structures. Sample fit parameters were refined to achieve the best calculated pattern fit on the measured diffractograms over 2θ range 6 - 39° . This while keeping the previously

solved $I(\theta)$ constant. The crystal structures for the phases used in the Rietveld fitting were obtained from the International Centre for Diffraction Data Powder Diffraction File-4+ 2016 (ICDD-PDF-4+) and Crystallography Open Databases (COD). The ICDD-PDF-4+ and COD database numbers for Fe carbide structures used for the R-QPA fitting are given in **Chapter 2**. Crystal structures from ICDD-PDF-4+ 2016 database, namely: α -Al₂O₃ (#04-004-2852), α -Fe₂O₃ (#04-006-6579), Fe₃O₄ (#04-012-7038), Fe_{0.974}O (#01-073-2143) and α -Fe (#04-007-9753) were also used.

Fit parameters of sample displacement, cylindrical 2θ correction,⁵⁴ Fe structures' lattice parameters, background (8th order Chebyshev polynomial) and diffraction peak size-strain broadening,^{48,50,51} and crystal structure scale factors,⁴⁵ were all refined simultaneously. The possible angular unit cell lattice parameters (α , β , γ) were not refined in order to avoid any lattice parameter correlation. Lattice parameters for the α -Al₂O₃ support material were not refined in order to avoid correlation between the sample displacement, the cylindrical 2θ correction and any of the Fe structures' lattice parameters. Parameter constraints were used to achieve the visually most representative fits on the measured diffractograms, when needed.

For fitting of the size-strain diffraction peak broadening on the Fe phases, only a single Lorentzian peak shape component was used to estimate the size broadening while ignoring the Gaussian peak shape component for the strain broadening.^{51,55} The strain broadening is more prominent at the high 2θ diffraction where the measured Fe carbides gave low diffraction intensities, with significant diffraction peak overlap between the carbide phases. This resulted in unrealistic values for both the size and strain and thus prevented the reliable determination of the Gaussian strain broadening component. The crystallite mean diameter (i.e. volume-weighted mean column length or domain size) was estimated from the Lorentzian peak's Integral Breadth with the Scherrer Equation. When the Integral Breadth is used, the Scherrer Equation shape factor k can be taken as $k = 1$.^{51,55-57} The lack of the fitted Gaussian strain component introduces an error to the determined crystallite mean diameters,⁵⁵ making the diameters only comparable in relative terms within this Dissertation. The size-strain peak broadening for the α -Al₂O₃ support material was fitted with both, Lorentzian size and Gaussian strain peak components for more accurate overall fitting.

Contribution from the amorphous diffraction/scattering, a broad peak with low intensity within range ≈ 8 -12° 2θ , was estimated with two or three individual Lorentzian peaks in order to aid the background fitting.

The crystalline phase quantification was performed using the refined scale factors,⁴⁵ with the database structures without any structure refinement. The obtained wt-%s for each crystalline Fe phase were normalized to the total sum of the Fe phase wt-%s for achieving comparable crystalline Fe phase percentages to the Fe phase spectral

Table 3.2

Overview of the catalyst treatments and the used shorthand notation in this Chapter. The treatments were performed on supported Fe(-Na-S)/ α -Al₂O₃ catalyst materials with or without the Na-S promotion.

Shorthand Notation	Catalyst Material Description
Calcin.	Calcining in air at 500°C for 6 h
H ₂	H ₂ reduction at 400°C for 5 h, after the calcining step
240, 290, 340, 390, 440	CO carburization (at 1 atm) temperature in °C, <i>after the reduction step</i>
340 h.p.	CO carburization at 25 bar at 340°C, <i>after the calcining step</i>
UP	Unpromoted Fe/ α -Al ₂ O ₃ catalyst
Na-S	Na-S promoted Fe-Na-S/ α -Al ₂ O ₃ catalyst

contributions from the MAS quantifications. Elemental Fe contents for the catalyst materials were calculated on the basis of the nominal molar amounts of Fe per fitted crystalline Fe phase.

For presenting the measured diffractograms and their calculated patterns, all of the diffraction patterns were aligned in 2θ to α -Al₂O₃ (#04-004-2852) peak (0 2 4) at 23.515° 2θ (at Mo K $_{\alpha 1}$) for correcting the sample displacement. Furthermore, the calculated background polynomials were subtracted and the diffractograms were normalized in counts to the maximum counts of the α -Al₂O₃ (0 2 4) peak for each diffractogram.

3.3 RESULTS AND DISCUSSION

In this Chapter, we have used ex-situ XRPD with R-QPA applied for the diffraction pattern Fe phase quantification on a set of Fe-based FTS reaction catalyst materials. The R-QPA results were compared to the respective ex-situ MAS quantifications. This was done in order to follow the formation of Fe carbides from α -Fe with CO carburization within the temperature range of 240-440°C. Furthermore, the effect of Na-S promotion on the Fe oxide and carbide formation was followed by exposing unpromoted Fe/ α -Al₂O₃ (shorthand *UP*) and Na-S promoted Fe-Na-S/ α -Al₂O₃ (*Na-S*) catalyst materials to identical CO carburization treatments. Additionally, morphological changes in the catalyst materials were followed with TEM while carbon deposition on the catalyst materials was quantified with the use of TGA-MS.

The shorthand notation of 240, 290, 340, 390 or 440 is used to refer to the applied CO carburization temperature of the H₂ reduced catalyst material, at atmospheric pressure. Catalyst materials CO carburized *directly* after the calcining step at 25 bar CO pressure at 340°C are noted in shorthand as 340 h.p.. Shorthand notation *Calcin.* is used for catalyst materials characterized directly after catalysts' calcining step. Notation *H₂* is used for the only H₂ reduced catalyst materials. The overview of the shorthand notation used within this Chapter is given **Table 3.2**.

Figure 3.2

Transmission Electron Microscopy (TEM) images for the Na-S (Fe-Na-S/ α -Al₂O₃) catalyst materials after the applied catalyst treatments. Images after a) Calcin. and b) H₂ treatments and after CO carburization treatments c) 240, and d) 290. The TEM images measured for the corresponding UP catalyst materials were similar and are not shown.

3.3.1 Probing Morphological Changes and Carbon Deposition with Transmission Electron Microscopy and Thermogravimetric Analysis – Mass Spectrometry

TEM images taken after the calcining, H₂ reduction and the carburizing 240 and 290 treatments are shown in **Figure 3.2** for the Na-S catalyst materials. TEM images taken after the higher temperature carburization treatments (340, 390, 440 and 340 h.p.) for the Na-S catalyst materials are shown in **Figure 3.3**. The TEM images for the UP catalyst materials after their respective treatments were very similar to their Na-S counterparts and are not shown. The number-weighted Fe particle mean diameters and the size

Figure 3.3

Transmission Electron Microscopy (TEM) images for Na-S (Fe-Na-S/ α -Al₂O₃) catalyst materials after the applied catalyst treatments. Images after CO carburization treatments a) 340, b) zoom to the region pointed with an arrow in (a), c) 390, d) 440, and e) 340 h.p.. The TEM images measured for the corresponding UP catalyst materials were similar and are not shown.

Figure 3.4

Transmission Electron Microscopy (TEM) images for the Na-S H₂ (Fe-Na-S/ α -Al₂O₃) catalysts materials on different locations. Despite a vast majority of Fe particles on the catalyst being clustered and poorly separated (**Figure 3.2b**), in some areas a) and b), the Fe particles were well separated.

distribution STDs obtained on the basis of the measured TEM images, are shown in **Figure 3.5**.

After the Calcin. (**Figure 3.2a**) and H₂ (**Figure 3.2b**) catalyst treatments, Fe is present on the α -Al₂O₃ support as clusters, rather than as individual Fe particles. Each Fe cluster was counted as a “Fe particle” by its longest diameter. In some, occasional regions the Na-S H₂ catalyst material however did show vastly different Fe distributions in where the Fe particles were individually separated (**Figure 3.4**). At 500°C, a shorter calcining time (≈ 1 h) might lessen the Fe clustering.^{58,59}

After applying the mildest CO carburization treatments 240 and 290 (**Figure 3.2c-d**), the Fe particles start to separate and resemble single Fe particles more than “a cluster of Fe particles”. This is reflected in the Fe particle size distribution values in **Figure 3.5**: from treatment Calcin. to 290, the Fe particle mean diameters and the STD values both decrease. That is, the Fe particles become smaller, with more homogenous size distribution. Both UP and Na-S catalysts show the same overall trend.

With CO carburization treatments with temperatures above 340°C, the Fe particles become encapsulated in carbon and invariably are not attached to the α -Al₂O₃ support (**Figure 3.3**). This is unlike with the Fe particles after the CO carburization treatments 240 and 290, which are still attached to the α -Al₂O₃ support. The catalyst materials after the treatments 340, 390, 440, and 340 h.p. resemble more of a composite system where the carbon-encapsulated Fe is incorporated to the α -Al₂O₃ support than a pure, metal

supported catalyst system.

From the treatment 340 to the higher temperature 440 treatment, a somewhat increasing trend in the Fe particle mean diameters and STD's can be observed for the Na-S catalyst materials. The Fe particle mean diameter growth with increasing carburization temperature seems to be significant for only the Na-S promoted materials (**Figure 3.5**). This is akin to a literature observation on the Na-S promotion effect increasing Fe particle diameters.⁶⁰

Furthermore, it is worth noting that it can be expected that the relatively small Fe particles of ≤ 60 nm within the catalyst materials described in this Chapter (**Figure 3.5**), after all catalyst treatments, prevent any C atom diffusion problems to the α -Fe lattice. This allows complete, unrestricted Fe carburization. If bulk Fe catalyst materials were used instead, C atom diffusion problems might arise thus decreasing the degree of Fe carburization.^{5,6,15}

The TGA measured carbon deposition as wt-%s and the average carbon deposition rates after each applied carburization treatment are shown in **Figure 3.6**. The simultaneously measured MS data for the total CO₂ released and the catalyst material weight loss fractions during the TGA runs are given in the **Figure 3.7**. The quantification results of the CO₂ released in the TGA measurements (**Figure 3.7c**) are in perfect agreement with the deposited carbon wt-% results (**Figure 3.6a**). That is, the TGA observed weight decrease on the catalyst materials is due to carbon deposition during

Figure 3.5

Transmission Electron Microscopy (TEM) image based, Fe particle a) (number-weighted) mean diameters and b) size distribution Standard Deviations (STDs) after the respective catalyst treatments of the UP and Na-S (Fe(-Na-S)/ α -Al₂O₃) catalyst materials.

Figure 3.6

Thermogravimetric Analysis (TGA) derived carbon deposition with UP and Na-S ($\text{Fe}(-\text{Na-S})/\alpha\text{-Al}_2\text{O}_3$) catalyst materials, after the CO carburization catalyst treatments. The results for a) total wt-% of carbon deposited and b) carbon deposition rate.

the carburization treatments.

Some trends in the carbon deposition can be observed as (**Figure 3.6**): i) treatments 240 and 290 show small total amounts of deposited carbon but with high rates of carbon deposition, and ii) from the treatment 340 to 440 the carbon deposition rate increases with increasing carburization temperature and iii) the effect of Na-S promotion is to increase the carbon deposition rate within the temperature range of 340–390°C. The Na-S promotion effect however diminishes with increasing carburization treatment temperature. In addition, iv) the high-pressure treatment 340 h.p. at 25 bar CO has around the same carbon deposition rates as the corresponding treatment 340 with atmospheric CO pressure.

With the treatments 240 and 290, the “carbon deposition” is due to carbide formation and dissolution of C atoms into the Fe lattice, a process which is very fast with $\alpha\text{-Fe}$.^{15,61} The dissolution of C to the Fe lattice is not affected by the Na-S promotion (**Figure 3.6b**).

From the treatment 340 to 440, the Boudouard reaction (i.e. CO disproportionation into C and CO_2) takes over and starts to deposit carbon on the catalyst materials, in agreement with both the TGA (**Figure 3.6**) and TEM results (**Figure 3.3**). Carbon deposition via the Boudouard reaction becomes significant with Fe-based catalyst materials at $\geq 300^\circ\text{C}$.^{16,62–65} From the TGA-MS observations it can be devised that the Na-S promotion increases the carbon deposition rates at $\approx 340^\circ\text{C}$ and with increasing

Figure 3.7

Thermogravimetric Analysis – Mass Spectrometry (TGA-MS) measurements for UP and Na-S (Fe(-Na-S)/ α -Al₂O₃) catalyst materials after each respective catalyst treatment. TGA weight loss fractions for a) UP and b) Na-S catalyst materials, and the corresponding c) MS-derived CO₂ peak areas (m/z 44) on the total CO₂ released during the TGA measurements, as normalized to the initial catalyst material amount.

temperature (≥ 390 – 440°C) the Na-S promotion effect diminishes and disappears (**Figure 3.6b**). From literature, the addition of alkali elements has been observed intrinsically to increase the carbon deposition.^{16,62,66} Therefore, the Na-S promotion behaves akin to alkali-only addition within the temperature range of 340– 390°C , increasing the carbon deposition with CO carburization via the Boudouard reaction.

By comparing the treatments 340 and 340 h.p., the average carbon deposition rates are the same i.e. the higher 25 bar CO pressure does not seem to increase the rate of the carbon deposition. However, under H₂:CO atmosphere i.e. in the FTS reaction, increased reaction pressure does increase, at least the initial, carbon deposition rate on the Fe-based catalyst materials.^{16,67}

For further research on the effect of Na-S promotion on the Boudouard reaction during the FTS reaction, the amount of deposited carbon should be compared in CO conversion normalized terms to unpromoted catalysts. Otherwise, the carbon deposition rates and amounts will merely follow the CO conversion levels in the FTS reaction, not the intrinsic Boudouard reaction rate.

Figure 3.8

R_{wp}-values for the differences between the X-ray Powder Diffractometry (XRPD) measured and Rietveld Quantitative Phase Analysis (R-QPA) calculated diffractograms. R_{wp}- and R_{wp'}-values for a) UP and b) Na-S (Fe-(Na-S)/ α -Al₂O₃) catalyst materials, after the respective catalyst treatment.

3.3.2 Phase Quantification with X-ray Powder Diffractometry/Rietveld Quantitative Phase Analysis and Mössbauer Absorption Spectroscopy

Background corrected, ex-situ XRPD measured and the Rietveld method calculated diffraction patterns with their difference to the experimentally measured XRPD patterns, for the Calcin. and H₂ catalyst materials are shown in **Figure 3.9**. The diffraction patterns after the CO carburization treatments are given in **Figure 3.10** for the UP and in **Figure 3.11** for the Na-S catalyst materials. For sake of clarity, only the range 13-29° 2 θ Mo K α , where the Fe carbides show their most intense diffraction peaks, is shown in the figures. R-weighted pattern (R_{wp}) values for the Rietveld fits are given in the **Figure 3.8**.⁶⁸ The MAS spectra with fitted phase peaks for the UP catalyst materials after H₂ and carburizing 240-440 and 340 h.p. catalyst treatments are given in **Figure 3.12**. The MAS spectra for the Na-S catalyst materials are omitted.

The crystalline Fe phase quantifications with R-QPA and the corresponding quantification results as based on the MAS measurements are presented in **Figure 3.13**. The used MAS fit parameters are given in **Table 3.3** for the UP and in **Table 3.4** for the Na-S catalyst materials. The R-QPA and MAS quantifications are in good agreement with each other.

The R-QPA quantification results for the Fe phases in the Calcin. catalyst materials, which only quantified α -Fe₂O₃ (hematite) for both UP and Na-S catalysts, are excluded from the **Figure 3.13b**. These quantification results were nevertheless used for

Figure 3.9

Background corrected, ex-situ measured X-ray Powder Diffractometry (XRPD) and Rietveld method calculated diffraction patterns over a range 13-29° 2θ for UP a) Calcin. and c) H₂; and for Na-S b) Calcin. and d) H₂ treated catalyst materials (Fe(-Na-S)/ α -Al₂O₃). Normalized counts are on a square-root scale.

calculating the elemental Fe contributions for the UP and Na-S Calcin. catalyst materials in the **Figure 3.13c**.

The elemental Fe contributions do not change significantly for the studied catalyst materials. The mean elemental Fe wt-%s are for UP catalyst materials 6.4 ± 0.5 wt-% and for Na-S materials 6.7 ± 0.5 wt-%, in comparison between all of the applied treatments within the promotion groups (**Figure 3.13c**). This can be taken as an indication that all of the Fe phases present in the XRPD patterns have been fitted consistently with a calculated Fe crystal structure. ICP-OES quantification results indicated the presence of ≈ 6.6 wt-% of elemental Fe for both the parent UP and Na-S Calcin. catalyst materials (**Table 3.1**).

Figure 3.10

Background corrected, ex-situ measured X-ray Powder Diffraction (XRPD) and Rietveld method calculated diffraction patterns over a range 13 – 29° 2θ for the UP ($\text{Fe}/\alpha\text{-Al}_2\text{O}_3$) catalyst materials after the respective catalyst treatment. The diffraction patterns as after catalyst treatment a) 240, b) 290, c) 340, d) 390, e) 440 and f) 340 h.p.. Normalized counts are on a square-root scale.

Figure 3.11

Background corrected, ex-situ measured X-ray Powder Diffractometry (XRPD) and Rietveld method calculated diffraction patterns over a range 13-29° 2θ for the Na-S (Fe-Na-S/ α -Al₂O₃) catalyst materials after the respective catalyst treatment. The diffraction patterns as after catalyst treatment a) 240, b) 290, c) 340, d) 390, e) 440 and f) 340 h.p.. Normalized counts are on a square-root scale.

Figure 3.12

Ex-situ measured Mössbauer Absorption Spectroscopy (MAS) spectra with fitted patterns for the Fe phases for the UP (Fe/ α -Al₂O₃) catalyst materials. The MAS spectra as measured at room temperature (300 K) after catalyst treatment a) H₂, b) 240, c) 290, d) 340, e) 390, f) 440 and g) 340 h.p.. The Roman numbers (*I, II, III*) mark the different non-equal Fe positions fitted for the Fe phases. SPM = superparamagnetic.

By comparing the elemental Fe content after each catalyst treatment (**Figure 3.13c**) to the trends on deposited carbon (**Figure 3.6a**), it can be concluded that no significant amount of Fe is lost, despite the carbon deposition and Fe growing off the α -Al₂O₃ support material with CO treatments $\geq 340^\circ\text{C}$ (**Figure 3.3**).

As a general note on performing bulk characterization studies on zerovalent Fe-based materials: a ≈ 4 -5 nm Fe reoxidation shell layer is expected to form upon exposure of the catalyst material to air or other source of O atoms.^{69,70} Such layer on Fe is indeed observable in e.g. **Figure 3.3b**. This effectively decreases the crystalline content of the Fe carbides from what they were during the application of each catalyst treatment. That is, as a general recommendation: at least a ≈ 20 nm Fe particle diameter is needed in order to preserve sufficient quantities of the Fe carbides for a bulk technique study, as is done here (**Figure 3.5a**). Fe particles smaller than ≈ 10 nm by diameter would be increasingly or solely measured as Fe oxides in bulk quantification studies due to the reoxidation by O atoms, skewing the quantification results.^{13,71}

In the following discussion, the effects of each catalyst treatment on the Fe phases present in the studied catalyst materials are discussed based on the R-QPA and MAS quantification results. A discussion on the results for the Calcin. catalyst materials is omitted. First, catalyst materials after the applied H₂ reduction treatment are discussed. This discussion is followed with remarks on the effect of the CO carburization treatments 240-440.

The carburizing treatments are first discussed, i) regarding the effect of increasing CO carburization temperature, and after which ii) the effect of Na-S promotion in the CO carburization process is treated. The formation of θ -Fe₇C₃ with the catalyst treatment 340 h.p. is discussed separately after the other CO carburization treatments.

The discussion is concluded with collective comments on the Fe crystallite diameter evolution due to the applied treatments (**Figure 3.16**), in relation to the Fe particle diameter trends derived from the TEM images (**Figure 3.6**).

3.3.2.1 The Effect of H₂ Reduction

After the H₂ reduction catalyst treatment, both the UP and Na-S catalyst materials are well reduced into α -Fe. This observation is valid regardless of the reduction retarding effect of alkali in the Na-S catalysts,⁷² and possible catalyst material reoxidation upon exposure of the zerovalent Fe to air.^{69,70,73}

All of the catalysts under study were cooled down under N₂ or N₂:H₂ flow and flushed with N₂ at room temperature for a period of time, without a dedicated passivation step.⁷⁰ No detrimental reoxidation of α -Fe is observed in the H₂ treated catalyst materials, which implies that the O atom containing impurities in the input N₂ gas sufficiently passivate the catalysts for the present bulk Fe study purposes.

Figure 3.13

The Fe phase quantifications for UP and Na-S (Fe(-Na-S)/ α -Al₂O₃) catalyst materials after the applied catalyst treatments. Quantification results for a) room temperature (300 K) Mössbauer Absorption Spectroscopy (MAS), and b) Rietveld Quantitative Phase Analysis (R-QPA). R-QPA results were used to derive c) the elemental Fe wt-% loadings from the crystalline Fe phases. Percentage labels cut-off is set to <10%. SPM = superparamagnetic.

Furthermore, the Fe oxide content quantifications of 31 % of Fe₃O₄ (magnetite) with R-QPA and 15-17 % of Fe³⁺ (Superparamagnetic, SPM) with MAS are in discrepancy with each other. This Fe oxide content is likely due to the formed passivation layer,^{69,70} which is hard to quantify with the bulk characterization techniques applied in this

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Table 3.3

Ex-situ Mössbauer Absorption Spectroscopy (MAS) fitted parameters for the UP (Fe/ α -Al₂O₃) catalyst materials after the respective catalyst treatment. Measurements were done at room temperature (300 K).

Treatment	Isomer Shift	Quadrupole Splitting	Hyperfine Field	Line Width	Phase	Spectral Contribution
	(mm s ⁻¹)	(mm s ⁻¹)	(T)	(mm s ⁻¹)		
UP H ₂	0.00	-	33.0	0.29	Fe ⁰	83
	0.32	1.11	-	0.98	Fe ³⁺ (SPM)	17
UP 240	0.00	-	33.4	0.30	Fe ⁰	3
	0.20	-	23.6	0.82	ϵ -Fe ₃ C	20
	0.24	-	17.4	0.55	η -Fe ₂ C	50
	0.31	0.99	-	0.60	Fe ³⁺ (SPM)	27
UP 290	0.26	-	21.3	0.43	χ -Fe ₅ C ₂ (I)	16
	0.16	-	18.8	0.43	χ -Fe ₅ C ₂ (II)	17
	0.28	-	10.9	0.43	χ -Fe ₅ C ₂ (III)	10
	0.25	-	16.9	0.43	η -Fe ₂ C	32
	0.30	0.98	-	0.55	Fe ³⁺ (SPM)	25
UP 340	0.24	-	21.2	0.42	χ -Fe ₅ C ₂ (I)	40
	0.18	-	18.7	0.42	χ -Fe ₅ C ₂ (II)	32
	0.21	-	11.2	0.42	χ -Fe ₅ C ₂ (III)	17
	0.30	0.89	-	0.47	Fe ³⁺ (SPM)	11
UP 390	0.24	-	21.4	0.33	χ -Fe ₅ C ₂ (I)	21
	0.17	-	18.3	0.33	χ -Fe ₅ C ₂ (II)	18
	0.15	-	11.7	0.33	χ -Fe ₅ C ₂ (III)	11
	0.20	-	20.2	0.33	θ -Fe ₃ C	40
	0.30	0.81	-	0.51	Fe ³⁺ (SPM)	10
UP 440	0.24	-	20.9	0.32	χ -Fe ₅ C ₂ (I)	15
	0.17	-	18.8	0.32	χ -Fe ₅ C ₂ (II)	15
	0.20	-	11.0	0.32	χ -Fe ₅ C ₂ (III)	7
	0.18	-	20.3	0.32	θ -Fe ₃ C	54
	0.23	0.90	-	0.41	Fe _x C (SPM)	9
UP 340	0.25	0.08	21.4	0.32	χ -Fe ₅ C ₂ (I)	25
h.p.	0.26	-0.05	18.1	0.32	χ -Fe ₅ C ₂ (II)	23
	0.14	0.03	10.4	0.32	χ -Fe ₅ C ₂ (III)	19
	0.32	-0.28	22.4	0.32	θ -Fe ₇ C ₃ (I)	7
	0.19	0.29	16.3	0.32	θ -Fe ₇ C ₃ (II)	14
	0.25	0.03	19.8	0.32	θ -Fe ₇ C ₃ (III)	8
	0.15	0.89	-	0.30	Fe _x C (SPM)	4

Experimental uncertainties: Isomer Shift ± 0.01 mm s⁻¹, Quadrupole Splitting ± 0.01 mm s⁻¹, Line Width ± 0.01 mm s⁻¹, Hyperfine Field ± 0.1 T, Spectral Contribution ± 3 %. SPM = Superparamagnetic.

Chapter. As an example, for the Na-S 340 catalyst material, the ≈ 4 nm passivation layer can be seen in **Figure 3.3b** around the carbon encapsulated Fe particle.

MAS measurements at liquid He temperature at 4.2 K would improve the quantification accuracy of the Fe oxide/hydroxide surface layer with respect to the

room temperature MAS applied in this Chapter.^{73,74} XRPD-based data is naturally less accurate with poorly crystalline,^{42,75} and/or with small $\lesssim 4\text{-}5$ nm crystallite diameter phases. The R-QPA fitted Fe_3O_4 phase (**Figure 3.9c-d**), gives very weak and broad diffraction peaks with very small estimated crystallite diameters of ≈ 3 nm (**Figure 3.16**).

It is more likely that the MAS measurements quantify the Fe oxides in the H_2 treated catalyst materials more reliably in the presented results, despite the measurements at room temperature. Although Fe_3O_4 crystal structure is used in the R-QPA fits, ferrihydrite structures also gave similar overall R-QPA fits (the fits are not shown).⁷⁶

In the Na-S H_2 catalyst materials, the presence of 12 % of $\text{Fe}_{0.974}\text{O}$ (wüstite) phase is enhanced in the R-QPA phase quantification as a difference to the UP H_2 catalyst materials with only 5 % of the $\text{Fe}_{0.974}\text{O}$ phase present (**Figure 3.13b**). Various chemical interactions between the Fe and support materials or other added compounds, such as alkali K, can stabilize the wüstite phase.⁷⁷ Thus, the Na-S promotion somewhat stabilizes the $\text{Fe}_{0.974}\text{O}$ phase. The $\alpha\text{-Al}_2\text{O}_3$ support does not play a role in the stabilization as the UP H_2 catalyst material does not have a significant $\text{Fe}_{0.974}\text{O}$ phase content. No clear presence of the $\text{Fe}_{0.974}\text{O}$ phase was detected with any of the MAS quantifications (**Figure 3.13a**).

3.3.2.2 The Effect of the Carburization Temperature

The effect of increasing CO carburization temperature is to shift the Fe carbide phase formation from the $\alpha\text{-Fe}$ starting material in order of $\epsilon\text{-Fe}_3\text{C} < \eta\text{-Fe}_2\text{C} < \chi\text{-Fe}_5\text{C}_2 < \theta\text{-Fe}_3\text{C}$, as can be observed in the Fe phase quantification data (**Figure 3.13a-b**). This order is in agreement with the Fe carbide temperature evolution interpreted from the literature, following the nomenclature proposed for the Fe carbides in **Chapter 2**. With a short CO carburization time ≤ 3 h at low temperature $\leq 290^\circ\text{C}$, also Fe oxide phases are present in the catalyst materials, in addition to the Fe carbides.

A. Effect on Fe Oxides

When moving from the catalyst treatment H_2 to the treatments 240 and 290, the Fe oxide ($\text{Fe}_3\text{O}_4/\text{Fe}^{3+}$ SMP) content in the catalyst materials increase, according to the MAS quantification results (**Figure 3.13a**). When comparing the XRPD patterns for the catalyst treatments H_2 UP and Na-S (**Figure 3.9c-d**), 240 and 290 UP (**Figure 3.10a-b**) and 240 and 290 Na-S (**Figure 3.11a-b**), the diffraction originating from the fitted Fe_3O_4 phase (e.g. at $27.62^\circ 2\theta$) is increased after the catalyst treatments 240 and 290. The total MAS (Fe^{3+}) and R-QPA ($\text{Fe}_3\text{O}_4 + \text{Fe}_{0.974}\text{O}$) quantifications of the Fe oxide phases are in fair agreement for the catalyst treatments 240 and 290. Thus, the increased crystallinity of the Fe oxide phases ($\text{Fe}_3\text{O}_4 + \text{Fe}_{0.974}\text{O}$) in respect to the H_2 treated catalyst materials improves the R-QPA accuracy for the catalyst treatments 240 and 290

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Table 3.4

Ex-situ Mössbauer Absorption Spectroscopy (MAS) fitted parameters for the Na-S (Fe-Na-S/ α -Al₂O₃) catalyst materials after the respective catalyst treatment. Measurements were done at room temperature (300 K).

Treatment	Isomer Shift	Quadrupole Splitting	Hyperfine Field	Line Width	Phase	Spectral Contribution
	(mm s ⁻¹)	(mm s ⁻¹)	(T)	(mm s ⁻¹)		
Na-S H ₂	0.00	-	33.5	0.30	Fe ⁰	85
	0.32	1.22	-	0.98	Fe ³⁺ (SPM)	15
Na-S 240	0.00	-	33.2	0.30	Fe ⁰	8
	0.18	-	23.2	0.68	ϵ -Fe ₃ C	16
	0.23	-	17.5	0.53	η -Fe ₂ C	37
	0.38	1.01	-	0.89	Fe ³⁺ (SPM)	31
	0.38	0.39	45.1	1.08	Fe ³⁺	8
Na-S 290	0.23	-	21.8	0.43	χ -Fe ₅ C ₂ (I)	15
	0.17	-	19.3	0.43	χ -Fe ₅ C ₂ (II)	16
	0.22	-	11.4	0.43	χ -Fe ₅ C ₂ (III)	8
	0.23	-	17.2	0.43	η -Fe ₂ C	22
	0.34	1.02	-	0.68	Fe ³⁺ (SPM)	25
	0.38	0.17	44.9	1.44	Fe ³⁺	14
Na-S 340	0.27	-	21.6	0.44	χ -Fe ₅ C ₂ (I)	35
	0.20	-	18.8	0.44	χ -Fe ₅ C ₂ (II)	30
	0.18	-	11.5	0.44	χ -Fe ₅ C ₂ (III)	19
	0.19	1.03	-	0.39	Fe _x C (SPM)	8
	0.39	-0.03	48.0	1.07	Fe ³⁺	8
Na-S 390	0.27	-	21.3	0.38	χ -Fe ₅ C ₂ (I)	22
	0.20	-	18.4	0.38	χ -Fe ₅ C ₂ (II)	22
	0.18	-	11.7	0.38	χ -Fe ₅ C ₂ (III)	16
	0.16	-	20.9	0.38	θ -Fe ₃ C	34
	0.17	1.02	-	0.30	Fe _x C (SPM)	6
Na-S 440	0.23	-	21.7	0.35	χ -Fe ₅ C ₂ (I)	20
	0.18	-	18.7	0.35	χ -Fe ₅ C ₂ (II)	20
	0.15	-	11.8	0.35	χ -Fe ₅ C ₂ (III)	10
	0.20	-	20.7	0.36	θ -Fe ₃ C	44
	0.15	1.02	-	0.45	Fe _x C (SPM)	6
Na-S 340	0.27	-	21.6	0.35	χ -Fe ₅ C ₂ (I)	26
h.p.	0.23	-	17.9	0.35	χ -Fe ₅ C ₂ (II)	24
	0.16	-	10.2	0.35	χ -Fe ₅ C ₂ (III)	20
	0.32	-0.25	22.3	0.35	θ -Fe ₇ C ₃ (I)	7
	0.21	0.30	16.2	0.35	θ -Fe ₇ C ₃ (II)	11
	0.30	0.01	19.2	0.35	θ -Fe ₇ C ₃ (III)	5
	0.23	1.12	-	0.45	Fe _x C (SPM)	7

Experimental uncertainties: Isomer Shift ± 0.01 mm s⁻¹, Quadrupole Splitting ± 0.01 mm s⁻¹, Line Width ± 0.01 mm s⁻¹, Hyperfine Field ± 0.1 T, Spectral Contribution ± 3 %. SPM = Superparamagnetic.

quantification results.

As discussed with the H₂ treated catalyst materials, reoxidation of the (near-)zerovalent Fe i.e. α -Fe or carbides, is expected to take place upon air exposure after the respective carburization treatments.^{69,70} The more accurate MAS quantification results with regard to the Fe oxides show roughly a doubling in the quantified Fe oxide content from 15-17 % to 25-39 % (**Figure 3.13a**), when comparing the H₂ to 240 and 290 treated catalyst materials. As the Fe oxide content increases quite a bit in comparison to the “reoxidation baseline case” of the H₂ treated catalyst materials, other phenomena than simply a Fe reoxidation by air exposure, are also likely to play a role.

The increased Fe oxidation can possibly be due to the O from CO dissociation during the CO carburization behaving as an oxidation agent.⁷⁸ As possible explanations: i) the O dissociated from CO is poorly removed as CO₂,^{79,80} with short applied CO treatment time of <3 h and/or due to low reaction temperature of <290°C, and/or ii) the O-removal product CO₂ causes oxidation of α -Fe downstream in the catalyst bed.^{16,27,81-83}

Any reoxidized Fe is expected to reduce poorly back to α -Fe for recarburization by CO, with the applied reduction temperatures $\leq 290^\circ\text{C}$.⁷⁷ Low amounts of ($\approx 1\%$) H₂ in the CO stream increase the CO dissociation rate over α -Fe.^{84,85} This effect as H₂ possibly removes surface O from dissociated CO as H₂O more efficiently than CO does as CO₂. When low temperature ($\leq 235^\circ\text{C}$) carburization is done with a H₂:CO mixture, instead of pure CO, the resulting Fe oxidization degree in the Fe carburization process might be decreased.¹² Or alternatively, O-free hydrocarbons can also be used for the α -Fe carburization to decrease Fe reoxidation.⁷⁸

Thus, indirectly, the quantification results for 240 and 290 catalyst materials can be interpreted to support the thought of the Fe oxidation via poor removal of O from CO dissociation by CO only. In addition, the oxidative effect by CO₂ can participate to the Fe reoxidation process but this effect is harder to determine based on the results. Worth noting is that the addition of Na-S promoters increases the Fe oxide formation after the catalyst treatments 240 and 290, from 25-27 % with UP to 39 % with Na-S catalyst materials, on the basis of the MAS quantifications (**Figure 3.13a**). This oxidation effect will be discussed more later on in the Chapter along with rest of the Na-S promotion effects on Fe carburization.

The Fe oxide content decreases in respect to the H₂ catalyst materials with the catalyst treatments with longer CO exposure times of ≥ 16 h and above temperature of 340°C, i.e. with the treatments 340, 390, 440. This is observed with both the R-QPA and MAS quantifications (**Figure 3.13a-b**). That is, the catalyst materials’ oxidation by O from the CO dissociation does not play a role, and the catalyst materials’ reoxidation by air exposure is also decreased. Both the higher carburization temperature and the increased CO exposure time are expected to improve the O removal as CO₂, and to increase the re-reduction of any reoxidized α -Fe.⁷⁷ Thus the overall carburization

extent increases as observed. Also, the observed increase in the carbon deposition by the Boudouard reaction (**Figure 3.6**),^{16,62–64,66} likely decreases the Fe phases propensity for reoxidation upon exposure to air.

B. Fe Carbide Formation below $\approx 300^\circ\text{C}$

After the mildest CO carburization treatment 240, ϵ -Fe₃C and η -Fe₂C are the major Fe carbide phases formed on the catalyst materials (**Figure 3.13a-b**). Small amounts of residual α -Fe can be detected as a sign of incomplete carburization for both UP and Na-S 240 catalyst materials. With R-QPA, also small amounts of χ -Fe₅C₂ (8–9 %) after the catalyst treatment 240 could be quantified (**Figure 3.13b**). However, MAS did not quantify any of the χ -Fe₅C₂ phase for either the UP or the Na-S catalyst materials (**Figure 3.13a**). In the XRPD patterns for the 240 catalyst materials, weak diffraction peaks originating from the χ -Fe₅C₂ phase can be seen, perhaps best, from the two small peaks at $\approx 21.3^\circ$ and $\approx 22.5^\circ$ 2θ (**Figure 3.10a** and **Figure 3.11a**).

With further increasing the catalyst CO carburization time and temperature with the catalyst treatment 290, the contribution from the χ -Fe₅C₂ phase increases. At the same time, the η -Fe₂C phase is still present, while the ϵ -Fe₃C phase is no longer observed with either R-QPA or MAS (**Figure 3.13a-b**).

The ϵ -Fe₃C phase is expected to form within a carburization the temperature range of 100 – 265°C ,^{30,31,34,73,86–89} and the η -Fe₂C phase between 160 – 300°C .^{2,19,30–32,34,87–90} Thus, the R-QPA and MAS quantification results with regard to the ϵ -Fe₃C and η -Fe₂C phases are in good agreement with the literature.

Furthermore, in literature, the formation of the χ -Fe₅C₂ phase has been observed to start, with α -Fe as the starting material, from temperatures of ≈ 250 – 260°C .^{86,87,91} As a notable discrepancy, Niemantsverdriet et al. have observed the formation of the χ -Fe₅C₂ phase to already start from a temperature of 190°C .² This temperature is a lot lower than expected, on the basis of both the R-QPA and MAS quantifications (**Figure 3.13a-b**) and the literature.

With the use of MAS, Niemantsverdriet et al. observed formation of Fe carbides from α -Fe under H₂:CO 1:1 at 1 bar as (when following our nomenclature): at 190°C (24 h) unknown quantity of η -Fe₂C and 36 % χ -Fe₅C₂, at 240°C (24 h) 35 % η -Fe₂C and 65 % χ -Fe₅C₂, at 350°C (3 h) 12 % η -Fe₂C, 47 % χ -Fe₅C₂ and 41 % θ -Fe₃C and at 450°C (1.5 h) 100 % θ -Fe₃C.² When comparing the results by Niemantsverdriet et al. to the quantification results for the Fe carbides in **Figure 3.13a-b**, it can be observed that the results by Niemantsverdriet et al. would compare more reasonably, if a constant temperature shift of $\approx +50^\circ\text{C}$ is applied to their data.

With FTS reaction under H₂:CO 2:1 at 1.03 bar at 200°C (3.9 h) Boellaard, van der Kraan and Geus,³⁰ quantified Fe carbides with MAS as 18 % ϵ -Fe₃C and 54 % η -Fe₂C. No observation of the χ -Fe₅C₂ phase was made. In a similar manner, with MAS

quantification, Amelse et al. observed only the ε -Fe₃C and η -Fe₂C phases after exposing α -Fe to H₂:CO 3:1 at 250°C (2.5 h) at atmospheric pressure, without observing any presence of the χ -Fe₅C₂ phase.⁷³ At higher carburization temperatures, Jiang et al. have quantified with MAS 14 % Fe₃O₄, 25 % η -Fe₂C and 61 % χ -Fe₅C₂ after H₂:CO 1:1 at 10 bar at 300°C (50 h) with pre-reduced K promoted Fe catalyst materials.⁹⁰ The results at 240°C (24 h) by Niemantsverdriet et al. seem very similar to the results by Jiang et al. at 300°C (50 h), and are the best match to the R-QPA and MAS results with the catalyst treatment 290 (CO, 290°C, 3 h) (**Figure 3.13a-b**). Again, all the above literature examples were interpreted to follow our nomenclature for the Fe carbide phases.

Thus, we shall presume a temperature offset of +50°C to all of the results by Niemantsverdriet et al.,² after which their quantifications are in a good agreement with the R-QPA and MAS results in **Figure 3.13a-b**, and also with the above literature examples.

The exception in the results by Niemantsverdriet et al. in comparison to the R-QPA and MAS quantifications in **Figure 3.13a-b**, is that even with the +50°C shift some η -Fe₂C (12 %) should be present even after carburizing reaction at 400°C (3 h). Furthermore, Wezendonk et al. have observed the η -Fe₂C phase at 340°C (≥ 24 h) in their Fe carburization and FTS reaction studies.¹³ We could not observe any η -Fe₂C with $\geq 340^\circ\text{C}$ CO carburization temperature, i.e. with the catalyst treatments 340-440. The common denominator for both of the cited studies is that the η -Fe₂C phase is *performed* first at a lower carburization temperature and then heated subsequently to a higher reaction temperature. Thus, if a η -Fe₂C phase is present a priori to the FTS reaction, some of it *may remain stable* i.e. its carbide-to-carbide transition is hindered with reaction temperatures higher than 300°C. However, on the basis of the quantification results in **Figure 3.13a-b**: η -Fe₂C does not directly form at 340°C when α -Fe is used as the starting phase for the carburization.

Thus, we assign 160-300°C as formation temperature for the η -Fe₂C phase from α -Fe. Nonetheless, a maximum thermal stability of the phase can reach at least $\approx 340^\circ\text{C}$ if the η -Fe₂C phase is preformed prior to the temperature increase. We acknowledge but exclude the rather high 400°C maximum thermal stability for the η -Fe₂C phase as observed by Niemantsverdriet et al. for now, due to possible uncertainty in the reaction temperature.

C. Fe Carbide Formation above $\approx 300^\circ\text{C}$

With increasing severity of the CO carburization with treatments 340, 390, and 440, only χ -Fe₅C₂ and θ -Fe₃C are observed as the Fe carbide phases with both R-QPA and MAS quantifications (**Figure 3.13a-b**). Some SPM, poorly crystalline Fe_xC phases are also observed with MAS quantifications after the higher temperature catalyst carburization treatments (**Figure 3.13a**). These phases are not observable with XRPD-

based R-QPA (**Figure 3.13b**). The poorly crystalline Fe_xC phases could perhaps be related to intergrowth structures of the χ -Fe₅C₂ and θ -Fe₃C phases.⁹²⁻⁹⁴

After the catalyst treatment 340, only the χ -Fe₅C₂ phase is observed as the sole carbide phase and the treatment 340 is the only one to form a near pure, single Fe carbide phase catalyst. Both R-QPA and MAS agree on the quantification (**Figure 3.13a-b**), and the XRPD patterns do not show any unassigned diffraction peaks (**Figure 3.10c** and **Figure 3.11c**). The expected formation temperature range for the χ -Fe₅C₂ phase is about 250-400°C as based on the experimental literature observations.^{6,15,22,73,86-88,90,91,95}

With both R-QPA and MAS quantifications, formation of the χ -Fe₅C₂ phase from α -Fe is still observed with the catalyst treatment 440. That is, the χ -Fe₅C₂ phase forms at as high as the temperature of 440°C with 16 h CO exposure time (**Figure 3.13a-b**). This temperature is $\approx$ +40°C higher than the highest observations in literature for the χ -Fe₅C₂ phase's high temperature formation. Nagakura observed preservation of the χ -Fe₅C₂ phase after heating their precursor carbide at 400°C for 0.1 h.⁸⁶ With the assumption of the previously discussed +50°C temperature shift, 400°C is also the highest observation temperature for the χ -Fe₅C₂ phase by Niemantsverdriet et al.²

As viewing from the diffraction patterns in **Figure 3.10c-d** and **Figure 3.11c-d**, the increasing amount of the θ -Fe₃C phase overlaps with the diffraction from the most intense peaks of the χ -Fe₅C₂ phase, obfuscating its presence. Moreover, with the increasing carburization temperature the crystallite diameters of the χ -Fe₅C₂ phase also decrease (**Figure 3.16**), further complicating its identification from the XRPD patterns. Nevertheless, the weak diffraction peaks at $\approx$ 21.3° 2 θ and $\approx$ 22.5° 2 θ originating from the χ -Fe₅C₂ phase, make the presence of the phase clear in the XRPD patterns even after the catalyst treatment 440 (**Figure 3.10e** and **Figure 3.11e**). The mentioned χ -Fe₅C₂ phase diffraction peak obfuscating effects in relation to the presence of the θ -Fe₃C phase might explain the lack of literature observations for χ -Fe₅C₂ up to temperature of 440°C, at least for the diffraction based methods.

Thus, together with the quantification of the χ -Fe₅C₂ phase after the low temperature catalyst treatment 240, we shall assign the formation temperature range for χ -Fe₅C₂ as about 240-440°C (**Figure 3.13a-b**). This is somewhat higher but close to the temperature range expected from the literature. However, we did not test for high-end thermal stability for the χ -Fe₅C₂ phase by heating the phase up until decomposition. That is, the χ -Fe₅C₂ phase is stable and forms *at least* up to 440°C reaction temperature, although even higher formation and stability temperature cannot be excluded.

The presence of θ -Fe₃C is expected within the temperature range of 310-600°C on the basis of literature.^{2,23,86,96} However, we could not observe any presence of the θ -Fe₃C phase in the catalyst materials with carburization treatment temperatures below

390°C.

The lowest observation temperatures for the θ -Fe₃C phase from gas phase carburizations are by Nagakura with 350°C,⁸⁶ and Shultz et al. with 310°C.²³ Furthermore, in martensite tempering studies, formation of the θ -Fe₃C phase as low as 250-267°C has been observed.^{34,92} These formation temperatures for the θ -Fe₃C phase in the martensite tempering studies seem very low in comparison to other literature, and disagree with the R-QPA and MAS quantification results in **Figure 3.13a-b**. They are thus excluded from further discussion.

Observations on the formation of the θ -Fe₃C phase after carburizing polycrystalline α -Fe film with CO at 350°C (3 h) have been made by Nagakura, with the use of Electron Diffraction (ED).⁸⁶ The closest carburization conditions corresponding to Nagakura's reaction conditions are with the catalyst treatment 340, with which we could not form any observable amounts of θ -Fe₃C using the applied bulk characterization techniques (**Figure 3.13a-b**). That is, Nagakura's observations at 350°C could be very close to the precise lower temperature limit for the θ -Fe₃C formation.

With regard to the observations with XRPD by Shultz et al. on formation of θ -Fe₃C from α -Fe under H₂:CO 2:1 at 310°C (6 h),²³ no imminently clear explanation can be given for the deviation to the R-QPA and MAS Fe quantification results. However, possibly, in the study by Shultz et al., the α -Fe was exposed to the carburizing H₂:CO gas mixture *directly* at 310°C, which might have caused significant reactor bed heating as the exothermic FTS reaction is initiated. This idea would be supported by another experiment by Shultz et al. in the same publication, where by step-wise increasing the CO exposure temperature from 150°C to 350°C on the α -Fe starting material, only χ -Fe₅C₂ was formed.²³ This result by Shultz et al. would be in close agreement with the results in **Figure 3.13a-b**. Thus, we shall presume that the actual, efficient reactor bed temperature has been a lot higher than 310°C in the discussed experiment by Shultz et al.²³ Therefore, the 310°C data point is ignored from the expected low-end formation temperature for the θ -Fe₃C phase.

We did not test for the high-end temperature limit for the θ -Fe₃C phase formation or stability. With gas phase carburizations at 500°C: Shultz et al. observed θ -Fe₃C with 6 h carburization of α -Fe with CH₄,²³ while also under H₂:CO (1.5 h),² and CO (1 h),⁸⁶ the θ -Fe₃C phase has been detected. Jozwiak et al. reduced α -Fe₂O₃ with CO to α -Fe at 500°C *without* formation of the θ -Fe₃C phase.⁷⁷

By heat treating the preformed θ -Fe₃C phase Wood et al. have observed initial slow, at 377°C, and rapid decomposition of θ -Fe₃C to α -Fe above 527°C.⁹⁷ Other authors have still observed the θ -Fe₃C phase after heating their catalyst materials between 525-550°C.^{86,96} The highest stability temperature for the θ -Fe₃C phase has been observed by Nagakura, who observed the θ -Fe₃C phase even after heating a preformed Fe carbide

Figure 3.14

Fe carbide formation regions (*hatched fill*) as temperature versus treatment exposure time as based on the available experimental literature data and this Chapter. *Arrows*: Maximum thermal stability with preformed Fe carbides for (A) η -Fe₂C and (B) θ -Fe₃C. Formation temperatures for the θ -Fe₇C₃ phase are excluded. Figure is modified from **Chapter 2**.

for 16 h in vacuum at 600°C.⁸⁶

Podgurski et al. have noted that decomposition of a high temperature carbide, most likely θ -Fe₃C, to α -Fe takes place at 500°C. If a Fe particle surface oxide was formed e.g. possibly when CO is used as a carburizing agent in comparison to O-free hydrocarbons, the decomposition temperature of the carbide to α -Fe was increased.⁷⁸ Thus, the higher-end stability temperature of the θ -Fe₃C phase is dependent on how easily the C atoms can be expelled from the θ -Fe₃C lattice, allowing the carbide phase to decompose to α -Fe and C atoms. Thus, the presence or absence of carbide decomposition inhibiting shell oxide layers on θ -Fe₃C phase can be used to explain the discussed differences in the θ -Fe₃C phase stability between 500-600°C.

Finally, as based on the R-QPA and MAS quantifications (**Figure 3.13a-b**) and the discussion on the literature observations: we assign the formation temperature range for the θ -Fe₃C phase as 350-500°C. A preformed θ -Fe₃C phase can be stable up to 600°C if C atom expulsion from the θ -Fe₃C lattice is hindered due to a Fe oxide layer.⁷⁸ Without the Fe oxide layer, θ -Fe₃C decomposes readily to α -Fe and C species above 527°C.⁹⁷

The Fe carbide formation temperature regions have been updated from the purely literature based observations of noninterpreted data points in **Chapter 2** to the **Figure 3.14** as based on the presented discussion. The updated **Figure 3.14** also includes the R-QPA and MAS quantification based observations in this Chapter for the Fe carbides (**Figure 3.13a-b**). The rejected data points and the +50°C shift to the

≈100°C	≈160°C	≈240-265°C	≈300°C	≈350°C	≈420°C	≈500°C
ε-Fe ₃ C	ε-Fe ₃ C					
	η-Fe ₂ C	η-Fe ₂ C				
		χ-Fe ₅ C ₂	χ-Fe ₅ C ₂	χ-Fe ₅ C ₂		
				θ-Fe ₃ C	θ-Fe ₃ C	

Figure 3.15

The Fe carbide formation temperature ranges as estimated from the **Figure 3.14** at 5 h treatment time. The θ -Fe₇C₃ phase is excluded as its formation is a more complex, not a solely temperature dependent, phenomenon.

reaction temperatures in the results by Niemantsverdriet et al.,² have also been updated to the **Figure 3.14**. The complete list of source publications for the literature data points in **Figure 3.14** is given in **Chapter 2**.

With the applied modifications, the Fe carbide formation temperature regions are (**Figure 3.15**): ε-Fe₃C (100-265°C), η-Fe₂C (160-300°C), χ-Fe₅C₂ (240-420°C) and θ-Fe₃C (350-500°C), when compared at 5 h treatment time in the **Figure 3.14**. Furthermore, the χ-Fe₅C₂ high-end formation temperature can be as high as 440°C after a longer, 16 h CO carburization time. The preformed η-Fe₂C and θ-Fe₃C phases can be stable up to ≈340°C and ≈600°C, respectively, but do not directly form at these temperatures from α-Fe.

As a final note on the Fe carbide formation temperatures: for the formation of the ε-Fe₃C phase within the temperature range of ≈100-160°C, the synthesis route will likely need to go via martensite tempering (**Figure 3.14**). At these very low carburization temperatures CO adsorption/dissociation products do not necessarily desorb,⁹⁸ likely inhibiting α-Fe carburization via a gas phase CO.^{12,99}

3.3.2.3 The Effect of Na-S Promotion

When comparing the UP and Na-S catalyst materials for the formation of various Fe carbides with the catalyst treatments 240-440: the relative formation quantities for the different Fe carbides from α-Fe are not affected by the added Na-S promotion in any major way (**Figure 3.13a-b**).

Significant effects from the Na-S promotion on α-Fe carburization are (**Figure 3.13**): i) the increased Fe oxide contribution with treatments 240 and 290 and ii) the added Na-S promotion seems to increase the χ-Fe₅C₂ phase content with expense of the θ-Fe₃C phase with treatments 390 and 440. In MAS observations, a non-SPM (i.e. larger crystallite diameter) Fe phase with Fe³⁺ appeared after catalyst treatments 240 and 290 with the addition of the Na-S promotion (**Table 3.4**).

The increased Fe oxide contribution with Na-S 240 and Na-S 290 catalyst materials in relation to the respective UP catalyst materials is in agreement with both R-QPA and

MAS quantifications (**Figure 3.13a-b**). Addition of alkali in general decreases the reducibility of Fe oxides by H₂,^{26,72,100} possibly by stabilizing the oxides.⁷² Together with the earlier discussion on the possible oxidative effects due to the O atoms from CO dissociation, we thus assign the increased Fe oxidation with Na-S 240 and Na-S 290 catalyst materials to the increased stability for Fe oxide formation. From the treatment 340 upwards towards higher carburization temperatures and times, the Na-S effect is absent as the gas environment becomes more reducing with CO (and H₂).⁷⁷ The increased carburization/reduction temperature likely overcomes the possibly increased Fe oxide stability.

Regarding the relative stabilities of the χ -Fe₅C₂ and θ -Fe₃C phases, the Na-S promotion stabilizes the χ -Fe₅C₂ while decreasing the presence of the θ -Fe₃C phase with the high temperature catalyst treatments 390 and 440 (**Figure 3.13a-b**). In the R-QPA quantifications: the χ -Fe₅C₂ phase amount is increased $\approx +10\%$ in the Na-S catalyst materials after the treatments 390 and 440, with the expense of the θ -Fe₃C phase. The MAS quantifications also agree on the trend of the decreased θ -Fe₃C phase content after the catalyst treatments.

As further effects on the Na-S promotion in Fe carburization it can be mentioned that occasionally in literature the addition of alkali has been cited to increase the carburization of Fe catalysts, but the R-QPA and MAS results do not agree with this (**Figure 3.13a-b**). The observed differences can be explained with the starting Fe phase for the carburization, i.e. whether the carburization process is started with α -Fe or a Fe oxide.

Berry and Smith have observed, with MAS, that the added alkali K promotion aids in carburization of the starting α -Fe₂O₃ material.¹⁰¹ Under pure CO at 270°C after 12 h of CO exposure time, the added alkali K enhanced the Fe carbide formation from the α -Fe₂O₃ starting material in comparison to the unpromoted catalyst. Interestingly, with a short CO exposure time of 2 h at 270°C regardless of the K promotion, the authors observed that only Fe₃O₄ formed without any Fe carbides. The dependency of the extent of carburization on the CO exposure time would also explain the previously discussed increased Fe oxidation with Na-S 240 and Na-S 290 catalyst materials with the short exposure times (≤ 3 h) (**Figure 3.13a-b**). The increased CO carburization rate of α -Fe₂O₃ starting materials due to the alkali promotion has been also observed by Ribeiro et al.,¹⁰² and also can be seen in MAS quantification results by both O'Brien et al. and Bukur et al.^{26,83}

The addition of alkali (as Na or K) promotes CO₂ releasing Water-gas Shift (WGS) reaction with Fe catalyst materials.^{79,103,104} The addition of alkali has been observed to increase the exchangeability of surface O atoms with CO on K promoted Al₂O₃, especially at lower temperatures of $\approx 300^\circ\text{C}$.¹⁰⁵ Also, increase in the rate of the WGS reaction with

the same transition metal-free K/Al₂O₃ catalyst material has been observed.¹⁰⁶ That is, the addition of alkali seems to enhance the interaction of CO with the catalyst surface O atoms, while also increasing the WGS reaction rate. The enhanced O/CO interaction could also suggest a possibility for improved Fe oxide reduction by CO in presence of alkali.

Effectively then, according to the presented discussion, with the added alkali to a Fe oxide: the Fe oxide's reducibility to zerovalent Fe should be i) increased at low temperatures ($\approx 300^\circ\text{C}$) with CO as the reductant when sufficient CO exposure time (>3 h) is applied,^{26,101,105} and ii) decreased with H₂,^{26,72,100} due to Fe oxide stabilization by the alkali.

Indeed, in a XRPD study where a precursor $\alpha\text{-Fe}_2\text{O}_3$ was carburized directly with i) pure CO or, ii) a H₂:CO 100:1 mixture, the Fe reduction steps for the $\alpha\text{-Fe}_2\text{O}_3$ were modified.³ As reading from the XRPD patterns in the study; the Fe reduction steps can be seen to shift for $\alpha\text{-Fe}_2\text{O}_3 \rightarrow \text{Fe}_3\text{O}_4$ ($\approx +35^\circ\text{C}$), $\text{Fe}_3\text{O}_4 \rightarrow \text{Fe}_x\text{O}$ (wüstite) ($\approx +65^\circ\text{C}$) and $\text{Fe}_x\text{O} \rightarrow \text{Fe}_x\text{C}$ (i.e. $\alpha\text{-Fe}$) ($\approx +93^\circ\text{C}$) when switching the carburizing gas from pure CO to a 100:1 H₂:CO mixture. That is, the $\alpha\text{-Fe}_2\text{O}_3$ was more poorly reducible with the 100:1 H₂:CO mixture than with pure CO. Noteworthy is that in the study, the used $\alpha\text{-Fe}_2\text{O}_3$ catalyst materials were prepared using Na₂CO₃ as the precipitation agent which, despite a washing,¹⁰⁷ is likely to leave residual Na in the catalyst with sufficient concentration to act as a promoter. Furthermore, X-ray Fluorescence (XRF) spectrometer was used to evaluate the catalyst material purity, a technique which detects the Na elements poorly.¹⁰⁸ The inadvertent Na promotion would explain both: the more efficient reduction of the Fe oxides at lower temperatures by CO as discussed, and the observations on the Fe_xO (wüstite) phase during Fe reduction step.^{72,77} The Fe_{0.974}O phase is also seen to stabilize for the Na-S H₂ catalyst material (**Figure 3.13b**).

Therefore, in total, the increased carburization of alkali promoted Fe oxides can be explained with a more efficient Fe oxide reduction to $\alpha\text{-Fe}$ with CO. $\alpha\text{-Fe}$ then subsequently carburizes to Fe carbides with the available CO. That is, *the Fe reduction step to $\alpha\text{-Fe}$* is enhanced by alkali, *not the carburization step* when starting with a Fe oxide material under a carburizing atmosphere. This explains the lack of significant Na(-S) effect in the results on the $\alpha\text{-Fe}$ carburization with the applied CO treatments 240-440 (**Figure 3.13a-b**).

3.3.2.4 Formation of the $\theta\text{-Fe}_7\text{C}_3$ Phase

Low yet clearly observable amounts of 22-29 % of the $\theta\text{-Fe}_7\text{C}_3$ phase were formed after the catalyst treatments 340 h.p. (**Figure 3.13a-b**). With these treatments, the $\alpha\text{-Fe}_2\text{O}_3$ phase was used as the carburization starting Fe phase, directly for carburization reaction at 25 bar CO pressure at 340°C . The addition of the Na-S promotion did not

affect the formation of the θ -Fe₇C₃ phase. This while minding for the differences in the applied CO exposure times of 120 h for the UP and 168 h for the Na-S 340 h.p. catalyst materials.

The θ -Fe₇C₃ phase can be formed under rather extreme conditions,^{109–112} but may also form under milder FTS reaction conditions which are more relevant to the present discussion.^{16,24,113} In order to form the θ -Fe₇C₃ phase under mild conditions: Tajima and Hirano used Ba promoted Fe₃O₄ carburized with pure CO under unspecified pressure at 300–375°C.²⁴ Audier, Bowen and Jones were able to prepare single crystals of θ -Fe₇C₃ from α -Fe under CO:CO₂ 3:1 at 500°C,¹¹³ with undefined, yet presumably, at atmospheric pressure.

As Audier, Bowen and Jones were able to prepare the θ -Fe₇C₃ phase without a Fe oxide, Ba promotion or high CO pressure: the results suggests that the common required factor for preparing the θ -Fe₇C₃ phase is none of the mentioned parameters. A common factor for mild condition preparation of the θ -Fe₇C₃ phase might be the CO₂, as Audier, Bowen and Jones used CO₂ in their carburizing gas mixture.¹¹³

In the study by Tajima and Hirano,²⁴ perhaps, the role of Ba has been to aid the Fe oxide reduction by CO, akin to the earlier discussed alkali effect, releasing CO₂ in the reduction process. Ba promotes Fe oxides towards the WGS reaction,^{104,114,115} suggesting similar expected behavior for Ba promotion as for the earlier discussed alkali WGS promotion effect.

At Sasol, formation of the θ -Fe₇C₃ phase has been observed at higher pressure (>60 bar) under industrial FTS reaction conditions in end-of-life catalysts.¹⁶ The Fe-based FTS reaction catalysts have the tendency to reoxidize to WGS catalyzing Fe₃O₄ over time.^{16,22,81,82,104,116,117} The catalyst reoxidation could explain the formation of the θ -Fe₇C₃ phase at later stages of the catalyst life-time at Sasol along the WGS catalyzing Fe₃O₄,¹⁶ as the WGS reaction releases CO₂.^{104,116}

The formation of the θ -Fe₇C₃ phase with catalyst treatment 340 h.p. might then be explained with the increased concentration of CO₂ in the carburizing gas stream, due to the reduction of the Fe oxide with CO.⁷⁷ Perhaps, with the elevated CO pressure, the rate of the initial Fe oxide reduction is momentarily sufficiently high for increasing the CO₂ concentration and thus allowing the θ -Fe₇C₃ formation, irrespective of the added Na-S promotion. The formed quantity of the θ -Fe₇C₃ phase was not affected by the different carburization times (**Figure 3.13a-b**), i.e. 168 h for UP as opposed to 120 h for Na-S catalysts with the catalyst treatment 340 h.p.. This would suggest that the formation of θ -Fe₇C₃ does not take place during the steady state of the applied treatments, but perhaps, during the temperature ramp or early period of the catalyst treatment. This is also when then CO₂ concentration in the carburizing gas stream would be expected to be highest due to the Fe oxide reduction. As the carbon deposition

rates between the catalyst treatments 340 and 340 h.p. are very similar (**Figure 3.6b**), the deposited carbon from the Boudouard reaction probably does not play a major role in the formation of the $\theta\text{-Fe}_7\text{C}_3$ phase.

Thus, we speculate that the $\theta\text{-Fe}_7\text{C}_3$ formation is dependent on the presence of CO_2 in the gas mixture during the gas phase carburization. However, more research on the topic should be performed in the future by systematically carburizing $\alpha\text{-Fe}$ and Fe oxides with $\text{CO}:\text{CO}_2$ mixtures. This might reveal whether a CO_2 correlation to the $\theta\text{-Fe}_7\text{C}_3$ formation exists as proposed.

Solely based on the R-QPA and MAS quantifications in **Figure 3.13a-b**, the formation temperature ranges for the $\theta\text{-Fe}_7\text{C}_3$ phase cannot be devised. However, according to Tajima and Hirano: the $\theta\text{-Fe}_7\text{C}_3$ phase is only stable within the temperature range 300-375°C.²⁴ This temperature range is in agreement with the observation of the $\theta\text{-Fe}_7\text{C}_3$ phase forming with the catalyst treatment 340 h.p. at 340°C (**Figure 3.13a-b**). Although, the higher end temperature stability of the $\theta\text{-Fe}_7\text{C}_3$ phase might be dependent in the carbide phase's purity.¹¹² O atom impurity free $\theta\text{-Fe}_7\text{C}_3$ phase has been witnessed to survive temperatures up to $\approx 400\text{-}500^\circ\text{C}$ before decomposing to $\alpha\text{-Fe}$ and C atoms.¹¹²

3.3.2.5 Changes in Fe Phases' Crystallite Diameters

The Fe phase (volume-weighted) crystallite mean diameters obtained via the R-QPA, after each applied catalyst treatment, are shown in **Figure 3.16**.

Few observations are worth a short discussion. The addition of the Na-S promotion has the effect of (**Figure 3.16**): i) increasing the crystallite diameters for both $\alpha\text{-Fe}_2\text{O}_3$ (Calcin.) and $\alpha\text{-Fe}$ (H_2) and ii) decreasing the crystallite diameters for the $\theta\text{-Fe}_3\text{C}$ phase (catalyst treatments 390 and 440). Especially with the catalyst treatment 440, the crystallite diameter of the $\theta\text{-Fe}_3\text{C}$ phase is decreased from 28.1 ± 0.9 nm to 17.2 ± 0.8 nm with the added Na-S promotion. Only the $\theta\text{-Fe}_3\text{C}$ phase seems to be affected by the Na-S promotion, as the rest of the Fe carbides are nearly identical in their crystallite diameters when UP catalyst materials are contrasted with the Na-S materials. At the moment, no precise explanation for the observed crystallite diameter effects, as due to the Na-S promotion addition, can be given. Additional, fundamental research is warranted.

The $\varepsilon\text{-Fe}_3\text{C}$ phase possesses the largest Fe carbide crystallite mean diameters, while excluding the $\theta\text{-Fe}_3\text{C}$ phase in the UP 440 catalyst material. The $\varepsilon\text{-Fe}_3\text{C}$ phase's crystallite diameters are close to those of $\alpha\text{-Fe}$ in its UP or Na-S H_2 carburization starting materials (**Figure 3.16**). A similar observation has earlier been made by Nagakura with ED:⁸⁶ the $\varepsilon\text{-Fe}_3\text{C}$ phase forms from $\alpha\text{-Fe}$ as single crystals i.e. one $\alpha\text{-Fe}$ crystallite transforms into one $\varepsilon\text{-Fe}_3\text{C}$ crystallite. This explains the similarity between the $\alpha\text{-Fe}$ and $\varepsilon\text{-Fe}_3\text{C}$ crystallite diameters.

Figure 3.16

The Rietveld Quantitative Phase Analysis (R-QPA) derived Fe phase volume-weighted crystallite mean diameters, after each applied catalyst treatment for UP and Na-S (Fe(-Na-S)/ α -Al₂O₃) catalyst materials.

The χ -Fe₅C₂ phase seems to have rather uniform crystallite diameters after the applied catalyst treatments with the smallest mean diameters of all of the Fe carbides. This suggests that the χ -Fe₅C₂ phase forms by dividing its precursor Fe crystallites or particles into smaller fractions. An effect akin to this has been observed with Environmental-TEM (ETEM) where the χ -Fe₅C₂ phase formed as a belt-like phase, rather than uniformly over a single crystal or particle of the carburized α -Fe.¹¹⁸

Comparing the Fe particle mean diameters (i.e. from TEM) to the crystallite mean diameters (i.e. from R-QPA) is not straightforward as: i) a single Fe particle may contain several Fe crystallites (or “coherent scattering regions”),^{57,118,119} ii) Fe particle mean diameters are number-weighted while Fe crystallite mean diameters are volume-weighted values,^{57,119} iii) the Gaussian strain component for the diffraction peak size-strain broadening could not be determined with the R-QPA (see *Experimental Methods*),⁵⁵ and iv) the formed reoxidation layer (**Figure 3.3b**) reduces the possible Fe crystallite diameters by $\approx$ 8-10 nm in comparison to the Fe particle diameters.

Nevertheless, a few comments can be made when comparing the TEM-based Fe particle diameters to R-QPA originating crystallite diameters. The main trend together in the mean Fe particle (**Figure 3.5**) and Fe crystallite diameters (**Figure 3.16**) is to decrease towards the catalyst treatment 340. With the treatment 340, the decreasing diameters can be assigned to the Fe fragmentation effect due to the carbon deposition,^{120,121} as agreed by the TGA-MS (**Figure 3.6**) and TEM (**Figure 3.3**) results. With treatments ≤ 290 the initial “Fe clusters” transform into more clearly individually separated Fe particles. This process decreases the measured mean Fe particle and crystallite diameters. The particle separation takes place without any significant carbon deposition.

The TEM derived Fe particle mean diameters suggest that only the Na-S promoted catalyst materials show Fe particle growth when moving from the catalyst treatment 340 towards 440 (**Figure 3.5**). However, the R-QPA-based Fe crystallite diameter values disagree with this (**Figure 3.16**). With increasing the treatment temperature, the θ -Fe₃C phase crystallite diameter growth against χ -Fe₅C₂ can be observed for both the UP and Na-S 440 catalyst materials (**Figure 3.16**).

The largest Fe carbide crystallites of 28.1 ± 0.9 nm over all catalyst materials are the θ -Fe₃C crystallites in the UP 440 catalyst material. This crystallite diameter is larger than the Fe particle mean diameter of 24.2 nm from TEM-based results for the same catalyst material; a seemingly odd physical result. The discrepancy is due to the volume-weighting of the R-QPA crystallite mean diameter values, as the relatively few large volume Fe particles (e.g. in **Figure 3.3d**) with large crystallites contribute far more to the volume-weighted Fe crystallite mean diameters than to the number-weighted Fe particle mean diameters. Also, R-QPA derived values rely on far larger sample size and are less prone to sampling errors than are the TEM derived Fe particle mean diameter values.⁵⁷

Thus, the R-QPA crystallite diameters do also imply Fe particle growth for the UP 440 catalyst materials, and not only for the Na-S 440, as the TEM derived values would suggest (**Figure 3.5**). Then, when considering both the TEM and R-QPA results for Fe particle or crystallite diameters in total: catalyst treatment 440 causes increasing Fe particle or crystallite growth for both the UP and Na-S catalyst materials.

3.3.3 Assignment of Fe Carbide Properties with X-ray Powder Diffractometry/Rietveld Quantitative Phase Analysis and Mössbauer Absorption Spectroscopy

In the literature review done in **Chapter 2**, we have assigned the Fe carbide crystal structures and the corresponding MAS hyperfine fields, as based on our interpretation of the literature. The assignments establish a common Fe carbide nomenclature

Figure 3.17

The lattice parameters used in Rietveld Quantitative Phase Analysis (R-QPA) for the ϵ -Fe₃C and η -Fe₂C phases in the UP and Na-S (Fe(-Na-S)/ α -Al₂O₃) catalyst materials after the respective catalyst treatment. Lattice parameters *a*, *b*, and *c* for ϵ -Fe₃C are in a), c) and e); and for η -Fe₂C in b), d) and f), respectively.

between the XRPD and MAS techniques. The experimental MAS and XRPD based R-QPA quantifications are very much in line with each other (**Figure 3.13a-b**), and the R-QPA fittings to the measured diffractograms are very good with the employed Fe carbide crystal structures, as can be seen in **Figure 3.10** for UP and in **Figure 3.11** for Na-S catalyst materials. It is therefore safe to conclude that our original interpretation of the literature is a reasonable one.

That is, the Fe carbides encountered in the FTS research can be identified as ϵ -Fe₃C, η -Fe₂C, χ -Fe₅C₂, θ -Fe₃C and θ -Fe₇C₃, with the lattice parameters and the crystal structures by the listed authors in **Table 3.5**. The use of inaccurate nomenclature of assigning any of the Fe carbides as pseudo-hexagonal, “ ϵ -carbides”, (ϵ -)Fe₂C or ϵ' -Fe_{2.2}C is discouraged.

Figure 3.18

The lattice parameters used in Rietveld Quantitative Phase Analysis (R-QPA) for the χ -Fe₅C₂, θ -Fe₃C and θ -Fe₇C₃ phases in the UP and Na-S (Fe-(Na-S)/ α -Al₂O₃) catalyst materials after the respective catalyst treatment. Lattice parameters *a*, *b*, and *c* for χ -Fe₅C₂ are in a), d) and g); for θ -Fe₃C in b), e) and h); and for θ -Fe₇C₃ in c), f) and i), respectively.

3.3.3.1 Fe Carbide Lattice Parameters and Hyperfine Fields

The R-QPA fitted lattice parameters comparing the effect of the Na-S promotion on the different Fe carbide phases are given in **Figure 3.17** for the ϵ -Fe₃C and η -Fe₂C and in **Figure 3.18** for the χ -Fe₅C₂, θ -Fe₃C and θ -Fe₇C₃ phases. The R-QPA fitted and averaged Fe carbide lattice parameters, over all the observations per Fe carbide phase, are given in the **Table 3.5**.

The averaged MAS-based Fe hyperfine fields and relative fitted spectral contribution derived non-equivalent Fe site ratios are given in **Table 3.6** for the Fe carbides. Used MAS fit parameters are given in the **Table 3.3** for UP and in **Table 3.4** for Na-S catalyst

Identification of Iron Carbides in Fe(-Na-S)/ α -Al₂O₃ Fischer-Tropsch Synthesis Catalysts with X-ray Powder Diffractometry and Mössbauer Absorption Spectroscopy

Table 3.5

The averaged Fe carbide lattice parameters and crystal structures used in the Rietveld Quantitative Phase Analysis (R-QPA) with comparisons to the lattice parameters by the crystal structures' authors.

Fe Carbide Phase	Space Group		Lattice Parameters		Database Number	Author
			Author (Å)	This Study ^{a)} (Å)		
ϵ -Fe ₃ C	Hexagonal, P6 ₃ 22 (182)	a	4.767	4.76±0.00	04-008-9572	Nagakura (1959) [86]
		b	4.767	4.76±0.00		
		c	4.354	4.36±0.00		
η -Fe ₂ C ^{b)}	Orthorhombic, Pnnm (58)	a	4.862	4.84±0.01	04-013-9510	Hirotsu (1972) [19]
		b	4.360	4.35±0.00		
		c	2.755	2.76±0.00		
χ -Fe ₅ C ₂	Monoclinic, C2/c (15)	a	11.588	11.56±0.01	00-051-0997	Retief (1999) [11]
		b	4.579	4.57±0.01		
		c	5.059	5.07±0.00		
χ -Fe ₅ C ₂ (h.p.) ^{c)}	Monoclinic, C2/c (15)	a	-	11.61±0.01	-	-
		b	-	4.57±0.00		
		c	-	5.04±0.00		
θ -Fe ₃ C ^{d)}	Orthorhombic, Pnma (62)	a	5.081	5.07±0.01	9014027 ^{e)}	Wood (2004) [97]
		b	6.754	6.76±0.02		
		c	4.515	4.53±0.01		
θ -Fe ₇ C ₃ ^{d)}	Orthorhombic, Pnma (62)	a	4.540	4.52±0.00	04-002-8165	Fruchart (1965) ^{f)} [122]
		b	6.879	6.90±0.01		
		c	11.942	11.91±0.00		

a) The mean values over all observations of the Fe carbide phase with Standard Deviations (STDs).

b) The author's lattice parameters are translated, according to Hirotsu and Nagakura,²⁰ to correspond the Fe carbide observed by Barton and Gale.⁹

c) Formed from Fe oxide precursor (α -Fe₂O₃/ α -Al₂O₃) with the catalyst treatment 340 h.p.

d) Diffraction peak overlap with χ -Fe₅C₂ or χ -Fe₅C₂ (h.p.) causes inaccuracy on the lattice parameters.

e) Crystallography Open Database (COD) number.

f) The original article written in French by Fruchart et al. is not readily available but some discussion on the crystal lattice can be found in publication by Audier, Bowen and Jones.¹¹³

materials. The reference MAS values from experimental literature studies in **Table 3.6** are reproduced from **Chapter 2**. The addition of Na-S promotion did not have any significant effect, on either the fitted Fe carbide lattice parameters or the hyperfine fields.

The mean values of the lattice parameters used for the R-QPA fits in **Table 3.5** are in general in good agreement with the lattice parameters by the authors of the crystal structures. The crystal structure of η -Fe₂C by Hirotsu and Nagakura,¹⁹ with the unit cell lattice translation by the same authors,²⁰ to correspond the Fe carbide observed by Barton and Gale,⁹ is in near agreement to the fitted unit cell for the η -Fe₂C phase.

The most significant deviations from the authors' unit cells are with the χ -Fe₅C₂ and

Table 3.6

The averaged Mössbauer Absorption Spectroscopy (MAS) spectral contribution derived relative ratios for non-equivalent Fe positions and hyperfine fields per Fe carbide. Averaged, experimental literature values are also provided for comparison.

Fe Carbide Phase	Space Group	Non-equivalent Fe Positions			Hyperfine Field (at room temperature)	
		Tot. Count ^{b)}	Rel. Ratio		Literature (T)	This Study ^{a)} (T)
			Nomin. ^{c)}	Fitted ^{d)}		
ϵ -Fe ₃ C	Hexagonal, P6 ₃ 22 (182)	1	1	1	24.5±0.8	23.4±0.3
η -Fe ₂ C	Orthorhombic, Pnnm (58)	1	1	1	17.2±0.3	17.3±0.3
χ -Fe ₅ C ₂	Monoclinic, C2/c (15)	3		2	21.4±0.3	21.4±0.3
				2	18.1±0.4	18.7±0.3
				1	10.9±0.9	11.4±0.3
χ -Fe ₅ C ₂ (h.p.) ^{e)}	Monoclinic, C2/c (15)	3		2	-	21.5±0.1
				2	-	18.0±0.1
				1	-	10.3±0.1
θ -Fe ₃ C	Orthorhombic, Pnma (62)	2		(2)	20.8±0.3	-
				(1)	20.0±0.3	-
				Avg. ^{f)}	20.8±0.5	20.5±0.3
θ -Fe ₇ C ₃	Orthorhombic, Pnma (62)	5		(1)	22.9±0.1	22.4±0.1
				(2)	-	-
				(1)	0.9±0.3	19.5±0.4
				(2)	1.8±0.3	16.3±0.1
				(1)	-	(21.0) ^{g)}

a) Mean values over all observations of the phase with the Standard Deviations (STDs).

b) Determined based on the crystal structures from authors in **Table 3.5**.

c) Nominal ratios assigned per experimental MAS data, where assignments in parenthesis () are uncertain.

d) Averaged ratios derived from the spectral contributions per fitted hyperfine field.

e) Formed from Fe oxide precursor (α -Fe₂O₃/ α -Al₂O₃) with the treatment 340 h.p.

f) Commonly, an averaged hyperfine field is fitted for the θ -Fe₃C in the experimental literature data.

g) Uncertain assignments values.

θ -Fe₇C₃ phases. Especially noteworthy is the distinctively distorted χ -Fe₅C₂ (h.p.) phase formed with the catalyst treatment 340 h.p., in both the UP and Na-S catalyst materials. The θ -Fe₃C phase's mean lattice parameters have large STDs complicating discussion on the phase's parameters (**Table 3.5**).

The MAS hyperfine fields for the ϵ -Fe₃C, η -Fe₂C, χ -Fe₅C₂ and θ -Fe₃C phases are in good agreement with the expected experimental values interpreted from literature (**Table 3.6**). For the θ -Fe₃C phase, two Fe hyperfine fields should be assigned for each of the non-equivalent Fe positions. However, as the hyperfine fields are close to each

other, therefore commonly a single averaged field is used.

The distinctively distorted unit cell for the χ -Fe₅C₂ (h.p.) phase is formed after the catalyst treatment 340 h.p.. By comparing the Rietveld method calculated χ -Fe₅C₂ phase diffraction patterns (**Figure 3.10b-e** and **Figure 3.11b-e**) to the χ -Fe₅C₂ (h.p.)'s calculated phase pattern after the high-pressure treatment (**Figure 3.10f** and **Figure 3.11f**), a shift towards lower 2θ in the most intense diffraction peak can be observed. The shift towards lower 2θ signifies increase in, at least one, unit cell lattice parameter for the diffracting phase. Indeed, the χ -Fe₅C₂ (h.p.) phase's lattice parameter a is noticeably larger than the literature reference value by Retief (**Table 3.5**).

The formation of a distorted or modified χ -Fe₅C₂ phase from a Fe oxide as the carburization precursor has been previously observed in distorted XRPD patterns and in changes in the Hägg carbide's Curie Temperature by Cohn et al.⁶⁴ Cohn et al. suggested that some O atoms could be retained in the Hägg carbide lattice when the carburization was performed on a Fe oxide instead of a pre-reduced α -Fe.⁶⁴

Both, R-QPA and MAS quantifications, are in agreement that the formed crystal lattice for the χ -Fe₅C₂ phase is dependent on whether α -Fe e.g. with catalyst treatment 340, or α -Fe₂O₃ with treatment 340 h.p. is used as the CO carburization starting material (**Table 3.5** and **Table 3.6**). In comparison to the χ -Fe₅C₂, the χ -Fe₅C₂ (h.p.) phase has i) shifted lattice parameters a , from 11.56 ± 0.01 Å to 11.61 ± 0.01 Å and c , from 5.07 ± 0.00 Å to 5.04 ± 0.00 Å as read from the **Table 3.5**. Furthermore, ii) the non-equivalent Fe position ratios are distorted from 1.9:1.8:1.0 to 1.3:1.2:1.0 and iii) the hyperfine field corresponding to the Fe position with fraction 1.0 drops from 11.4 ± 0.3 T to 10.3 ± 0.1 T (**Table 3.6**). No precise explanation for these observations can be given at this time. That is, whether the differences in the lattices and hyperfine fields are due to retained O atoms in the lattice as proposed by Cohn et al., or due to something else.⁶⁴

Additionally, a lowered lattice parameter a can be observed for the χ -Fe₅C₂ phase formed from α -Fe with catalyst treatments 240-440, in comparison to Retief's lattice parameters for χ -Fe₅C₂ (**Table 3.5**). This can be tentatively explained with the used carburization conditions: with the use of pure CO carburization as opposed to Retief's H₂:CO carburization during the FTS reaction.¹¹

With respect to the θ -Fe₇C₃ discrepancies, the orthorhombic crystal structure by Fruchart et al.,¹²² gives a good fit for the diffraction patterns of the θ -Fe₇C₃ phase, in both peak intensity and positions. However, with different unit cell lattices than the original ones from the crystal structure's authors (**Table 3.5**).

The deviations on the lattice parameters for the θ -Fe₇C₃ phase could be, in part, due to inaccurate peak position determination. The θ -Fe₇C₃ phase contents are low (**Figure 3.13a-b**), and the θ -Fe₇C₃ peaks also overlap with the more abundant χ -Fe₅C₂ (h.p.) phase (**Figure 3.10f** and **Figure 3.11f**).

Using the hexagonal crystal structure by Herbstein and Snyman,¹⁸ instead of the orthorhombic structure by Fruchart et al.,¹²² for the Fe_7C_3 phase gave a clearly worse fit to the measured XRPD patterns with R-QPA (fits are not shown). That is, the Eckström-Adcock carbide $\theta\text{-Fe}_7\text{C}_3$ has an orthorhombic rather than a hexagonal crystal structure.¹¹³

As with the $\theta\text{-Fe}_7\text{C}_3$ phase, the diffraction peak overlap issues can also explain the large STD values for the lattice parameters of $\theta\text{-Fe}_3\text{C}$. For the UP and Na-S 390 catalyst materials, the $\theta\text{-Fe}_3\text{C}$ phase diffraction peaks are poorly defined and overlap with the $\chi\text{-Fe}_5\text{C}_2$ phase. This as can be seen in **Figure 3.10d** for the phases in UP and in **Figure 3.11d** for phases in Na-S catalyst materials. The overlap, therefore, results in large STDs in the determined lattice parameters (**Figure 3.18b, e, h** and **Table 3.5**).

Only three of the five expected non-equivalent Fe positions could be definitely assigned for the $\theta\text{-Fe}_7\text{C}_3$ phase on the basis of the MAS quantifications (**Table 3.6**). We assign the hyperfine fields 22.4 ± 0.1 T, 19.5 ± 0.4 T and 16.3 ± 0.1 T for spectral contributions in ratios $\approx 1.0:0.9:1.8$, respectively. As based on the nominal non-equivalent Fe position ratios derived from the crystal structures, this is plausible, as three positions can be assigned in ideal ratios of 1:1:2 with the used orthorhombic crystal structure for the $\theta\text{-Fe}_7\text{C}_3$ phase. For the hexagonal crystal lattice for Fe_7C_3 by Herbstein and Snyman,¹⁸ three non-equivalent Fe positions should be assigned in ratio 3:3:1. This is a further sign that the hexagonal lattice is not a correct one for the Fe_7C_3 phase.

The leftover two hyperfine fields, corresponding to the unassigned non-equivalent Fe positions, should be assigned in ratio of 2:1 for the $\theta\text{-Fe}_7\text{C}_3$ phase with orthorhombic structure. However, we could not conclusively assign these two missing hyperfine fields. A catalyst material with larger relative quantity of the $\theta\text{-Fe}_7\text{C}_3$ phase would be needed for assigning the remaining hyperfine fields for the phase.

3.3.3.2 Fe Carbide C Atom Order and Contents

Earlier in **Chapter 2**, as based on the crystal structures from literature, the $\varepsilon\text{-Fe}_3\text{C}$ phase was discussed to have C atoms occupying the Fe lattice interstitial spaces in a random, disordered manner. For the $\eta\text{-Fe}_2\text{C}$ phase the C atoms are in the interstitial spaces in a regular, ordered manner. According to discussion by Gatte and Phillips,¹²³ this interstitial C atom disorder should cause spectral broadening in the measured MAS spectra.

Indeed, in the fitted MAS results the expected spectral broadening can be seen from **Table 3.3** for UP and **Table 3.4** for Na-S catalyst materials: the $\varepsilon\text{-Fe}_3\text{C}$ phase has a mean line width of 0.75 ± 0.07 mm s⁻¹ versus a mean line width of 0.49 ± 0.06 mm s⁻¹ for the $\eta\text{-Fe}_2\text{C}$ phase over all of the catalysts. The MAS results are thus in agreement with the

expectations: in the ϵ -Fe₃C phase the C atoms occupy the interstitial spaces in a random, disordered manner,⁸⁶ and in the η -Fe₂C phase the C atoms occupy the interstitial spaces in a regular, ordered manner.¹⁹

The C atom content in the Fe carbide lattice can be indirectly determined from the fitted MAS hyperfine fields. Increasing amounts of C atoms in the Fe lattice interstitial spaces decrease the observed hyperfine fields for each non-equivalent Fe position.^{5,31,33,124,125} In **Figure 3.19** are depicted the MAS spectral contribution weighted mean hyperfine fields for each Fe carbide phase versus the unit cell volume normalized to the Fe atoms in the phase's unit cell. By adding C atoms to the α -Fe lattice via the carburization process, the cell volume per Fe atom increases while the hyperfine fields decrease (**Figure 3.19**), as would be expected.

The C atom content in the Fe carbide lattices follows increasing order, with decreasing hyperfine fields:

$$\begin{array}{ccccccccc}
 23.4 \pm 0.3 \text{ T} & 20.5 \pm 0.3 \text{ T} & 18.7 \pm 0.0 \text{ T} & 18.2 \pm 0.3 \text{ T} & 17.3 \pm 0.3 \text{ T} & 17.1 \pm 0.1 \text{ T} \\
 \epsilon\text{-Fe}_3\text{C} & < & \theta\text{-Fe}_3\text{C} & < & \theta\text{-Fe}_7\text{C}_3 & < & \chi\text{-Fe}_5\text{C}_2 & < & \eta\text{-Fe}_2\text{C} & \lesssim & \chi\text{-Fe}_5\text{C}_2 \\
 & & & & & & & & & & & \text{(h.p.)}
 \end{array}$$

as devised from the order of the MAS fitted, spectral contribution weighted mean hyperfine fields (**Figure 3.19**).

Interestingly, the distorted χ -Fe₅C₂ (h.p.) phase has the lowest averaged and weighted hyperfine field suggesting the highest C atom content in the Fe carbide lattice. Whether the observed lattice distortion effects for the χ -Fe₅C₂ (h.p.) phase with decreased hyperfine fields are truly due to increased C atom content and/or, e.g. due to the retained O atoms in the Fe carbide lattice as suggested by Cohn et al.,⁶⁴ cannot be

Figure 3.19

Mössbauer Absorption Spectroscopy (MAS)-based spectral contribution weighted mean hyperfine fields versus Rietveld Quantitative Phase Analysis (R-QPA)-based fitted unit cell volumes normalized to Fe atoms per unit cell for each Fe carbide phase and α -Fe. Standard Deviations (STDs) for the averaged data points are smaller than the data markers, and are omitted.

Figure 3.20

Rietveld method calculated Fe carbide phase diffraction patterns compared for UP (Fe/ α -Al₂O₃) catalyst materials. The Fe carbides as after catalyst treatment a) ϵ -Fe₃C 240, b) η -Fe₂C 240, c) ϵ -Fe₃C and η -Fe₂C 240, d) χ -Fe₅C₂ 340, e) θ -Fe₃C 440 and f) θ -Fe₇C₃ 340 h.p.. Normalization to the most intense diffraction peak.

conclusively determined as based on the work in this Chapter.

3.3.3.3 Fe Carbide Diffraction Patterns

Examples of the Rietveld method calculated Fe carbide diffraction patterns used in the R-QPA fitting are shown in **Figure 3.20** for the UP catalyst materials. The very similar R_{wp} -values for the UP and Na-S catalyst materials in **Figure 3.8** suggests that the Fe carbide crystal structures, i.e. the relative peak intensities, are little perturbed by the added Na-S promotion after the applied CO carburization treatments.

The R-QPA fitted, calculated diffraction patterns for the ϵ -Fe₃C and η -Fe₂C phases are compared in the **Figure 3.20c**. The differences between the diffraction patterns for the phases are rather small. Thus, when only XRPD is used for the phase identification of the ϵ -Fe₃C and η -Fe₂C phases, care needs to be taken for correctly identifying the carbides. In the inset graph in **Figure 3.20c** the weak superstructural diffraction peaks originating from the C atoms are marked with s.⁸⁶ With XRPD, the superstructural peaks are very weak, only about 1-2 % of the intensity of the most intense diffraction peak. These peaks are more pronounced with ED,⁸⁶ which is more sensitive to low atomic number elements (i.e. C atoms).

In summary, the calculated diffraction patterns reproduced in the **Figure 3.20** also hopefully serve as an aid for identifying the Fe carbide phases from XRPD patterns on past and future studies.

As a final remark, the behavior, crystal structures and diffraction patterns of the ϵ -Fe₃C and η -Fe₂C phases are very similar to their close, yet more stable, cousins of ϵ -Fe₃N and ζ -Fe₂N Fe nitrides.¹²⁶⁻¹³² A comparative study of the ϵ -Fe₃C and η -Fe₂C crystal structures in contrast to the structures of ϵ -Fe₃N and ζ -Fe₂N phases and phase properties would be an intriguing topic for a future study.

3.4 CONCLUSIONS

The XRPD patterns for H₂ reduced, CO carburized, supported Fe(-Na-S)/ α -Al₂O₃ catalyst materials were quantified with R-QPA for crystalline Fe phases. The R-QPA results were compared to the catalysts' corresponding MAS quantifications. The quantification results between the two characterization techniques were in a very good agreement. As a result, a common nomenclature between the Fe carbide crystalline structures, relative C atom contents, non-equivalent Fe position ratios and their corresponding MAS hyperfine fields could be established. As based on the experimental results, the Fe carbides observable in the FTS reaction research, with their crystal lattices, are as follows:

ε -Fe ₃ C	η -Fe ₂ C	χ -Fe ₅ C ₂	θ -Fe ₃ C	θ -Fe ₇ C ₃
Hexagonal, <i>P6₃22</i> (182)	Orthorhombic, <i>Pnnm</i> (58)	Monoclinic, <i>C2/c</i> (15)	Orthorhombic, <i>Pnma</i> (62)	Orthorhombic, <i>Pnma</i> (62)

The experimental result-based assignment of the Fe carbides is in agreement with our interpretation of the literature data, which was discussed in **Chapter 2**. The use of nomenclature such as pseudo-hexagonal, “ ε -carbides”, (ε -)Fe₂C or ε' -Fe_{2.2}C for describing the Fe carbides should not be used as it is inaccurate.

The formation of the observed Fe carbides follows an increasing α -Fe carburization temperature. The estimated carbide thermal formation regions from literature with comparison to the results in this Chapter are established as:

$$\begin{array}{ccccccc} \varepsilon\text{-Fe}_3\text{C} & < & \eta\text{-Fe}_2\text{C} & < & \chi\text{-Fe}_5\text{C}_2 & < & \theta\text{-Fe}_3\text{C} \\ 100\text{-}265^\circ\text{C} & & 160\text{-}300^\circ\text{C} & & 240\text{-}420^\circ\text{C} & & 350\text{-}500^\circ\text{C} \end{array}$$

while the formation of the θ -Fe₇C₃ phase is not solely temperature dependent.

As explained on the basis of literature observations: a preformed (alkali-free) η -Fe₂C phase may remain stable up to 340°C, and decomposition of θ -Fe₃C to α -Fe and C atoms becomes significant at >527°C in the absence of a carbide oxidation shell. A shell that can increase the θ -Fe₃C phase thermal stability up to 600°C.

The formation of the θ -Fe₇C₃ phase is speculated to be related to the presence of CO₂. The θ -Fe₇C₃ phase could only be formed with a high-pressure carburization (340°C, 25 bar, CO) with Fe oxide (α -Fe₂O₃/ α -Al₂O₃) as the carburization starting material. Additionally, a distinctly distorted χ -Fe₅C₂ (h.p.) Hägg carbide phase could be observed with both the R-QPA and MAS techniques after the high-pressure treatment, in addition to the presence of the θ -Fe₇C₃ phase. The formation temperature of 340°C for the θ -Fe₇C₃ phase matches literature observations.

With CO carburization of α -Fe, the added Na-S promotion did not affect the lattice parameters, the hyperfine fields or the formed phase quantities of any of the Fe carbides. In addition, the Fe carbide crystallite diameters remained largely unaffected by the Na-S promotion. In literature, added alkali is occasionally cited to improve the Fe carbide formation, however, the results in this Chapter do not agree with this. The literature observations were explained to be due to enhanced reduction of Fe oxides with CO when alkali is present. That is, alkali improves *the Fe oxide reduction step with CO not the Fe carburization step*. As the carburization treatments were performed with α -Fe as the starting material - with the exception of the high-pressure treatment - the lack of observable Na-S promotion effect on the Fe carburization can be accounted for.

However, few effects due to the Na-S promotion could be observed on the Fe phases

in the carburized catalyst materials. The added Na-S promotion i) increased the Fe oxidation, presumably by O from the CO dissociation acting as oxidation agent, with short, low temperature CO carburization treatments ($\leq 290^\circ\text{C}$, ≤ 3 h) and ii) decreased the crystallite diameter of θ -Fe₃C formed after CO treatment at 440°C .

The deposition and encapsulation of the Fe phases by carbon during the CO carburization treatments has the effect of i) fragmenting the Fe phases into smaller Fe particles (TEM) and crystallite diameters (R-QPA) and ii) detaching the Fe particles from the α -Al₂O₃ support. The carbon deposition becomes significant with catalyst treatments $\geq 340^\circ\text{C}$ (≥ 16 h). With the treatments $\leq 290^\circ\text{C}$ (≤ 3 h), the Fe phases are not significantly encapsulated by carbon and are attached to the α -Al₂O₃ support. The addition of the Na-S promotion increased the rate of carbon deposition from CO at $\geq 340^\circ\text{C}$, but the effect was carburization temperature dependent. The increased carbon deposition rate diminished at 390°C and disappeared when reaching the CO carburization temperature of 440°C . With the highest temperature carburization treatment at 440°C , growth of both larger and smaller Fe particles as well as θ -Fe₃C crystallite growth, could be observed.

For further study, the formation of the θ -Fe₇C₃ phase in relation to presence of CO₂ should be more systematically investigated. This in order to synthesize larger relative quantities of the Fe carbide for more detailed characterization studies. Although, we could identify the hyperfine fields for three of the five expected non-equivalent Fe positions in the θ -Fe₇C₃ crystal lattice; a purer, θ -Fe₇C₃ phase only catalyst materials would be needed for assigning the remaining two Fe positions with hyperfine fields.

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3.6 REFERENCES

- [1] de Smit, E. and Weckhuysen, B. M., "The renaissance of iron-based Fischer-Tropsch synthesis: on the multifaceted catalyst deactivation behaviour", *Chem. Soc. Rev.* **37**, 2758–2781 (2008).
- [2] Niemantsverdriet, J. W., van der Kraan, A. M., van Dijk, W. L. and van der Baan, H. S., "Behavior of Metallic Iron Catalysts during Fischer-Tropsch Synthesis Studied with Mössbauer Spectroscopy, X-ray Diffraction, Carbon Content Determination, and Reaction Kinetic Measurements", *J. Phys. Chem.* **84**, 3363–3370 (1980).
- [3] de Smit, E., Cinquini, F., Beale, A. M., Safonova, O. V., van Beek, W., Sautet, P. and Weckhuysen, B. M., "Stability and Reactivity of ϵ - χ - θ Iron Carbide Catalyst Phases in Fischer-Tropsch Synthesis:

- Controlling μ_c* , *J. Am. Chem. Soc.* **132**, 14928–14941 (2010).
- [4] Stanfield, R. M. and Delgass, W. N., "Mössbauer spectroscopy of supported Fe-Co alloy catalysts for Fischer-Tropsch synthesis", *J. Catal.* **72**, 37–50 (1981).
- [5] Le Caër, G., Dubois, J. M., Pijolat, M., Perrichon, V. and Bussière, P., "Characterization by Moessbauer Spectroscopy of Iron Carbides Formed by Fischer-Tropsch Synthesis", *J. Phys. Chem.* **86**, 4799–4808 (1982).
- [6] Jung, H. and Thomson, W. J., "Dynamic X-ray diffraction study of an unsupported iron catalyst in Fischer-Tropsch synthesis", *J. Catal.* **134**, 654–667 (1992).
- [7] Liu, X.-W., Cao, Z., Zhao, S., Gao, R., Meng, Y., Zhu, J.-X., Rogers, C., Huo, C.-F., Yang, Y., Li, Y.-W. and Wen, X.-D., "Iron Carbides in Fischer-Tropsch Synthesis: Theoretical and Experimental Understanding in Epsilon-Iron Carbide Phase Assignment", *J. Phys. Chem. C* **121**, 21390–21396 (2017).
- [8] Hofer, L. J. E., Cohn, E. M. and Peebles, W. C., "The Modifications of the Carbide, Fe_7C_3 ; Their Properties and Identification", *J. Am. Chem. Soc.* **71**, 189–195 (1949).
- [9] Barton, G. H. and Gale, B., "The structure of a pseudo-hexagonal iron carbide", *Acta Crystallogr.* **17**, 1460–1462 (1964).
- [10] Duggin, M. J. and Hofer, L. J. E., "Nature of χ -Iron Carbide", *Nature* **212**, 248–248 (1966).
- [11] Retief, J. J., "Powder diffraction data and Rietveld refinement of Hägg-carbide, χ - Fe_7C_3 ", *Powder Diffr.* **14**, 130–132 (1999).
- [12] Wang, P., Chen, W., Chiang, F., Dugulan, A. I., Song, Y., Pestman, R., Zhang, K., Yao, J., Feng, B., Miao, P., Xu, W. and Hensen, E. J. M., "Synthesis of stable and low- CO_2 selective ϵ -iron carbide Fischer-Tropsch catalysts", *Sci. Adv.* **4**, eaau2947 (2018).
- [13] Wezendonk, T. A., Sun, X., Dugulan, A. I., van Hoof, A. J. F., Hensen, E. J. M., Kapteijn, F. and Gascon, J., "Controlled formation of iron carbides and their performance in Fischer-Tropsch synthesis", *J. Catal.* **362**, 106–117 (2018).
- [14] Hofer, L. J. E. and Cohn, E. M., "Some Reactions in the Iron-Carbon System: Application to the Tempering of Martensite", *Nature* **167**, 977–978 (1951).
- [15] Hofer, L. J. E., "Nature of the carbides of iron", *U.S. Bureau of Mines Bulletin* **631** (1966). Available at: <http://www.onemine.org/document/abstract.cfm?docid=186163&title=Nature-Of-The-Carbides-Of-Iron> (Accessed: February 2014).
- [16] Dry, M. E., "The Fischer-Tropsch Synthesis" in *Catalysis - Science and Technology* (eds. Anderson, J. R. & Boudart, M.) **1**, 159–256 (Springer-Verlag, Berlin, 1981).
- [17] Eckstrom, H. C. and Adcock, W. A., "A New Iron Carbide in Hydrocarbon Synthesis Catalysts", *J. Am. Chem. Soc.* **72**, 1042–1043 (1950).
- [18] Herbstein, F. H. and Snyman, J. A., "Identification of Eckstrom-Adcock Iron Carbide as Fe_7C_3 ", *Inorg. Chem.* **3**, 894–896 (1964).
- [19] Hirotsu, Y. and Nagakura, S., "Crystal structure and morphology of the carbide precipitated from martensitic high carbon steel during the first stage of tempering", *Acta Metall.* **20**, 645–655 (1972).
- [20] Hirotsu, Y. and Nagakura, S., "Electron Microscopy and Diffraction Study of the Carbide Precipitated at the First Stage of Tempering of Martensitic Medium Carbon Steel", *Trans. Japan Inst. Met.* **15**, 129–134 (1974).
- [21] de Smit, E., Beale, A. M., Nikitenko, S. and Weckhuysen, B. M., "Local and long range order in promoted iron-based Fischer-Tropsch catalysts: A combined in situ X-ray absorption spectroscopy/wide angle X-ray scattering study", *J. Catal.* **262**, 244–256 (2009).
- [22] Shultz, J. F., Hall, W. K., Seligman, B. and Anderson, R. B., "Studies of the Fischer-Tropsch Synthesis. XIV. Hägg Carbide as Catalysts", *J. Am. Chem. Soc.* **77**, 213–221 (1955).

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- [23] Shultz, J. F., Hall, W. K., Dubs, T. A. and Anderson, R. B., "Studies of the Fischer-Tropsch Synthesis. XV. Cementite as Catalysts", *J. Am. Chem. Soc.* **78**, 282–285 (1956).
- [24] Tajima, S. and Hirano, S., "Synthesis and Magnetic Properties of Fe-C₃ Particles with High Saturation Magnetization", *Jpn. J. Appl. Phys.* **29**, 662–668 (1990).
- [25] Dictor, R. and Bell, A. T., "Fischer-Tropsch synthesis over reduced and unreduced iron oxide catalysts", *J. Catal.* **97**, 121–136 (1986).
- [26] O'Brien, R. J., Xu, L., Milburn, D. R., Li, Y.-X., Klabunde, K. J. and Davis, B. H., "Fischer-Tropsch synthesis: Impact of potassium and zirconium promoters on the activity and structure of an ultrafine iron oxide catalyst", *Top. Catal.* **2**, 1–15 (1995).
- [27] Ning, W., Koizumi, N., Chang, H., Mochizuki, T., Itoh, T. and Yamada, M., "Phase transformation of unpromoted and promoted Fe catalysts and the formation of carbonaceous compounds during Fischer-Tropsch synthesis reaction", *Appl. Catal. A Gen.* **312**, 35–44 (2006).
- [28] Mogorosi, R. P., Fischer, N., Claeys, M. and van Steen, E., "Strong-metal-support interaction by molecular design: Fe-silicate interactions in Fischer-Tropsch catalysts", *J. Catal.* **289**, 140–150 (2012).
- [29] Königer, A., Hammerl, C., Zeitler, M. and Rauschenbach, B., "Formation of metastable iron carbide phases after high-fluence carbon ion implantation into iron at low temperatures", *Phys. Rev. B* **55**, 8143–8147 (1997).
- [30] Boellaard, E., van der Kraan, A. M. and Geus, J. W., "Behaviour of a cyanide-derived Fe/Al₂O₃ catalyst during Fischer-Tropsch synthesis", *Appl. Catal. A Gen.* **147**, 229–245 (1996).
- [31] Pijolat, M., Perrichon, V. and Bussière, P., "Study of the carburization of an iron catalyst during the Fischer-Tropsch synthesis: Influence on its catalytic activity", *J. Catal.* **107**, 82–91 (1987).
- [32] Amelse, J. A., Butt, J. B. and Schwartz, L. H., "Carburization of supported iron synthesis catalysts", *J. Phys. Chem.* **82**, 558–563 (1978).
- [33] Liu, X.-W., Zhao, S., Meng, Y., Peng, Q., Dearden, A. K., Huo, C.-F., Yang, Y., Li, Y.-W. and Wen, X.-D., "Mössbauer Spectroscopy of Iron Carbides: From Prediction to Experimental Confirmation", *Sci. Rep.* **6**, 26184 (2016).
- [34] Williamson, D. L., Nakazawa, K. and Krauss, G., "A study of the early stages of tempering in an Fe-1.2 Pct alloy", *Metall. Trans. A* **10**, 1351–1363 (1979).
- [35] Botes, G. F., Bromfield, T. C., Coetzer, R. L. J., Crous, R., Gibson, P. and Ferreira, A. C., "Development of a chemical selective iron Fischer Tropsch catalyst", *Catal. Today* **275**, 40–48 (2016).
- [36] Crous, R., Bromfield, T. C. and Booyens, S., "Olefin Selective FT Catalyst Composition and Preparation Thereof", Patent WO2010066386A1 (2010).
- [37] Johnson, J. Y., "Improvements in the Manufacture and Production of Unsaturated Hydrocarbons of Low Boiling Point", Patent GB322284A (1929).
- [38] Torres Galvis, H. M., Bitter, J. H., Khare, C. B., Ruitenbeek, M., Dugulan, A. I. and de Jong, K. P., "Supported Iron Nanoparticles as Catalysts for Sustainable Production of Lower Olefins", *Science* **335**, 835–838 (2012).
- [39] Pendyala, V. R. R., Graham, U. M., Jacobs, G., Hamdeh, H. H. and Davis, B. H., "Fischer-Tropsch Synthesis: Deactivation as a Function of Potassium Promoter Loading for Precipitated Iron Catalyst", *Catal. Lett.* **144**, 1704–1716 (2014).
- [40] An, X., Wu, B., Wan, H.-J., Li, T.-Z., Tao, Z.-C., Xiang, H.-W. and Li, Y.-W., "Comparative study of iron-based Fischer-Tropsch synthesis catalyst promoted with potassium or sodium", *Catal. Commun.* **8**, 1957–1962 (2007).
- [41] Klencsár, Z., Kuzmann, E. and Vértes, A., "User-friendly software for Mössbauer spectrum analysis", *J.*

- Radioanal. Nucl. Chem. Artic.* **210**, 105–118 (1996).
- [42] León-Reina, L., García-Maté, M., Álvarez-Pinazo, G., Santacruz, I., Vallcorba, O., De la Torre, A. G. and Aranda, M. A. G., "Accuracy in Rietveld quantitative phase analysis: a comparative study of strictly monochromatic Mo and Cu radiations", *J. Appl. Crystallogr.* **49**, 722–735 (2016).
- [43] Jenkins, R. and Snyder, R. L., "Introduction to X-ray Powder Diffractometry", *Introduction to X-ray Powder Diffractometry* **138** (John Wiley & Sons, Inc., Hoboken, NJ, USA, 1996).
- [44] Rietveld, H. M., "A profile refinement method for nuclear and magnetic structures", *J. Appl. Crystallogr.* **2**, 65–71 (1969).
- [45] Hill, R. J. and Howard, C. J., "Quantitative phase analysis from neutron powder diffraction data using the Rietveld method", *J. Appl. Crystallogr.* **20**, 467–474 (1987).
- [46] Bish, D. L. and Post, J. E., "Quantitative Mineralogical Analysis Using the Rietveld Full- Pattern Fitting Method", *Am. Mineral.* **78**, 932–940 (1993).
- [47] Taupin, D., "Automatic peak determination in X-ray powder patterns", *J. Appl. Crystallogr.* **6**, 266–273 (1973).
- [48] Balzar, D., "Voigt-function model in diffraction line-broadening analysis" in *Microstructure Analysis from Diffraction* (eds. Snyder, R. L., Bunge, H. J. & Fiala, J.), 808 (International Union of Crystallography, 1999).
- [49] Cheary, R. W., Coelho, A. A. and Cline, J. P., "Fundamental parameters line profile fitting in laboratory diffractometers", *J. Res. Natl. Inst. Stand. Technol.* **109**, 1 (2004).
- [50] Langford, J. I., Delhez, R., de Keijser, T. H. and Mittemeijer, E. J., "Profile Analysis for Microcrystalline Properties by the Fourier and Other Methods", *Aust. J. Phys.* **41**, 173 (1988).
- [51] Mittemeijer, E. J. and Welzel, U., "The "state of the art" of the diffraction analysis of crystallite size and lattice strain", *Zeitschrift für Krist.* **223**, 552–560 (2008).
- [52] Hubbard, C. R., Swanson, H. E. and Mauer, F. A., "NIST Certificate - Standard Reference Material 640", (1974).
- [53] Le Bail, A., "Whole powder pattern decomposition methods and applications: A retrospection", *Powder Diffraction* **20**, 316–326 (2005).
- [54] Sabine, T. M., Hunter, B. A., Sabine, W. R. and Ball, C. J., "Analytical Expressions for the Transmission Factor and Peak Shift in Absorbing Cylindrical Specimens", *J. Appl. Crystallogr.* **31**, 47–51 (1998).
- [55] Balzar, D., Audebrand, N., Daymond, M. R., Fitch, A., Hewat, A., Langford, J. I., Le Bail, A., Louër, D., Masson, O., McCowan, C. N., Popa, N. C., Stephens, P. W. and Toby, B. H., "Size-strain line-broadening analysis of the ceria round-robin sample", *J. Appl. Crystallogr.* **37**, 911–924 (2004).
- [56] Stokes, A. R. and Wilson, A. J. C., "The diffraction of X rays by distorted crystal aggregates - I", *Proc. Phys. Soc.* **56**, 174–181 (1944).
- [57] Matyi, R. J., Schwartz, L. H. and Butt, J. B., "Particle Size, Particle Size Distribution, and Related Measurements of Supported Metal Catalysts", *Catal. Rev.* **29**, 41–99 (1987).
- [58] Butt, J. B., "Carbide phases on iron-based Fischer-Tropsch synthesis catalysts part I: Characterization studies", *Catal. Lett.* **7**, 61–82 (1990).
- [59] Zhou, X., Ji, J., Wang, D., Duan, X., Qian, G., Chen, D. and Zhou, X., "Hierarchical structured α -Al₂O₃ supported S-promoted Fe catalysts for direct conversion of syngas to lower olefins", *Chem. Commun.* **51**, 8853–8856 (2015).
- [60] Xie, J., Yang, J., Dugulan, A. I., Holmen, A., Chen, D., De Jong, K. P. and Louwerse, M. J., "Size and Promoter Effects in Supported Iron Fischer-Tropsch Catalysts: Insights from Experiment and Theory", *ACS Catal.* **6**, 3147–3157 (2016).

- [61] Butt, J. B., "Carbide phases on iron-based Fischer-Tropsch synthesis catalysts part II: Some reaction studies", *Catal. Lett.* **7**, 83–106 (1990).
- [62] Dry, M. E., Shingles, T. and van H. Botha, C. S., "Factors influencing the formation of carbon on iron Fischer-Tropsch catalysts I. The influence of promoters", *J. Catal.* **17**, 341–346 (1970).
- [63] Dry, M. E., Shingles, T., Boshoff, L. J. and van H. Botha, C. S., "Factors influencing the formation of carbon on iron Fischer-Tropsch catalysts. II. The effect of temperature and of gases and vapors present during Fischer-Tropsch synthesis", *J. Catal.* **17**, 347–354 (1970).
- [64] Cohn, E. M., Bean, E. H., Mentser, M., Hofer, L. J. E., Pontello, A., Peebles, W. C. and Jack, K. H., "The carburization of iron oxide with carbon monoxide: Modifications of Hägg iron carbide", *J. Appl. Chem.* **5**, 418–425 (1955).
- [65] Sancier, K. M., Isakson, W. E. and Wise, H., "Carburization Studies of Iron Fischer-Tropsch Catalysts" in *Hydrocarbon Synthesis from Carbon Monoxide and Hydrogen* (eds. Kugler, E. L. & Steffgen, F. W.) **178**, 129–145 (American Chemical Society, Washington, 1979).
- [66] Berry, T. F., Ames, R. N. and Snow, R. B., "Influence of Impurities and Role of Iron Carbides in Deposition of Carbon from Carbon Monoxide", *J. Am. Ceram. Soc.* **39**, 308–318 (1956).
- [67] Koeken, A. C. J., Torres Galvis, H. M., Davidian, T., Ruitenbeek, M. and de Jong, K. P., "Suppression of Carbon Deposition in the Iron-Catalyzed Production of Lower Olefins from Synthesis Gas", *Angew. Chem., Int. Ed.* **51**, 7190–7193 (2012).
- [68] Toby, B. H., "R factors in Rietveld analysis: How good is good enough?", *Powder Diffr.* **21**, 67–70 (2006).
- [69] Janbroers, S., Louwen, J. N., Zandbergen, H. W. and Kooyman, P. J., "Insights into the nature of iron-based Fischer-Tropsch catalysts from quasi in situ TEM-EELS and XRD", *J. Catal.* **268**, 235–242 (2009).
- [70] Shroff, M. D. and Datye, A. K., "The importance of passivation in the study of iron Fischer-Tropsch catalysts", *Catal. Lett.* **37**, 101–106 (1996).
- [71] Xie, J., Torres Galvis, H. M., Koeken, A. C. J., Kirilin, A., Dugulan, A. I., Ruitenbeek, M. and de Jong, K. P., "Size and Promoter Effects on Stability of Carbon-Nanofiber-Supported Iron-Based Fischer-Tropsch Catalysts", *ACS Catal.* **6**, 4017–4024 (2016).
- [72] Li, J., Cheng, X., Zhang, C., Chang, Q., Wang, J., Wang, X., Lv, Z., Dong, W., Yang, Y. and Li, Y., "Effect of alkalis on iron-based Fischer-Tropsch synthesis catalysts: Alkali-FeO_x interaction, reduction, and catalytic performance", *Appl. Catal. A Gen.* **528**, 131–141 (2016).
- [73] Amelse, J. A., Grynkewich, G., Butt, J. B. and Schwartz, L. H., "Moessbauer spectroscopic study of passivated small particles of iron and iron carbide", *J. Phys. Chem.* **85**, 2484–2488 (1981).
- [74] Sirimanathan, N., Hamdeh, H. H., Zhang, Y. and Davis, B. H., "Fischer-Tropsch Synthesis; Changes in Phase and Activity during Use", *Catal. Lett.* **82**, 181–191 (2002).
- [75] León-Reina, L., De la Torre, A. G., Porras-Vázquez, J. M., Cruz, M., Ordonez, L. M., Alcobé, X., Gispert-Guirado, F., Larrañaga-Varga, A., Paul, M., Fuellmann, T., Schmidt, R. and Aranda, M. A. G., "Round robin on Rietveld quantitative phase analysis of Portland cements", *J. Appl. Crystallogr.* **42**, 906–916 (2009).
- [76] Michel, F. M., Ehm, L., Antao, S. M., Lee, P. L., Chupas, P. J., Liu, G., Strongin, D. R., Schoonen, M. A. A., Phillips, B. L. and Parise, J. B., "The Structure of Ferrihydrite, a Nanocrystalline Material", *Science* **316**, 1726–1729 (2007).
- [77] Jozwiak, W. K., Kaczmarek, E., Maniecki, T. P., Ignaczak, W. and Maniukiewicz, W., "Reduction behavior of iron oxides in hydrogen and carbon monoxide atmospheres", *Appl. Catal. A Gen.* **326**, 17–27 (2007).
- [78] Podgurski, H. H., Kummer, J. T., DeWitt, T. W. and Emmett, P. H., "Preparation, Stability and

- Adsorptive Properties of the Carbides of Iron*", *J. Am. Chem. Soc.* **72**, 5382–5388 (1950).
- [79] Krishnamoorthy, S., Li, A. and Iglesia, E., "Pathways for CO₂ Formation and Conversion During Fischer–Tropsch Synthesis on Iron-Based Catalysts", *Catal. Lett.* **80**, 77–86 (2002).
- [80] Davis, B. H., "Fischer–Tropsch Synthesis: Reaction mechanisms for iron catalysts", *Catal. Today* **141**, 25–33 (2009).
- [81] Shultz, J. F., Abelson, M., Stein, K. C. and Anderson, R. B., "Studies of the Fischer–Tropsch Synthesis. XVIII. Influence of Catalyst Geometry on Synthesis on Iron Catalysts", *J. Phys. Chem.* **63**, 496–500 (1959).
- [82] O'Brien, R. J., Xu, L., Spicer, R. L. and Davis, B. H., "Activation Study of Precipitated Iron Fischer–Tropsch Catalysts", *Energy & Fuels* **10**, 921–926 (1996).
- [83] Bukur, D. B., Okabe, K., Rosynek, M. P., Li, C. P., Wang, D. J., Rao, K. R. P. M. and Huffman, G. P., "Activation Studies with a Precipitated Iron Catalyst for Fischer–Tropsch Synthesis. I. Characterization Studies", *Journal of Catalysis* **155**, 353–365 (1995).
- [84] Arakawa, H. and Bell, A. T., "Effects of potassium promotion on the activity and selectivity of iron Fischer–Tropsch catalysts", *Ind. Eng. Chem. Process Des. Dev.* **22**, 97–103 (1983).
- [85] Olsson, R. G. and Turkdogan, E. T., "Catalytic effect of iron on decomposition of carbon monoxide: II. Effect of additions of H₂, H₂O, CO₂, SO₂ and H₂S", *Metall. Trans.* **5**, 21–26 (1974).
- [86] Nagakura, S., "Study of Metallic Carbides by Electron Diffraction Part III. Iron Carbides", *J. Phys. Soc. Japan* **14**, 186–195 (1959).
- [87] Raupp, G. B. and Delgass, W. N., "Mössbauer Investigation of Supported Fe and FeNi Catalysts II. Carbides Formed by Fischer–Tropsch Synthesis", *J. Catal.* **58**, 348–360 (1979).
- [88] Tau, L. M., Borcar, S., Bianchi, D. and Bennett, C. O., "Investigation of supported iron Fischer–Tropsch synthesis catalysts by Mössbauer spectroscopy", *J. Catal.* **87**, 36–54 (1984).
- [89] Xu, K., Sun, B., Lin, J., Wen, W., Pei, Y., Yan, S., Qiao, M., Zhang, X. and Zong, B., "ε-Iron carbide as a low-temperature Fischer–Tropsch synthesis catalyst", *Nat. Commun.* **5**, 5783 (2014).
- [90] Jiang, F., Zhang, M., Liu, B., Xu, Y. and Liu, X., "Insights into the influence of support and potassium or sulfur promoter on iron-based Fischer–Tropsch synthesis: understanding the control of catalytic activity, selectivity to lower olefins, and catalyst deactivation", *Catal. Sci. Technol.* **7**, 1245–1265 (2017).
- [91] Riedel, T., Schulz, H., Schaub, G., Jun, K.-W., Hwang, J.-S. and Lee, K.-W., "Fischer–Tropsch on Iron with H₂/CO and H₂/CO₂ as Synthesis Gases: The Episodes of Formation of the Fischer–Tropsch Regime and Construction of the Catalyst", *Top. Catal.* **26**, 41–54 (2003).
- [92] Nagakura, S., Hirotsu, Y., Kusunoki, M., Suzuki, T. and Nakamura, Y., "Crystallographic study of the tempering of martensitic carbon steel by electron microscopy and diffraction", *Metall. Trans. A* **14**, 1025–1031 (1983).
- [93] Bauer-Grosse, E. and Le Caër, G., "Crystallisation of amorphous Fe_{1-x}C_x alloys (0.30 ≤ x ≤ 0.32) and Chemical Twinning", *J. Phys. F Met. Phys.* **16**, 399–406 (1986).
- [94] Nagakura, S., Suzuki, T. and Kusunoki, M., "Structure of the Precipitated Particles at the Third Stage of Tempering of Martensitic Iron–Carbon Steel Studied by High Resolution Electron Microscopy", *Trans. Japan Inst. Met.* **22**, 699–709 (1981).
- [95] du Plessis, H. E., de Villiers, J. P. R., Kruger, G. J., Steuwer, A. and Brunelli, M., "Rietveld and pair distribution function study of Hägg carbide using synchrotron X-ray diffraction", *J. Synchrotron Radiat.* **18**, 266–271 (2011).
- [96] Cohn, E. M. and Hofer, L. J. E., "Mode of Transition from Hägg Iron Carbide to Cementite", *J. Am. Chem. Soc.* **72**, 4662–4664 (1950).

- [97] Wood, I. G., Vočadlo, L., Knight, K. S., Dobson, D. P., Marshall, W. G., Price, G. D. and Brodholt, J., "Thermal expansion and crystal structure of cementite, Fe₃C, between 4 and 600 K determined by time-of-flight neutron powder diffraction", *J. Appl. Crystallogr.* **37**, 82–90 (2004).
- [98] de Smit, E., van Schooneveld, M. M., Cinquini, F., Bluhm, H., Sautet, P., de Groot, F. M. F. and Weckhuysen, B. M., "On the Surface Chemistry of Iron Oxides in Reactive Gas Atmospheres", *Angew. Chem., Int. Ed.* **50**, 1584–1588 (2011).
- [99] Bordet, A., Soulantika, A. and Chaudret, B., "Iron carbide nanoparticles, method for preparing same and use thereof for heat generation", Patent WO 2017/103492 A2 (2017).
- [100] Li, J., Cheng, X., Zhang, C., Yang, Y. and Li, Y., "Effects of alkali on iron-based catalysts for Fischer-Tropsch synthesis: CO chemisorptions study", *J. Mol. Catal. A Chem.* **396**, 174–180 (2015).
- [101] Berry, F. J. and Smith, M. R., "A Mössbauer investigation of iron-containing catalysts prepared at low temperatures and active for carbon monoxide hydrogenation", *J. Chem. Soc. Faraday Trans. 1 Phys. Chem. Condens. Phases* **85**, 467–477 (1989).
- [102] Ribeiro, M. C., Jacobs, G., Davis, B. H., Cronauer, D. C., Kropf, A. J. and Marshall, C. L., "Fischer-Tropsch Synthesis: An In-Situ TPR-EXAFS/XANES Investigation of the Influence of Group I Alkali Promoters on the Local Atomic and Electronic Structure of Carburized Iron/Silica Catalysts", *J. Phys. Chem. C* **114**, 7895–7903 (2010).
- [103] Ngantsoe-Hoc, W., Zhang, Y., O'Brien, R. J., Luo, M. and Davis, B. H., "Fischer-Tropsch synthesis: activity and selectivity for Group I alkali promoted iron-based catalysts", *Appl. Catal. A Gen.* **236**, 77–89 (2002).
- [104] Ratnasamy, C. and Wagner, J. P., "Water Gas Shift Catalysis", *Catal. Rev.* **51**, 325–440 (2009).
- [105] Krupay, B. W. and Amenomiya, Y., "Alkali-promoted Alumina Catalysts I. Chemisorption and oxygen exchange of carbon monoxide and carbon dioxide on potassium-promoted alumina catalysts", *J. Catal.* **67**, 362–370 (1981).
- [106] Amenomiya, Y. and Pleizier, G., "Alkali-promoted Alumina Catalysts II. Water-Gas Shift Reaction", *J. Catal.* **76**, 345–353 (1982).
- [107] Anderson, R. B., Karn, F. S. and Shultz, J. F., "Factors in sulfur poisoning of iron catalysts in Fischer-Tropsch synthesis", *J. Catal.* **4**, 56–63 (1965).
- [108] Towett, E. K., Shepherd, K. D. and Cadisch, G., "Quantification of total element concentrations in soils using total X-ray fluorescence spectroscopy (TXRF)", *Sci. Total Environ.* **463–464**, 374–388 (2013).
- [109] Tsuzuki, A., Sago, S., Hirano, S.-I. and Naka, S., "High temperature and pressure preparation and properties of iron carbides Fe₇C₃ and Fe₃C", *J. Mater. Sci.* **19**, 2513–2518 (1984).
- [110] Bi, X.-X., Ganguly, B., Huffman, G. P., Huggins, F. E., Endo, M. and Eklund, P. C., "Nanocrystalline α -Fe, Fe₃C, and Fe₇C₃ produced by CO₂ laser pyrolysis", *J. Mater. Res.* **8**, 1666–1674 (1993).
- [111] Yamada, Y., Yoshida, H., Kouno, K. and Kobayashi, Y., "Iron carbide films produced by laser deposition", *J. Phys. Conf. Ser.* **217**, 012096 (2010).
- [112] Sethuraman, A. R., "In-situ high temperature X-ray diffraction studies of nanocrystalline iron carbides", *Nanostructured Mater.* **4**, 79–92 (1994).
- [113] Audier, M., Bowen, P. and Jones, W., "Transmission electron microscopic study of single crystals of Fe₇C₃", *J. Cryst. Growth* **63**, 125–134 (1983).
- [114] Lywood, W. J. and Twigg, M. V., "Hydrogen production including a shift reaction process", Patent EP0361648A1 (1990).
- [115] Luo, M. and Davis, B. H., "Fischer-Tropsch synthesis: Group II alkali-earth metal promoted catalysts", *Appl. Catal. A Gen.* **246**, 171–181 (2003).
- [116] Rhodes, C., Hutchings, G. J. and Ward, A. M., "Water-gas shift reaction: finding the mechanistic

- boundary", *Catal. Today* **23**, 43–58 (1995).
- [117] Anderson, R. B., Hofer, L. J. E., Cohn, E. M. and Seligman, B., "Studies of the Fischer—Tropsch Synthesis. IX. Phase Changes of Iron Catalysts in the Synthesis", *J. Am. Chem. Soc.* **73**, 944–946 (1951).
- [118] Liu, X., Zhang, C., Li, Y., Niemantsverdriet, J. W., Wagner, J. B. and Hansen, T. W., "Environmental Transmission Electron Microscopy (ETEM) Studies of Single Iron Nanoparticle Carburization in Synthesis Gas", *ACS Catal.* **7**, 4867–4875 (2017).
- [119] Kril, C. E. and Birringer, R., "Estimating grain-size distributions in nanocrystalline materials from X-ray diffraction profile analysis", *Philos. Mag. A* **77**, 621–640 (1998).
- [120] Steynberg, A. P., Espinoza, R. L., Jager, B. and Vosloo, A. C., "High temperature Fischer–Tropsch synthesis in commercial practice", *Appl. Catal. A Gen.* **186**, 41–54 (1999).
- [121] Sarkar, A., Seth, D., Dozier, A. K., Neathery, J. K., Hamdeh, H. H. and Davis, B. H., "Fischer–Tropsch Synthesis: Morphology, Phase Transformation and Particle Size Growth of Nano-scale Particles", *Catal. Lett.* **117**, 1–17 (2007).
- [122] Fruchart, R., Senateur, J. P., Bouchaud, J. P. and Michel, A., "A propos de la structure exacte du carbure de fer Fe_7C_3 ", *Bull. Soc. Chim. Fr.* **2**, 392 (1965).
- [123] Gatte, R. R. and Phillips, J., "The influence of particle size and structure on the Mössbauer spectra of iron carbides formed during Fischer–Tropsch synthesis", *J. Catal.* **104**, 365–374 (1987).
- [124] Foct, J., Senateur, J. P., Dubois, J. M. and Le Caër, G., "Mössbauer Spectroscopy of Different Interstitial Compounds and Solid Solutions Containing ^{57}Fe ", *Le J. Phys. Colloq.* **40**, 647–649 (1979).
- [125] Dubois, J. M. and Le Caër, G., "Electron diffraction and Mossbauer studies of the ϵ phase retained in splat-quenched Fe–C and Fe–C–Si alloys", *Acta Metall.* **25**, 609–618 (1977).
- [126] Shultz, J. F., Abelson, M., Shaw, L. and Anderson, R. B., "Fischer–Tropsch Synthesis. Nitrides and Carbonitrides of Iron as Catalysts", *Ind. Eng. Chem.* **49**, 2055–2060 (1957).
- [127] Niewa, R., Rau, D., Wosylus, A., Meier, K., Hanfland, M., Wessel, M., Dronskowski, R., Dzivenko, D. A., Riedel, R. and Schwarz, U., "High-Pressure, High-Temperature Single-Crystal Growth, Ab initio Electronic Structure Calculations, and Equation of State of ϵ - Fe_3N_{1+x} ", *Chem. Mater.* **21**, 392–398 (2009).
- [128] Leineweber, A., Shang, S., Liu, Z.-K., Widenmeyer, M. and Niewa, R., "Crystal structure determination of Hägg carbide, χ - Fe_5C_2 by first-principles calculations and Rietveld refinement", *Zeitschrift für Krist.* **227**, 207–220 (2012).
- [129] Jack, K. H., "The iron–nitrogen system: the crystal structures of ϵ -phase iron nitrides", *Acta Crystallogr.* **5**, 404–411 (1952).
- [130] Rechenbach, D. and Jacobs, H., "Structure determination of ζ - Fe_2N by neutron and synchrotron powder diffraction", *J. Alloys Compd.* **235**, 15–22 (1996).
- [131] Jacobs, H., Rechenbach, D. and Zachwieja, U., "Structure determination of γ' - Fe_4N and ϵ - Fe_3N ", *J. Alloys Compd.* **227**, 10–17 (1995).
- [132] Nagakura, S. and Tanehashi, K., "Electronic Structure of Iron Nitrides Studied by Electron Diffraction. II. ϵ - Fe_2N and ζ - Fe_2N ", *J. Phys. Soc. Japan* **25**, 840–846 (1968).

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Chapter 4

On the Role of Iron Carbides in the Fischer-Tropsch Synthesis with Fe(-Na-S)/ α -Al₂O₃ Catalysts

The Fischer-Tropsch Synthesis (FTS) reaction converts a H₂:CO gas mixture with e.g. Fe-based catalysts into hydrocarbons. Fe carbides, ϵ -Fe₃C, η -Fe₂C, χ -Fe₅C₂, θ -Fe₃C and/or θ -Fe₇C₃, form the active phases in Fe-based FTS reaction catalysts. We aim to probe in to each of the Fe carbides' catalysis properties, in combination to the effect of Na-S promotion on the Fe carbide phases in 10 bar FTS reaction at 340°C. Supported Fe(-Na-S)/ α -Al₂O₃ catalyst materials with preformed Fe carbides were tested for their FTS reaction performance. The catalysts were characterized ex-situ after the FTS reaction by using X-ray Powder Diffractometry (XRPD) with Rietveld Quantitative Phase Analysis (R-QPA) and Transmission Electron Microscopy (TEM). In the FTS reaction, Na-S promotion stabilizes the η -Fe₂C and destabilizes the θ -Fe₃C phase. Regardless of the Na-S promotion, the χ -Fe₅C₂ and θ -Fe₇C₃ phases were stable and the ϵ -Fe₃C phase unstable. Any specific Fe carbide did not directly imply enhanced FTS reaction activity. This property was primarily enhanced by the added Na-S promotion. By the differences in the observed lattice parameters, the η -Fe₂C and χ -Fe₅C₂ phases were divided into subtypes and the subtypes primary formation requirements were assigned. Indications on the FTS reaction hydrocarbon selectivity dependency on Fe carbide subtypes and/or phases could be observed, warranting further research.

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4.1 INTRODUCTION

Fe carbides form the active phases for the Fe-based Fischer-Tropsch Synthesis (FTS) reaction polymerizing a $\text{H}_2\text{:CO}$ mixture (i.e. syngas) into various hydrocarbons. The Fe carbides observable in the FTS reaction research field have been identified with their crystal lattices as: $\epsilon\text{-Fe}_3\text{C}$ $P6_322$ (182), $\eta\text{-Fe}_2\text{C}$ $Pnnm$ (58), $\chi\text{-Fe}_5\text{C}_2$ $C2/c$ (15), $\theta\text{-Fe}_3\text{C}$ $Pnma$ (62) and $\theta\text{-Fe}_7\text{C}_3$ $Pnma$ (62) on the basis of the literature (**Chapter 2**) and performed CO carburization experiments at various reaction temperatures (**Chapter 3**).

Different FTS reaction activities for the various Fe carbides have been proposed in the past. That is, that not all of the Fe carbides perform equally in the FTS reaction. The most commonly observed Fe carbide phase in the FTS reaction is the $\chi\text{-Fe}_5\text{C}_2$ phase (the Hägg carbide),^{1–6} which is usually taken as a FTS reaction active carbide phase. The “ ϵ -carbides” (i.e. $\epsilon\text{-Fe}_3\text{C}$ and/or $\eta\text{-Fe}_2\text{C}$) have been proposed to be more FTS active than the $\chi\text{-Fe}_5\text{C}_2$ phase,⁷ or can be present in a deactivated catalyst material.⁸ $\theta\text{-Fe}_3\text{C}$ phase (cementite) has indirectly been associated to the deactivation of the Fe-based FTS catalyst materials,⁹ or possesses somewhat a lower FTS activity than the $\chi\text{-Fe}_5\text{C}_2$ phase, yet still being active for the FTS reaction.¹⁰ The less studied and more rare Fe_7C_3 (i.e. $\theta\text{-Fe}_7\text{C}_3$) phase has also been associated to the FTS active catalyst materials.^{11,12} In contrast to this, the Fe_7C_3 phase has also been encountered in the industrially applied Fe-based FTS reaction catalyst materials near their end-of-life.¹³

However, whether a single, bulk Fe carbide phase or a Fe phase mixture can simply be associated to a catalyst material's FTS reaction performance has been questioned before.^{8,14–16} Intertwined deactivation processes, e.g. carbon deposition,^{8,13,17–19} Fe particle sintering,^{20,21} and/or Fe reoxidation into inactive oxides can simultaneously take place for Fe-based FTS reaction catalyst materials.^{3,4,8,13,21–25} The variety of the possible deactivation processes complicate the interpretation of the effect of the Fe carbide phases' individual performance in the FTS reaction.

The hydrocarbon product selectivity in the FTS reaction can be altered, besides changing the reaction conditions:^{26,27} with the addition of promoters,^{8,22,28–33} or to some extent with different Fe phases as the FTS reaction's starting materials (i.e. with catalyst pretreatment or conditioning).^{4,34–36} Especially, Na-S promotion has been observed as an effective way for increasing the FTS reaction's hydrocarbon products' olefin content while suppressing the undesired CH_4 product selectivity.^{28–30,37–40}

In this Chapter, we aim to systematically probe further to the effect that the initial Fe carbide phase(s), with and without the Na-S promotion, have on the catalyst materials' FTS reaction catalysis performance. The changes in the initial Fe carbide phase(s) after the FTS reaction are followed and further evaluated in respect to their FTS reaction performance (**Figure 4.1**). Especially, the Fe carbides' lattice parameters

and their changes, under the FTS reaction or CO carburization conditions are often an overlooked Fe carbide property. This, despite the X-ray Powder Diffractometry (XRPD), a technique capable of probing to the Fe carbide lattice changes, has been widely applied in the FTS research field.^{1,4,9,11,12,15,19,26,34,41,42} As an example, various and significantly different lattice parameters have been observed for the χ -Fe₅C₂ phase.^{43–46} That is, more than one type of the χ -Fe₅C₂ phase may exist, with an unclear relation to their FTS reaction performance.

Therefore, with the use of ex-situ XRPD with Rietveld Quantitative Phase Analysis (R-QPA), we explore the effect of Na-S promotion on the preformed Fe carbides (i.e. ϵ -Fe₃C, η -Fe₂C, χ -Fe₅C₂, θ -Fe₃C and θ -Fe₇C₃) on CO carburized Fe(-Na-S)/ α -Al₂O₃ catalyst materials applied in the FTS reaction at 340°C. For reference, Fe carbide free, H₂ reduced only catalyst materials are also studied. The R-QPA is used to obtain the Fe

Figure 4.1

A schematic of the approach applied in this Chapter. Various Fe carbide phases were preformed on unpromoted and Na-S promoted Fe(-Na-S)/ α -Al₂O₃ catalyst materials. The catalysts are (a) tested for their catalytic performance in the Fischer-Tropsch Synthesis (FTS) reaction and (b) subsequently characterized ex-situ with X-ray Powder Diffractometry (XRPD). Rietveld Quantitative Phase Analysis (R-QPA) is applied to the XRPD patterns in order to (c) quantify the Fe carbide phases and their crystallite diameters and lattice parameters in the catalyst materials after their application in the FTS reaction. The quantification results are then (d) compared to the catalyst materials FTS reaction catalysis performances.

phase quantities, crystallite diameters and lattice parameters. As a complementary technique, Fe particle diameters and catalyst morphology are followed for the selected FTS reaction catalyst materials using Transmission Electron Microscopy (TEM). Both R-QPA and TEM obtained results are compared to the results for the catalyst materials before the FTS reaction, as reported in **Chapter 3**. These characterization results for the catalyst materials are then related to their FTS reaction catalysis performance in terms of both activity and selectivity.

4.2 EXPERIMENTAL METHODS

4.2.1 Catalyst Preparation

The details of the synthesis, CO carburization (within 240-440°C) or only H₂ reduction of the nominal 7 weight percent (wt-%) Fe on alpha alumina supported (Fe-(Na-S)/ α -Al₂O₃) catalyst materials, with or without Na-S promotion, are described in **Chapter 3**. The CO carburized or H₂ reduced FTS reaction catalyst materials within this Chapter are from the same catalyst material synthesis batches as studied in **Chapter 3**.

4.2.2 Catalyst Testing

A high-throughput Avantium Flowrence catalyst testing set-up with 16 parallel fixed bed reactors was used for testing the prepared CO carburized or H₂ reduced catalyst materials in the FTS reaction.

The catalyst materials ($\approx$ 25 mg, 212-425 μ m particle size) were diluted with SiC ($\approx$ 125 mg, 212-425 μ m). The resulting catalyst material/SiC mixtures were loaded into stainless steel reactor tubes with an inner diameter of 2 mm, giving catalyst beds with heights within $\approx$ 33-34 mm. Each catalyst material/SiC mixture was loaded into two reactors for testing the data reproducibility. Additionally, two reactor tubes were loaded with SiC only and used as blank reactors.

The FTS reaction was performed at 340°C at 10 bar H₂:CO:He (2.0:1.0:0.33 volume ratio) total pressure. The nominal input gas flows for each reactor were 5.28 ml/min H₂, 2.64 ml/min CO and 0.88 ml/min He giving gas hourly space velocity (GHSV, as total input gas flow per total catalyst bed volume) of $\approx$ 5 000 h⁻¹. The reactor pressurizing was done with the H₂:CO:He gas mixture at 120°C up to the desired 10 bar total reaction pressure. Upon reaching the 10 bar pressure, the reactor temperature was increased from 120°C to 340°C (2°C/min) to start the FTS reaction test run. The FTS reaction was considered to start when the 340°C reaction temperature was reached. After 72 h of the FTS reaction, the input gas flow was switched to pure He and the reactor temperature and pressure were lowered to ambient conditions. The spent catalyst material/SiC mixtures were removed from the reactors and exposed to air. The catalysts were

separated from the SiC diluent using a magnet. The H₂ and He gas purities were grade 5.0 (99.999 % pure) and for CO grade 2.5 (99.5 % pure).

On-line gas chromatography (GC) with Thermal Conductivity (TCD) and Flame Ionization Detectors (FIDs) were used for determining the H₂ and CO conversions, CO₂ and hydrocarbon (+methanol) (mol C-%) selectivities for each of the tested catalyst materials. H₂ and CO conversion percentages were calculated from the difference of the outlet H₂ and CO TCD peak areas between the average of the blank reactors and the reactors with loaded catalyst materials. Fe Time Yield (FTY) was calculated as based on the nominal converted input CO flow and the elemental Fe loadings of the parent (**Chapter 3**), as-synthesized calcined catalyst materials. Usage Ratio H₂:CO was calculated as the ratio of the converted H₂ and CO. The CO conversion towards hydrocarbons was estimated by normalizing the cumulative total chromatogram FID peak areas per GC injection to the respective converted CO area as per TCD data.

TCD data was used to obtain the CO₂ selectivities. The reported, CO₂-free, methanol and C₁-C₄ hydrocarbon selectivities were obtained as identified chromatogram peak area per chromatogram cumulative total peak area using the FID data. The C₅+ hydrocarbon selectivity was taken as 100 - (C₁-C₄ + methanol selectivities). Furthermore, individual C₁-C₈ hydrocarbon selectivities were calculated from the FID data and used for obtaining the Anderson-Schulz-Flory (ASF) distribution α -value via the **Equation 2.1** by using a linear fit to the C₃-C₇ range.

All of the TCD and FID peak areas were normalized to the variable GC injection volumes using the He peak area. Bad GC injections (i.e. outlying data points) were filtered out with taking 5-point median values over the FTS reaction time. Data points with distance $\geq 2 \times$ Standard Deviation (STD) of the median value were rejected.

4.2.3 Catalyst Characterization

The catalyst materials collected after the 72 h FTS reaction were analyzed ex-situ with bright field TEM and XRPD. The term X-ray Powder Diffractometry (XRPD) is used to refer to X-ray diffraction phenomena based characterization experiments that are done under powder diffraction conditions.⁴⁷ R-QPA was applied on the obtained XRPD patterns, for both crystalline Fe phase quantifications and determining the crystallite diameters for the Fe phases. The Fe particles counted from the TEM images were used for determining the Fe particle size distributions. The experimental details on the application of TEM, XRPD and R-QPA have been explained earlier within **Chapter 3** and the techniques are applied in an identical manner within this Chapter.

With R-QPA, in addition to the technique application details in **Chapter 3**, residual SiC phases from the catalyst material dilution for the FTS reaction gave occasional, random (non-powder diffraction), diffraction peaks. These SiC diffraction peaks were

Table 4.1

Overview of the used shorthand notation for the catalyst materials used in this Chapter. The catalyst materials after the applied H_2 reduction or CO carburization treatments are discussed more in detail in **Chapter 3**.

Shorthand Notation	Catalyst Material Description
H_2	H_2 reduction at 400°C for 5 h
240, 290, 340, 390, 440	CO carburization (at 1 atm) temperature in °C, <i>after H_2 reduction</i>
340 h.p.	CO carburization at 25 bar at 340°C, <i>after calcining</i>
UP	Unpromoted Fe/ α - Al_2O_3 catalyst
Na-S	Na-S promoted Fe-Na-S/ α - Al_2O_3 catalyst
Carb.	Catalyst material after H_2 reduction or CO carburization (“fresh catalyst”)
FTS	Catalyst material after 72 h 340°C, 10 bar FTS reaction (“spent catalyst”)

fitted with individual Lorentzian peaks i.e. without a crystal structure or space group constrains.

4.3 RESULTS AND DISCUSSION

In this Chapter, we have used ex-situ XRPD for collecting X-ray diffraction patterns on Fe-based catalyst materials *after* their catalytic performance testing in the FTS reaction (340°C, 10 bar, H_2 :CO:He 2.0:1.0:0.33 v/v, GHSV 5 000 h⁻¹). R-QPA was employed on the XRPD patters for quantifying the Fe phases present in the catalyst materials applied in the FTS reaction. Fe particle diameter changes have been followed with TEM. The results have been compared to the R-QPA and TEM results for the respective catalyst materials *before* the FTS reaction reported in **Chapter 3**. This approach has been applied on both unpromoted Fe/ α - Al_2O_3 (shorthand *UP*) and the Na-S promoted Fe-Na-S/ α - Al_2O_3 (*Na-S*) catalyst materials. These catalyst materials have been CO carburized in **Chapter 3** to contain various Fe carbide phases, or only reduced with H_2 to non-carbide α -Fe/ Fe_xO_y phases for comparison purposes.

The shorthand notation of 240, 290, 340, 390 or 440 is used to refer to catalyst material with the CO carburization done at the implied temperature in °C, at atmospheric pressure. Catalyst materials CO carburized *directly* after a catalyst calcining step at 25 bar CO pressure at 340°C are noted in shorthand as 340 h.p.. The notation H_2 is used for the only H_2 reduced catalyst materials.

For the catalyst material characterizations done after the 72 h FTS reaction run, shorthand notation *FTS* (i.e. “spent catalyst”) is used. For the CO carburized or H_2 reduced catalyst materials before the FTS reaction shorthand *Carb.* (i.e. “fresh catalyst”) is used collectively. The used shorthand notations for the catalyst materials under study are summarized in **Table 4.1**

4.3.1 Morphological Changes Probed with Transmission Electron Microscopy

Examples of the measured TEM images for the selected catalyst materials (H₂, 240, 340, 440) are compared for the UP FTS in **Figure 4.2** and in **Figure 4.3** for the Na-S FTS catalysts. The Fe particle (number-weighted) mean diameters for the FTS catalyst materials, as derived from the measured TEM images, are given in **Figure 4.4**. The values in **Figure 4.4** are compared to the respective values for the Carb. catalyst materials from **Chapter 3** before the FTS reaction.

The catalyst morphology, for both the UP and Na-S FTS catalyst materials, behaves as would be expected based on the discussion in **Chapter 3**. At 340°C (the FTS reaction temperature) the Fe particles are encapsulated by carbon and detached from the α -Al₂O₃ support,⁴⁸ for all the UP (**Figure 4.2**) and Na-S catalyst materials (**Figure 4.3**)

Figure 4.2

Transmission Electron Microscopy (TEM) images for the selected UP FTS (Fe/ α -Al₂O₃) catalyst materials after 72 h of the Fischer-Tropsch Synthesis (FTS) reaction. Images for the catalyst materials a) H₂, b) 240, c) 340 and d) 440.

Figure 4.3

Transmission Electron Microscopy (TEM) images for selected Na-S FTS (Fe-Na-S/ α -Al₂O₃) catalyst materials after 72 h of the Fischer-Tropsch Synthesis (FTS) reaction. Images for the catalyst materials a) H₂, b) 240, c) 340 and d) 440.

applied in the FTS reaction. Especially with the UP H₂ and 240 (**Figure 4.2a-b**) and Na-S H₂ and 240 Carb. catalyst materials (**Figure 4.3a-b**), for which the Fe particles were attached to the support α -Al₂O₃ without carbon encapsulation before the FTS reaction (**Chapter 3**), the change is significant. Likewise, as with the Carb. catalyst materials, the FTS catalyst materials show ≈ 4 nm Fe oxidation layer due to the catalyst exposure to air.^{49,50}

Some elongated, cylindrical Fe particles and filamentous carbon can be observed in the TEM images for the FTS catalyst materials (e.g. **Figure 4.3c-d**), which were not present in any of the Carb. catalysts. Under pure CO, i.e. with Carb. catalyst materials, carbon forms as a Fe encapsulating overlayer. For the FTS catalyst materials in the presence of both C and H under H₂:CO (or C₂H₂) atmosphere, filamentous carbon growth can take place.⁵¹⁻⁵³ As has been visualized with use of Environmental TEM

Figure 4.4

Transmission Electron Microscopy (TEM)-based, Fe particle (number-weighted) mean diameters compared for selected UP and Na-S (Fe(-Na-S)/ α -Al₂O₃) catalyst materials before (Carb.) and after 72 h Fischer-Tropsch Synthesis (FTS) reaction for a) UP and c) Na-S catalysts. The respective size distribution Standard Deviations (STDs) are given for b) UP and d) Na-S catalyst materials. The percentage changes for UP and Na-S catalysts as FTS versus Carb. for e) Fe particle mean diameters and the respective f) size distribution STDs.

(ETEM) by Mazzucco et al., the filamentous carbon growth causes elongation in the Fe particles.⁵³ This could explain the observations of more cylindrical Fe particles in the FTS catalyst materials.

The size distribution derived Fe particle mean diameters (**Figure 4.4a**) or Fe particle size distribution STDs (**Figure 4.4b**) do not change for the UP FTS catalyst materials in any significant manner in comparison to the respective Carb. catalysts (**Figure 4.4e-f**). Neither, no significant change is observed for the Na-S H₂ and Na-S 440 catalyst materials after the FTS reaction (**Figure 4.4c-f**). But, for the Na-S 240 FTS and Na-S 340 FTS catalyst materials the Fe particle mean diameters increase by $\approx +28\%$ and $\approx +48\%$ (**Figure 4.4e**), respectively, in comparison to the respective Carb. catalysts.

Furthermore, the Fe particle size distribution STD for Na-S 340 FTS catalyst material increases by $\approx +78\%$ in comparison to the Na-S 340 Carb. catalyst (**Figure 4.4f**). The increase in the STD signifies increased variation in the Fe particle diameters in the catalyst material.

The addition of Na-S promotion has previously been observed to increase the Fe particle mean diameters for catalyst materials applied in the FTS reaction.²⁰ This observation is akin to the results for the FTS catalyst materials Na-S 240 and Na-S 340. However, for the Na-S H₂ and Na-S 440 catalysts, only negligible changes in both mean Fe particle diameters (**Figure 4.4c, e**) and size distribution STDs (**Figure 4.4d, f**) can be observed despite the Na-S promotion.

As the catalytic performances (**Figure 4.20**), as will be discussed in a later section, are reasonably comparable for the selected Na-S (H₂, 240, 340 and 440) FTS catalyst materials: the differences e.g. in catalytic activity do not explain the variability in the Fe particle growth. The causality when and why the Na-S promotion causes Fe particle growth is unclear from the results but may or may not occur if Na-S promotion is applied. Thus, possibly: Fe particle growth may not be an intrinsic property of the Na-S promotion.

4.3.2 Phase Quantification with X-ray Powder Diffractometry/Rietveld Quantitative Phase Analysis

The background corrected, ex-situ measured XRPD and Rietveld method (i.e. R-QPA) calculated diffraction and difference patterns, for the catalyst materials are given in **Figure 4.6** (UP and Na-S H₂ FTS), **Figure 4.7** (UP FTS) and **Figure 4.8** (Na-S FTS) over the range $13-29^\circ 2\theta$ with Mo K α . The R-QPA refinements were done over the measured X-ray diffraction pattern range of $6-39^\circ 2\theta$ for all of the catalyst materials under study.

The Fe carbide phases encountered in FTS research field have been identified to be ϵ -Fe₃C *P6₃22* (182), η -Fe₂C *Pnnm* (58), χ -Fe₅C₂ *C2/c* (15) (the Hägg carbide), θ -Fe₃C *Pnma* (62) (cementite) and θ -Fe₇C₃ *Pnma* (62) (Eckström-Adcock Carbide) on basis of the literature survey in **Chapter 2** and with experimental validation in **Chapter 3**.

The Rietveld method calculated diffraction patterns resulted in a good agreement with the experimentally measured patterns, with fitting mismatches mainly originating from the support material α -Al₂O₃ phase. Thus, the named Fe carbides represent the Fe phases formed in the FTS reaction accurately. R-weighted pattern (R_{wp}) values for the Rietveld fits are given in **Figure 4.5**.⁵⁴ The R-QPA quantification results for the crystalline Fe phase contents are given in the **Figure 4.9**. Crystallite diameters for each Fe phase are given for UP catalyst materials in **Figure 4.17**, and for Na-S catalysts in **Figure 4.18**. The respective R-QPA quantification results for the catalysts before the FTS reaction, i.e. for the Carb. catalyst materials, are reproduced from **Chapter 3** for

comparison into **Figure 4.9**.

4.3.2.1 Fe Phase Rietveld Quantitative Phase Analysis Quantification Changes

The most prominent Fe carbide to form at $\approx 340^\circ\text{C}$ reaction temperature under a carburizing gas atmosphere is the χ -Fe₅C₂ phase.^{4,6,41,55–61} This is reflected in the R-QPA Fe phase quantification results when comparing the observed Fe phases in the Carb. and FTS catalyst materials in **Figure 4.9**.

After the 72 h FTS reaction at 340°C with the UP catalyst materials, the α -Fe/Fe_xO_y phases preferentially carburize to the χ -Fe₅C₂ phase, as can most prominently be seen for the catalyst UP H₂ FTS in **Figure 4.9a**. The ε -Fe₃C and η -Fe₂C phases are generally unstable above $\approx 265^\circ\text{C}$ and $\approx 300^\circ\text{C}$, respectively, and preferentially transform to the χ -Fe₅C₂ phase at 340°C , as can be observed for the UP 240 FTS and UP 290 FTS catalysts (**Figure 4.9a**).

The θ -Fe₃C phase in the UP 390 FTS and UP 440 FTS catalyst materials does not transform in the FTS reaction to the χ -Fe₅C₂ phase as it is thermally more stable than the χ -Fe₅C₂ phase at 340°C (**Chapter 3**). The UP 390 FTS and UP 440 FTS catalysts' θ -Fe₃C phase quantities thus remain unchanged in the FTS reaction. However, as will be discussed later, the θ -Fe₃C crystallite diameters *do decrease* in UP 390 FTS and UP 440 FTS catalyst materials (**Figure 4.18**). This, perhaps signaling at least some θ -Fe₃C phase instability under the applied FTS reaction conditions.

Although, the UP catalyst materials follow the expected thermal stabilities of the Fe carbides, the Na-S promoter addition changes the situation. With the Na-S catalyst

Figure 4.5

R_{wp}-values for the differences between the measured and Rietveld method calculated diffractograms, for the catalysts after 72 h Fischer-Tropsch Synthesis (FTS) reaction. R_{wp}- and R_{wp}- (background corrected) values for a) UP (Fe/ α -Al₂O₃) and b) Na-S (Fe-Na-S/ α -Al₂O₃) catalyst materials.

materials, after the 72 h FTS reaction at 340°C, two interesting differences in comparison to the UP catalysts can be observed: the Na-S promotion i) *stabilizes* the η -Fe₂C phase and ii) *destabilizes* the θ -Fe₃C phase. These effects regardless of the expectations on the thermal stability of the Fe carbides (**Chapter 3**).

For the catalyst materials Na-S 240 FTS and Na-S 290 FTS, the η -Fe₂C content is significantly higher (53 % and 35 %) after the FTS reaction than for the respective UP catalysts (21 % and 13 %). This despite the UP Carb. catalyst materials having higher η -Fe₂C contents before the FTS reaction (**Figure 4.9a-b**). Only the η -Fe₂C but not the ϵ -Fe₃C phase is stabilized with the Na-S promotion under the used FTS reaction conditions. None of the Na-S or UP FTS catalyst materials shows any presence of the ϵ -Fe₃C phase. This, albeit the ϵ -Fe₃C phase being present in the 240 Na-S and UP Carb. catalyst materials at the start of the FTS reaction.

The alkali stabilizing effect on “ ϵ -carbides” has also been previously observed in-line with the R-QPA results in **Figure 4.9a-b**.^{8,15,22} Moreover, by inspecting the XRPD results by Dictor and Bell, the η -Fe₂C phase can be identified in their K/Fe₂O₃ catalyst material after it has been applied in the FTS reaction.²⁶ In the results by Dictor and Bell, peak position 2.18 Å (d/n) (*Fig 17*. in their publication) belongs to the η -Fe₂C plane (0 2 0) (2.18 Å, or 18.74° 2 θ in Mo K α), not to the Hägg carbide as after their assignment. If no K promotion was used, in their study, the XRPD peak 2.18 Å (d/n) i.e. the η -Fe₂C phase

Figure 4.6

Background corrected, ex-situ measured X-ray Powder Diffractometry (XRPD) and Rietveld method calculated diffraction patterns over a range 13–29° 2 θ for the a) UP H₂ and b) Na-S H₂ (Fe(-Na-S)/ α -Al₂O₃) catalyst materials after 72 h Fischer-Tropsch Synthesis (FTS) reaction. Normalized counts on a square-root scale.

Figure 4.7

Background corrected, ex-situ measured X-ray Powder Diffraction (XRPD) and Rietveld method calculated diffraction patterns over a range 13-29° 2θ for the UP FTS (Fe/ α -Al₂O₃) catalyst materials after 72 h Fischer-Tropsch Synthesis (FTS) reaction: a) 240, b) 290, c) 340, d) 390, e) 440 and f) 340 h.p.. Normalized counts on a square-root scale.

Figure 4.8

Background corrected, ex-situ measured X-ray Powder Diffractometry (XRPD) and Rietveld method calculated diffraction patterns over a range 13-29° 2θ for the Na-S FTS (Fe-Na-S/ α - Al_2O_3) catalyst materials after 72 h Fischer-Tropsch Synthesis (FTS) reaction: a) 240, b) 290, c) 340, d) 390, e) 440 and f) 340 h.p.. Normalized counts on a square-root scale.

Figure 4.9

The Rietveld Quantitative Phase Analysis (R-QPA) Fe phase quantifications before (Carb.) and after 72 h Fischer-Tropsch Synthesis (FTS) reaction. Crystalline Fe phase fractions for a) UP and b) Na-S (Fe(-Na-S)/ α -Al₂O₃) catalyst materials, and c) the elemental Fe wt-% loadings on basis of the crystalline Fe phases. Data for the Carb. catalyst materials, prior to FTS reaction is reproduced from **Chapter 3**. Percentage labels cut-off is set to <10 %.

is missing after the applied FTS reaction.²⁶

The other interesting case on the basis of the R-QPA results is the Na-S promotion imposed θ -Fe₃C instability in the FTS reaction. For both, the Na-S 390 and Na-S 440 FTS catalyst materials the θ -Fe₃C quantity has decreased relative $\approx$ 40 % from the original

quantity of the θ -Fe₃C phase before the FTS reaction.

That is, the θ -Fe₃C phase fractions decreased from 35 % to 21 % for Na-S 390 FTS, and from 54 % to 32 % for Na-S 440 FTS catalysts in comparison to the respective Na-S Carb. catalyst materials. While at the same time, the χ -Fe₅C₂ phase content increased (**Figure 4.9b**).

Thus, the Na-S promotion promotes the θ -Fe₃C transformation to χ -Fe₅C₂ at 340°C while this conversion does not take place without the Na-S promotion. That is, not at least with a noticeable rate within the applied 72 h FTS reaction runs.

No Fe oxides were present in any detectable quantities in the FTS catalyst materials (**Figure 4.9**). The measured XRPD patterns are well explained with the Fe phases used for the R-QPA fitting. This is equally valid for the UP and Na-S H₂ (**Figure 4.6**) and for all of the carburized UP (**Figure 4.7**) and Na-S catalyst materials (**Figure 4.8**). The CO conversion with the UP catalyst materials (2-5 %, **Table 4.4**) was too low during the FTS reaction for increasing the H₂O:H₂ or CO₂:CO ratios above levels sufficient for the Fe carbide oxidation.^{3,4,13,23,24,62} The Na-S catalyst materials exhibited higher CO conversion levels (33-55 % **Table 4.4**) i.e. higher H₂O concentrations, and also higher CO₂ selectivities (**Table 4.5**). However, added alkali Na(-S) decreases the Fe carbide oxidation tendency under the FTS reaction conditions.^{8,22} Therefore, no Fe oxides are observed neither on any of the Na-S FTS catalyst materials.

As compared in the **Figure 4.9c**, the elemental Fe content remains unchanged for the UP FTS but decreases for the Na-S FTS catalyst materials in comparison to their respective Carb. catalyst materials before the FTS reaction. For the Na-S FTS catalyst materials (excluding the 340 h.p.), the elemental Fe content is decreased by a mean value of 0.76±0.30 wt-% of Fe.

The unchanged elemental Fe loading for the UP FTS catalyst materials is a good sign that all the Fe phases present in the catalyst materials have been correctly accounted for in the R-QPA fittings. The systematic decrease in the elemental Fe loading with the Na-S FTS catalyst materials hints of either: i) lost Fe during the FTS reaction, ii) Fe is in phase(s) with too small crystallites to give clear Bragg diffraction or, iii) a possibly inaccurate or a missing Fe phase structure(s) used for the Rietveld fitting. Which of the options is the most correct answer, cannot be straightforwardly be devised from the R-QPA results.

Nevertheless, as was mentioned, as the Rietveld calculated diffraction patterns represent the measured XRPD patterns well: a Fe phase missing from the R-QPA fits can be excluded as a reason for the decreased elemental Fe loading with the Na-S FTS catalyst materials.

Table 4.2

Overview of the Fe carbide phases with their space groups and mean lattice parameters used for the Rietveld Quantitative Phase Analysis (R-QPA). In **bold** are highlighted the lattice parameters for which definite distortion by Na-S promotion could be observed.

Fe Carbide Phase ^{a)}	Space Group		Lattice Parameters ^{b)}			
			UP Carb. (Å)	Na-S Carb. (Å)	UP FTS (Å)	Na-S FTS (Å)
η -Fe ₂ C	Orthorhombic, Pnnm (58)	a	4.84±0.00	4.83±0.00	4.84±0.00	4.86±0.01
		b	4.35±0.00	4.35±0.00	4.35±0.00	4.35±0.00
		c	2.76±0.00	2.76±0.00	2.75±0.00	2.76±0.01
χ -Fe ₅ C ₂	Monoclinic, C2/c (15)	a	11.55±0.01	11.56±0.01	11.56±0.01	11.58±0.00
		b	4.57±0.01	4.57±0.01	4.57±0.01	4.58±0.00
		c	5.07±0.00	5.06±0.00	5.06±0.01	5.05±0.00
χ -Fe ₅ C ₂ (h.p.)	Monoclinic, C2/c (15)	a	11.60	11.61	11.61	11.62
		b	4.57	4.58	4.58	4.58
		c	5.05	5.04	5.05	5.04
θ -Fe ₃ C	Orthorhombic, Pnma (62)	a	5.08±0.01	5.07±0.01	5.07±0.02	5.07±0.00
		b	6.76±0.02	6.76±0.02	6.76±0.03	6.79±0.01
		c	4.53±0.01	4.54±0.01	4.54±0.01	4.55±0.00
θ -Fe ₇ C ₃ ^{c)}	Orthorhombic, Pnma (62)	a	4.52	4.52	4.53	4.54
		b	6.89	6.91	6.89	6.90
		c	11.91	11.91	11.89	11.89

a) The authors for the used crystal structures are listed in **Chapter 3**.

b) Mean values over all observations within the catalyst material group of the phase with STDs. Values for Carb. catalyst materials reproduced from the results obtained in **Chapter 3**.

c) Low phase quantities and peak overlap with the χ -Fe₅C₂ (h.p.) phase results in inaccuracy on the measured lattice parameters.

4.3.2.2 Fe Carbide Lattice Changes

The Fe carbide mean crystal lattice parameters with their STDs used in the R-QPA for are listed in **Table 4.2** for both the Carb. (with the results from **Chapter 3**) and the FTS catalyst materials. As the most significant lattice parameter phenomenon, the Na-S promotion caused expansion in the lattice parameters for the η -Fe₂C and χ -Fe₅C₂ phases in the Na-S FTS catalyst materials, as is marked with **bold** in the **Table 4.2**. As exceptions, the χ -Fe₅C₂ phase in UP 240 FTS and UP 290 FTS catalyst materials showed similar lattice expansion effects as did the Na-S promoted χ -Fe₅C₂ phase in the Na-S FTS catalyst materials (**Figure 4.13b, d, f**). This peculiarity will be commented more later on. The distinctively distorted χ -Fe₅C₂ (h.p.) phase in the 340 h.p. catalyst materials did not show any significant modification trends in the lattice parameters between the UP or Na-S Carb. and the UP or Na-S FTS catalyst materials (**Table 4.2**).

Due to the relatively low phase amounts (18-22 %, **Figure 4.9a-b**), and the

Figure 4.10

The lattice parameters used in the Rietveld Quantitative Phase Analysis (R-QPA) fitting of the θ -Fe₃C and θ -Fe₇C₃ phases before (Carb.) and after 72 h Fischer-Tropsch Synthesis (FTS) reaction for UP (Fe/ α -Al₂O₃) catalyst materials. Lattice parameters for UP θ -Fe₃C are in a) a, b) b and c) c and for UP θ -Fe₇C₃ in d) a, e) b and f) c.

overlapping diffraction peaks with the χ -Fe₅C₂ (h.p.) phase UP (**Figure 4.7f**) and Na-S catalysts (**Figure 4.8f**): discussion on the θ -Fe₇C₃ lattice shifts is omitted due to the uncertainty in determining the its precise diffraction peak positions and therefore the θ -Fe₇C₃ phase lattice parameters.

In a similar manner, the θ -Fe₃C phase diffraction peaks largely overlap with the χ -Fe₅C₂ phase in all UP (**Figure 4.7d**) and Na-S catalyst materials (**Figure 4.8d-e**), with the θ -Fe₃C phase in the UP 440 FTS catalyst material being an exception (**Figure 4.7e**). The peak overlapping results in significant STDs for the mean θ -Fe₃C lattice parameters (**Table 4.2**). This makes the determination of the relative lattice parameter changes for the θ -Fe₃C phase inaccurate. Therefore, the discussion on the θ -Fe₃C phase's lattice parameter changes is also omitted.

The comparison of individual lattice parameters used in the R-QPA fitting of the θ -Fe₃C and θ -Fe₇C₃ phases in UP and Na-S Carb. and FTS catalyst materials is given in **Figure 4.10** (for UP) and in **Figure 4.11** (for Na-S catalyst materials).

As examples of the observed lattice shifts in relation to the diffraction peak shifts, in **Figure 4.12** are compared the Rietveld fitted, calculated diffraction patterns for the η -Fe₂C and χ -Fe₅C₂ phases in the UP 240 and UP 340, and Na-S 240 and Na-S 340, Carb. and FTS catalyst material. The respective measured XRPD diffraction patterns for the catalyst materials are also given in the figure.

Figure 4.11

The lattice parameters used in the Rietveld Quantitative Phase Analysis (R-QPA) fitting for the θ -Fe₃C and θ -Fe₇C₃ phases before (Carb.) and after 72 h Fischer-Tropsch Synthesis (FTS) reaction for Na-S (Fe-Na-S/ α -Al₂O₃) catalyst materials. Lattice parameters for Na-S θ -Fe₃C are in a) a, b) *b* and c) *c* and for Na-S θ -Fe₇C₃ in d) *a*, e) *b* and f) *c*.

Before the FTS reaction, the η -Fe₂C phase in the 240 Carb. (**Figure 4.12a**) and the χ -Fe₅C₂ phase in the 340 Carb. (**Figure 4.12b**), in both UP and Na-S catalyst materials, gave nearly identical Rietveld calculated diffraction patterns. After the FTS reaction, however, the phases' peak positions have shifted as depending on the addition of the Na-S promotion. For the η -Fe₂C phase the most intense diffraction peak shifts towards a lower 2θ (19.42° Carb. $\rightarrow$ 19.38° FTS) after the FTS reaction when Na-S promotion is applied (**Figure 4.12a, c**). For the χ -Fe₅C₂ phase, a similar shift for two peaks (marked with #, **Figure 4.12d**) towards a lower 2θ (19.95° Carb. $\rightarrow$ 19.92° FTS and 17.86° Carb. $\rightarrow$ 17.83° FTS) takes place (**Figure 4.12b, d**).

In **Figure 4.13** are compared the individual R-QPA fitted lattice parameters with their R-QPA fit error estimates for the η -Fe₂C and χ -Fe₅C₂ phases in the UP Carb. and FTS, and in **Figure 4.14** for the Na-S Carb. and FTS catalysts materials. For both the η -Fe₂C and χ -Fe₅C₂ phases, anisotropic lattice parameter changes can be observed which are assignable to be due to the Na-S promotion. These lattice changes reflect the examples of the diffraction peak position changes in the diffraction patterns in **Figure 4.12**.

The added Na-S promotion increases the lattice parameter *a* by ≈ 0.02 Å for both the η -Fe₂C and χ -Fe₅C₂ phases in the FTS catalyst materials, in comparison to the respective phases in the Carb. catalyst materials (**Table 4.2** and **Figure 4.14a-b**). For the χ -Fe₅C₂

Figure 4.12

Background corrected, ex-situ measured X-ray Powder Diffraction (XRPD) patterns with Rietveld method calculated η -Fe₂C and χ -Fe₅C₂ phase patterns over a range 13-25° 2θ for both UP and Na-S (Fe(-Na-S)/ α -Al₂O₃) catalyst materials before (Carb.) and after 72 h Fischer-Tropsch Synthesis (FTS) reaction. The diffraction patterns for the η -Fe₂C phase in UP and Na-S 240 catalysts compared a) before and c) after 72 h FTS reaction, and for χ -Fe₅C₂ phase in UP and Na-S 340 catalysts compared b) before and d) after 72 h FTS reaction. Normalized counts on a square-root scale.

phase, the lattice parameter c decreases by ≈ 0.01 Å with Na-S catalyst materials while the lattice parameter b experiences lesser changes (**Table 4.2** and **Figure 4.14d, f**). The lattice parameters c and b for the η -Fe₂C phase do not change consistently (**Table 4.2** and **Figure 4.14c, e**).

The η -Fe₂C phase does not show any decisive crystal lattice expansion or contraction in comparison between the UP Carb. and FTS catalyst materials. Although, the R-QPA fit error estimates for the lattice parameters for the η -Fe₂C phases in the UP FTS catalyst materials are rather high (**Figure 4.13a, c, e**). This is due the η -Fe₂C phase

Figure 4.13

The lattice parameters used in Rietveld Quantitative Phase Analysis (R-QPA) for η -Fe₂C and χ -Fe₅C₂ phases compared before (Carb.) and after 72 h Fischer-Tropsch Synthesis (FTS) reaction for UP (Fe/ α -Al₂O₃) catalyst materials. Lattice parameters *a*, *b*, and *c* for η -Fe₂C in a), c) and e), and for χ -Fe₅C₂ in b), d) and f), respectively.

content being low (**Figure 4.9a**), as the η -Fe₂C phase is unstable without Na-S promotion at 340°C in the FTS reaction. Thus, some uncertainty remains in the exact crystal lattice behavior for the η -Fe₂C phase in the UP FTS catalyst materials.

In an earlier study, Dry and Ferreira determined the lattice expansion for (cubic) Fe₃O₄ due to Na promotion being ≤ 0.03 Å with the amount of the lattice expansion depending on the used Na concentration.⁶³ The Fe₃O₄ lattice expansion was interpreted to be due to Na forming a solid solution with the Fe₃O₄ phase. Thus, the observed ≈ 0.01 - 0.02 Å changes in the lattice parameters for the η -Fe₂C and χ -Fe₅C₂ phases are within an expected range, if the Na in the added Na-S promotion enters the Fe lattice interstitial spaces. Granting that the literature reference value is for a Fe₃O₄ lattice, not for a Fe carbide.

Figure 4.14

The lattice parameters used in Rietveld Quantitative Phase Analysis (R-QPA) for η -Fe₂C and χ -Fe₅C₂ phases compared before (Carb.) and after 72 h Fischer-Tropsch Synthesis (FTS) reaction for Na-S (Fe-Na-S/ α -Al₂O₃) catalyst materials. Lattice parameters *a*, *b*, and *c* for η -Fe₂C in a), c) and e), and for χ -Fe₅C₂ in b), d) and f), respectively.

However, as a peculiarity, also the χ -Fe₅C₂ phase in the UP 240 FTS and UP 290 FTS catalyst materials show similar changes in its lattice parameters as the χ -Fe₅C₂ phase with Na-S promotion does. That is, lattice parameters *a*: increase (≈ 0.02 Å), *b*: unchanged, *c*: decrease (≈ 0.01 Å) (**Figure 4.13b, d, f**). The Rietveld calculated diffraction patterns for the χ -Fe₅C₂ phase in the UP 240 FTS and Na-S 340 FTS catalyst materials are compared in **Figure 4.15**.

The patterns are near identical with each other, i.e. a R-QPA fitting error does not explain the lattice shifts. With the increasing CO treatment temperature ($\geq 340^\circ\text{C}$) applied in the initial catalyst carburization, the lattice expansion effect disappears for the UP FTS catalyst materials. The χ -Fe₅C₂ phase lattice parameters then become nearly identical between the UP 340-440 Carb. and FTS catalyst materials (**Figure 4.13b, d, f**).

Figure 4.15

Background corrected, ex-situ measured X-ray Powder Diffractometry (XRPD) patterns with Rietveld method calculated η -Fe₂C and χ -Fe₅C₂ phase patterns over the range 13–25° 2 θ for UP 240 and Na-S 340 (Fe(-Na-S)/ α -Al₂O₃) catalyst materials after 72 h Fischer-Tropsch Synthesis (FTS) reaction. Normalized counts on a square-root scale.

Why the χ -Fe₅C₂ phase crystal lattice parameters in the UP 240 FTS and UP 290 FTS catalyst materials behaves akin to the Na-S promoted catalyst materials, is not clear from the results. Na(-S) contamination can be excluded, as the catalyst materials in question do not show any alkali or Na-S promotion effects in their FTS reaction catalysis performance, as will be discussed later on (**Table 4.4** and **Table 4.5**).

4.3.2.3 Assignment of Fe Carbide Subtypes

As based on the differences in the η -Fe₂C, χ -Fe₅C₂ and χ -Fe₅C₂ h.p. phases lattice parameter a 's (**Table 4.2**), the carbides can be divided to subtypes and assigned with their primary formation conditions (**Table 4.3**).

The χ -Fe₅C₂ subtypes defined by lattice parameter a can be divided as: *Type I*: ≈ 11.56 Å which is observed either after CO carburization of α -Fe (UP and Na-S Carb.) or after FTS reaction *without* Na-S promotion (UP FTS), *Type II*: ≈ 11.58 Å is observed in Na-S FTS catalyst materials, and *Type III*: ≈ 11.61 Å if a Fe oxide (α -Fe₂O₃) is carburized with CO at high-pressure (340 h.p.). The Type III is also stable in the FTS reaction *regardless* of the Na-S promotion.

The lattice parameters (a : 11.562 Å, b : 4.573 Å, c : 5.060 Å) corresponding to the χ -Fe₅C₂ Type I have earlier been reported by Jack and Wild.⁴⁶ Similar values have also been reported by Duggin and Hofer,⁴⁵ on the basis of χ -Fe₅C₂ phase prepared from α -Fe via CO carburization.⁶⁴

Table 4.3

Overview of the different subtypes (*I, II, III*) of η -Fe₂C and χ -Fe₅C₂ phases as divided by their observed lattice parameters in the UP and Na-S Carb. and FTS catalyst materials. The lattice parameters are taken as the mean value over all observations of the subtype. Value after ($\pm$) is the Standard Deviation (STD) of the mean value.

Fe Carbide Phase	Space Group	Lattice Parameters		
		Type I (Å)	Type II (Å)	Type III (Å)
η -Fe ₂ C	Orthorhombic, a	4.84±0.01	4.86±0.01	4.704
	Pnnm (58) b	4.35±0.00	4.35±0.00	4.318
	c	2.76±0.00	2.76±0.01	2.830
Observed in catalyst	UP Carb.	x		Tempering of martensitic steel ^{a)}
	Na-S Carb.	x		
	UP FTS	x		
	Na-S FTS		x	
χ -Fe ₅ C ₂	Monoclinic, a	11.56±0.01	11.58±0.00	11.61±0.01
	C2/c (15) b	4.57±0.01	4.58±0.00	4.58±0.00
	c	5.06±0.00	5.05±0.00	5.05±0.01
Observed in catalyst	UP Carb.	x		x ^{c)}
	Na-S Carb.	x		x ^{c)}
	UP FTS	x	x ^{b)}	x ^{c)}
	Na-S FTS		x	x ^{c)}

a) The η -Fe₂C Type III carbide has been observed as a precipitate in tempering of martensitic steel at 120°C,^{65,66} and is included here for completeness.

b) With UP FTS catalyst materials, the χ -Fe₅C₂ Type II could be observed only with catalysts 240 and 290.

c) The χ -Fe₅C₂ Type III was only observed in catalyst materials 340 h.p.. The phase is also labelled as χ -Fe₅C₂ (h.p.) in **Table 4.2** and in **Chapter 3**.

Lattice parameters (a : 11.588 Å, b : 4.579 Å, c : 5.059 Å and β = 97.75°) close to the χ -Fe₅C₂ Type II have been determined by Retief with a proprietary Fe-based catalyst material extracted from a Sasol pilot plant, after FTS reaction (320°C, 20 bar, H₂:CO 1:2.3).⁴⁴ Although, even as Fe₃O₄ was used as the FTS reaction starting material by Retief, the resulting χ -Fe₅C₂ phase gave lattice parameters more akin to χ -Fe₅C₂ Type II than to the Type III. The Type III would be expected based on our results.

By following the catalyst material Curie Temperature and XRPD patterns, a distorted χ -Fe₅C₂ phase was observed to form from a Fe₃O₄ starting material with CO carburization by Cohn et al.¹⁹ The observation by Cohn et al. is alike to the formation of the distorted χ -Fe₅C₂ h.p. phase with the UP and Na-S 340 h.p. catalyst materials, which were not reduced with H₂ to α -Fe a priori to the CO carburization. Rather, the α -Fe₂O₃ on the calcined catalyst materials was carburized directly (**Table 4.1**). Cohn et al. did not report lattice parameters on the basis of their XRPD patterns. We shall presume, nevertheless, that the distorted χ -Fe₅C₂ h.p. phase is the same phase as the Cohn et al.'s

distorted χ -Fe₅C₂ phase. This distorted phase corresponds to the χ -Fe₅C₂ Type III subtype with mean lattice parameters defined as: a : 11.61±0.01 Å, b : 4.58±0.00 Å, c : 5.05±0.01 Å and β = 97.75°.

Cohn et al. presumably used atmospheric CO pressure for forming the distorted χ -Fe₅C₂ phase,¹⁹ not 25 bar CO as used in the carburization of the 340 h.p. Carb. catalyst materials. That is, a high CO pressure may not be required for the formation of the χ -Fe₅C₂ Type III (i.e. the χ -Fe₅C₂ h.p. phase) from a Fe oxide. Directly carburizing a Fe oxide with CO might be the sole requirement for the formation of the χ -Fe₅C₂ Type III subtype.

As the distorted χ -Fe₅C₂ phase by Cohn et al. would form a more crystalline χ -Fe₅C₂ phase after an extended CO exposure period or increased carburization treatment temperature. After these observations, Cohn et al. speculated, among other possibilities, that the distortion could be due to O atoms being retained in the distorted χ -Fe₅C₂ lattice.¹⁹ The recrystallization behavior also could explain why the χ -Fe₅C₂ phase observed by Retief resembles the Type II and not the Type III χ -Fe₅C₂ subtype,⁴⁴ despite Retief having started the FTS reaction with a Fe₃O₄ phase.

Likewise to the χ -Fe₅C₂, the η -Fe₂C phase can be divided to carbide subtypes following the distinct ranges of lattice parameter a 's as: *Type I*: $\approx$ 4.83 Å with UP and Na-S Carb. and UP FTS catalyst materials, and *Type II*: $\approx$ 4.86 Å with Na-S FTS catalyst materials. The η -Fe₂C phase *Type III* precipitates from martensitic steel with lattice parameter a of 4.704 Å have been observed in tempering studies at 120°C.^{65,66} The η -Fe₂C phase Type III has not been observed in the FTS reaction related studies - for best of the author's knowledge - but is included here for sake of completeness (**Table 4.3**).

The η -Fe₂C Type II matches well with the "pseudo-hexagonal Fe carbide", detected by Barton and Gale in a K-promoted Fe-based catalyst after the FTS reaction.⁶⁷ With the orthorhombic unit cell translation for the η -Fe₂C phase by Hirotsu and Nagakura,⁶⁸ the lattice parameters corresponding Barton and Gale's Fe carbide are: a : 4.862 Å, b : 4.360 Å, and c : 2.755 Å. These lattices parameters are a good match to the η -Fe₂C Type II subtype formed with the Na-S FTS catalyst materials (**Table 4.2**).

For the η -Fe₂C Type I, no matching lattice parameters could be found from the literature, despite the author's best efforts. Thus, we shall assign the η -Fe₂C Type I in the UP and Na-S 240 and 290 Carb. and in UP 240 and 290 FTS catalyst materials with mean lattice parameters as: a : 4.84±0.01 Å, b : 4.35±0.00 Å and c : 2.76±0.00 Å. That is, the η -Fe₂C Type I forms *regardless* of the Na-S promotion with CO carburization $\leq$ 290°C.

Thus, under FTS reaction conditions: *without Na-S promotion* the η -Fe₂C Type I prevails (UP FTS), while *with Na-S promotion* transformation to the η -Fe₂C Type II takes over (Na-S FTS). These conclusions, however, are drawn while acknowledging the large lattice parameter fit errors for the η -Fe₂C phases in the UP FTS catalyst materials (**Figure 4.13a, c, e**).

Figure 4.16

Rietveld method calculated phase diffraction pattern examples of the η -Fe₂C and χ -Fe₅C₂ phase subtypes over a range of 16–22° 2 θ fitted for Na-S (Fe-Na-S/ α -Al₂O₃) catalyst materials before (Carb.) and after 72 h Fischer-Tropsch Synthesis (FTS) reaction. The calculated phase diffraction patterns for a) η -Fe₂C Type I-II and b) χ -Fe₅C₂ Type I-III, as following the nomenclature in **Table 4.3**. The calculated patterns are normalized to the carbide subtype's most intense diffraction peak. Normalized counts on a square-root scale.

In **Figure 4.16** are overlaid examples of the Rietveld calculated phase diffraction patterns for the η -Fe₂C Types I-II and χ -Fe₅C₂ Types I-III, as based on the R-QPA fits on the indicated Na-S catalyst materials. When comparing the calculated phase diffraction patterns between the η -Fe₂C Type I versus Type II: a shoulder (marked with *) appears to the diffraction pattern of the η -Fe₂C Type II (**Figure 4.16a**). This shoulder is likely the origins of the “double peak” observations by Barton and Gale on their “pseudo-hexagonal Fe carbide”,⁶⁷ i.e. on the η -Fe₂C phase. Barton and Gale obtained their X-ray diffraction patterns with Co K α radiation which provides significantly better diffraction peak separation than the Mo K α in capillary geometry applied in our study does. Thus, the shoulder in the **Figure 4.16a** would be a well separated diffraction peak in Barton and Gale's diffraction patterns.

For the χ -Fe₅C₂ Types I-III the calculated diffraction patterns show clear differences, especially, in the most intense diffraction peaks (**Figure 4.16b**). The fundamental origins of these differences, however, are unclear at the time being.

In total, a monochromatic synchrotron radiation based XRPD study on the crystal structural details on the origins of the differences in the η -Fe₂C and the χ -Fe₅C₂ phases subtypes would be of future interested.

Figure 4.17

Rietveld Quantitative Phase Analysis (R-QPA) determined Fe phase (volume-weighted) crystallite mean diameters derived from the X-ray Powder Diffractometry (XRPD) patterns for UP (Fe/ α -Al₂O₃) catalyst materials after 72 h Fischer-Tropsch Synthesis (FTS) reaction. The respective mean Fe crystallite diameters before the FTS reaction (Carb.) are reproduced from **Chapter 3** for comparison.

4.3.2.4 Changes in Fe Phases' Crystallite Diameters

The R-QPA determined Fe phase (volume-weighted) crystallite mean diameters are given in **Figure 4.17** for the UP FTS catalyst materials with the respective UP Carb. results reproduced from **Chapter 3** for comparison. Likewise, crystallite mean diameters for the Na-S FTS catalyst materials are given in **Figure 4.18**. As a general observation: no clear, straightforward trends seem to exist in the crystallite mean diameters when comparison is done between the UP or Na-S, Carb. and FTS catalyst materials.

However, few comments can be made when comparing the Fe phases crystallite diameters in the Carb. and FTS catalyst materials to each other: i) in general, the χ -Fe₅C₂ phase crystallite mean diameter increases in the FTS reaction for the UP (**Figure 4.17**) and Na-S catalyst materials (**Figure 4.18**), ii) for UP FTS catalyst materials, the

Figure 4.18

Rietveld Quantitative Phase Analysis (R-QPA) determined Fe phase (volume-weighted) crystallite mean diameters derived from the X-ray Powder Diffractometry (XRPD) patterns for Na-S (Fe-Na-S/ α -Al₂O₃) catalyst materials after 72 h Fischer-Tropsch Synthesis (FTS) reaction. The respective mean Fe crystallite diameters before the FTS reaction (Carb.) are reproduced from **Chapter 3** for comparison.

crystallite mean diameters *decrease* for both η -Fe₂C and θ -Fe₃C phases (**Figure 4.17**), and iii) for Na-S FTS catalyst materials, the η -Fe₂C phase crystallite mean diameters remain largely unchanged while the θ -Fe₃C diameters *decrease significantly* (**Figure 4.18**).

The general increase in the χ -Fe₅C₂ crystallite mean diameters, i.e. the point i), is due to the χ -Fe₅C₂ phase being the most thermally stable carbide phase at the used FTS reaction temperature of 340 °C (**Chapter 3**). The χ -Fe₅C₂ phase is present in both the UP and Na-S FTS catalyst materials in larger relative quantities than in the respective Carb. catalysts (**Figure 4.9a-b**). Therefore, this is resulting in larger crystallite diameters for the χ -Fe₅C₂ phase.

Both, the points ii) and iii), also follow the development of the Fe phase quantities in **Figure 4.9a-b**. As the phase η -Fe₂C is unstable in the FTS reaction with the UP catalyst materials, the phase's quantity decreases, and so does the phase's crystallite

mean diameter (**Figure 4.17**). In the Na-S FTS catalyst materials the η -Fe₂C phase is stable, thus the crystallite mean diameters do not decrease nor notably increase (**Figure 4.18**), despite the increased η -Fe₂C phase content (**Figure 4.9b**).

With regard to the θ -Fe₃C phase crystallite mean diameters, the Na-S promotion destabilizes and decreases the θ -Fe₃C phase content in the Na-S FTS catalyst material resulting in severely decreased crystallite mean diameters (**Figure 4.18**). Interestingly, also in the UP FTS catalysts the θ -Fe₃C crystallite mean diameters decrease in comparison to the Carb. catalysts, albeit less than in the Na-S catalyst materials. In relative terms, the θ -Fe₃C phase crystallite diameters decrease: -30 % for UP 390 and -23 % for UP 440; and -64 % for Na-S 390 and -75 % for Na-S 440 catalysts when comparing the respective Carb. to the FTS catalyst materials. That is, the decreasing θ -Fe₃C crystallite mean diameters also without the Na-S promotion might suggest that under the used reaction conditions, the θ -Fe₃C phase is unstable. However, its demise is greatly hastened by the presence of Na-S promotion.

The Na-S 240 FTS and Na-S 340 FTS catalyst materials showed significant increases in the TEM-based Fe particle mean diameters in comparison to the respective Carb. catalysts (**Figure 4.4e**). However, the R-QPA-based Fe crystallite mean diameters do not show any comparable increase for any of the Fe phases in the same catalyst materials (**Figure 4.18**).

Furthermore, the TEM-based Fe particle mean diameters for the UP and Na-S 440 FTS catalysts show an *increase* of +8 % and +23 %, respectively, in the Fe particle mean diameters in comparison to the respective Carb. catalyst materials (**Figure 4.4e**). The R-QPA-based Fe crystallite mean diameters show an opposite trend: for both UP and Na-S 440 FTS catalyst materials the θ -Fe₃C phase crystallite diameters *decrease* (-23 %, and -75 %, respectively, see earlier paragraph) while the χ -Fe₅C₂ phase crystallite diameters remain relatively unchanged. Likewise, no connection between the Fe particle (**Figure 4.4e**) and crystallite mean diameters exist for the UP (**Figure 4.17**) and Na-S H₂ catalyst materials (**Figure 4.18**).

That is, the Fe particle and crystallite mean diameters give opposing trends for the mentioned catalyst materials. The lack of common trends could be interpreted to suggest that *a single Fe particle is not a single Fe carbide crystallite*. In literature, examples of this have been observed.^{43,69–71}

As a final comment in the current section, comparing the TEM Fe particle based and R-QPA (i.e. XRPD-based) Fe crystallite diameters data is not straightforward,^{69,72,73} as is shortly yet more in detail discussed in **Chapter 3**. Thus, drawing any further conclusions on the Fe particle (TEM), in comparison to the Fe crystallite diameter (R-QPA) results is not attempted within the current context.

Table 4.4

Median Fischer-Tropsch Synthesis (FTS) reaction activity data over Time-on-Stream (ToS) 33-72 h for UP and Na-S (Fe(-Na-S)/ α -Al₂O₃) catalyst materials. Value after ($\pm$) is the Standard Deviation (STD) of the median value.

Promotion Group	Catalyst	CO Conversion	Fe Time Yield (FTY)	Usage Ratio H ₂ :CO	CO to Hydrocarbons Na-S versus UP ^{a)}
		(%)	(10 ⁻⁴ mol _{CO} /g _{FeS})	(-)	(-)
UP	H ₂	3 $\pm$ 0	0.4 $\pm$ 0.1	2.1 $\pm$ 0.4	N/A
	240	5 $\pm$ 0	0.6 $\pm$ 0.1	1.8 $\pm$ 0.2	N/A
	290	3 $\pm$ 1	0.4 $\pm$ 0.1	2.3 $\pm$ 0.4	N/A
	340	2 $\pm$ 0	0.3 $\pm$ 0.0	1.9 $\pm$ 0.5	N/A
	390	4 $\pm$ 0	0.5 $\pm$ 0.1	2.1 $\pm$ 0.3	N/A
	440	3 $\pm$ 0	0.3 $\pm$ 0.1	2.2 $\pm$ 0.7	N/A
	340 h.p.	2 $\pm$ 1	0.3 $\pm$ 0.2	2.1 $\pm$ 1.1	N/A
Na-S	H ₂	53 $\pm$ 3	5.9 $\pm$ 0.3	0.7 $\pm$ 0.1	0.45 $\pm$ 0.22
	240	40 $\pm$ 0	4.8 $\pm$ 0.0	0.7 $\pm$ 0.0	0.47 $\pm$ 0.11
	290	34 $\pm$ 3	3.7 $\pm$ 0.3	0.7 $\pm$ 0.1	0.45 $\pm$ 0.16
	340	45 $\pm$ 5	5.3 $\pm$ 0.5	0.7 $\pm$ 0.1	0.42 $\pm$ 0.20
	390	24 $\pm$ 2	2.8 $\pm$ 0.3	0.8 $\pm$ 0.1	0.43 $\pm$ 0.15
	440	33 $\pm$ 1	4.0 $\pm$ 0.1	0.8 $\pm$ 0.0	0.42 $\pm$ 0.14
	340 h.p.	3 $\pm$ 0	0.4 $\pm$ 0.0	1.1 $\pm$ 0.5	0.61 $\pm$ 0.49

FTS conditions: 340°C, 10 bar, H₂:CO:He 2.0:1.0:0.33 v/v, $\approx$ 5 000 h⁻¹.

a) Change in fraction of CO converted to hydrocarbons with addition of Na-S promotion (Na-S) versus the respective unpromoted (UP) catalyst material.

4.3.3 Catalytic Performance

The catalytic activity profiles as FTYs for each of the catalyst materials over the 72 h FTS reaction are given in **Figure 4.20**. The median CO conversions, FTYs and Usage Ratios H₂:CO over Time-on-Stream (ToS) 33-72 h, over relatively steady FTYs, for each catalyst material are tabulated in **Table 4.4**. In addition, for comparing the effect of Na-S promotion to the relative FTS reaction C pathways (**Chapter 2**), the changes in CO converted towards hydrocarbons between the Na-S and the corresponding UP catalyst materials are reported in the **Table 4.4**. The median CO₂ and CO₂-free hydrocarbon selectivities over ToS 33-72 h are given in the **Table 4.5**.

For each catalyst material, each of the duplicate reactors used for the FTS reaction runs gave identical results with the exceptions of the catalyst materials Na-S H₂ and Na-S 440. For these catalyst materials the FTY profiles differed in respect to their duplicate reactors (**Figure 4.19**). For the catalysts with differing duplicate reactor results the catalyst reactors with higher overall FTY are discussed. Moreover, the catalyst Na-S H₂ also gave a differing C₂H₄/C₂H₆ ratio in comparison to its duplicate FTS reactor (**Table 4.5**).

Table 4.5

Median Fischer-Tropsch Synthesis (FTS) reaction selectivity data over Time-on-Stream (ToS) 33-72 h for UP and Na-S (Fe(-Na-S)/ α -Al₂O₃) catalyst materials. Value after ($\pm$) is the Standard Deviation (STD) of the median value.

Promotion Group	Catalyst	CO ₂	CH ₄	C ₂ -C ₄ Olefin	C ₂ -C ₄ Paraffin	C ₅ +	C ₂ H ₄ /C ₂ H ₆	ASF α -value
		(%)	(%)	(%)	(%)	(%)	(-)	(a.u)
UP	H ₂	< dl	56 $\pm$ 2	33 $\pm$ 1	7 $\pm$ 0	4 $\pm$ 3	2.8 $\pm$ 0.1	0.36 $\pm$ 0.05
	240	11 $\pm$ 4	52 $\pm$ 1	34 $\pm$ 1	8 $\pm$ 0	5 $\pm$ 2	2.4 $\pm$ 0.0	0.29 $\pm$ 0.04
	290	16 $\pm$ 2	53 $\pm$ 1	35 $\pm$ 1	7 $\pm$ 0	5 $\pm$ 2	2.9 $\pm$ 0.1	0.34 $\pm$ 0.07
	340	< dl	58 $\pm$ 3	30 $\pm$ 1	9 $\pm$ 0	4 $\pm$ 5	2.2 $\pm$ 0.1	0.30 $\pm$ 0.02
	390	9 $\pm$ 3	55 $\pm$ 0	28 $\pm$ 0	14 $\pm$ 1	3 $\pm$ 1	1.0 $\pm$ 0.1	0.25 $\pm$ 0.03
	440	14 $\pm$ 0	55 $\pm$ 0	28 $\pm$ 0	13 $\pm$ 0	3 $\pm$ 1	1.2 $\pm$ 0.1	0.28 $\pm$ 0.01
	340 h.p.	< dl	69 $\pm$ 1	19 $\pm$ 1	10 $\pm$ 0	2 $\pm$ 2	1.2 $\pm$ 0.1	0.18 $\pm$ 0.05
Na-S ^{a)}	H ₂	43 $\pm$ 6	10 $\pm$ 0	44 $\pm$ 0	4 $\pm$ 0	41 $\pm$ 0	(6.5 $\pm$ 0.3) ^{b)}	0.77 $\pm$ 0.00
	240	43 $\pm$ 2	9 $\pm$ 0	46 $\pm$ 1	4 $\pm$ 0	41 $\pm$ 1	9.1 $\pm$ 0.3	0.76 $\pm$ 0.01
	290	42 $\pm$ 3	8 $\pm$ 0	47 $\pm$ 0	4 $\pm$ 0	41 $\pm$ 0	10.5 $\pm$ 0.6	0.76 $\pm$ 0.01
	340	41 $\pm$ 8	9 $\pm$ 0	45 $\pm$ 1	4 $\pm$ 0	42 $\pm$ 1	9.3 $\pm$ 0.1	0.78 $\pm$ 0.01
	390	38 $\pm$ 2	9 $\pm$ 0	48 $\pm$ 1	4 $\pm$ 0	39 $\pm$ 2	10.4 $\pm$ 0.1	0.75 $\pm$ 0.01
	440	40 $\pm$ 2	8 $\pm$ 0	46 $\pm$ 1	4 $\pm$ 0	41 $\pm$ 1	10.0 $\pm$ 0.2	0.77 $\pm$ 0.01
	340 h.p.	15 $\pm$ 4	18 $\pm$ 0	56 $\pm$ 4	3 $\pm$ 0	23 $\pm$ 4	11.3 $\pm$ 0.2	0.52 $\pm$ 0.01

FTS conditions: 340°C, 10 bar, H₂:CO:He 2.0:1.0:0.33 v/v, $\approx$ 5 000 h⁻¹.

< dl – Below detection limit.

a) For all of the Na-S catalysts the MeOH (methanol) selectivity was $\approx$ 0.4 %, and for all of the UP catalysts the MeOH selectivity was below detection limit.

b) For the duplicate reactor the value is 9.6 $\pm$ 1.0.

In the following, first the effect of Na-S addition on the catalytic performance of the materials under study is discussed. This is followed with remarks on the dependency of the catalytic performance on the catalyst materials themselves i.e. on the FTS reaction starting Fe phase(s). The observed catalytic performance trends are then related to the characterization results.

4.3.3.1 The Effect of Na-S Promotion

In terms of the catalytic activity in the FTS reaction (**Table 4.4**) and the hydrocarbon product selectivities (**Table 4.5**), the addition of the combined Na-S promotion acts as expected on the basis of the literature. That is, i) the overall CO conversion (and FTY) is increased,^{29,30,74,75} ii) CH₄ selectivity is decreased below expectations from the ASF distribution,^{28,29} iii) the olefin content of the hydrocarbon product slate is increased.^{28,29,37,39} The hydrocarbon chain length (i.e. the α -value) is increased with the Na-S promotion addition, but less than it would be if only Na was added.^{30,37,38}

For the Na-S 340 h.p. catalyst, the Na-S addition shows a mixed effect: increased olefin selectivity but with far lower CO conversion than for the other Na-S catalyst

Figure 4.19

Fe Time Yield (FTY) profiles for two catalyst materials that gave differing catalytic activity profiles between the duplicate reactors. In a) Na-S H_2 , and b) Na-S 440 ($\text{Fe-Na-S}/\alpha\text{-Al}_2\text{O}_3$) catalyst materials. For both, FTY profiles and the associated Fischer-Tropsch Synthesis (FTS) performance data from the Reactor #2 are discussed in the main text.

materials. Moreover, the α -value is lower than for the other catalysts within the Na-S promotion group. The UP 340 h.p. catalyst material also behaves differently in comparison to other catalysts within the UP promotion group. The trend breaking 340 h.p. catalyst materials, for both Na-S and UP catalysts, will be discussed more later on in the section, and ignored for now.

For rest of the Na-S catalyst materials, the 8-10 % CH_4 and 48-52 % total $\text{C}_2\text{-C}_4$ selectivities match well with the “High Na – Low S” promotion (≈ 8 % CH_4 , ≈ 50 % $\text{C}_2\text{-C}_4$) by Botes et al. with experiments done at Sasol.²⁸ The total $\text{C}_2\text{-C}_4$ selectivity is ≈ 10 % higher than is predicted by the ASF distribution with the measured CH_4 selectivity. This is the unique feature of the combined Na-S promotion.²⁸

The Na-S catalysts also show a marked decrease in Usage Ratios $\text{H}_2\text{:CO}$: from ≈ 1.8 -2.3 to ≈ 0.7 -0.8 in comparison to the UP catalyst materials (**Table 4.4**). The CO_2 selectivity increases to 38-43 % with the Na-S addition, which is a significant CO_2 selectivity increase in comparison to the UP catalysts with ≤ 16 % CO_2 selectivity (**Table 4.5**). The decreased Usage Ratios $\text{H}_2\text{:CO}$ from the ideal ≈ 2 ,^{27,76} in the FTS reaction are an indicator for additional reactions consuming CO besides the ideal FTS hydrocarbon chain polymerization.

Water-gas Shift (WGS) reaction converts $\text{CO} + \text{H}_2\text{O}$ to $\text{H}_2 + \text{CO}_2$.^{2,32,76-78} Above 300°C , the Boudouard reaction converts CO to inactive carbon deposits releasing CO_2 .^{13,17-19}

With the pure CO only carburization in **Chapter 3**, the rate of carbon deposition on

the catalyst materials at 340°C increased with Na-S promotion. Thus, increase in the Boudouard reaction by the Na-S promotion is also possible under the FTS reaction conditions. Solely based on the FTS performance results in this Chapter, the definite Boudouard reaction rate changes due to the Na-S promotion cannot be determined.

For the WGS reaction at 340°C, the Fe₃O₄ is the active phase and not the Fe carbides.^{62,78–80} We cannot observe any Fe₃O₄ or other Fe oxides in the FTS catalysts materials (**Figure 4.9**). Therefore, another phase/site needs to be active for the WGS reaction in the Na-S catalyst materials in order for the WGS reaction to be contributing on the decreased Usage Ratios H₂:CO. Previously, alkali added as K on Al₂O₃ (ALON), has been observed to provide WGS activity via a proposed potassium formate/carbonate intermediate $\geq 300^\circ\text{C}$ mechanism.^{81,82} Noteworthy is that this pathway does not require a presence of Fe or any other transition metal. The presence of alkali is sufficient for the WGS activity.

Formate-like species with K-promoted bulk Fe FTS reaction catalyst materials using in-situ Raman Spectroscopy (200°C, H₂:CO 5:1) have been observed by Zhang and Schrader.⁸³ Zhang and Schrader do not assign their formate-like species directly to a K-site adsorption, but do observe Raman Shifts within a region 1586-1600 cm⁻¹. Raman Shifts which are possibly assignable to a potassium formate/carbonate phases. Alkali-free Fe-based catalysts produce less CO₂ via the WGS reaction,^{36,84,85} than alkali containing Fe-based catalysts.^{32,85} Also, an alkali effect promoting the WGS reaction is present with Ni-based catalysts.⁸⁶ The possibility of K-sites as the directly WGS active sites has been earlier discussed in publication by Arakawa and Bell.⁸⁷ Na and K behave in a similar manner regarding their WGS reaction activity promotion.³²

Thus, for the Na-S catalyst materials the Na-S promotion most likely induces WGS activity, where alkali-Na could provide direct WGS reaction sites. Therefore, the WGS reaction may contribute to the lowered Usage Ratio H₂:CO with the Na-S promoted catalyst in comparison to the UP catalyst materials (**Table 4.4**).

The addition of Na-S promotion decreases the CO conversion to hydrocarbons to a fraction of ≈ 0.42 -0.47 in comparison to the respective UP catalysts (**Table 4.4**). This is in agreement if the Boudouard and/or WGS reactions are more active for the Na-S than UP catalysts converting CO to non-hydrocarbon products. However, precise changes due to the Na-S promotion on the relative FTS/WGS/Boudouard reaction rates cannot be determined from the results in this Chapter.

Nevertheless, despite the decreased selectivity and thus in overall decreased C efficiency towards the FTS reaction: still, the increased FTY for the Na-S catalyst materials increases the total production of hydrocarbons per unit of time. When comparing the catalysts with the highest median FTY's, i.e. UP 240 versus Na-S H₂, in their respective promotion groups (**Table 4.4**), correcting the Na-S H₂ FTY value with

Figure 4.20

The catalytic activity profiles as Fe Time Yields (FTYs) for the UP and Na-S ($\text{Fe}(-\text{Na-S})/\alpha\text{-Al}_2\text{O}_3$) catalyst materials over the 72 h Fischer-Tropsch Synthesis (FTS) reaction. FTY profiles for a) UP and c) Na-S H_2 , 240 and 290 catalysts, and for b) UP and d) Na-S 340, 390, 440 and 340 h.p. catalysts. FTS conditions: 340°C, 10 bar $\text{H}_2:\text{CO}:\text{He}$ 2.0:1.0:0.33 v/v, $\approx 5\,000\text{ h}^{-1}$.

the CO to hydrocarbons conversion factor of 0.45 versus the UP 230 catalyst, gives a FTY value of $\approx 2.7 \times 10^{-4}\text{ mol}_{\text{CO}}/\text{g}_{\text{Fe}}\text{s}$. This is ≈ 4.4 times the FTY of the UP 240 catalyst material.

Consequently, in total, for the production of hydrocarbons per unit of time the Na-S promotion addition is still advantageous with respect to the CO conversion. That is, if the lost CO towards non-FTS reaction C pathways i.e. Boudouard and/or WGS reactions and the associated decrease in the FTS reaction C efficiency can be tolerated.

4.3.3.2 The Effect of Used Catalyst

The catalytic performance of the tested catalysts is mainly governed by the Na-S promotion, regarding both the CO conversion and hydrocarbon selectivities. The applied catalyst material i.e. the combination of Fe phases (Fe carbides/ α -Fe/Fe oxides)

at the start of the catalytic run has a lesser effect on catalyst activity (**Table 4.4**) and selectivity (**Table 4.5**). Nevertheless, especially if the Na-S promotion is applied, the FTY profiles can be affected as depending on the used catalyst and its preparation method (**Figure 4.20**).

First, if the catalyst materials UP and Na-S 340 h.p. with heavy carbon deposits are ignored, for the UP catalysts the median FTY values over ToS 33-72 h are related as:

$$\text{UP 340} \lesssim \text{UP H}_2 \approx \text{UP 290} \approx \text{UP 440} \lesssim \text{UP 390} \lesssim \text{UP 240}$$

while for the Na-S catalyst materials, the relation follows:

$$\text{Na-S 390} < \text{Na-S 440} \lesssim \text{Na-S 290} < \text{Na-S 240} < \text{Na-S 340} < \text{Na-S H}_2.$$

No clear trends emergence of which of the used catalysts with different starting Fe phases leads to the highest FTY values over the near steady ToS range of 33-72 h. That is, no clear correlation between the initial Fe phase(s) and steady FTY activity exists for the studied catalyst materials.

Mogorosi et al. have estimated for a “ ϵ -carbide” phase (“ ϵ -Fe₂C””) being about +25 % more active per carbide surface area in the FTS reaction (250°C, 20 bar, H₂:CO 2:1) than the χ -Fe₅C₂ phase.⁷ The Na-S 240 FTS catalyst material contains the highest amount of the η -Fe₂C phase (a “ ϵ -carbide”, **Chapter 2**) with 53 % of η -Fe₂C (**Figure 4.9b**). However, lower median FTY value than for the Na-S 340 FTS and Na-S H₂ FTS catalysts with 100 % and 73 % of the χ -Fe₅C₂ phase, respectively, is obtained. Thus, for the studied catalyst materials: a high η -Fe₂C content does not imply a high FTY value or a higher value than for χ -Fe₅C₂-rich catalysts.

In an opposing view, a “ ϵ -carbide” phase (“Fe_{2.2}C”) has also been associated to a deactivating FTS reaction catalyst with lower intrinsic FTS reaction activity than a catalyst with higher χ -Fe₅C₂ phase content.⁸ For the Na-S 240 FTS catalyst material, the presence of the η -Fe₂C phase does not either lead to deactivation (**Figure 4.20c**). As Pendyala et al. also discuss, simply associating a bulk Fe carbide phase to the FTS reaction’s CO conversion activity can be misleading. In Pendyala et al.’s case the lowering CO conversion and bulk phase transformation to a “ ϵ -carbide” phase (“Fe_{2.2}C”) also coincided with heavy carbon deposition, which likely caused the catalyst’s deactivation in the FTS reaction.

The θ -Fe₃C phase has been proposed to be related to the FTS catalyst deactivation.⁹ For the UP 440 FTS catalyst material the presence of 64 % of the θ -Fe₃C phase does not lead to a lower FTY than for e.g. UP H₂ FTS catalyst material (**Table 4.4**) with 100 % χ -Fe₅C₂ phase content (**Figure 4.9a**). That is, the presence of θ -Fe₃C does not imply

catalyst deactivation or low FTY for the studied catalyst materials.

Thus, according to the results obtained in this Chapter and as noted also in literature:^{8,14–16} *a single bulk Fe carbide phase in the FTS reaction does not correlate with the FTY*. However, as will be discussed shortly, the different Fe carbide phases and their subtypes can cautiously be associated to differences in hydrocarbon selectivities (**Table 4.3**).

A noteworthy detail to highlight is that despite the Fe being detached from the support material α -Al₂O₃, either before; as for the 340, 390 and 440 catalysts (**Chapter 3**), or during the FTS reaction; as for the H₂, 240 and 290 catalyst materials (**Figure 4.2** and **Figure 4.3**). Neither were significant quantities of elemental Fe lost from the catalyst materials in the FTS reaction (**Figure 4.9c**). Furthermore, the FTY profiles during the FTS reaction for the UP and Na-S FTS catalyst materials are relatively stable (**Figure 4.20**). Thus, direct Fe interaction with the α -Al₂O₃ support in the FTS reaction is not a prerequisite for a FTS stable catalyst. For comparison, Fe encapsulated to carbon via Metal Organic Framework (MOF) pyrolysis has also been shown to be a stable and active Fe-based FTS reaction catalyst.^{36,88}

Some further effects warranting a discussion on the catalytic performance due to the used catalyst material can be mentioned as: i) within the UP promotion group the catalysts start active but lose activity within the first ≈ 20 h ToS (**Figure 4.20a-b**), ii) within the Na-S promotion group the catalysts either show steady (**Figure 4.20c**) or iii) increasing FTY within the first ≈ 20 h ToS (**Figure 4.20d**). With regard to the product selectivities (**Table 4.5**): iv) within the UP promotion group catalysts 390 and 440 show a modest $\approx +5$ % increase towards C₂-C₄ paraffin formation with decreased C₂H₄/C₂H₆ ratio and v) the 340 h.p. catalysts have differing product selectivities within the UP and Na-S promotion groups in comparison to the other catalysts in the respective promotion groups.

No definite, clear reasoning for the UP catalyst materials' FTY profiles, for starting initially active and followed by deactivation, can be given here. In general, variable FTY profiles depending on the initial state of the catalysts at the start of the FTS reaction, have been observed.^{35,89} Assigning clear cut reasons for the FTY profiles, is in general challenging due to the intertwined processes in the FTS reaction.^{2,77}

Nevertheless, few comments can be made. Regardless of the UP starting catalysts i.e. the initial Fe phases (**Figure 4.9a**), amount of initial carbon deposited on the catalyst or the initial Fe particle diameters (**Chapter 3**): all of the UP catalyst materials have decreasing FTY profiles with < 20 h ToS. The FTYs' are roughly halved from the start before reaching a steady state > 20 h ToS in the FTS reaction.

Fe particle diameter growth has been given as a one possible reason for the initially decreasing FTY profiles.²⁰ That is, the gradual sintering of the Fe particles results in

decreased active Fe surface area available for catalyzing the FTS reaction, thus decreasing the FTY's gradually. For longer reaction (≈ 600 h ToS) times, continuous Fe particle diameter growth has been observed by Sarkar et al. along with catalyst deactivation. However, the catalyst deactivation was associated by Sarkar et al. to be due to Fe carbide reoxidation to Fe₃O₄, not to the Fe sintering.²¹

For the UP catalyst materials, the Fe particle diameters do not significantly change in the FTS reaction (**Figure 4.4e-f**). Therefore, the Fe particle sintering is not a plausible explanation for the initially decreased FTY's for the studied UP catalyst materials. Furthermore, no elemental Fe is lost during the FTS reaction (**Figure 4.9c**) i.e. loss of the FTS active Fe does not either explain the decreasing FTYs within the first ≈ 20 h ToS. Neither, no Fe reoxidation to Fe₃O₄ is observed (**Figure 4.9a**). The possibility for the catalyst deactivation due to carbon deposition cannot be devised from the results in this Chapter.

For the Na-S catalyst materials the FTY profiles either stay nearly steady; as for the H₂, 240 and 290 catalysts (**Figure 4.20c**), or; increase for the 340, 390 and 440 catalysts within the first $\lesssim 20$ h ToS (**Figure 4.20d**). This behavior could be associated on the carbon deposited on the catalysts during the initial CO carburization for preparing the catalyst materials (**Chapter 3**). The Na-S H₂, 240 and 290 catalysts do not, but the Na-S 340, 390 and 440 catalyst materials do have initial deposits of carbon from the CO carburization. We therefore associate the initially increasing FTY profiles for the Na-S 340, 390 and 440 catalyst materials to the initial changes in the carbon deposit overlayer. Perhaps, the carbon overlayer gradually exposes more of the Fe carbide surface for the FTS reaction. H₂ may hydrogenate and remove carbon deposits $> 350^\circ\text{C}$.¹³ Very high amount of initial carbon deposits can also be used to explain the low FTY value for the Na-S 340 h.p. catalyst material in comparison to the rest of the catalysts in the Na-S promotion group (**Table 4.4**).

Despite the increased Fe particle mean diameters after the 72 h FTS reaction (**Figure 4.4**), the Na-S 240 (increase of +28 %) and Na-S 340 (+48 %) catalyst materials do not show significant catalyst deactivation in their FTY profiles (**Figure 4.20c-d**). The result is unlike as has been observed for the Fe-Na-S/CNT (Carbon Nanotube) catalyst materials.²⁰ In the study it was concluded that the Na-S promotion lead to a significant Fe particle growth and to decreasing FTY's and thus to catalyst deactivation. The results obtained within this study do not agree with this conclusion.

4.3.3.3 The Role of the Fe Carbides and their Subtypes in Fischer-Tropsch Synthesis Hydrocarbon Selectivity

With regard to the roles of the different Fe carbides (**Figure 4.9**) and their subtypes (**Table 4.3**) in the FTS reaction's hydrocarbon selectivity, some conclusions can be

made. Such as: i) the presence of the θ -Fe₃C phase can be associated to increased hydrocarbon paraffin selectivity (UP 390 FTS and UP 440 FTS catalysts), ii) the η -Fe₂C and χ -Fe₅C₂ Type II's with Na-S promotion can be associated to increased hydrocarbon olefin selectivity and decreased CH₄ with increased α -value (Na-S FTS) and, iii) possibly, χ -Fe₅C₂ Type III can be associated to decreased α -value (UP and Na-S 340 h.p. FTS), and with Na-S promotion also to increased olefin selectivity (Na-S 340 h.p. FTS).

The first conclusion is rather straightforward, as for the UP 390 FTS and UP 440 FTS catalysts the θ -Fe₃C phase is relatively stable and is present in significant quantities in comparison to the other UP catalysts (**Figure 4.9a**). That is, the $\approx$ +5 % increased C₂-C₄ paraffin selectivity and the decreased C₂H₄/C₂H₆ ratio can be associated to the θ -Fe₃C phase (**Table 4.5**). The Na-S 390 and Na-S 440 catalysts, for which the θ -Fe₃C phase is not stable and is converted to χ -Fe₅C₂ Type II during the FTS reaction (**Figure 4.9b**), do not show any deviations in the paraffin selectivities within the Na-S promotion group.

The result for the θ -Fe₃C phase is in disagreement with earlier data by Shultz et al,^{4,10} where Hägg carbide (χ -Fe₅C₂) and cementite (θ -Fe₃C) were the initial phases in the used FTS reaction catalyst materials. No increase in the paraffin selectivity (i.e. decrease in bromine number) can be observed in their selectivity data for the θ -Fe₃C phase as the catalyst.¹⁰ As a bulk Fe catalyst (Fe:MgO:K₂O:SiO₂:Cr₂O₃) containing K was used for the studies, it might be suspected that their θ -Fe₃C phase was converted towards χ -Fe₅C₂ during the FTS reaction, akin to the results for the Na-S FTS catalyst materials. This would explain the lack of selectivity effect from the θ -Fe₃C phase in the results by Shultz et al..

Both η -Fe₂C and χ -Fe₅C₂ Type II's in their respective Na-S FTS catalyst materials can be associated to increased olefin and decreased CH₄ selectivity, as well as to increased α -value. Interestingly, also the UP 240 FTS and UP 290 FTS catalysts showed the presence of η -Fe₂C and χ -Fe₅C₂ Type II's. However, without the mentioned changes in the hydrocarbon selectivities in respect to the other UP FTS catalysts with the χ -Fe₅C₂ Type I. That is, without the Na-S promotion the χ -Fe₅C₂ Type I and χ -Fe₅C₂ Type II do not seem to differ in their FTS reaction hydrocarbon selectivity. Thus, the χ -Fe₅C₂ Type II lattice may not by itself lead to differences in the hydrocarbon selectivities in comparison to the Type I, but the Type II might be the favored lattice in the presence of Na-S promotion. Further studies, e.g. akin to the Density Functional Theory (DFT) calculations by Xie et al.,⁴⁰ on how the Na-S promotion occupies the surface and the bulk positions of the different χ -Fe₅C₂ sublattice types would be of interest.

4.3.3.4 Behavior of the 340 h.p. Catalysts

The final item of interest is the catalytic behavior of the UP and Na-S 340 h.p. catalyst materials in the FTS reaction, as they break the general hydrocarbon selectivity trends

in their respective promotion groups (**Table 4.5**). Both show a decreased α -value; the UP 340 h.p. catalyst shows a C₂H₄/C₂H₆ ratio in-line with the UP 390 and UP 440 catalysts; and the Na-S 340 h.p. catalysts shows slightly increased C₂H₄/C₂H₆ ratio in comparison to the other Na-S FTS catalysts (**Table 4.5**).

Bukur et al. have observed increased olefin selectivity with a bulk Rührchemie (Fe:Cu:K:SiO₂) FTS catalyst material pretreated with CO (at 280°C) or H₂:CO (at 310°C) without a prior H₂ reduction step, in comparison to the catalysts reduced with H₂ prior to the FTS reaction. Also, Bukur et al.'s selectivity data suggests increased α -value (decreased CH₄, increased C₁₂) for the CO and H₂:CO pretreated catalysts.³⁵

The increased olefin selectivity observed by Bukur et al. matches the results with the alkali containing catalyst Na-S 340 h.p., which has been directly carburized with CO without first reducing the as-synthesized Fe oxide (α -Fe₂O₃) with H₂ (**Table 4.1**). For all of the 340 h.p. catalyst materials, the χ -Fe₅C₂ Type III is majority Fe carbide (**Figure 4.9a-b** and **Table 4.3**). Thus, when the χ -Fe₅C₂ Type III is combined with the Na-S promotion, the hydrocarbon selectivity might be steered towards olefin formation more effectively than with the Na-S promotion in combination with the χ -Fe₅C₂ Type II. Especially, the highest C₂H₄/C₂H₆ ratio of 11.3±0.2 is achieved with the Na-S promoted χ -Fe₅C₂ Type III in the Na-S 340 h.p. catalysts. This value is higher than with any of the Na-S promoted χ -Fe₅C₂ Type II's in the other Na-S catalyst materials (**Table 4.5**).

Although, this conclusion needs to be taken with care for the time being. In comparison to the results by Bukur et al.: the subtype of the χ -Fe₅C₂ phase cannot be deduced from the characterization results on the Bukur et al.'s FTS catalyst material,³⁴ nor do the Bukur et al.'s α -value changes match the changes for UP or Na-S 340 h.p. catalysts.³⁵ Also, CO conversions are very much higher for Bukur et al.'s catalyst (52-61 %) than for the Na-S 340 h.p. catalyst material (3±0). Although, the CO conversion levels should not affect the hydrocarbon selectivities directly.^{27,32} Furthermore, it would be expected that the heavy initial carbon deposits in the Na-S 340 h.p. catalyst (**Chapter 3**) block the available Fe surface, reducing possibility for secondary reactions, and thus possibly increasing the olefin content.^{26,27} However, the UP 340 h.p. catalyst shows *decreased* olefin selectivity within the UP promotion group. This, thus, going against the blocking of surface via secondary reactions argument.

For the UP and Na-S FTS 340 h.p. catalyst materials the minority θ -Fe₇C₃ phase (UP 19 %, Na-S 18 %) (**Figure 4.9a-b**), is unlikely to any play major a role in the FTS reaction catalysis performance results, and therefore is left uncommented. The results, nevertheless, can be taken as a demonstration, that the θ -Fe₇C₃ phase may form under relatively mild conditions and is stable in the FTS reaction, without a need for industrial FTS reactors.¹³ More studies on the rather understudied θ -Fe₇C₃ phase as the major FTS catalysis phase, with and without Na(-S) promotion, should be conducted in the future.

4.4 CONCLUSIONS

Supported Fe(-Na-S)/ α -Al₂O₃ catalyst materials, with or without Na-S promotion, prepared via CO carburization at various temperatures (240–440°C) or via H₂ reduction in **Chapter 3** were tested in 72 h FTS reaction (340°C, 10 bar H₂:CO:He 2.0:1.0:0.33 v/v, GHSV $\approx$ 5 000 h⁻¹). Ex-situ measured XRPD patterns collected after the FTS reaction runs were quantified using R-QPA. The Fe carbide phases of, as identified in **Chapter 2**, η -Fe₂C *Pnnm* (58), χ -Fe₅C₂ *C2/c* (15), θ -Fe₃C *Pnma* (62) and θ -Fe₇C₃ *Pnma* (62) were observed in the studied catalyst materials. The phase ϵ -Fe₃C *P6₃22* (182) was not stable in the FTS reaction. No other Fe phases besides the Fe carbides, such as Fe oxides, were observed in the catalyst materials after the FTS reaction.

In relation to the formation of the Fe carbides, addition of Na-S promotion: i) *stabilizes* the η -Fe₂C phase, and ii) *destabilizes* the θ -Fe₃C phase, under the used FTS reaction conditions.

Furthermore, the Na-S promotion addition causes a maximum $\approx$ 0.02 Å anisotropic changes in the crystal lattice parameters for the η -Fe₂C and χ -Fe₅C₂ phases after the FTS reaction. Observed lattice parameter changes are within the limits what might be expected if Na forms a solid solution with the Fe carbides. However, as exceptions: unpromoted catalyst materials prepared by CO carburization at 240°C or 290°C, showed similar lattice shifts for the χ -Fe₅C₂ phase after the FTS reaction, as would be expected with the Na-S promotion. Possible Na(-S) contamination could be ruled out based on the catalyst materials' catalytic performance. Whether similar lattice distortions due to the Na-S promotion exists for the θ -Fe₃C and θ -Fe₇C₃ phases, could not be conclusively determined. The distinctively distorted χ -Fe₅C₂ (h.p.) phase (i.e. Type III) prepared via CO carburization of Fe oxide (α -Fe₂O₃) at high-pressure, prevailed unchanged in the FTS reaction.

As based on the observed lattice parameters, the η -Fe₂C and χ -Fe₅C₂ phases can be divided into subtypes with their typical formation conditions as:

χ -Fe₅C₂

- Type I** After CO carburization, or FTS *without* Na-S promotion,
- Type II** After FTS *with* Na-S promotion,
- Type III** After CO carburization of Fe oxide (α -Fe₂O₃), the subtype is stable in FTS *regardless* of the Na-S promotion,

η -Fe₂C

- Type I** After CO carburization, or FTS *without* Na-S promotion,
- Type II** After FTS *with* Na-S promotion,
- Type III** After martensite tempering at 120°C. *Not observed in FTS.*

The η -Fe₂C Type III is not observed in this study but is included from literature for completeness.

In the terms of FTS reaction performance, the Na-S promotion has the general effects of i) increased CO conversion, ii) $\approx +10$ % increased C₂-C₄ selectivity with significantly suppressed CH₄ selectivity below the ASF expectations, iii) increased olefin content and iv) increased α -value, in comparison to unpromoted catalyst materials. As adverse effects for the FTS reaction, with the Na-S promotion: i) CO₂ selectivity increases from ≤ 16 % to ≈ 38 -43 % and ii) fraction of CO converted to hydrocarbons drops to ≈ 0.42 -0.47 in relation to the unpromoted catalyst materials. Also, the Usage Ratios H₂:CO decrease from ≈ 1.8 -2.3 to ≈ 0.7 -0.8 with the added Na-S promotion as a sign of increased, CO₂ releasing, Boudouard and/or WGS reactions consuming the input CO. Despite the CO diverted to non-FTS reaction C pathways, ≈ 4.4 times more hydrocarbons are still converted from CO per unit of time, when comparing the catalysts with the highest FTY's with and without Na-S promotion. This, while taking into account the decreased fraction of CO to hydrocarbons conversion for the Na-S promoted catalysts.

No WGS reaction active Fe₃O₄, or other Fe oxides, were observed in any of the catalyst materials after the FTS reaction. The WGS reaction may contribute to the observed decrease in the Usage Ratio H₂:CO by Na(-S) promotion directly providing active sites for the WGS reaction. This was explained with observations from literature in combination with the catalytic performance data.

Under the applied FTS reaction conditions, for all of the studied catalyst materials the Fe is encapsulated in carbon and detached from the support α -Al₂O₃, as observed with TEM. This, however, did not affect the catalyst materials' FTY profiles versus ToS in the FTS reaction. No significant amounts of elemental Fe was lost during the 72 h FTS reaction, as quantified with R-QPA. Neither, no connection between the Fe particle mean diameter changes and FTY profiles were observed e.g. increasing Fe particle mean diameters did not correlate with decreases in the catalyst materials FTY profiles.

Fe crystallite mean diameters for each phase (R-QPA) in comparison to the Fe particle mean diameters (TEM) did not show any common trends. This suggests that a single Fe particle is not a single Fe phase crystallite.

No direct correlation between any of the bulk Fe carbide phases and the catalyst materials' FTYs' could be observed. However, hydrocarbon selectivity-wise cautious associations can be made as: i) the θ -Fe₃C phase mildly ($\approx +5$ %) increases hydrocarbon product slate paraffin content, ii) with Na-S promotion, η -Fe₂C Type II and χ -Fe₅C₂ Type II are present in high olefin and low CH₄ selective FTS reaction catalyst materials, and iii) χ -Fe₅C₂ Type III, when combined with Na-S promotion, might increase the olefin selectivity more than the χ -Fe₅C₂ Type II with Na-S promotion does. No conclusions on the role of the θ -Fe₇C₃ phase in the FTS reaction could be drawn, due to the minor phase

quantities present in the studied FTS catalyst materials.

For further research: i) the general connection between, but especially for the χ -Fe₅C₂ phase, crystal lattice subtypes and Na-S promotion to hydrocarbon selectivities, and also ii) investigating the understudied role of the θ -Fe₇C₃ phase as a major phase for the FTS reaction catalysis, with and without Na-S promotion, are interesting topics for further research.

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4.6 REFERENCES

- [1] de Smit, E., Cinquini, F., Beale, A. M., Safonova, O. V., van Beek, W., Sautet, P. and Weckhuysen, B. M., "Stability and Reactivity of ϵ - χ - θ Iron Carbide Catalyst Phases in Fischer-Tropsch Synthesis: Controlling μ_c ", *J. Am. Chem. Soc.* **132**, 14928–14941 (2010).
- [2] de Smit, E. and Weckhuysen, B. M., "The renaissance of iron-based Fischer-Tropsch synthesis: on the multifaceted catalyst deactivation behaviour", *Chem. Soc. Rev.* **37**, 2758–2781 (2008).
- [3] Anderson, R. B., Hofer, L. J. E., Cohn, E. M. and Seligman, B., "Studies of the Fischer-Tropsch Synthesis. IX. Phase Changes of Iron Catalysts in the Synthesis", *J. Am. Chem. Soc.* **73**, 944–946 (1951).
- [4] Shultz, J. F., Hall, W. K., Seligman, B. and Anderson, R. B., "Studies of the Fischer-Tropsch Synthesis. XIV. Hägg Carbide as Catalysts", *J. Am. Chem. Soc.* **77**, 213–221 (1955).
- [5] Le Caër, G., Dubois, J. M., Pijolat, M., Perrichon, V. and Bussière, P., "Characterization by Moessbauer Spectroscopy of Iron Carbides Formed by Fischer-Tropsch Synthesis", *J. Phys. Chem.* **86**, 4799–4808 (1982).
- [6] Niemantsverdriet, J. W., van der Kraan, A. M., van Dijk, W. L. and van der Baan, H. S., "Behavior of Metallic Iron Catalysts during Fischer-Tropsch Synthesis Studied with Mössbauer Spectroscopy, X-ray Diffraction, Carbon Content Determination, and Reaction Kinetic Measurements", *J. Phys. Chem.* **84**, 3363–3370 (1980).
- [7] Mogorosi, R. P., Fischer, N., Claeys, M. and van Steen, E., "Strong-metal-support interaction by molecular design: Fe-silicate interactions in Fischer-Tropsch catalysts", *J. Catal.* **289**, 140–150 (2012).
- [8] Pendyala, V. R. R., Graham, U. M., Jacobs, G., Hamdeh, H. H. and Davis, B. H., "Fischer-Tropsch Synthesis: Deactivation as a Function of Potassium Promoter Loading for Precipitated Iron Catalyst", *Catal. Lett.* **144**, 1704–1716 (2014).
- [9] de Smit, E., Beale, A. M., Nikitenko, S. and Weckhuysen, B. M., "Local and long range order in promoted iron-based Fischer-Tropsch catalysts: A combined in situ X-ray absorption spectroscopy/wide angle X-ray scattering study", *J. Catal.* **262**, 244–256 (2009).
- [10] Shultz, J. F., Hall, W. K., Dubs, T. A. and Anderson, R. B., "Studies of the Fischer-Tropsch Synthesis. XV. Cementite as Catalysts", *J. Am. Chem. Soc.* **78**, 282–285 (1956).
- [11] Datye, A. K., Jin, Y., Mansker, L. D., Motjope, R. T., Dlamini, T. H. and Coville, N. J., "The nature of the active phase in iron Fischer-Tropsch catalysts" in *Studies in Surface Science and Catalysis* **130**, 1139–1144 (2000).

- [12] Mansker, L. D., Jin, Y., Bukur, D. B. and Datye, A. K., "Characterization of slurry phase iron catalysts for Fischer-Tropsch synthesis", *Appl. Catal. A Gen.* **186**, 277–296 (1999).
- [13] Dry, M. E., "The Fischer-Tropsch Synthesis" in *Catalysis - Science and Technology* (eds. Anderson, J. R. & Boudart, M.) **1**, 159–256 (Springer-Verlag, Berlin, 1981).
- [14] Sirimanothan, N., Hamdeh, H. H., Zhang, Y. and Davis, B. H., "Fischer-Tropsch Synthesis; Changes in Phase and Activity during Use", *Catal. Lett.* **82**, 181–191 (2002).
- [15] O'Brien, R. J., Xu, L., Milburn, D. R., Li, Y.-X., Klabunde, K. J. and Davis, B. H., "Fischer-Tropsch synthesis: Impact of potassium and zirconium promoters on the activity and structure of an ultrafine iron oxide catalyst", *Top. Catal.* **2**, 1–15 (1995).
- [16] Rao, K. R. P. M., Huggins, F. E., Huffman, G. P., Gormley, R. J., O'Brien, R. J. and Davis, B. H., "Mössbauer Study of Iron Fischer-Tropsch Catalysts during Activation and Synthesis", *Energy & Fuels* **10**, 546–551 (1996).
- [17] Dry, M. E., Shingles, T. and van H. Botha, C. S., "Factors influencing the formation of carbon on iron Fischer-Tropsch catalysts I. The influence of promoters", *J. Catal.* **17**, 341–346 (1970).
- [18] Dry, M. E., Shingles, T., Boshoff, L. J. and van H. Botha, C. S., "Factors influencing the formation of carbon on iron Fischer-Tropsch catalysts. II. The effect of temperature and of gases and vapors present during Fischer-Tropsch synthesis", *J. Catal.* **17**, 347–354 (1970).
- [19] Cohn, E. M., Bean, E. H., Mentser, M., Hofer, L. J. E., Pontello, A., Peebles, W. C. and Jack, K. H., "The carburization of iron oxide with carbon monoxide: Modifications of Hägg iron carbide", *J. Appl. Chem.* **5**, 418–425 (1955).
- [20] Xie, J., Torres Galvis, H. M., Koeken, A. C. J., Kirilin, A., Dugulan, A. I., Ruitenbeek, M. and de Jong, K. P., "Size and Promoter Effects on Stability of Carbon-Nanofiber-Supported Iron-Based Fischer-Tropsch Catalysts", *ACS Catal.* **6**, 4017–4024 (2016).
- [21] Sarkar, A., Seth, D., Dozier, A. K., Neathery, J. K., Hamdeh, H. H. and Davis, B. H., "Fischer-Tropsch Synthesis: Morphology, Phase Transformation and Particle Size Growth of Nano-scale Particles", *Catal. Lett.* **117**, 1–17 (2007).
- [22] An, X., Wu, B., Wan, H.-J., Li, T.-Z., Tao, Z.-C., Xiang, H.-W. and Li, Y.-W., "Comparative study of iron-based Fischer-Tropsch synthesis catalyst promoted with potassium or sodium", *Catal. Commun.* **8**, 1957–1962 (2007).
- [23] O'Brien, R. J., Xu, L., Spicer, R. L. and Davis, B. H., "Activation Study of Precipitated Iron Fischer-Tropsch Catalysts", *Energy & Fuels* **10**, 921–926 (1996).
- [24] Shultz, J. F., Abelson, M., Stein, K. C. and Anderson, R. B., "Studies of the Fischer-Tropsch Synthesis. XVIII. Influence of Catalyst Geometry on Synthesis on Iron Catalysts", *J. Phys. Chem.* **63**, 496–500 (1959).
- [25] Ning, W., Koizumi, N., Chang, H., Mochizuki, T., Itoh, T. and Yamada, M., "Phase transformation of unpromoted and promoted Fe catalysts and the formation of carbonaceous compounds during Fischer-Tropsch synthesis reaction", *Appl. Catal. A Gen.* **312**, 35–44 (2006).
- [26] Dictor, R. and Bell, A. T., "Fischer-Tropsch synthesis over reduced and unreduced iron oxide catalysts", *J. Catal.* **97**, 121–136 (1986).
- [27] Todic, B., Nowicki, L., Nikacevic, N. and Bukur, D. B., "Fischer-Tropsch synthesis product selectivity over an industrial iron-based catalyst: Effect of process conditions", *Catal. Today* **261**, 28–39 (2016).
- [28] Botes, G. F., Bromfield, T. C., Coetzer, R. L. J., Crous, R., Gibson, P. and Ferreira, A. C., "Development of a chemical selective iron Fischer Tropsch catalyst", *Catal. Today* **275**, 40–48 (2016).
- [29] Torres Galvis, H. M., Bitter, J. H., Khare, C. B., Ruitenbeek, M., Dugulan, A. I. and de Jong, K. P., "Supported Iron Nanoparticles as Catalysts for Sustainable Production of Lower Olefins", *Science* **335**, 835–838 (2012).

- [30] Torres Galvis, H. M., Koeken, A. C. J., Bitter, J. H., Davidian, T., Ruitenbeek, M., Dugulan, A. I. and de Jong, K. P., "Effects of sodium and sulfur on catalytic performance of supported iron catalysts for the Fischer-Tropsch synthesis of lower olefins", *J. Catal.* **303**, 22–30 (2013).
- [31] Dry, M. E. and Oosthuizen, G. J., "The correlation between catalyst surface basicity and hydrocarbon selectivity in the Fischer-Tropsch synthesis", *J. Catal.* **11**, 18–24 (1968).
- [32] Ngantsoue-Hoc, W., Zhang, Y., O'Brien, R. J., Luo, M. and Davis, B. H., "Fischer-Tropsch synthesis: activity and selectivity for Group I alkali promoted iron-based catalysts", *Appl. Catal. A Gen.* **236**, 77–89 (2002).
- [33] Luo, M. and Davis, B. H., "Fischer-Tropsch synthesis: Group II alkali-earth metal promoted catalysts", *Appl. Catal. A Gen.* **246**, 171–181 (2003).
- [34] Bukur, D. B., Okabe, K., Rosynek, M. P., Li, C. P., Wang, D. J., Rao, K. R. P. M. and Huffman, G. P., "Activation Studies with a Precipitated Iron Catalyst for Fischer-Tropsch Synthesis. I. Characterization Studies", *Journal of Catalysis* **155**, 353–365 (1995).
- [35] Bukur, D. B., Nowicki, L., Manne, R. K. and Lang, X. S., "Activation Studies with a Precipitated Iron Catalyst for Fischer-Tropsch Synthesis II. Reaction Studies", *J. Catal.* **155**, 366–375 (1995).
- [36] Wezendonk, T. A., Sun, X., Dugulan, A. I., van Hoof, A. J. F., Hensen, E. J. M., Kapteijn, F. and Gascon, J., "Controlled formation of iron carbides and their performance in Fischer-Tropsch synthesis", *J. Catal.* **362**, 106–117 (2018).
- [37] Johnson, J. Y., "Improvements in the Manufacture and Production of Unsaturated Hydrocarbons of Low Boiling Point", Patent GB322284A (1929).
- [38] Crous, R., Bromfield, T. C. and Booyens, S., "Olefin Selective FT Catalyst Composition and Preparation Thereof", Patent WO2010066386A1 (2010).
- [39] Myddleton, W. W., "Improvements Relating to the Catalytic Synthesis of Hydrocarbon Oils from Gaseous Mixtures of Carbon Monoxide and Hydrogen", Patent GB509325A (1939).
- [40] Xie, J., Yang, J., Dugulan, A. I., Holmen, A., Chen, D., De Jong, K. P. and Louwerse, M. J., "Size and Promoter Effects in Supported Iron Fischer-Tropsch Catalysts: Insights from Experiment and Theory", *ACS Catal.* **6**, 3147–3157 (2016).
- [41] Jung, H. and Thomson, W. J., "Dynamic X-ray diffraction study of an unsupported iron catalyst in Fischer-Tropsch synthesis", *J. Catal.* **134**, 654–667 (1992).
- [42] McCartney, J. T., Hofer, L. J. E., Seligman, B., Lecky, J. A., Peebles, W. C. and Anderson, R. B., "Electron and X-Ray Diffraction Studies of Iron Fischer-Tropsch Catalysts", *J. Phys. Chem.* **57**, 730–736 (1953).
- [43] Leineweber, A., Shang, S., Liu, Z.-K., Widenmeyer, M. and Niewa, R., "Crystal structure determination of Hägg carbide, χ -Fe₅C₂ by first-principles calculations and Rietveld refinement", *Zeitschrift für Krist.* **227**, 207–220 (2012).
- [44] Retief, J. J., "Powder diffraction data and Rietveld refinement of Hägg-carbide, χ -Fe₅C₂", *Powder Diffr.* **14**, 130–132 (1999).
- [45] Duggin, M. J. and Hofer, L. J. E., "Nature of χ -Iron Carbide", *Nature* **212**, 248–248 (1966).
- [46] Jack, K. H. and Wild, S., "Nature of χ -Carbide and Its Possible Occurrence in Steels", *Nature* **212**, 248–250 (1966).
- [47] Jenkins, R. and Snyder, R. L., "Introduction to X-ray Powder Diffractometry", *Introduction to X-ray Powder Diffractometry* **138** (John Wiley & Sons, Inc., Hoboken, NJ, USA, 1996).
- [48] Koeken, A. C. J., Torres Galvis, H. M., Davidian, T., Ruitenbeek, M. and de Jong, K. P., "Suppression of Carbon Deposition in the Iron-Catalyzed Production of Lower Olefins from Synthesis Gas", *Angew. Chem., Int. Ed.* **51**, 7190–7193 (2012).
- [49] Janbroers, S., Louwen, J. N., Zandbergen, H. W. and Kooyman, P. J., "Insights into the nature of iron-

- based Fischer-Tropsch catalysts from quasi in situ TEM-EELS and XRD", *J. Catal.* **268**, 235–242 (2009).
- [50] Shroff, M. D. and Datye, A. K., "The importance of passivation in the study of iron Fischer-Tropsch catalysts", *Catal. Lett.* **37**, 101–106 (1996).
- [51] Alstrup, I., Tavares, M. T., Bernardo, C. A., Sørensen, O. and Rostrup-Nielsen, J. R., "Carbon formation on nickel and nickel-copper alloy catalysts", *Mater. Corros.* **49**, 367–372 (1998).
- [52] Nolan, P. E., Lynch, D. C. and Cutler, A. H., "Catalytic disproportionation of CO in the absence of hydrogen: Encapsulating shell carbon formation", *Carbon* **32**, 477–483 (1994).
- [53] Mazzucco, S., Wang, Y., Tanase, M., Picher, M., Li, K., Wu, Z., Irle, S. and Sharma, R., "Direct evidence of active and inactive phases of Fe catalyst nanoparticles for carbon nanotube formation", *J. Catal.* **319**, 54–60 (2014).
- [54] Toby, B. H., "R factors in Rietveld analysis: How good is good enough?", *Powder Diffr.* **21**, 67–70 (2006).
- [55] Nagakura, S., "Study of Metallic Carbides by Electron Diffraction Part III. Iron Carbides", *J. Phys. Soc. Japan* **14**, 186–195 (1959).
- [56] Amelse, J. A., Grynkewich, G., Butt, J. B. and Schwartz, L. H., "Moessbauer spectroscopic study of passivated small particles of iron and iron carbide", *J. Phys. Chem.* **85**, 2484–2488 (1981).
- [57] Jiang, F., Zhang, M., Liu, B., Xu, Y. and Liu, X., "Insights into the influence of support and potassium or sulfur promoter on iron-based Fischer-Tropsch synthesis: understanding the control of catalytic activity, selectivity to lower olefins, and catalyst deactivation", *Catal. Sci. Technol.* **7**, 1245–1265 (2017).
- [58] Raupp, G. B. and Delgass, W. N., "Mössbauer Investigation of Supported Fe and FeNi Catalysts II. Carbides Formed by Fischer-Tropsch Synthesis", *J. Catal.* **58**, 348–360 (1979).
- [59] Tau, L. M., Borcar, S., Bianchi, D. and Bennett, C. O., "Investigation of supported iron Fischer-Tropsch synthesis catalysts by Mössbauer spectroscopy", *J. Catal.* **87**, 36–54 (1984).
- [60] du Plessis, H. E., de Villiers, J. P. R., Kruger, G. J., Steuwer, A. and Brunelli, M., "Rietveld and pair distribution function study of Hägg carbide using synchrotron X-ray diffraction", *J. Synchrotron Radiat.* **18**, 266–271 (2011).
- [61] Hofer, L. J. E., "Nature of the carbides of iron", *U.S. Bureau of Mines Bulletin* **631** (1966). Available at: <http://www.onemine.org/document/abstract.cfm?docid=186163&title=Nature-Of-The-Carbides-Of-Iron> (Accessed: February 2014).
- [62] Rhodes, C., Hutchings, G. J. and Ward, A. M., "Water-gas shift reaction: finding the mechanistic boundary", *Catal. Today* **23**, 43–58 (1995).
- [63] Dry, M. E. and Ferreira, L. C., "The distribution of promoters in magnetite catalysts", *J. Catal.* **7**, 352–358 (1967).
- [64] Hofer, L. J. E., Cohn, E. M. and Peebles, W. C., "The Modifications of the Carbide, Fe₂C; Their Properties and Identification", *J. Am. Chem. Soc.* **71**, 189–195 (1949).
- [65] Hirotsu, Y. and Nagakura, S., "Crystal structure and morphology of the carbide precipitated from martensitic high carbon steel during the first stage of tempering", *Acta Metall.* **20**, 645–655 (1972).
- [66] Nagakura, S., Hirotsu, Y., Kusunoki, M., Suzuki, T. and Nakamura, Y., "Crystallographic study of the tempering of martensitic carbon steel by electron microscopy and diffraction", *Metall. Trans. A* **14**, 1025–1031 (1983).
- [67] Barton, G. H. and Gale, B., "The structure of a pseudo-hexagonal iron carbide", *Acta Crystallogr.* **17**, 1460–1462 (1964).
- [68] Hirotsu, Y. and Nagakura, S., "Electron Microscopy and Diffraction Study of the Carbide Precipitated

- at the First Stage of Tempering of Martensitic Medium Carbon Steel*", *Trans. Japan Inst. Met.* **15**, 129–134 (1974).
- [69] Matyi, R. J., Schwartz, L. H. and Butt, J. B., "Particle Size, Particle Size Distribution, and Related Measurements of Supported Metal Catalysts", *Catal. Rev.* **29**, 41–99 (1987).
- [70] Liu, X., Zhang, C., Li, Y., Niemantsverdriet, J. W., Wagner, J. B. and Hansen, T. W., "Environmental Transmission Electron Microscopy (ETEM) Studies of Single Iron Nanoparticle Carburization in Synthesis Gas", *ACS Catal.* **7**, 4867–4875 (2017).
- [71] Pendyala, V. R. R., Graham, U. M., Jacobs, G., Hamdeh, H. H. and Davis, B. H., "Fischer-Tropsch Synthesis: Morphology, Phase Transformation, and Carbon-Layer Growth of Iron-Based Catalysts", *ChemCatChem* **6**, 1952–1960 (2014).
- [72] Balzar, D., Audebrand, N., Daymond, M. R., Fitch, A., Hewat, A., Langford, J. I., Le Bail, A., Louër, D., Masson, O., McCowan, C. N., Popa, N. C., Stephens, P. W. and Toby, B. H., "Size-strain line-broadening analysis of the ceria round-robin sample", *J. Appl. Crystallogr.* **37**, 911–924 (2004).
- [73] Kril, C. E. and Birringer, R., "Estimating grain-size distributions in nanocrystalline materials from X-ray diffraction profile analysis", *Philos. Mag. A* **77**, 621–640 (1998).
- [74] Anderson, R. B., Karn, F. S. and Shultz, J. F., "Factors in sulfur poisoning of iron catalysts in Fischer-Tropsch synthesis", *J. Catal.* **4**, 56–63 (1965).
- [75] Torres Galvis, H. M., Koeken, A. C. J., Bitter, J. H., Davidian, T., Ruitenbeek, M., Dugulan, A. I. and De Jong, K. P., "Effect of precursor on the catalytic performance of supported iron catalysts for the Fischer-Tropsch synthesis of lower olefins", *Catal. Today* **215**, 95–102 (2013).
- [76] Dry, M. E., "The Fischer-Tropsch process: 1950–2000", *Catal. Today* **71**, 227–241 (2002).
- [77] van der Laan, G. P. and Beenackers, A. A. C. M., "Kinetics and Selectivity of the Fischer-Tropsch Synthesis: A Literature Review", *Catal. Rev.* **41**, 255–318 (1999).
- [78] Ratnasamy, C. and Wagner, J. P., "Water Gas Shift Catalysis", *Catal. Rev.* **51**, 325–440 (2009).
- [79] Chianese, S., Loipersböck, J., Malits, M., Rauch, R., Hofbauer, H., Molino, A. and Musmarra, D., "Hydrogen from the high temperature water gas shift reaction with an industrial Fe/Cr catalyst using biomass gasification tar rich synthesis gas", *Fuel Process. Technol.* **132**, 39–48 (2015).
- [80] Lywood, W. J. and Twigg, M. V., "Hydrogen production including a shift reaction process", Patent EP0361648A1 (1990).
- [81] Amenomiya, Y. and Pleizier, G., "Alkali-promoted Alumina Catalysts II. Water-Gas Shift Reaction", *J. Catal.* **76**, 345–353 (1982).
- [82] Krupay, B. W. and Amenomiya, Y., "Alkali-promoted Alumina Catalysts I. Chemisorption and oxygen exchange of carbon monoxide and carbon dioxide on potassium-promoted alumina catalysts", *J. Catal.* **67**, 362–370 (1981).
- [83] Zhang, H.-B. and Schrader, G. L., "Characterization of a fused iron catalyst for Fischer-Tropsch synthesis by in situ laser Raman spectroscopy", *J. Catal.* **95**, 325–332 (1985).
- [84] Wang, P., Chen, W., Chiang, F., Dugulan, A. I., Song, Y., Pestman, R., Zhang, K., Yao, J., Feng, B., Miao, P., Xu, W. and Hensen, E. J. M., "Synthesis of stable and low-CO₂ selective ϵ -iron carbide Fischer-Tropsch catalysts", *Sci. Adv.* **4**, eaau2947 (2018).
- [85] Krishnamoorthy, S., Li, A. and Iglesia, E., "Pathways for CO₂ Formation and Conversion During Fischer-Tropsch Synthesis on Iron-Based Catalysts", *Catal. Lett.* **80**, 77–86 (2002).
- [86] Hwang, K.-R., Lee, C.-B. and Park, J.-S., "Advanced nickel metal catalyst for water-gas shift reaction", *J. Power Sources* **196**, 1349–1352 (2011).
- [87] Arakawa, H. and Bell, A. T., "Effects of potassium promotion on the activity and selectivity of iron Fischer-Tropsch catalysts", *Ind. Eng. Chem. Process Des. Dev.* **22**, 97–103 (1983).

- [88] Wezendonk, T. A., Santos, V. P., Nasalevich, M. A., Warringa, Q. S. E., Dugulan, A. I., Chojecki, A., Koeken, A. C. J., Ruitenbeek, M., Meima, G., Islam, H.-U., Sankar, G., Makkee, M., Kapteijn, F. and Gascon, J., "Elucidating the Nature of Fe Species during Pyrolysis of the Fe-BTC MOF into Highly Active and Stable Fischer-Tropsch Catalysts", *ACS Catal.* **6**, 3236–3247 (2016).
- [89] Davidian, T., Ruitenbeek, M., Koeken, A. C. J., Vos, M. and Wielemaker, M. F., "Novel Iron-based Catalysts and Treatment Process therefor for Use in Fischer-Tropsch Reactions", Patent WO2014210089A1 (2014).

Chapter 5

On the Effect of the Reaction Pressure in Fischer-Tropsch Synthesis with Fe(-Na-S)/ α -Al₂O₃ Catalysts

Fe-based catalysts catalyze Fischer-Tropsch Synthesis (FTS) reaction producing hydrocarbons from an input H₂:CO gas mixture. The catalysts' FTS performance is modifiable by varying e.g. reaction conditions, catalyst pretreatment and added chemical promoters. We follow the combined effects of the FTS reaction pressure, catalyst H₂ pre-reduction and Na-S promotion on the catalysts' FTS performance. Especially, formation of Fe carbides and their subtypes defined by distinct lattice parameters, are followed. Supported, Na-S promoted and unpromoted Fe(-Na-S)/ α -Al₂O₃ catalysts were tested at 3, 10 and 20 bar FTS reaction at 340°C. Catalysts were either H₂ pre-reduced or directly exposed to H₂:CO in the FTS reaction. X-ray Powder Diffractometry (XRPD) with Rietveld Quantitative Phase Analysis (R-QPA) was applied for Fe phase quantification and Transmission Electron Microscopy (TEM) for determining catalyst morphology. Na-S promotion induced a lowered 10 bar reaction pressure threshold for boosted catalyst activity and also decreased both Usage Ratio H₂:CO and CH₄ selectivity. 20 bar reaction pressure was required for unpromoted catalyst for similar effects. Regardless of Na-S promotion, catalysts directly exposed to H₂:CO showed increased C₂H₄/C₂H₆ ratio, which was attributed to the presence of χ -Fe₅C₂ Type III. The results contribute towards understanding Na-S promotion reaction pressure dependency, especially in relation to the associated Fe phase/carbide subtype changes.

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5.1 INTRODUCTION

With Fischer-Tropsch Synthesis (FTS) reaction a $\text{H}_2\text{:CO}$ gas mixture (i.e. syngas) can be catalytically converted into hydrocarbon products. A wide variety of different hydrocarbons can be produced via the FTS reaction.¹⁻⁵ With the use of Fe-based catalyst materials in the FTS reaction, increased amount of olefins (i.e. unsaturated hydrocarbons) as the synthesis hydrocarbon products can be attained.^{1,3,4}

Fe-based catalyst materials can operate over a varied range of FTS reaction conditions.^{1,3,4,6} By altering the exact FTS reaction conditions, e.g. reaction pressure,⁵⁻⁸ temperature,^{4,5,7,9-11} or input $\text{H}_2\text{:CO}$ ratio,^{4,5,7,10} the hydrocarbon product slate can be steered towards the desired products. Besides the FTS reaction conditions, the hydrocarbon product selectivities can also be adjusted with use of chemical promoters added on the FTS catalyst materials.^{4,5,12-17} An added element from the alkali metal group, commonly Na or K, is the most common chemical catalyst promoter applied in the Fe-based FTS reaction. The alkali alters the hydrocarbon product selectivities towards longer chained hydrocarbons with increased olefinicity.^{4,5,11,12,15-18} Furthermore, combining an alkali element with S is especially well-suited for steering the FTS reaction hydrocarbon products towards increased olefinicity, while simultaneously suppressing undesired CH_4 selectivity.¹⁹⁻²⁵

The active phases for the Fe-based FTS reaction are Fe carbides. Fe carbides with their crystal lattices encountered in FTS research are (**Chapter 2**): $\epsilon\text{-Fe}_3\text{C}$ $P6_322$ (182), $\eta\text{-Fe}_2\text{C}$ $Pnnm$ (58), $\chi\text{-Fe}_5\text{C}_2$ $C2/c$ (15), $\theta\text{-Fe}_3\text{C}$ $Pnma$ (62) and $\theta\text{-Fe}_7\text{C}_3$ $Pnma$ (62). The $\eta\text{-Fe}_2\text{C}$ and $\chi\text{-Fe}_5\text{C}_2$ phases can further be divided into subtypes after differences in their crystal lattice parameters, as induced by different formation conditions (**Chapter 4**). The Fe carbide subtype formation was observed to depend on the presence of Na-S promotion, the initial Fe phase used for carburization ($\alpha\text{-Fe}_2\text{O}_3$ or $\alpha\text{-Fe}$) and whether a Fe carbide was exposed to FTS reaction conditions (340°C, 10 bar, $\text{H}_2\text{:CO}$ 2:1) or only CO carburized. The Fe carbide subtype divisions can be used to explain the various lattice parameters,²⁶⁻²⁹ and a distorted form,³⁰ of the $\chi\text{-Fe}_5\text{C}_2$ phase observed in the literature.

The presence of any specific Fe carbide phase does not directly predict the FTS reaction performance of the applied catalyst.^{16,31-33} Nevertheless, without a known or direct correlation to any specific Fe carbide phase(s), the Fe-based catalysts FTS reaction performance can be altered with an applied catalyst pretreatment. That is, by altering the Fe phase(s) present in the catalyst material at the initiation of the FTS reaction.³⁴⁻³⁸ As examples, exposing a Fe-based FTS reaction catalyst material in its oxidic form directly to CO or $\text{H}_2\text{:CO}$ without a prior H_2 reduction of the catalyst, can induce an $\approx +10\%$ increase in the achieved $\text{C}_2\text{-C}_4$ olefin hydrocarbon product fraction,³⁵

Figure 5.1

A schematic of the approach applied in this Chapter. Na-S promoted and unpromoted Fe(-Na-S)/ α -Al₂O₃ catalyst materials are either H₂ reduced prior (α -Fe) or exposed directly as calcined only (α -Fe₂O₃) catalysts to (a) Fischer-Tropsch Synthesis (FTS) reaction at reaction pressures of 3, 10 or 20 bar at 340°C. The catalyst materials are (b) subsequently characterized after the FTS reaction with ex-situ X-ray Powder Diffractometry (XRPD). Rietveld Quantitative Phase Analysis (R-QPA) is applied to the XRPD patterns in order to (c) quantify the Fe carbide phases and lattice parameters in the catalyst materials. Special attention is given on the Fe carbide subtypes, which are defined by their lattice parameters. The quantification results are then (d) compared to the catalyst materials FTS reaction catalysis performances.

or decrease the catalyst's hydrogenation ability.³⁸ Origins of this effect, however, are not fundamentally understood. Especially, whether a connection between the Fe carbide subtypes and Fe-based FTS reaction catalysts' catalytic performance exists is unknown. The precise Fe carbide crystal lattice parameters, defining the Fe carbide subtypes, are commonly overlooked in the literature. This, despite the wide application of the X-ray Powder Diffractometry (XRPD) technique within the research field of Fe-based FTS reaction.^{10,30,32,34,36,39-44}

Within this Chapter, with use of supported Fe(-Na-S)/ α -Al₂O₃ catalyst materials with and without Na-S promotion, we probe the combined effects of i) Na-S promotion, ii) FTS reaction pressure and iii) α -Fe₂O₃ (hematite) or H₂ pre-reduced α -Fe phases as the FTS reaction's starting Fe phases. The observations are correlated to the catalyst

Table 5.1

Inductively Coupled Plasma - Optical Emission Spectrophotometry (ICP-OES) results of elemental analysis on the used Fe(III) nitrate nonahydrate precursor $\text{Fe}(\text{NO}_3)_3 \cdot 9\text{H}_2\text{O}$ (Acros, 423710030) and the unpromoted (UP) and Na-S promoted (Na-S) catalysts materials after calcining (Calcin.). The nitrate precursor was measured at Mikrolab Kolbe and the UP and Na-S Calcin. materials at Universiteit Utrecht (UU) GeoLab.

	Elemental Analysis (weight-ppm)							
	Co	Cr	Mn	Fe	Ca	K	Na	S
$\text{Fe}(\text{NO}_3)_3 \cdot 9\text{H}_2\text{O}$	-	-	-	132 200	-	42	126	145
(UP) $\text{Fe}/\alpha\text{-Al}_2\text{O}_3$	2	457	16	130 105	188	< dl	< dl	392
(Na-S) $\text{Fe-Na-S}/\alpha\text{-Al}_2\text{O}_3$	2	446	22	137 297	203	< dl	5 268	1 184

< dl - Below detection limit.

(-) - Not determined.

materials' subsequent FTS reaction performance (**Figure 5.1**). The Fe phases present in the catalyst materials before and after the FTS reaction are quantified by applying Rietveld Quantitative Phase Analysis (R-QPA) on the ex-situ measured XRPD patterns on the catalysts. The reaction performances of the catalysts under study are then correlated to the quantified Fe phases, and especially to the Fe carbide subtypes defined by their crystal lattice parameters. Additionally, Fe phases' crystallite diameters are also determined with the R-QPA. Transmission Electron Microscopy (TEM) is applied to obtain the Fe particle mean diameters and catalyst morphology for the studied catalyst materials. Quasi-In-situ Transmission Mössbauer Absorption Spectroscopy (MAS) is also applied as a complementary characterization technique for verifying some of the R-QPA-based Fe phase identification results on the studied catalyst materials.

5.2 EXPERIMENTAL METHODS

5.2.1 Catalyst Preparation

5.2.1.1 Catalyst Synthesis

Supported catalyst materials with a nominal 15 weight percent (wt-%) Fe loading, with and without added Na-S promotion, were prepared using Incipient Wetness Impregnation (IWI) method on alpha-alumina ($\alpha\text{-Al}_2\text{O}_3$) support material (BASF, 7 m²/g, 212-425 μm particle size). The impregnation solution was prepared using Fe(III) nitrate nonahydrate (Acros, 423710030) as Fe precursor, Fe(II) sulfate heptahydrate (Merck, 103965) as S precursor and Na tribasic citrate dihydrate (Sigma-Aldrich, S4641) as Na precursor. Inductively Coupled Plasma Optical Emission Spectrophotometry (ICP-OES) was used for elemental analysis of the Fe precursor Fe(III) nitrate nonahydrate (**Table 5.1**).

The precursor solution used for the preparation of the Na-S promoted catalyst material was prepared to a glass vial by individually solvating 3.823 g of Fe, 0.272 g of S and 0.941 g of Na precursors to 0.8 ml of demineralized water. The precursor solution for the unpromoted catalyst material was prepared only with 3.833 g of the Fe precursor. Any insoluble crystals were dissolved by heating the closed precursor solution containing glass vial at 60°C for few minutes. The catalyst materials nominal weight loadings for the added Na and S promoters were 0.62 wt-% Na and 0.09 wt-% S.

3.00 g of the α -Al₂O₃ support material was placed to a round-bottom boiling flask with a magnetic stirring rod. In three sequential impregnation steps, $\approx$ 1.0 ml, $\approx$ 0.8 ml and $\approx$ 0.7 ml of the precursor solution was dropwise added on the α -Al₂O₃ support with a syringe. The α -Al₂O₃ support material was simultaneously stirred with the magnetic rod. Each impregnation step was followed by drying the impregnated α -Al₂O₃ support at 120°C, for at least 4 h. The precursor solution containing glass vial was washed with $\approx$ 0.1 ml of demineralized water within the last impregnation step. After each drying step, any catalyst particle aggregates formed were gently broken down with a mortar. In case of any precursor recrystallization and precipitation taking place in between the impregnation steps, the precursor solution was heated to 60°C for few minutes for dissolving the appeared crystals. The impregnation procedure was individually repeated twice for both unpromoted and Na-S promoted catalyst materials. After their final drying steps, the prepared unpromoted and Na-S promoted catalyst batches were respectively combined.

5.2.1.2 Catalyst Calcining

Catalyst material calcining was done under flowing air in an open quartz vessel by heating (10°C/min) the dried catalyst materials from room temperature to 500°C, and holding the temperature for 6 h. In order to avoid any gas diffusion limitations, the catalyst materials were calcined in batches of $\leq$ 3.0 g. Each calcining batch lost $\approx$ 3-4 % of its weight during the calcining step. The calcined catalyst materials were recombined within the unpromoted and Na-S promoted batches and re-sieved to a catalyst particle fraction of 212-425 μ m in order to obtain the ready, calcined catalyst materials. Results for the elemental ICP-OES analysis on the calcined catalyst materials are given in **Table 5.1**.

5.2.1.3 Catalyst Reduction

Reduction of the calcined catalyst materials was performed with use of a plug flow quartz reactor. For each reduction treatment, 1.0 g of calcined catalyst material was mixed with 5.0 g of SiC and the catalyst material/SiC mixture was loaded into the quartz reactor. The reactor was heated up (10°C/min) from room temperature to 350°C under N₂:H₂ flow (85:165 ml/min, at atmospheric pressure) and held at 350°C for 17 h. After

the reduction, the reactor was cooled down to room temperature under N₂:H₂ flow and subsequently flushed with N₂ for couple of hours to passivate the catalysts. The reduced catalyst material was removed from reactor and exposed to air. The catalyst material and SiC diluent were separated using a magnet. Both the H₂ and N₂ gas purities were Grade 5.0 (99.999 % pure) and were supplied by Linde Gas Benelux.

5.2.2 Catalyst Testing

A high-throughput Avantium Flowrence catalyst testing set-up with 16 parallel fixed bed reactors was used for testing the calcined only and the calcined and subsequently H₂ reduced catalyst materials in the FTS reactions.

The catalyst materials (≈ 25 mg, 212-425 μm) were diluted with SiC (≈ 125 mg, 212-425 μm). The resulting catalyst material/SiC mixtures were loaded into stainless steel reactor tubes with an inner diameter of 2 mm, giving catalyst beds with heights within ≈ 31 -33 mm. Each catalyst material/SiC mixture was loaded to two reactors for testing the data reproducibility. Two reactor tubes were loaded as blanks, one with the α -Al₂O₃ support material (212-425 μm) and the other one with the SiC (212-425 μm) diluent.

The FTS reactions were performed at 340°C, in separate 72 h runs with 3, 10 and 20 bar H₂:CO:He (1.0:1.0:0.2 volume ratio) total reaction pressure. Nominal input gas flows for each reactor were 4.0 ml/min H₂, 4.0 ml/min CO and 0.8 ml/min He giving gas hourly space velocity (GHSV, as total input gas flow per total catalyst bed volume) of $\approx 5\,500\text{ h}^{-1}$. The loaded reactors were heated up (2°C/min) under pure He flow from room temperature to 270°C. At 270°C, the reactor was pressurized with the H₂:CO:He gas mixture to the desired, 3, 10 or 20 bar FTS reaction total pressure. Upon reaching the reaction pressure, the reactor temperature was increased from 270°C to 340°C (2°C/min) to start the FTS reaction test run. After 72 h of the FTS reaction, the input gas flow was switched to pure He and the reactor temperature and pressure were lowered to ambient conditions. The spent catalyst material/SiC mixtures were removed from the reactor tubes and exposed to air. The catalyst materials were separated from the SiC diluent using a magnet. The used H₂ and He gas purities were grade 5.0 (99.999 % pure) and for CO grade 2.5 (99.5 % pure) gas was used.

On-line gas chromatography (GC) with Thermal Conductivity (TCD) and Flame Ionization Detector (FID) were used for analyzing the reactor outlet gas compositions. The on-line GC-based catalytic performance data analysis was performed in an identical manner to the analysis described in *Chapter 4*.

5.2.3 Catalyst Characterization

The catalyst materials collected after the 72 h FTS reaction were analyzed ex-situ with bright field TEM and XRPD. The term X-ray Powder Diffractometry (XRPD) is used to

refer to X-ray diffraction phenomena based characterization experiments that are done under powder diffraction conditions.⁴⁵ R-QPA was applied on the obtained XRPD patterns for crystalline Fe phase quantifications, i.e. for determining phase quantities, lattice parameters and crystallite diameters for each Fe phase. Fe particles counted from the TEM images were used for determining the Fe particle size distributions. The details for application of TEM, XRPD and R-QPA have been given earlier in **Chapter 3**.

With R-QPA, in addition to the technique application details in **Chapter 3**, residual SiC (#00-029-1129 and #00-029-1131) diffraction was fitted using the crystal structures from International Centre for Diffraction Data Powder Diffraction File-4+ 2016 database (ICDD-PDF-4+). The residual amounts of large SiC crystallites did not fully comfort to the random diffraction requirements for powder diffraction. That is, some SiC diffraction peaks were missing, were systematically shifted and/or appeared with enhanced intensity (i.e. “rocks-in-the-dust”).⁴⁶ Thus, preferential orientation correction (March-Dollase) was applied with the SiC structures and SiC lattice parameters were refined in an arbitrary manner to match the shifted SiC diffraction peak positions. Furthermore, additional, individual Lorentzian peaks were used to fit the SiC diffraction when needed. In addition, in some of the studied catalyst materials, diffraction peaks from crystallized hydrocarbons were identified with crystal lattice of n-heptacosane (#00-057-1555). The crystallized hydrocarbons were fitted with individual Lorentzian peaks, if needed.

5.2.3.1 Quasi-In-situ Mössbauer Absorption Spectroscopy

Quasi-In-situ Transmission ⁵⁷Fe MAS was performed with the Mössbauer spectra collected at liquid He temperature (4.2 K). A sinusoidal velocity spectrometer using a ⁵⁷Co(Rh) source was used. Velocity calibration was carried out using an α -Fe foil, at room temperature. The source and the absorbing catalyst materials were kept at the same temperature during the MAS measurements. The Mössbauer spectra were fitted using the Mosswinn 4.0 software.⁴⁷

In the Quasi-In-situ MAS experiments, all of the catalyst materials were reduced under H₂:Ar 2:1 flow at 350°C for 12 h. The applied FTS reaction conditions were 340°, 3 or 20 bar, H₂:CO 1:1 for 48 h. After the FTS reaction, the catalyst materials were cooled down from the reaction conditions to the liquid He temperature for collecting the Mössbauer spectra.

5.3 RESULTS AND DISCUSSION

Ex-situ XRPD has been applied for collecting X-ray diffraction patterns on Fe-based catalyst materials *before* and *after* their catalyst testing in the FTS reaction. The FTS

Table 5.2

Overview of the used shorthand notation within this Chapter. Nominal elemental loadings used for the catalyst materials are 15 wt-% of Fe and when added, 0.62 wt-% of Na and 0.09 wt-% of S promoters.

Shorthand Notation	Catalyst Material Description
Calcin.	Calcined in air at 500°C for 6 h
H ₂	H ₂ reduced at 350°C for 17 h, after the calcining step
UP	Unpromoted Fe/ α -Al ₂ O ₃ catalyst material
Na-S	Na-S promoted Fe-Na-S/ α -Al ₂ O ₃ catalyst material
Fresh	Catalyst material before the FTS reaction ("i.e. fresh catalyst")
3, 10, 20 bar	Catalyst material after the 72 h 340°C FTS reaction with the indicated reaction pressure ("i.e. spent catalyst")

reactions were performed at different reaction pressures of 3, 10 or 20 bar (340°C, H₂:CO:He 1.0:1.0:0.2, GHSV 5 500 h⁻¹). R-QPA was employed on the XRPD patterns for quantifying the Fe phases present in the catalyst materials. This approach has been applied on both unpromoted Fe/ α -Al₂O₃ (shorthand *UP*) and the Na-S promoted Fe-Na-S/ α -Al₂O₃ (*Na-S*) catalyst materials. These catalyst materials have been either only calcined (*Calcin.*) or also H₂ reduced (*H₂*) prior to the FTS reactions. The catalyst materials FTS reaction performance has been correlated to the characterization results. This has been done, by systematically comparing the catalysts' FTS reaction performance on the changes in the Fe carbide subtypes, which are defined by their distinct crystal lattice parameters.

For catalyst material characterizations done before the FTS reaction, shorthand notation *Fresh* is used. The shorthand notation *3, 10* or *20 bar* is used for indicating a

Figure 5.2

Transmission Electron Microscopy (TEM) images for the Na-S (Fe-Na-S/ α -Al₂O₃) catalyst materials before the Fischer-Tropsch Synthesis (FTS) reaction (*Fresh*). Images after a) calcining (*Calcin.*) and b) H₂ reduction (*H₂*) treatments for the catalyst materials.

Figure 5.3

Transmission Electron Microscopy (TEM) images for the Na-S (Fe-Na-S/ α -Al₂O₃) catalyst materials after 72 h Fischer-Tropsch Synthesis (FTS) reactions. Images for calcined only (Calcin.) catalyst materials after a) 3 bar, c) 10 bar and e) 20 bar FTS reaction. Images for H₂ reduced (H₂) catalysts after b) 3 bar, d) 10 bar and f) 20 bar FTS reaction.

Figure 5.4

Transmission Electron Microscopy (TEM)-based, Fe particle size distribution derived values for UP and Na-S (Fe(-Na-S)/ α -Al₂O₃) catalyst materials. Fe particle (number-weighted) mean diameters for a) calcined only (Calcin.) and c) H₂ reduced catalysts (H₂), before (Fresh) and after the 72 h Fischer-Tropsch Synthesis (FTS) reactions (3, 10, 20 bar). Corresponding size distribution Standard Deviations (STDs) for b) Calcin. and d) H₂ catalyst materials.

FTS reaction spent catalyst material and the applied reaction pressure. The overview of the shorthand notations used in this Chapter is given in the **Table 5.2**.

The catalysts used in this Chapter have been prepared using a *Fe nitrate precursor*, in comparison to the use of *Fe citrate precursor* in other Chapters. Differences in the FTS reaction performance of catalyst materials prepared with the nitrate and citrate precursors by impregnating the α -Al₂O₃ support have been studied earlier by Torres Galvis et al.⁴⁸

5.3.1 Morphological Changes Probed with Transmission Electron Microscopy

TEM images of the Na-S Calcin. and H₂ Fresh catalyst materials before FTS reaction are given in **Figure 5.2**. The TEM images taken after the Na-S Calcin. and H₂ catalyst materials' use in the 72 h FTS reaction at 3, 10 or 20 bar are in turn given in **Figure 5.3**. The TEM images for the UP catalyst materials are not shown, as they did not differ in their morphology from their respective Na-S catalyst material counterparts. The TEM-based particle size distribution derived Fe particle number-weighted mean diameters with their respective size distribution Standard Deviations (STDs) for the UP and Na-S catalyst materials before (Fresh) and after (3, 10 or 20 bar) FTS reaction are given in **Figure 5.4**.

The Fe particles in the Na-S (and UP) catalyst materials before the FTS reaction are as clusters of Fe particles rather than as individual particles on the α -Al₂O₃ support material (**Figure 5.2**). With regard to the catalyst morphologies observed with TEM after the 3, 10 or 20 bar FTS reaction: in all of the Na-S (and UP) catalyst materials the Fe particles capsulated in carbon and have grown off from the α -Al₂O₃ support (**Figure 5.3**). These TEM results are analogous with observations in **Chapter 4**, and with observations in literature for the used catalyst type.⁴⁹

With increasing reaction pressure, for Na-S catalyst materials the Fe particle mean diameters and size distribution STDs increase in comparison to the respective UP catalysts (**Figure 5.4**). This behavior takes place irrespective to the catalyst materials prior Calcin. or H₂ treatment. Similarly, after 4 h FTS reaction (340°C, 20 bar, H₂:CO (1:1) Na-S promotion induced Fe particle growth has been observed in the literature.⁵⁰ The precise reasons for this possible Na-S promotion induced Fe particle growth are not clear. Nevertheless, the particle growth does have a reaction pressure dependency (**Figure 5.4**).

5.3.2 Phase Quantification with X-ray Powder Diffractometry/Rietveld Quantitative Phase Analysis

The background corrected, ex-situ measured XRPD and Rietveld method calculated diffraction and difference patterns are given in **Figure 5.5** for the UP and Na-S, Calcin. and H₂ Fresh catalyst materials. The diffraction patterns for the catalyst materials measured after their application in the 72 h FTS reaction at reaction pressures of 3, 10 or 20 bar, are given in **Figure 5.6** for the UP, and in **Figure 5.7** for the Na-S catalyst materials. Only the diffraction pattern range of 13-29° 2 θ (Mo K α) is visualized but the R-QPA fittings were done over the full XRPD measurement range of 6-39° 2 θ .

The XRPD diffraction pattern derived R-QPA Fe phase quantification results for the crystalline Fe phases and the R-QPA derived elemental Fe loadings are given in **Figure 5.10**. The R_{wp}-values for all of the R-QPA fits are given in **Figure 5.8**.⁵¹ R-QPA determined Fe phase (volume-weighted) crystallite mean diameters are given in **Figure 5.9**. A detailed discussion on the Fe phase crystallite diameters is omitted in this Chapter.

The Rietveld method calculated diffraction patterns represent the measured XRPD patterns in overall well, for all of the studied catalyst materials, both before (**Figure 5.5**) and after the FTS reactions for all of the UP (**Figure 5.6**) and Na-S catalyst materials (**Figure 5.7**). That is, it is unlikely that any significant Fe phases are missing from the R-QPA Fe phase quantifications in **Figure 5.10**.

However, for all of the UP and Na-S Calcin. catalyst materials, systematic misfits in the calculated relative diffraction peak intensities for the χ -Fe₅C₂ phase could be

Figure 5.5

Background corrected, ex-situ measured X-ray Powder Diffractometry (XRPD) and Rietveld method calculated diffraction patterns over a range 13-29° 2θ for UP and Na-S (Fe(-Na-S)/α-Al₂O₃) catalyst materials before the Fischer-Tropsch Synthesis (FTS) reaction (Fresh). Diffraction patterns for calcined only (Calcin.) a) UP and b) Na-S, and for H₂ reduced (H₂) c) UP and d) Na-S catalyst materials. Normalized counts on a square-root scale.

observed. Examples of these misfits are marked with * for phases in UP (**Figure 5.6a, c, e**) and Na-S catalysts (**Figure 5.7a, c, e**). The misfits will be discussed more later on; when the χ -Fe₅C₂ phase crystal lattice changes are discussed. Furthermore, imperfect fitting of large crystallite SiC residue phases caused large R_{wp} -values for the UP Calcin. 3, 10 and 20 bar catalyst materials, as well as for the UP H₂ 10 bar catalyst material (**Figure 5.8**).

Each of the FTS reaction used catalysts' duplicate reactors were also measured with XRPD and quantified with R-QPA. The results (data not shown) were well comparable to the Fe phase quantification results in **Figure 5.10**.

Figure 5.6

Background corrected, ex-situ measured X-ray Powder Diffractometry (XRPD) and Rietveld method calculated diffraction patterns over a range 13-29° 2 θ for UP (Fe/ α -Al₂O₃) catalysts after 72 h Fischer-Tropsch Synthesis (FTS) reaction (3, 10, 20 bar). Calcined catalysts (Calcin.) after a) 3 bar, c) 10 bar and e) 20 bar, and H₂ reduced (H₂) after b) 3 bar, d) 10 bar and f) 20 bar FTS reaction. Peak intensity misfit (*) for χ -Fe₅C₂ phase. Normalized counts on a square-root scale.

Figure 5.7

Background corrected, ex-situ measured X-ray Powder Diffraction (XRPD) and Rietveld method calculated diffraction patterns over a range 13-29° 2θ for Na-S (Fe-Na-S/ $\alpha\text{-Al}_2\text{O}_3$) materials after 72 h Fischer-Tropsch Synthesis (FTS) reaction (3, 10, 20 bar). Calcined catalysts (Calcin.) after a) 3 bar, c) 10 bar and e) 20 bar and H_2 reduced (H_2) after b) 3 bar, d) 10 bar and f) 20 bar FTS reaction. Peak intensity misfit (*) for $\chi\text{-Fe}_5\text{C}_2$ phase. Normalized counts on a square-root scale.

Figure 5.8

R_{wp}-values for the differences between the X-ray Powder Diffractometry (XRPD) measured and Rietveld method calculated diffractograms, for calcined only (Calcin.) and H₂ reduced catalysts (H₂), before (Fresh) and after the 72 h Fischer-Tropsch Synthesis (FTS) reactions (3, 10, 20 bar). R_{wp}-values for UP and Na-S (Fe(-Na-S)/ α -Al₂O₃) catalyst materials a) without and b) with diffraction pattern background correction.

The R-QPA crystalline Fe phase quantification derived elemental Fe wt-%s vary somewhat: the average Fe wt-%s with STDs are 13.2 ± 2.1 wt-% over all of the UP catalysts and 14.2 ± 2.4 wt-% over all of the Na-S catalysts materials (**Figure 5.10c, f**).

The high STDs for the elemental Fe wt-%s can be taken as an indication of some inaccuracy in the R-QPA Fe phase quantifications. This is, likely, mainly due to the interference from the residual SiC content and a rather complex diffraction pattern background.

However, the identified Fe phases present in the R-QPA quantifications are correct as the diffraction peaks were well accounted for in the quantified XRPD patterns. Whether any elemental Fe was lost from any of the catalyst materials during the FTS reactions, cannot reliably be deduced from the R-QPA quantification results for the studied catalyst materials.

5.3.2.1 Crystalline Fe Phase Quantifications

For the UP and Na-S Calcin. Fresh catalyst materials, the only Fe phase present is α -Fe₂O₃ (hematite), as would be expected after a calcining treatment (**Figure 5.10a-b**). Both, the UP and Na-S H₂ Fresh catalyst materials exhibit α -Fe as the major phase (64-68 %), with some oxidic Fe as Fe₃O₄ (magnetite) and Fe_{0.974}O (wüstite) also present (**Figure 5.10d-e**). Alkali stabilizes the Fe_{0.974}O phase,⁵² explaining its presence in the Na-S H₂ Fresh catalyst material. The presence of Fe_{0.974}O in the UP H₂ Fresh catalyst material might indicate occurrence of some impurities, e.g. the alkali or Si,^{52,53} stabilizing the Fe_{0.974}O phase.

With regard to the crystalline Fe phases in the catalysts' Fe phase compositions after the FTS reactions, three Fe carbide phases can be quantified: η -Fe₂C *Pnnm* (58), χ -Fe₅C₂

Figure 5.9

Rietveld Quantitative Phase Analysis (R-QPA) determined Fe phase (volume-weighted) crystallite mean diameters before (Fresh) and after 72 h Fischer-Tropsch Synthesis (FTS) reactions (3, 10, 20 bar). Crystallite diameters for UP ($\text{Fe}/\alpha\text{-Al}_2\text{O}_3$) catalyst materials with a) calcining only (Calcin.) and c) H_2 reduction (H_2), and for Na-S ($\text{Fe-Na-S}/\alpha\text{-Al}_2\text{O}_3$) materials after b) Calcin. and d) H_2 treatments.

C2/c (15) (the Hägg carbide) and $\theta\text{-Fe}_7\text{C}_3$ $Pnma$ (62) (the Eckström-Adcock carbide) (**Figure 5.10a-b, d-e**). The identification and nomenclature of the Fe carbide phases is discussed in detail in **Chapter 2**.

After the 3 bar FTS reaction, only the $\chi\text{-Fe}_5\text{C}_2$ phase is detected as a Fe carbide and as the sole Fe phase regardless of the Na-S promotion or the Calcin. or H_2 catalyst treatments (**Figure 5.10a-b, d-e**). After 10 bar FTS reaction, the addition of Na-S promotion induces the appearance of the $\eta\text{-Fe}_2\text{C}$ alongside the $\chi\text{-Fe}_5\text{C}_2$ phase. The Na(-S) promotion's $\eta\text{-Fe}_2\text{C}$ phase stabilizing effect in the FTS reaction is in agreement to “ ϵ -carbide” (i.e. $\eta\text{-Fe}_2\text{C}$) stabilizing alkali effect observations in literature.^{16,32,54} The expected maximum thermal stability for the $\eta\text{-Fe}_2\text{C}$ phase is $\lesssim 300^\circ\text{C}$ (**Chapter 3**), but with the applied Na-S promotion, the stability is increased, at least, to the used FTS reaction temperature of 340°C .

In the Na-S Calcin. 10 bar catalyst material the $\eta\text{-Fe}_2\text{C}$ phase contribution is higher

Figure 5.10

Rietveld Quantitative Phase Analysis (R-QPA) Fe phase quantifications before (Fresh) and after 72 h Fischer-Tropsch Synthesis (FTS) reactions (3, 10, 20 bar) for calcined only (Calcin.) and H₂ reduced (H₂) catalyst materials. Crystalline Fe phase fractions for UP (Fe/ α -Al₂O₃) a) Calcin. and d) H₂, and for Na-S (Fe-Na-S/ α -Al₂O₃) b) Calcin. and e) H₂ catalyst materials. The elemental Fe wt-% loadings on basis of the crystalline Fe phases for c) Calcin. and f) H₂ materials. Percentage labels cut-off is set to <10 %.

(46 %) than in the Na-S H₂ 10 bar catalyst (27 %). That is, α -Fe₂O₃ as the FTS reaction and carburization starting material favors the formation or the FTS reaction stability of the η -Fe₂C phase. As no η -Fe₂C stabilizing effect with the Na-S addition is observed for the 3 bar FTS catalyst materials (**Figure 5.10a-b, d-e**): a >3 bar FTS reaction pressure is needed, for an unknown reason, for observing the η -Fe₂C phase stabilization effect by Na-S promotion addition. The η -Fe₂C phase's stability dependency on the FTS reaction pressure and Na-S promotion was also observed with R-QPA independent Quasi-In-situ MAS measurements (**Table 5.3**).

It is worthy to emphasize the perfect fit of the Rietveld method calculated η -Fe₂C phase in the XRPD patterns of the Na-S Calcin. 10 bar catalyst material (**Figure 5.7c**). Thus, the crystal structure solution by Hirotsu and Nagakura is a very good one for the

Table 5.3

Quasi-In-situ Mössbauer Absorption Spectroscopy (MAS) fitted parameters for the UP and Na-S (Fe-(Na-S)/ α -Al₂O₃) catalyst materials. Catalyst reduction (H₂) was done at 350°C for 12 h under H₂:Ar 2:1. Fischer-Tropsch Synthesis (FTS) reaction conditions of 340°C, 3 or 20 bar, H₂:CO 1:1 for 48 h, were used. MAS measurements were done at the liquid He temperature (4.2 K).

Treatment	Isomer Shift	Quadrupole Splitting	Hyperfine Field	Line Width	Phase	Spectral Contribution
	(mm s ⁻¹)	(mm s ⁻¹)	(T)	(mm s ⁻¹)		(%)
UP H ₂	0.24	-0.03	50.8	0.41	Fe ₃ O ₄ (I)	36
	0.54	0.04	51.7	0.60	Fe ₃ O ₄ (II)	31
	0.84	-0.74	48.0	0.60	Fe ₃ O ₄ (III)	16
	0.77	0.84	41.1	0.60	Fe ₃ O ₄ (IV)	8
	1.04	-0.01	46.7	0.60	Fe ₃ O ₄ (V)	9
UP H ₂	0.26	-	25.6	0.39	χ -Fe ₅ C ₂ (I)	41
3 bar	0.16	-	21.5	0.50	χ -Fe ₅ C ₂ (II)	37
	0.20	-	12.9	0.48	χ -Fe ₅ C ₂ (III)	22
UP H ₂	0.24	-	25.4	0.39	χ -Fe ₅ C ₂ (I)	40
20 bar	0.18	-	22.0	0.52	χ -Fe ₅ C ₂ (II)	38
	0.19	-	13.5	0.56	χ -Fe ₅ C ₂ (III)	22
Na-S H ₂	0.00	-	34.2	0.34	Fe ⁰	100
Na-S H ₂	0.24	-	25.4	0.61	χ -Fe ₅ C ₂ (I)	44
3 bar	0.17	-	21.0	0.61	χ -Fe ₅ C ₂ (II)	33
	0.13	-	12.8	0.61	χ -Fe ₅ C ₂ (III)	23
Na-S H ₂	0.26	-	18.3	0.35	η -Fe ₂ C	60
20 bar	0.27	-	25.7	0.43	χ -Fe ₅ C ₂ (I)	17
	0.19	-	20.7	0.44	χ -Fe ₅ C ₂ (II)	13
	0.22	-	10.1	0.41	χ -Fe ₅ C ₂ (III)	10

Experimental uncertainties: Isomer Shift ± 0.02 mm s⁻¹, Quadrupole Splitting ± 0.02 mm s⁻¹, Line Width ± 0.03 mm s⁻¹, Hyperfine Field ± 0.1 T, Spectral Contribution ± 3 %.

carbide.^{55,56} The η -Fe₂C phase corresponds to the “pseudo-hexagonal Fe carbide” observed by Barton and Gale in a Fe-based catalyst material after the FTS reaction.^{57,58}

After the 20 bar FTS reaction, the η -Fe₂C is present with the χ -Fe₅C₂ phase for both Na-S Calcin. and Na-S H₂ catalyst materials. Thus, the η -Fe₂C phase’s presence after the FTS reaction again requires the added Na-S promotion (**Figure 5.10a-b, d-e**). Intriguingly, in the Na-S Calcin. 20 bar catalyst material; a small amount (8 %) of the rare θ -Fe₇C₃ phase is quantified (**Figure 5.10b**). This observation is interesting, as the θ -Fe₇C₃ phase only appears with the Na-S promoted catalyst material but not with the respective unpromoted UP Calcin. 20 bar catalyst.

In **Chapter 3**, with CO carburization of an initial α -Fe₂O₃(/ α -Al₂O₃) Fe phase at 25 bar, the Na-S promotion *was not required* for the formation of the θ -Fe₇C₃ phase. The θ -Fe₇C₃ phase formed from the oxide precursor regardless of the Na-S promotion. In a comparable manner to the Na-S addition requirement, Tajima and Hirano observed

formation of θ -Fe₇C₃ with CO carburization of Ba promoted Fe₃O₄. However, without Ba, no θ -Fe₇C₃ phase was formed.⁵⁹ As a similarity to the results in **Chapter 3**, only the Na-S Calcin. catalyst material forms any of the θ -Fe₇C₃ phase. That is, a Fe oxide precursor is required for the θ -Fe₇C₃ phase formation also in this Chapter. The topic of the θ -Fe₇C₃ phase formation is more thoroughly discussed in **Chapter 3**. Nevertheless, the rare θ -Fe₇C₃ phase may form under the relatively mild 20 bar FTS reaction conditions applied in this Chapter, and use of an industrial scale FTS reactor is not required.⁴

Moreover, after the 20 bar FTS reaction, the UP and Na-S Calcin. catalyst materials exhibit significant amounts of Fe₃O₄. In contrary, the Fe₃O₄ phase is absent from the H₂ reduced, UP and Na-S H₂ 20 bar catalyst materials (**Figure 5.10a-b, d-e**). In the 20 bar FTS reaction, the initial α -Fe₂O₃ ($/\alpha$ -Al₂O₃) phase may not be fully reduced to zerovalent α -Fe but converts to Fe₃O₄ at the FTS reaction temperature, and thus is not subsequently fully carburized. A possible explanation could be in mass transport limitations. With the 20 bar FTS reaction pressure and the used H₂:CO 1:1 ratio, the likely high initial inactive carbon deposition for the catalyst,⁴⁹ might prevent the diffusion of the reducing H₂:CO atmosphere into the inner parts of the catalyst particles. Alternatively, carbon deposition might create preferential flows to the catalyst bed preventing parts of it being reduced.

Fe carbide reoxidation by the oxidative H₂O from the FTS reaction or by CO₂ from the Water-gas Shift (WGS) reaction,^{4,16,36,54,60-65} is not a plausible explanation for the Fe₃O₄ formation in the UP and Na-S Calcin. 20 bar catalyst materials. The UP and Na-S H₂ 20 bar catalyst materials have higher or equal Fe Time Yields (FTYs) (**Figure 5.13**), Usage Ratios H₂:CO (**Figure 5.14b**) and CO₂ selectivities (**Figure 5.15e**) in comparison to the UP and Na-S Calcin. 20 bar catalysts. Thus, all of the H₂ and Calcin. 20 bar catalysts have comparable H₂O and CO₂ concentrations in the reactor gas atmosphere. Despite this, the H₂ 20 bar catalyst material does not show any signs of Fe₃O₄ as a carbide reoxidation product (**Figure 5.10d-e**). The catalytic performance results for the studied catalyst materials will be discussed more in a later section.

The addition of elements from the alkali metal group, e.g. as in Na-S promotion, increases the Fe oxides reducibility by CO at low temperatures ($\approx 270^\circ\text{C}$).⁶⁶ In the Na-S Calcin. 20 bar catalyst (**Figure 5.10a-b**): a lesser amount of Fe₃O₄ (27 %) observed in comparison to Fe₃O₄ (46 %) in the UP Calcin. 20 bar catalyst material. This can be explained by more efficient α -Fe₂O₃ ($/\text{Fe}_3\text{O}_4$) low temperature reduction upon the catalyst exposure to the reducing H₂:CO mixture at 270°C, when the reactor is pressurized for the FTS reaction (*Experimental methods*). When the reactor temperature is ramped to $\geq 300^\circ\text{C}$, inactive carbon deposition becomes significant,^{4,30,67,68} and possible mass transportation limitations for the H₂:CO gas

mixture might begin to appear, therefore hindering Fe phases reduction.

Before moving on, the discussion on the Fe phase quantifications so far can be summarized as: i) Na-S promotion stabilizes the η -Fe₂C phase when FTS reaction pressure ≥ 10 bar is applied, while after 3 bar FTS reaction, no η -Fe₂C phase was present regardless of the Na-S promotion; ii) the θ -Fe₇C₃ phase could only be observed in the Na-S Calcin. 20 bar catalyst material; and iii) only in UP and Na-S Calcin. 20 bar catalyst materials could Fe₃O₄ be observed. The presence of Na-S promotion reduced the amount of the quantified Fe₃O₄ phase in the Calcin. 20 bar catalysts.

5.3.2.2 Fe Phase Lattice Changes

As discussed in **Chapter 4**, both of the η -Fe₂C and χ -Fe₅C₂ phases can be categorized by their crystal lattice parameter a 's into different carbide subtypes. The lattice parameters used for the R-QPA fits for the η -Fe₂C and χ -Fe₅C₂ phases within the current Chapter are given in **Figure 5.11** (for η -Fe₂C) and **Figure 5.12** (for χ -Fe₅C₂). Markers for the carbide subtype defining lattice parameter a 's are included in the figures. For the single observation of the θ -Fe₇C₃ phase in the Na-S Calcin. 20 bar catalyst material, lattice parameters of a : 4.537 ± 0.007 Å, b : 6.900 ± 0.016 Å and c : 11.910 ± 0.030 Å were used, where the value after $\pm$ is the R-QPA fit error estimate.

For the η -Fe₂C phase, which was only observed in the presence of the added Na-S promotion, the lattice parameters a are close to the η -Fe₂C Type II for both the Calcin. and H₂ catalyst materials (**Figure 5.11a**). The η -Fe₂C Type II (a : 4.86 ± 0.01 Å, b : 4.35 ± 0.00 Å, c : 2.76 ± 0.01 Å, with STDs) is expected to form in the FTS reaction with Na-S promotion, while the Type I (a : 4.84 ± 0.01 Å, b : 4.35 ± 0.00 Å, c : 2.76 ± 0.00 Å) is expected to form under CO carburization regardless of the Na-S promotion (**Chapter 4**). Thus, as would be expected, only a η -Fe₂C Type II carbide is observed after the FTS reactions (**Figure 5.11a**). The lattice parameters for the η -Fe₂C Type II correspond to the “pseudo-hexagonal Fe carbide” observed by Barton and Gale,⁵⁷ with lattice parameters defined by Hirotsu and Nagakura (a : 4.862 Å, b : 4.360 Å, c : 2.755 Å).⁵⁶

Although, after the 10 bar FTS reaction for both Na-S Calcin. and Na-S H₂ catalyst materials, the lattice parameter a is larger (a : 4.88 ± 0.00 Å, with STD) than what would be expected for the η -Fe₂C Type II (**Figure 5.11a**). As mentioned before, the Rietveld method calculated η -Fe₂C phase pattern is especially well fitting to the XRPD pattern for the Na-S Calcin. 10 bar material (**Figure 5.7c**). The larger lattice parameter a is therefore not due to inaccurate peak position fit. We shall take the η -Fe₂C phase with the larger lattice parameter a of 4.88 ± 0.00 Å as a member of the subtype Type II i.e. the η -Fe₂C subtype forming in the FTS reaction in the presence of Na-S promotion.

The χ -Fe₅C₂ phase lattice parameter a changes largely follow the carbide phase's subtype expectations set in **Chapter 4** (**Figure 5.12a**). Type I (a : 11.56 ± 0.01 Å, b :

Figure 5.11

The lattice parameters used in Rietveld Quantitative Phase Analysis (R-QPA) for the η -Fe₂C phase compared for Na-S (Fe-Na-S/ α -Al₂O₃), calcined only (Calcin.) and H₂ reduced (H₂), catalyst materials after 72 h Fischer-Tropsch Synthesis (FTS) reactions (3, 10, 20 bar). Lattice parameters *a*, *b*, and *c* in a), b) and c), respectively. Lattice parameters *a* for the η -Fe₂C subtypes I-II, as defined in **Chapter 4**, are also marked in a). No η -Fe₂C formed during the FTS reactions without Na-S promotion.

4.57±0.01 Å, *c*: 5.06±0.00 Å) forms in the FTS reaction (or via CO carburization) *without* Na-S promotion. *Type II* (*a*: 11.58±0.00 Å, *b*: 4.58±0.00 Å, *c*: 5.05±0.00 Å) forms in the FTS reaction *with* Na-S promotion. Moreover, *Type III* (*a*: 11.61±0.01 Å, *b*: 4.58±0.00 Å, *c*: 5.05±0.01 Å) forms in the FTS reaction (or via CO carburization) if a Fe oxide (α -Fe₂O₃) is used as the initial carburizing Fe phase *regardless* of the Na-S promotion. As observable discrepancies on the χ -Fe₅C₂ subtype formation (**Figure 5.12**): i) with catalyst Na-S H₂ 3 bar, χ -Fe₅C₂ Type I is formed instead of the expected Type II and ii) χ -Fe₅C₂ Type III lattice distortion increases with increasing FTS reaction pressure with the UP and Na-S Calcin. catalyst materials.

First, as was the case for the Na-S promotion induced formation of the η -Fe₂C phase – the phase was not observed after 3 bar FTS reaction (**Figure 5.10**) – the Na-S promotion requiring χ -Fe₅C₂ Type II also requires higher than 3 bar FTS reaction pressure to form (**Figure 5.12a**). After 3 bar FTS reaction, only the χ -Fe₅C₂ Type I is observed, regardless of the Na-S promotion. This is rather interesting, as will be discussed more in the next section when the catalytic performance data is treated, but shortly: Na-S H₂ 3 bar catalyst is only meagerly active in the FTS reaction while the Na-S H₂ 10 bar catalyst shows a significantly higher FTY. The FTS activity increase coincides with χ -Fe₅C₂ subtype transition from Type I to Type II (**Figure 5.12a**). The crystal lattice change results point towards that Na-S promotion induced formation of χ -Fe₅C₂ Type II is a FTS reaction pressure dependent phenomena, akin to the stabilization and appearance of the η -Fe₂C phase.

Figure 5.12

The lattice parameters used in Rietveld Quantitative Phase Analysis (R-QPA) for the χ -Fe₅C₂ phase compared for UP and Na-S (Fe(-Na-S)/ α -Al₂O₃), calcined only (Calcin.) and H₂ reduced (H₂), catalyst materials after 72 h Fischer-Tropsch Synthesis (FTS) reactions (3, 10, 20 bar). Lattice parameters *a*, *b*, and *c* in a), b) and c), respectively. Lattice parameters *a* for χ -Fe₅C₂ subtypes I-III, as defined in **Chapter 4**, are also marked in a).

The formation of χ -Fe₅C₂ Type III by carburizing a Fe oxide has been explained, possibly, to be due to the retained O atoms in the χ -Fe₅C₂ lattice causing lattice distortion.³⁰ The χ -Fe₅C₂ Type III forms for all of the Calcin. catalyst materials tested in the FTS reactions, regardless of the Na-S promotion or the applied FTS reaction pressure (**Figure 5.12a**). The systematic shift in the most intense diffraction peak position for the χ -Fe₅C₂ phase in Calcin., in comparison to H₂, 3, 10 and 20 bar catalyst materials is clear (**Figure 5.6** and **Figure 5.7**). This peak shift is quantified as the change, especially, in the crystal lattice parameter *a*'s for the χ -Fe₅C₂ phase (**Figure 5.12a**).

The lattice parameter *a* increases for the χ -Fe₅C₂ phase in the Calcin. catalyst materials, in a nearly linear fashion, with the applied FTS reaction pressure (**Figure 5.12a**). In the earlier section, mass transfer limitations due to inactive carbon formation were offered as a possible explanation for the appearance of the Fe₃O₄ phase with the UP and Na-S Calcin. 20 bar catalysts (**Figure 5.10a-b**). Thus, perhaps, the fundamental origins of the increasing χ -Fe₅C₂ Type III lattice parameter *a* and the appearance of Fe₃O₄ with the 20 bar FTS reaction are the same. Increasing carbon deposition with increasing reaction pressure,⁴⁹ inhibits the removal of the O atoms from the initial Fe oxide (α -Fe₂O₃/ α -Al₂O₃) lattice in the Calcin. catalyst materials. Thus possibly, the increasingly retained O atoms in the χ -Fe₅C₂ Type III lattice during its formation resulting in the progressively increasing lattice parameter *a*.

Besides the rather large lattice parameter *a* for the χ -Fe₅C₂ Type III in relation to the χ -Fe₅C₂ Types I and II, also the χ -Fe₅C₂ Type III crystal structure is systematically

distorted in comparison to the crystal structures matching the χ -Fe₅C₂ Types I and II. The χ -Fe₅C₂ crystal structure (monoclinic $C2/c$, 15) used in the R-QPA fitting was solved by Retief,²⁷ whose structure solution corresponds to the χ -Fe₅C₂ Type II (**Chapter 4**). By refining the lattice parameters during the R-QPA fitting: the χ -Fe₅C₂ Type III peak positions are correctly fitted (i.e. monoclinic space group $C2/c$, 15, is correct). However, the relative χ -Fe₅C₂ Type III diffraction peak intensities are systematically changed (i.e. the crystal structure is systematically distorted). As an example, in **Figure 5.6a, c, e** and in **Figure 5.7a, c, e**, systematic diffraction peak intensity misfits for the χ -Fe₅C₂ (Type III) phase plane (3 1 2) ($\approx 22.52^\circ$ Mo K α_1) are marked with * for all of the Calcin. catalyst materials. For all of the H₂ catalyst materials, no clear χ -Fe₅C₂ (Types I and II) phase diffraction peak intensity misfits are observable (**Figure 5.6b, d, f** and **Figure 5.7b, d, f**). Further work for solving a more accurate crystal structure for the χ -Fe₅C₂ Type III should be performed. Diffraction patterns obtained with monochromatic synchrotron radiation or electron diffraction should preferably be used for the work.

The Fe carbide lattice changes and the associated carbide subtype FTS reaction formation conditions can be summarized, in a following manner: i) η -Fe₂C Type II forms in the FTS reaction with reaction pressure ≥ 10 bar and added Na-S promotion, in both Calcin. and H₂ catalysts; ii) χ -Fe₅C₂ Type I forms in the FTS reaction with 3 bar pressure *regardless* of Na-S promotion in H₂ catalysts; iii) χ -Fe₅C₂ Type II requires ≥ 10 bar FTS reaction pressure with Na-S promotion for transition from χ -Fe₅C₂ Type I to Type II in H₂ catalysts; iv) χ -Fe₅C₂ Type III forms on all of the Calcin. catalysts in the FTS reaction *regardless* of Na-S promotion or the FTS reaction pressure. Moreover, iv) with increasing FTS reaction pressure (3 $\rightarrow$ 20 bar) the χ -Fe₅C₂ Type III lattice parameter a increases progressively in the Calcin. catalysts *regardless* of Na-S promotion. This observation is speculated to be due to increasingly retained O atoms in the χ -Fe₅C₂ Type III lattice from the initially carburizing α -Fe₂O₃ (α -Al₂O₃) phase.

5.3.3 Catalytic Performance

The catalytic performance results for the UP and Na-S, for both Calcin. and H₂ catalyst materials at the reaction pressures of 3, 10 or 20 bar are given in terms of FTY profiles in **Figure 5.13** over the 72 h FTS reaction runs. Median values for the FTYs, Usage Ratios H₂:CO and estimates for total CO to hydrocarbons (HC) conversion ratios are plotted in **Figure 5.14** for each of the studied catalyst for each applied FTS reaction pressure. The median CO₂ and CO₂-free hydrocarbon selectivities and C₂H₄/C₂H₆ (ethene/ethane) selectivity ratios for the catalyst materials at different reaction pressures are given in the **Figure 5.15**. Median Anderson-Schulz-Flory (ASF) distribution α -values are summarized in **Figure 5.16**. All of the catalytic performance median values are taken over Time-on-Stream (ToS) of 33-72 h, and plotted with their

Figure 5.13

Fe Time Yield (FTY) profiles for the UP and Na-S ($\text{Fe}(-\text{Na-S})/\alpha\text{-Al}_2\text{O}_3$), calcined only (Calcin.) and H_2 reduced (H_2) catalyst materials over the 72 h Fischer-Tropsch Synthesis (FTS) reactions. The FTS reaction FTY profiles with a) 3 bar, b) 10 bar and c) 20 bar reaction pressure. FTS conditions: 340°C , 3, 10 or 20 bar, $\text{H}_2:\text{CO}:\text{He}$ 1.0:1.0:0.2 v/v, $\approx 5\,500\text{ h}^{-1}$.

STDs as the error bars. The median values are also tabulated in **Table 5.4** for the FTS activity and in **Table 5.5** for FTS reaction selectivity results.

In the following, the FTS reaction activity results are first discussed with reflections on the characterization results. The activity dialogue is then followed with likewise remarks on the obtained FTS reaction selectivity data.

Discussion on the $\theta\text{-Fe}_7\text{C}_3$ phase is omitted, as only minor quantity (8 %) of the phase was formed with the Na-S Calcin. 20 bar catalyst material (**Figure 5.10b**). This amount is unlikely sufficient for playing any relevant role in the catalyst's FTS reaction performance.

5.3.3.1 Catalyst Activity

Assigning precise causality for the FTY profiles representing the catalytic activity over the course of the FTS reactions is a complex task. Such processes e.g. as $\geq 300^\circ\text{C}$ inactive carbon deposition,^{4,30,49,67,68} possible Fe particle diameter changes changing the available Fe surface area for the FTS reaction catalysis,^{50,69,70} and/or Fe phases carburization/reoxidation,^{4,16,36,54,60,63–65,69} can all affect the observed FTY profiles simultaneously. Also, depending on how the FTS reaction is initiated, the FTY profiles can be significantly affected.^{35,37} Thus, a comprehensive discussion on the FTY profile differences is challenging and not attempted in this Chapter in exhaustive detail. Nevertheless, few observations on the FTY profiles are worth a discussion.

The FTY profile developments of interest are (**Figure 5.13**): i) ≥ 10 bar FTS reaction pressure is required for a significant activity gain from the Na-S promotion, irrespective

Figure 5.14

Fischer-Tropsch Synthesis (FTS) activity values for UP and Na-S (Fe(-Na-S)/ α -Al₂O₃) calcined only (Calcin.) and H₂ reduced (H₂) catalyst materials with 3, 10 and 20 bar FTS reaction pressures. Median values with their Standard Deviations (STDs) over Time-on-Stream (ToS) 33-72 h for: a) Fe Time Yield (FTY), b) Usage Ratio H₂:CO and c) CO to hydrocarbons (HC) values. Missing values for UP 3 bar catalysts are omitted due to high STDs.

to the Calcin. and H₂ catalyst materials, ii) with 20 bar FTS reaction pressure, the UP catalysts gain a significant boost in their FTYs, irrespective to the Calcin. or H₂ treatments, iii) Na-S H₂ catalyst deactivates very fast with 20 bar FTS reaction pressure and iv) with 20 bar FTS reaction pressure, the H₂ catalysts give higher initial FTYs than the Calcin. catalyst materials, regardless of the Na-S promotion.

With the increase of the applied FTS reaction pressure from 3 to 10 bar, the Na-S Calcin. and H₂ catalyst materials gain significantly in their FTYs (**Figure 5.13a-b**). For the Na-S H₂ catalyst, the FTY boost coincides with transition from χ -Fe₅C₂ Type I to Type II (**Figure 5.12a**). For the Na-S Calcin. catalyst material, the χ -Fe₅C₂ Type III can also be associated to increased FTY when the FTS reaction pressure is at least 10 bar (**Figure 5.12a**). When the FTS reaction pressure is increased to 20 bar (**Figure 5.13c**): the χ -Fe₅C₂ Type I (UP H₂) and χ -Fe₅C₂ Type III (UP Calcin.), without Na-S promotion, can also be associated as active phases correlating with the increased overall FTYs for the catalysts. The Na-S promotion also results in stabilization of the η -Fe₂C Type II with ≥ 10 bar reaction pressure (**Figure 5.10b, e**). However, the presence of the η -Fe₂C Type II in the catalyst material does not correlate with FTYs: the η -Fe₂C (Type II) phase content is 46 % for Na-S Calcin. and 27 % for Na-S H₂ catalyst, after the 10 bar FTS reaction (**Figure 5.10b, e**). Despite this, the FTYs are virtually identical for the catalyst materials at the end of the FTS reaction runs (**Figure 5.13b**).

Thus, in simplified and succinct terms: the addition of Na-S promotion shifts the pressure threshold for increased FTY attainable in the FTS reaction to a lower reaction

pressure. Possibly, Na-S promotion i) might sensitize the χ -Fe₅C₂ Type III towards lower reaction pressure (20 → 10 bar) FTS reactivity and ii) aids in transition for χ -Fe₅C₂ Type I to Type II, where the Type II might possess properties for lower pressure (20 → 10 bar) FTS reaction activity. Without Na-S promotion, χ -Fe₅C₂ Type I and χ -Fe₅C₂ Type III require 20 bar FTS reaction pressure for significant catalytic activity in the FTS reaction. The presence of η -Fe₂C Type II phase does predict FTS reaction activity at any reaction pressure.

The increased FTYs for the UP catalyst materials with 20 bar FTS reaction pressure do not come for free. When the FTS reaction pressure is increased from 10 to 20 bar, the increase in the FTY values with the UP catalysts is also associated to both: decreases in the Usage Ratio H₂:CO and in CO to HC conversion estimate (**Figure 5.14**). The drop in Usage Ratio H₂:CO from ≈2 signifies CO consuming activity also from other reactions than the hydrocarbon producing FTS.^{7,8} This is agreed by CO to HC conversion estimate. That is, less CO is directed towards the FTS hydrocarbon production, decreasing the FTS reaction's C efficiency towards hydrocarbon production with UP catalysts at 20 bar FTS reaction.

Likewise, but already with lower 10 bar reaction pressure: the Na-S promotion decreases the Usage Ratio H₂:CO and thus CO to HC conversion (**Figure 5.14**). Na(-S)

Table 5.4

Median Fischer-Tropsch Synthesis (FTS) activity data over Time-on-Stream (ToS) 33-72 h for UP and Na-S (Fe(-Na-S)/ α -Al₂O₃) calcined only (Calcin.) and H₂ reduced (H₂) catalyst materials. Values after (±) are the Standard Deviations (STDs) of the median values.

Reaction Pressure	Catalyst	CO Conversion	Fe Time Yield (FTY)	Usage Ratio H ₂ :CO	CO to Hydrocarbons Na-S versus UP ^{a)}
		(%)	(10 ⁻⁴ mol _{CO} /g _{Fe-S})	(-)	(-)
3 bar	UP Calcin.	(0±0)	(0.02±0.03)	(1.6±2.5)	N/A
	UP H ₂	0±0	0.03±0.01	(1.4±0.9)	N/A
	Na-S Calcin.	0±0	0.04±0.02	1.1±0.7	(0.61±2.60)
	Na-S H ₂	1±0	0.08±0.02	1.1±0.2	(0.68±0.80)
10 bar	UP Calcin.	2±0	0.1±0.0	1.8±0.3	N/A
	UP H ₂	4±0	0.3±0.0	1.7±0.1	N/A
	Na-S Calcin.	45±5	3.5±0.4	0.6±0.0	0.44±0.24
	Na-S H ₂	49±6	3.9±0.5	0.6±0.0	0.47±0.08
20 bar	UP Calcin.	50±6	3.8±0.5	1.0±0.1	N/A
	UP H ₂	67±3	5.1±0.2	0.8±0.0	N/A
	Na-S Calcin.	36±3	2.8±0.3	0.6±0.0	0.67±0.04
	Na-S H ₂	37±10	2.9±0.8	0.6±0.0	0.79±0.02

FTS conditions: 340°C, 3, 10 or 20 bar, H₂:CO:He 1.0:1.0:0.2 v/v, ≈5 500 h⁻¹.

() – Values in parentheses are rough estimates due to high associated STDs.

a) Change in fraction of CO converted to hydrocarbons with addition of Na-S promotion (Na-S) versus the respective unpromoted (UP) catalyst materials.

promotion offers directly active sites for the WGS reaction,^{18,71,72} and/or increases the CO conversion to carbon deposits via the Boudouard reaction.⁴ All of the UP catalyst materials regardless of the reaction pressure convert larger fraction of CO to hydrocarbons than do the Na-S promoted catalysts (**Table 5.4** and **Figure 5.14c**).

The discussed changes in the Usage Ratios H₂:CO and in CO to HC conversions are accompanied by increased CO₂ selectivities for the Na-S 10 bar and 20 bar, and UP 20 bar catalyst materials (**Figure 5.15e**). The increased amount of consumed CO is converted to CO₂, and possibly to inactive carbon deposits on the catalysts, rather than to desired FTS hydrocarbon products.

No Fe₃O₄,^{61,62,73,74} or significant amounts of alkali (**Table 5.1**),^{12,18,71,72} is present with the UP H₂ 20 bar catalyst offering WGS active sites. CO₂ then predominantly likely comes from the increased Boudouard reaction for the catalyst material.^{4,30,49,67,68} For both UP Calcin. and H₂ 20 bar catalyst materials, the origins of the CO₂ are likely the same as the Usage Ratios H₂:CO, CO to HC conversion values (**Figure 5.14b-c**) and CO₂ selectivities are very similar between the catalysts (**Figure 5.15e**). This despite the presence of, but yet seemingly inaccessible as discussed earlier, WGS active Fe₃O₄ in the UP Calcin. 20 bar catalyst (**Figure 5.10a**).

The fast deactivation of the Na-S H₂ 20 bar catalyst has reminiscence to results by van Dijk et al. and Zhou et al., where fast initial drop in catalysts' FTS activity was remedied by added S.^{75,76} The remedying effect by S can be interpreted to be via a S poisoning effect, decreasing CO conversion and the initial catalyst bed heating and therefore the inactive carbon deposition.⁷⁷ For the Na-S H₂ 20 bar catalyst materials, thus, the initially high FTY possibly causes excessive reactor bed heating, deactivating the catalyst rather fast. The FTS initiation procedure for the Na-S H₂ 20 bar catalyst needs adjustment for attaining a more sustained FTS reaction activity.

As a final comment on the measured FTS reaction activity indicators, only with the 20 bar FTS reaction does the application of Calcin., in comparison to the H₂ catalysts, make a difference in case of both the Na-S and UP catalyst materials (**Figure 5.13**). In the 3 and 10 bar FTS reaction runs, the UP and Na-S Calcin. and H₂ catalyst materials behave FTS reaction activity-wise essentially the same within their respective promotion groups. In turn, when the H₂ catalysts are applied in the 20 bar FTS reaction run, both UP and Na-S catalysts show higher initial FTY values in comparison to the respective Calcin. catalyst materials applied in the 20 bar FTS reaction (**Figure 5.13c**). This can be associated to the presence of the inaccessible Fe₃O₄ in the Na-S and UP Calcin. 20 bar catalysts (**Figure 5.10a-b, d-e**), as commented earlier. Due to the presence of Fe₃O₄, less CO dissociating near-zerovalent Fe carbides are available for the FTS reaction in the Calcin. than in the H₂ 20 bar catalyst materials. This explains the difference in the initial FTY profiles.

Figure 5.15

Fischer-Tropsch Synthesis (FTS) selectivity results for UP and Na-S (Fe(-Na-S)/ α -Al₂O₃) calcined only (Calcin.) and H₂ reduced (H₂) catalyst materials for 3, 10 and 20 bar FTS reaction pressures. Median selectivity values with their Standard Deviations (STDs) over Time-on-Stream (ToS) 33-72 h for a) CH₄, b) C₂-C₄ olefin, c) C₂-C₄ paraffin, d) C₅+ and e) CO₂. In f) C₂H₄/C₂H₆ ratio is compared. Missing values for the catalyst materials are below detection limit.

Fe particle growth has been proposed to be responsible for the deactivation of the Na-S promoted FTS catalysts.⁵⁰ However, no clear connection between the catalysts' morphology, Fe particle diameter (**Figure 5.4**) and FTS reaction activity (**Figure 5.13**) can be derived from the results in this Chapter.

5.3.3.2 Catalyst Selectivity

The added Na-S promotion has the overall reaction pressure independent effects on the catalysts' FTS reaction hydrocarbon selectivities of (**Figure 5.15**): i) decreased CH₄, ii) in general increased C₂-C₄ olefin and decreased C₂-C₄ paraffin, iii) increased C₅+ selectivity, and iv) increased C₂H₄/C₂H₆ ratio. As would be expected from the changes in the hydrocarbon chain-length selectivities, with the Na-S promotion, the ASF distribution α -value is in overall increased in comparison to the UP catalyst materials for all of the tested FTS reaction pressures (**Figure 5.16**). All of the mentioned selectivity effects are akin to alkali only promotion effects.^{4,5,11,12,15-18}

Furthermore, as a specific property with the combined Na-S promotion, the CH₄ selectivity is especially suppressed to values below the expectations from the ASF distribution.^{19,20,25}

This can be also observed in the results for the Na-S promoted catalyst materials (**Figure 5.15a** and **Table 5.5**). Both, the Calcin. and H₂ catalyst materials show the same Na-S promotion dependent trends. An exception, however, is being the C₂H₄/C₂H₆ ratio that shows a possible Calcin. versus H₂ catalyst treatment dependency for catalyst materials with ≥ 10 bar FTS reaction pressure (**Figure 5.15f**). The C₂H₄/C₂H₆ ratio Calcin. versus H₂ catalyst dependency will be discussed in more detail shortly.

As a reference point, for the Na-S Calcin. and H₂ 20 bar catalyst materials, the FTS reaction hydrocarbon selectivities compare well with the results by Koeken et al. under similar FTS reaction conditions (340°C, 20 bar, H₂:CO 1:1, 4 200 h⁻¹) with a Fe-Na-S/ α -Al₂O₃ catalyst.⁴⁹

Also, as a general note, FTS reaction hydrocarbon selectivities are not directly affected by the CO conversion levels within range ≈ 10 -80 %.^{7,12} Thus, despite the different FTYs for the studied catalyst materials, the selectivity results can be compared.

For High-temperature Fischer-Tropsch (HTFT, 320-375°C), the CH₄ selectivity correlates with average partial pressures p in the reactor after **Equation 5.1**:^{5,8}

$$F_{CH_4} = \frac{p_{H_2}^{0.25}}{p_{CO} + 0.7p_{CO_2} + 0.6p_{H_2O}} \quad CH_4 \text{ Correlation in HTFT} \quad (\text{Eq. 5.1})$$

where a decreasing factor F_{CH_4} correlates with decreasing CH₄ selectivity. This is in agreement with the observed results of decreasing CH₄ correlating with increasing CO₂ selectivities (**Figure 5.15a, e**). More fundamentally, CO₂ and H₂O are thought to compete the FTS reaction reactants H₂ and CO for the catalyst's Fe surface adsorption sites, effectively decreasing the Fe surface H:C ratio and thus decreasing CH₄ selectivity.^{5,8} The rest of the FTS hydrocarbon chain-length selectivities follow the implications from the CH₄ selectivity.^{5,8} That is, when CH₄ decreases, total C₂-C₄ and C₅+ selectivities generally increase (**Figure 5.15a-d**) due to the requirements from the ASF distribution.^{3,78}

With the FTS reaction pressure increase from 10 to 20 bar (**Figure 5.15a, e** and **Table 5.5**): for the Na-S Calcin. and H₂ catalyst materials the CO₂ selectivity remains constant (43-46 %) as does the CH₄ selectivity (4-9 %); while for the UP Calcin. and H₂ catalysts the CO₂ selectivity increases from below detection limit to 37-42 % and CH₄ selectivity decreases from 41-46 % to 23-24 %. That is, with total FTS reaction pressure within 10-20 bar: the Na-S catalysts are *independent* of the reaction pressure and the

UP catalyst materials pressure *dependent*, in regard to the hydrocarbon CH₄, C₂-C₄ (olefin and paraffin), C₅₊ and CO₂ selectivities (**Figure 5.15a-e**). With 3 bar FTS reaction pressure, the CO₂ selectivities are below detection limit for both UP and Na-S catalyst materials and increased CH₄ selectivities are observed (**Figure 5.15a, e**). This is in-line with expectations of increased CH₄ selectivity for low FTS reaction pressure (<6 bar).⁶

The CH₄ selectivity independency of the alkali promoted catalysts from the total FTS reaction pressure has also been observed previously with bulk Rhrchemie (Fe:Cu:K:SiO₂) catalyst (260C, 15-25 bar, H₂:CO 2:3),⁷ and with K-promoted Fe-based catalyst material (240C, 6-25 bar, H₂:CO 2:1),⁶ for Low-temperature Fischer-Tropsch (LTFT, 200-250C). With testing done on a Fe-Na-S/ α -Al₂O₃ catalyst (5-20 bar, 350C), the threshold pressure for CH₄ selectivity independency can also be observed to be depended on the applied H₂:CO ratio (see *Fig. S16*, in the cited article).⁴⁹

Alkali (as Na or K) intrinsically increases the CO₂ releasing, inactive carbon depositing Boudouard reaction,^{4,67,79} and the WGS activity converting CO + H₂O to H₂ + CO₂.^{12,14,17,18} Both reactions affect the presence of CO₂, and the WGS reaction also affects the H₂O concentration in the FTS reaction and according to the **Equation 5.1** alter the (hydrocarbon and) CH₄ selectivity. The different total FTS reaction pressure responses with the Na-S and UP catalysts on the CH₄ selectivity are then most likely related to the WGS and Boudouard reaction promotion ability of the Na(-S) addition.

The threshold pressure for the CH₄ selectivity independency, with regard to the χ -Fe₅C₂ subtypes, follows the discussion on the FTY pressure dependency. The Na-S promotion induced transition of χ -Fe₅C₂ Type I to Type II and addition of Na-S promotion to χ -Fe₅C₂ Type III (**Figure 5.12a**) correlate with lowered, 10 bar threshold for the CH₄ selectivity independency (**Figure 5.15a-d**), as well as with the related FTY boost discussed earlier (**Figure 5.13**). Without Na-S promotion, χ -Fe₅C₂ Type I and Type III do not show comparable behavior in either the FTYs or FTS reaction selectivities. The quantity of η -Fe₂C (Type II) phase (**Figure 5.10a-b, d-e**) does not correlate with the FTS reaction hydrocarbon selectivities (**Figure 5.15**). Whether the different χ -Fe₅C₂ subtypes favor e.g. different lattice/surface positions for the Na-S promoters, possibly explaining the observations FTS performance differences, would be worthy of future research interest.

So far in the discussion, whether either the Calcin. or H₂ catalyst material was applied in the FTS reaction, did not make any difference selectivity-wise versus the FTS reaction pressure. The Na-S promotion has been the catalysts' FTS reaction selectivity defining feature. The exception to this rule, however, comes with the C₂H₄/C₂H₆ selectivity ratio (**Figure 5.15f**). C₂H₄ is reactive, and may be hydrogenated to C₂H₆ via secondary reactions i.e. via its readsorption on the Fe surface which is followed by hydrogenation or oligomerization reaction.^{4,7,10,78} In general it can be observed that

increasing FTS reaction pressure decreases the C₂H₄/C₂H₆ ratio for all of the studied catalyst materials (**Figure 5.15f**). This, while minding a to-be discussed exemption with the Na-S H₂ 20 bar catalyst material (**Figure 5.15f**).

For all of the studied Na-S catalyst materials, the ASF α -value (**Figure 5.16**), and the C₂H₄/C₂H₆ ratio is increased over the tested pressure range in comparison to the UP catalysts (**Figure 5.15f**). This is what would be expected to be the case with Na(-S) promotion.^{4,5,10–12,17,18} The more interesting point, however, is the increase in the C₂H₄/C₂H₆ ratio with the Calcin. catalysts in comparison to H₂ catalyst materials at the FTS reaction pressure of 10 bar *regardless* of the Na-S promotion (**Figure 5.15f**). The duplicate reactors tested for the data reproducibility gave comparable results for the ToS resolved C₂H₄/C₂H₆ ratio results in **Figure 5.17**. The observation, therefore, is not due a “random” occurrence.

A result akin to the increased C₂H₄/C₂H₆ ratio with Calcin. 10 bar catalyst materials has been previously observed by Bukur et al.³⁵ By treating their bulk Rührchemie (Fe:Cu:K:SiO₂) FTS catalyst with CO (at 280°C) or H₂:CO (at 310°C) prior to the FTS reaction (250°C, 14.8 bar, H₂:CO 2:3), a $\approx +10$ % increase in C₂-C₄ fraction olefin content could be achieved. This in comparison to the same catalysts reduced with H₂ prior to the FTS reaction. The result by Bukur et al. is not perfectly the same as in this study: for their catalyst, the C₂-C₄ olefin fraction increased, while for the Calcin. 10 bar catalysts the C₂H₄/C₂H₆ ratio is increased (**Figure 5.15f**) without a marked increase in the total C₂-C₄ range olefin selectivity (**Figure 5.15b**). Furthermore, Wezendonk et al. have observed decreased hydrogenation ability for their catalyst material, when an initial γ -Fe₂O₃@C catalyst was directly carburized (340°C, H₂:CO 1:1) in comparison to a prior H₂ reduction before the FTS reaction (230°C, 20 bar, H₂:CO 1:1).³⁸

Together with the literature observations, the results for the Calcin. catalyst materials with 10 bar FTS reaction are intriguing. Recalling from the discussion in R-QPA results section that *regardless of the Na-S promotion*, the χ -Fe₅C₂ Type III subtype is formed with all of the Calcin. catalyst materials. With all of the studied H₂ catalyst materials, either χ -Fe₅C₂

Figure 5.16
Median Anderson-Schulz-Flory (ASF) distribution α -values with their Standard Deviations (STDs) over Time-on-Stream (ToS) 33-72 h compared for UP and Na-S (Fe(-Na-S)/ α -Al₂O₃) calcined only (Calcin.) and H₂ reduced (H₂) catalyst materials for 3, 10 and 20 bar Fischer-Tropsch Synthesis (FTS) reaction pressures.

Table 5.5

Median Fischer-Tropsch Synthesis (FTS) selectivity data over Time-on-Stream (ToS) 33-72 h for UP and Na-S (Fe(-Na-S)/ α -Al₂O₃) calcined only (Calcin.) and H₂ reduced (H₂) catalyst materials. Values after ($\pm$) are the Standard Deviations (STDs) of the median values.

Reaction Pressure	Catalyst ^{a)}	CO ₂	CH ₄	C ₂ -C ₄ Olefin	C ₂ -C ₄ Paraffin	C ₅ +	C ₂ H ₄ /C ₂ H ₆	ASF α -value
		(%)	(%)	(%)	(%)	(%)	(-)	(a.u)
3 bar	UP Calcin.	< dl	77 $\pm$ 0	22 $\pm$ 0	2 $\pm$ 0	-	8.2 $\pm$ 0.4	0.16 $\pm$ 0.03
	UP H ₂	< dl	74 $\pm$ 0	24 $\pm$ 0	2 $\pm$ 0	-	7.5 $\pm$ 0.4	0.19 $\pm$ 0.01
	Na-S Calcin.	< dl	38 $\pm$ 12	47 $\pm$ 7	2 $\pm$ 0	11 $\pm$ 4	11.6 $\pm$ 1.7	0.54 $\pm$ 0.02
	Na-S H ₂	< dl	18 $\pm$ 3	56 $\pm$ 6	3 $\pm$ 0	23 $\pm$ 9	13.6 $\pm$ 0.7	0.59 $\pm$ 0.03
10 bar	UP Calcin.	< dl	46 $\pm$ 5	34 $\pm$ 4	6 $\pm$ 1	13 $\pm$ 10	3.6 $\pm$ 0.1	0.62 $\pm$ 0.22
	UP H ₂	< dl	41 $\pm$ 2	37 $\pm$ 2	10 $\pm$ 1	11 $\pm$ 4	2.0 $\pm$ 0.1	0.54 $\pm$ 0.10
	Na-S Calcin.	45 $\pm$ 0	6 $\pm$ 0	35 $\pm$ 0	3 $\pm$ 0	55 $\pm$ 1	8.6 $\pm$ 0.2	0.84 $\pm$ 0.00
	Na-S H ₂	46 $\pm$ 0	9 $\pm$ 1	35 $\pm$ 1	4 $\pm$ 0	51 $\pm$ 1	5.4 $\pm$ 0.9	0.82 $\pm$ 0.01
20 bar	UP Calcin.	37 $\pm$ 2	23 $\pm$ 0	26 $\pm$ 0	18 $\pm$ 1	34 $\pm$ 0	0.4 $\pm$ 0.0	0.57 $\pm$ 0.01
	UP H ₂	42 $\pm$ 0	24 $\pm$ 1	25 $\pm$ 0	19 $\pm$ 0	33 $\pm$ 1	0.3 $\pm$ 0.0	0.58 $\pm$ 0.02
	Na-S Calcin.	43 $\pm$ 0	7 $\pm$ 0	33 $\pm$ 0	4 $\pm$ 0	56 $\pm$ 0	5.3 $\pm$ 0.1	0.66 $\pm$ 0.02
	Na-S H ₂	44 $\pm$ 1	4 $\pm$ 0	38 $\pm$ 1	3 $\pm$ 0	55 $\pm$ 1	10.8 $\pm$ 1.0	0.67 $\pm$ 0.05

FTS conditions: 340°C, 3, 10 or 20 bar, H₂:CO:He 1.0:1.0:0.2 v/v, $\approx$ 5 500 h⁻¹.

< dl – Below detection limit.

a) 10 bar: MeOH (methanol) selectivity was 1.3-1.4 % for Na-S Calcin. and H₂, and 0.3-0.4 % for UP Calcin. and H₂ catalysts. 3 and 20 bar: MeOH selectivity was $\leq$ 0.1 % for all catalyst materials.

Type I or Type II forms but *no* Type III (**Figure 5.12a**). From the characterization results by Bukur et al. or Wezendonk et al., it cannot be deduced which χ -Fe₅C₂ subtypes may have formed in their studies with the applied H₂, CO or H₂:CO treatments.^{34,38}

With the CO or H₂:CO treatments applied before the FTS reaction, Bukur et al. mainly detected χ -Fe₅C₂ and Fe₃O₄ phases, while with H₂ treatments a “ ϵ' -Fe_{2.2}C” phase (i.e. η -Fe₂C) was detected as the major Fe carbide phase after the FTS reaction.³⁴ With the applied carburizing H₂:CO treatment, Wezendonk et al. characterized the χ -Fe₅C₂ as being the major Fe carbide phase, with a minor contribution from “ ϵ' -Fe_{2.2}C”. Thus, despite the enriched presence of the η -Fe₂C phase in the Na-S Calcin. 10 bar catalyst it unlikely plays a role in the enhanced C₂H₄/C₂H₆ ratio. The η -Fe₂C phase is also missing from the UP Calcin. 10 bar catalyst material after the FTS reaction (**Figure 5.10a-b**) but enhanced C₂H₄/C₂H₆ ratio is still observed (**Figure 5.17b**).

We, therefore, assign the increased C₂H₄/C₂H₆ ratio as an intrinsic property, i.e. being independent of the Na-S promotion, to the χ -Fe₅C₂ Type III phase when the FTS reaction pressure is around 10 bar (**Figure 5.15f**). This would also explain the literature observations: when a Fe oxide is directly exposed to carburizing atmosphere, χ -Fe₅C₂ Type III phase forms, resulting in the catalyst material's decreased hydrogenation ability.^{35,38}

Figure 5.17

C_2H_4/C_2H_6 ratio Time-on-Stream (ToS) profiles for the UP and Na-S (Fe(-Na-S)/ α -Al₂O₃), calcined only (Calcin.) and H₂ reduced (H₂) catalysts over the 72 h Fischer-Tropsch Synthesis (FTS) reactions. FTS reaction C_2H_4/C_2H_6 ratio profiles for a) 3 bar, b) 10 bar and c) 20 bar FTS reaction pressures.

With 3 bar results for the UP and Na-S Calcin. catalyst materials, no positive effect towards olefin formation can be associated to the χ -Fe₅C₂ Type III phase (**Figure 5.15f**). An explanation for the C_2H_4/C_2H_6 ratio trend breaking Na-S H₂ 20 bar catalyst (**Figure 5.15f**) could be suggested when contrasting the Na-S H₂ 20 bar catalyst's C_2H_4/C_2H_6 ratio ToS profile (**Figure 5.17c**) to the catalyst's corresponding FTY profile (**Figure 5.13c**). After the ToS resolved results for the catalyst material, the increasing C_2H_4/C_2H_6 ratio has an inverse relation with the decreasing FTY profile. Rather fast decrease in the FTY profile might indicate inactive carbon deposition blocking the catalyst surface, when FTS reaction conditions of 20 bar H₂:CO 1:1 are applied.⁴⁹ Carbon deposition could decrease the available Fe sites for the C₂H₄ readsorption and thus decrease its secondary reactions.^{10,75} This would result in the increasing the C_2H_4/C_2H_6 ratio (**Figure 5.17c**). Thus, whether the Na-S Calcin. 20 bar catalyst exhibits olefin favoring C_2H_4/C_2H_6 ratio in comparison to the Na-S H₂ 20 bar catalyst material cannot be judged due to lack of reference point. For the UP Calcin. 20 bar catalyst material; the overall 20 bar FTS reaction pressure suppresses the C_2H_4/C_2H_6 ratio (**Figure 5.17**).

In total, the favorable, Na-S promotion independent, properties towards C₂H₄ formation with the χ -Fe₅C₂ Type III phase seem to be FTS reaction pressure dependent. The response of the χ -Fe₅C₂ Type III phase to the reaction conditions, and to C₂H₄ and overall olefin production is well worth further investigation in the future.

5.4 CONCLUSIONS

Supported Fe(-Na-S)/ α -Al₂O₃ catalyst materials, with and without Na-S promotion,

were prepared, characterized and tested. The catalysts were either calcined only, or subsequently to calcining also H_2 reduced, prior to the catalytic performance testing in the FTS reaction. The FTS reactions were separately ran for 72 h at either 3, 10 or 20 bar total reaction pressure at otherwise identical reaction conditions (340°C , $H_2:CO:He$ 1.0:1.0:0.2 v/v, GHSV $\approx 5\,500\text{ h}^{-1}$). XRPD patterns of each of the studied catalyst materials were collected ex-situ after the FTS reaction runs and Fe phases present were quantified from the XRPD patterns using R-QPA.

Before performing the FTS reactions, both the unpromoted and Na-S promoted, calcined only catalyst materials only contained $\alpha\text{-Fe}_2\text{O}_3$ as the sole Fe phase. The subsequently H_2 reduced catalysts consisted of $\alpha\text{-Fe}$ as the major Fe phase with both Fe_3O_4 and $\text{Fe}_{0.974}\text{O}$ also present. After the FTS reactions, the Fe carbide phases identified in the catalyst materials were $\eta\text{-Fe}_2\text{C}$ *Pnnm* (58), $\chi\text{-Fe}_5\text{C}_2$ *C2/c* (15) and/or $\theta\text{-Fe}_7\text{C}_3$ *Pnma* (62).

On all of the applied catalyst materials after the FTS reactions, the $\chi\text{-Fe}_5\text{C}_2$ phase was quantified as the major Fe carbide phase. Na-S promotion altered the Fe carbide formation by i) inducing appearance of the $\eta\text{-Fe}_2\text{C}$ phase in 10 and 20 bar FTS reaction runs *but not* with the 3 bar FTS run, and ii) with 10 bar FTS reaction pressure the Na-S promoted and calcined only catalyst materials showed more tendency towards the $\eta\text{-Fe}_2\text{C}$ formation than the Na-S promoted and H_2 reduced catalysts did. Also, iii) combining the Na-S promotion with the calcined only catalyst with 20 bar FTS reaction pressure induced formation of a minor quantity (8 %) of the $\theta\text{-Fe}_7\text{C}_3$ phase.

In **Chapter 4**, the $\eta\text{-Fe}_2\text{C}$ and $\chi\text{-Fe}_5\text{C}_2$ phase subtypes were defined by their crystal lattice parameters. Within this Chapter, the carbide subtype formation largely follows the set expectations. With respect to the FTS reaction pressure, the Fe carbide subtype formation takes place as follows:

$\chi\text{-Fe}_5\text{C}_2$

Type I *Without* Na-S promotion *regardless* of reaction pressure, or with 3 bar FTS reaction pressure *regardless* of Na-S promotion,

Type II *With* Na-S promotion, and ≥ 10 bar FTS reaction pressure,

Type III Fe oxide ($\alpha\text{-Fe}_2\text{O}_3$) as the FTS starting material *regardless* of the Na-S promotion or the FTS reaction pressure,

$\eta\text{-Fe}_2\text{C}$

Type II *With* Na-S promotion, and ≥ 10 bar FTS reaction pressure.

Increasing the FTS reaction pressure increased lattice parameter *a* distortion for the $\chi\text{-Fe}_5\text{C}_2$ Type III. The $\chi\text{-Fe}_5\text{C}_2$ Type III distortion is conceivably due to increasingly retained O atoms in the $\chi\text{-Fe}_5\text{C}_2$ Type III crystal lattice. In addition to the phase's lattice

parameter distortion, the crystal structure of the χ -Fe₅C₂ Type III was systematically altered in comparison to the crystal structures of χ -Fe₅C₂ Type I and Type II.

The catalysts' FTS performance dependency on the reaction pressure was mainly altered by the Na-S promotion. Whether the catalyst was only calcined or also H₂ reduced, had a lesser influence on its catalytic performance. As reaction pressure independent, Na-S promotion effects: CH₄ selectivity was suppressed, and ASF α -value and overall hydrocarbon product slate olefin content both increased, in comparison to all of the unpromoted catalyst materials.

The Na-S promotion combined with 10 bar FTS reaction pressure threshold, had the effects of that: i) catalysts showed a significant boost in the FTYs, ii) Usage Ratio H₂:CO, CO converted to hydrocarbons and hydrocarbon selectivities became reaction pressure independent, and iii) CO₂ selectivity was increased significantly. These FTS performance changes correlate with Na-S induced transition of χ -Fe₅C₂ Type I to Type II, and to the presence of χ -Fe₅C₂ Type III with Na-S promoters. For unpromoted catalysts, 20 bar FTS reaction pressure threshold was required for attaining similar FTS catalysis effects as were observed with the Na-S promoted catalyst materials with ≥ 10 bar reaction pressure. For these changes, χ -Fe₅C₂ Type I and unpromoted Type III were present as the χ -Fe₅C₂ phase subtypes. With 3 bar reaction pressure, none of the studied catalyst materials showed significant FTYs regardless of the Na-S promotion.

For all of the catalyst materials under study: the CH₄ selectivity inversely correlated with CO₂ selectivity, as was expected from literature. The presence of η -Fe₂C Type II did not correlate with any of the FTS catalytic performance - activity or selectivity - indicators.

For both, Na-S promoted and unpromoted catalyst materials, the observed reaction pressure dependent FTY boosts were also accompanied by decreased Usage Ratios H₂:CO and CO conversion to hydrocarbons. That is, less CO was converted towards the desired FTS reaction produced hydrocarbons but was instead released as unwanted CO₂, as an adverse effect to the boosted FTYs.

Regardless of the Na-S promotion, when employing calcined only catalyst materials in the FTS reaction: i) increased C₂H₄/C₂H₆ ratio with 10 bar FTS reaction pressure and ii) decreased overall FTYs with 20 bar reaction pressure in comparison to the H₂ reduced catalysts were observed. The increased C₂H₄/C₂H₆ ratio can be independently of the Na-S promotion associated to the presence of χ -Fe₅C₂ Type III with 10 bar reaction pressure. That is, the χ -Fe₅C₂ Type III correlates with catalyst material's decreased hydrogenation ability. Decreased FTYs in turn correlate with the presence of Fe₃O₄, in the calcined only, 20 bar FTS catalysts. The presence of the Fe₃O₄ phase possibly originates from mass transfer limited reduction of the initial α -Fe₂O₃ (α -Al₂O₃) phase. Na-S promotion combined with H₂ reduction and 20 bar FTS reaction pressure

resulted in high initial FTY with, however, FTY decreasing fast over the course of the FTS reaction.

For future research, the χ -Fe₅C₂ Type III should be investigated in more detail for: i) an improved crystal structure solution, and ii) the carbide subtype's association to the increased C₂H₄/C₂H₆ ratio. The general relation e.g. whether Na-S promoters occupy different surface or crystal lattice positions in the χ -Fe₅C₂ subtypes, is a further topic of interest. The observed fast deactivation of the H₂ reduced, Na-S promoted catalysts in the 20 bar FTS reaction perhaps could be prevented with altered reaction initiation, which is another subject for a further study.

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5.6 REFERENCES

- [1] Torres Galvis, H. M. and de Jong, K. P., "Catalysts for Production of Lower Olefins from Synthesis Gas: A Review", *ACS Catal.* **3**, 2130–2149 (2013).
- [2] Dry, M. E., "High quality diesel via the Fischer-Tropsch process - a review", *J. Chem. Technol. Biotechnol.* **77**, 43–50 (2001).
- [3] van der Laan, G. P. and Beenackers, A. A. C. M., "Kinetics and Selectivity of the Fischer-Tropsch Synthesis: A Literature Review", *Catal. Rev.* **41**, 255–318 (1999).
- [4] Dry, M. E., "The Fischer-Tropsch Synthesis" in *Catalysis - Science and Technology* (eds. Anderson, J. R. & Boudart, M.) **1**, 159–256 (Springer-Verlag, Berlin, 1981).
- [5] Dry, M. E., "Chemical concepts used for engineering purposes" in *Studies in Surface Science and Catalysis - Fischer-Tropsch Technology* (eds. Steynberg, A. P. & Dry, M. E.) **152**, 196–257 (Elsevier B.V., Amsterdam, 2004).
- [6] Botes, G. F., Niemantsverdriet, J. W. and van de Loosdrecht, J., "A comparison of cobalt and iron based slurry phase Fischer-Tropsch synthesis", *Catal. Today* **215**, 112–120 (2013).
- [7] Todic, B., Nowicki, L., Nikacevic, N. and Bukur, D. B., "Fischer-Tropsch synthesis product selectivity over an industrial iron-based catalyst: Effect of process conditions", *Catal. Today* **261**, 28–39 (2016).
- [8] Dry, M. E., "The Fischer-Tropsch process: 1950–2000", *Catal. Today* **71**, 227–241 (2002).
- [9] Dry, M. E., "Commercial conversion of carbon monoxide to fuels and chemicals", *J. Organomet. Chem.* **372**, 117–127 (1989).
- [10] Dictor, R. and Bell, A. T., "Fischer-Tropsch synthesis over reduced and unreduced iron oxide catalysts", *J. Catal.* **97**, 121–136 (1986).
- [11] Jiang, F., Zhang, M., Liu, B., Xu, Y. and Liu, X., "Insights into the influence of support and potassium or sulfur promoter on iron-based Fischer-Tropsch synthesis: understanding the control of catalytic activity, selectivity to lower olefins, and catalyst deactivation", *Catal. Sci. Technol.* **7**, 1245–1265 (2017).

- [12] Ngantsoue-Hoc, W., Zhang, Y., O'Brien, R. J., Luo, M. and Davis, B. H., "*Fischer-Tropsch synthesis: activity and selectivity for Group I alkali promoted iron-based catalysts*", *Appl. Catal. A Gen.* **236**, 77–89 (2002).
- [13] Dry, M. E. and Oosthuizen, G. J., "*The correlation between catalyst surface basicity and hydrocarbon selectivity in the Fischer-Tropsch synthesis*", *J. Catal.* **11**, 18–24 (1968).
- [14] Luo, M. and Davis, B. H., "*Fischer-Tropsch synthesis: Group II alkali-earth metal promoted catalysts*", *Appl. Catal. A Gen.* **246**, 171–181 (2003).
- [15] Pendyala, V. R. R., Graham, U. M., Jacobs, G., Hamdeh, H. H. and Davis, B. H., "*Fischer-Tropsch Synthesis: Morphology, Phase Transformation, and Carbon-Layer Growth of Iron-Based Catalysts*", *ChemCatChem* **6**, 1952–1960 (2014).
- [16] Pendyala, V. R. R., Graham, U. M., Jacobs, G., Hamdeh, H. H. and Davis, B. H., "*Fischer-Tropsch Synthesis: Deactivation as a Function of Potassium Promoter Loading for Precipitated Iron Catalyst*", *Catal. Lett.* **144**, 1704–1716 (2014).
- [17] Bukur, D. B., Mukesh, D. and Patel, S. A., "*Promoter effects on precipitated iron catalysts for Fischer-Tropsch synthesis*", *Ind. Eng. Chem. Res.* **29**, 194–204 (1990).
- [18] Arakawa, H. and Bell, A. T., "*Effects of potassium promotion on the activity and selectivity of iron Fischer-Tropsch catalysts*", *Ind. Eng. Chem. Process Des. Dev.* **22**, 97–103 (1983).
- [19] Botes, G. F., Bromfield, T. C., Coetzer, R. L. J., Crous, R., Gibson, P. and Ferreira, A. C., "*Development of a chemical selective iron Fischer Tropsch catalyst*", *Catal. Today* **275**, 40–48 (2016).
- [20] Torres Galvis, H. M., Bitter, J. H., Khare, C. B., Ruitenbeek, M., Dugulan, A. I. and de Jong, K. P., "*Supported Iron Nanoparticles as Catalysts for Sustainable Production of Lower Olefins*", *Science* **335**, 835–838 (2012).
- [21] Torres Galvis, H. M., Koeken, A. C. J., Bitter, J. H., Davidian, T., Ruitenbeek, M., Dugulan, A. I. and de Jong, K. P., "*Effects of sodium and sulfur on catalytic performance of supported iron catalysts for the Fischer-Tropsch synthesis of lower olefins*", *J. Catal.* **303**, 22–30 (2013).
- [22] Johnson, J. Y., "*Improvements in the Manufacture and Production of Unsaturated Hydrocarbons of Low Boiling Point*", Patent GB322284A (1929).
- [23] Crous, R., Bromfield, T. C. and Booyens, S., "*Olefin Selective FT Catalyst Composition and Preparation Thereof*", Patent WO2010066386A1 (2010).
- [24] Myddleton, W. W., "*Improvements Relating to the Catalytic Synthesis of Hydrocarbon Oils from Gaseous Mixtures of Carbon Monoxide and Hydrogen*", Patent GB509325A (1939).
- [25] Xie, J., Yang, J., Dugulan, A. I., Holmen, A., Chen, D., De Jong, K. P. and Louwerse, M. J., "*Size and Promoter Effects in Supported Iron Fischer-Tropsch Catalysts: Insights from Experiment and Theory*", *ACS Catal.* **6**, 3147–3157 (2016).
- [26] Leineweber, A., Shang, S., Liu, Z.-K., Widenmeyer, M. and Niewa, R., "*Crystal structure determination of Hägg carbide, χ -Fe₅C₂ by first-principles calculations and Rietveld refinement*", *Zeitschrift für Krist.* **227**, 207–220 (2012).
- [27] Retief, J. J., "*Powder diffraction data and Rietveld refinement of Hägg-carbide, χ -Fe₅C₂*", *Powder Diff.* **14**, 130–132 (1999).
- [28] Duggin, M. J. and Hofer, L. J. E., "*Nature of χ -Iron Carbide*", *Nature* **212**, 248–248 (1966).
- [29] Jack, K. H. and Wild, S., "*Nature of χ -Carbide and Its Possible Occurrence in Steels*", *Nature* **212**, 248–250 (1966).
- [30] Cohn, E. M., Bean, E. H., Mentser, M., Hofer, L. J. E., Pontello, A., Peebles, W. C. and Jack, K. H., "*The carburization of iron oxide with carbon monoxide: Modifications of Hägg iron carbide*", *J. Appl. Chem.* **5**, 418–425 (1955).

- [31] Sirimanothan, N., Hamdeh, H. H., Zhang, Y. and Davis, B. H., "Fischer-Tropsch Synthesis; Changes in Phase and Activity during Use", *Catal. Lett.* **82**, 181–191 (2002).
- [32] O'Brien, R. J., Xu, L., Milburn, D. R., Li, Y.-X., Klabunde, K. J. and Davis, B. H., "Fischer-Tropsch synthesis: Impact of potassium and zirconium promoters on the activity and structure of an ultrafine iron oxide catalyst", *Top. Catal.* **2**, 1–15 (1995).
- [33] Rao, K. R. P. M., Huggins, F. E., Huffman, G. P., Gormley, R. J., O'Brien, R. J. and Davis, B. H., "Mössbauer Study of Iron Fischer-Tropsch Catalysts during Activation and Synthesis", *Energy & Fuels* **10**, 546–551 (1996).
- [34] Bukur, D. B., Okabe, K., Rosynek, M. P., Li, C. P., Wang, D. J., Rao, K. R. P. M. and Huffman, G. P., "Activation Studies with a Precipitated Iron Catalyst for Fischer-Tropsch Synthesis. I. Characterization Studies", *Journal of Catalysis* **155**, 353–365 (1995).
- [35] Bukur, D. B., Nowicki, L., Manne, R. K. and Lang, X. S., "Activation Studies with a Precipitated Iron Catalyst for Fischer-Tropsch Synthesis II. Reaction Studies", *J. Catal.* **155**, 366–375 (1995).
- [36] Shultz, J. F., Hall, W. K., Seligman, B. and Anderson, R. B., "Studies of the Fischer-Tropsch Synthesis. XIV. Hägg Carbide as Catalysts", *J. Am. Chem. Soc.* **77**, 213–221 (1955).
- [37] Davidian, T., Ruitenbeek, M., Koeken, A. C. J., Vos, M. and Wielemaker, M. F., "Novel Iron-based Catalysts and Treatment Process therefor for Use in Fischer-Tropsch Reactions", Patent WO2014210089A1 (2014).
- [38] Wezendonk, T. A., Sun, X., Dugulan, A. I., van Hoof, A. J. F., Hensen, E. J. M., Kapteijn, F. and Gascon, J., "Controlled formation of iron carbides and their performance in Fischer-Tropsch synthesis", *J. Catal.* **362**, 106–117 (2018).
- [39] de Smit, E., Cinquini, F., Beale, A. M., Safonova, O. V., van Beek, W., Sautet, P. and Weckhuysen, B. M., "Stability and Reactivity of ϵ - χ - θ Iron Carbide Catalyst Phases in Fischer-Tropsch Synthesis: Controlling μ c", *J. Am. Chem. Soc.* **132**, 14928–14941 (2010).
- [40] de Smit, E., Beale, A. M., Nikitenko, S. and Weckhuysen, B. M., "Local and long range order in promoted iron-based Fischer-Tropsch catalysts: A combined in situ X-ray absorption spectroscopy/wide angle X-ray scattering study", *J. Catal.* **262**, 244–256 (2009).
- [41] Datye, A. K., Jin, Y., Mansker, L. D., Motjope, R. T., Dlamini, T. H. and Coville, N. J., "The nature of the active phase in iron Fischer-Tropsch catalysts" in *Studies in Surface Science and Catalysis* **130**, 1139–1144 (2000).
- [42] Mansker, L. D., Jin, Y., Bukur, D. B. and Datye, A. K., "Characterization of slurry phase iron catalysts for Fischer-Tropsch synthesis", *Appl. Catal. A Gen.* **186**, 277–296 (1999).
- [43] Jung, H. and Thomson, W. J., "Dynamic X-ray diffraction study of an unsupported iron catalyst in Fischer-Tropsch synthesis", *J. Catal.* **134**, 654–667 (1992).
- [44] McCartney, J. T., Hofer, L. J. E., Seligman, B., Lecky, J. A., Peebles, W. C. and Anderson, R. B., "Electron and X-Ray Diffraction Studies of Iron Fischer-Tropsch Catalysts", *J. Phys. Chem.* **57**, 730–736 (1953).
- [45] Jenkins, R. and Snyder, R. L., "Introduction to X-ray Powder Diffractometry", *Introduction to X-ray Powder Diffractometry* **138** (John Wiley & Sons, Inc., Hoboken, NJ, USA, 1996).
- [46] De La Torre, A. G., Bruque, S. and Aranda, M. A. G., "Rietveld quantitative amorphous content analysis", *J. Appl. Crystallogr.* **34**, 196–202 (2001).
- [47] Klencsár, Z., Kuzmann, E. and Vértes, A., "User-friendly software for Mössbauer spectrum analysis", *J. Radioanal. Nucl. Chem. Artic.* **210**, 105–118 (1996).
- [48] Torres Galvis, H. M., Koeken, A. C. J., Bitter, J. H., Davidian, T., Ruitenbeek, M., Dugulan, A. I. and De Jong, K. P., "Effect of precursor on the catalytic performance of supported iron catalysts for the Fischer-Tropsch synthesis of lower olefins", *Catal. Today* **215**, 95–102 (2013).

- [49] Koeken, A. C. J., Torres Galvis, H. M., Davidian, T., Ruitenbeek, M. and de Jong, K. P., "*Suppression of Carbon Deposition in the Iron-Catalyzed Production of Lower Olefins from Synthesis Gas*", *Angew. Chem., Int. Ed.* **51**, 7190–7193 (2012).
- [50] Xie, J., Torres Galvis, H. M., Koeken, A. C. J., Kirilin, A., Dugulan, A. I., Ruitenbeek, M. and de Jong, K. P., "*Size and Promoter Effects on Stability of Carbon-Nanofiber-Supported Iron-Based Fischer-Tropsch Catalysts*", *ACS Catal.* **6**, 4017–4024 (2016).
- [51] Toby, B. H., "*R factors in Rietveld analysis: How good is good enough?*", *Powder Diffr.* **21**, 67–70 (2006).
- [52] Jozwiak, W. K., Kaczmarek, E., Maniecki, T. P., Ignaczak, W. and Maniukiewicz, W., "*Reduction behavior of iron oxides in hydrogen and carbon monoxide atmospheres*", *Appl. Catal. A Gen.* **326**, 17–27 (2007).
- [53] Mogorosi, R. P., Fischer, N., Claeys, M. and van Steen, E., "*Strong-metal-support interaction by molecular design: Fe-silicate interactions in Fischer-Tropsch catalysts*", *J. Catal.* **289**, 140–150 (2012).
- [54] An, X., Wu, B., Wan, H.-J., Li, T.-Z., Tao, Z.-C., Xiang, H.-W. and Li, Y.-W., "*Comparative study of iron-based Fischer-Tropsch synthesis catalyst promoted with potassium or sodium*", *Catal. Commun.* **8**, 1957–1962 (2007).
- [55] Hirotsu, Y. and Nagakura, S., "*Crystal structure and morphology of the carbide precipitated from martensitic high carbon steel during the first stage of tempering*", *Acta Metall.* **20**, 645–655 (1972).
- [56] Hirotsu, Y. and Nagakura, S., "*Electron Microscopy and Diffraction Study of the Carbide Precipitated at the First Stage of Tempering of Martensitic Medium Carbon Steel*", *Trans. Japan Inst. Met.* **15**, 129–134 (1974).
- [57] Barton, G. H. and Gale, B., "*The structure of a pseudo-hexagonal iron carbide*", *Acta Crystallogr.* **17**, 1460–1462 (1964).
- [58] Niemantsverdriet, J. W., van der Kraan, A. M., van Dijk, W. L. and van der Baan, H. S., "*Behavior of Metallic Iron Catalysts during Fischer-Tropsch Synthesis Studied with Mössbauer Spectroscopy, X-ray Diffraction, Carbon Content Determination, and Reaction Kinetic Measurements*", *J. Phys. Chem.* **84**, 3363–3370 (1980).
- [59] Tajima, S. and Hirano, S., "*Synthesis and Magnetic Properties of Fe₇C₃ Particles with High Saturation Magnetization*", *Jpn. J. Appl. Phys.* **29**, 662–668 (1990).
- [60] O'Brien, R. J., Xu, L., Spicer, R. L. and Davis, B. H., "*Activation Study of Precipitated Iron Fischer-Tropsch Catalysts*", *Energy & Fuels* **10**, 921–926 (1996).
- [61] Ratnasamy, C. and Wagner, J. P., "*Water Gas Shift Catalysis*", *Catal. Rev.* **51**, 325–440 (2009).
- [62] Rhodes, C., Hutchings, G. J. and Ward, A. M., "*Water-gas shift reaction: finding the mechanistic boundary*", *Catal. Today* **23**, 43–58 (1995).
- [63] Shultz, J. F., Abelson, M., Stein, K. C. and Anderson, R. B., "*Studies of the Fischer-Tropsch Synthesis. XVIII. Influence of Catalyst Geometry on Synthesis on Iron Catalysts*", *J. Phys. Chem.* **63**, 496–500 (1959).
- [64] Anderson, R. B., Hofer, L. J. E., Cohn, E. M. and Seligman, B., "*Studies of the Fischer-Tropsch Synthesis. IX. Phase Changes of Iron Catalysts in the Synthesis*", *J. Am. Chem. Soc.* **73**, 944–946 (1951).
- [65] Ning, W., Koizumi, N., Chang, H., Mochizuki, T., Itoh, T. and Yamada, M., "*Phase transformation of unpromoted and promoted Fe catalysts and the formation of carbonaceous compounds during Fischer-Tropsch synthesis reaction*", *Appl. Catal. A Gen.* **312**, 35–44 (2006).
- [66] Berry, F. J. and Smith, M. R., "*A Mössbauer investigation of iron-containing catalysts prepared at low temperatures and active for carbon monoxide hydrogenation*", *J. Chem. Soc. Faraday Trans. 1 Phys. Chem. Condens. Phases* **85**, 467–477 (1989).

- [67] Dry, M. E., Shingles, T. and van H. Botha, C. S., "*Factors influencing the formation of carbon on iron Fischer-Tropsch catalysts I. The influence of promoters*", *J. Catal.* **17**, 341–346 (1970).
- [68] Dry, M. E., Shingles, T., Boshoff, L. J. and van H. Botha, C. S., "*Factors influencing the formation of carbon on iron Fischer-Tropsch catalysts. II. The effect of temperature and of gases and vapors present during Fischer-Tropsch synthesis*", *J. Catal.* **17**, 347–354 (1970).
- [69] Sarkar, A., Seth, D., Dozier, A. K., Neathery, J. K., Hamdeh, H. H. and Davis, B. H., "*Fischer-Tropsch Synthesis: Morphology, Phase Transformation and Particle Size Growth of Nano-scale Particles*", *Catal. Lett.* **117**, 1–17 (2007).
- [70] Steynberg, A. P., Espinoza, R. L., Jager, B. and Vosloo, A. C., "*High temperature Fischer-Tropsch synthesis in commercial practice*", *Appl. Catal. A Gen.* **186**, 41–54 (1999).
- [71] Amenomiya, Y. and Pleizier, G., "*Alkali-promoted Alumina Catalysts II. Water-Gas Shift Reaction*", *J. Catal.* **76**, 345–353 (1982).
- [72] Krupay, B. W. and Amenomiya, Y., "*Alkali-promoted Alumina Catalysts I. Chemisorption and oxygen exchange of carbon monoxide and carbon dioxide on potassium-promoted alumina catalysts*", *J. Catal.* **67**, 362–370 (1981).
- [73] Chianese, S., Loipersböck, J., Malits, M., Rauch, R., Hofbauer, H., Molino, A. and Musmarra, D., "*Hydrogen from the high temperature water gas shift reaction with an industrial Fe/Cr catalyst using biomass gasification tar rich synthesis gas*", *Fuel Process. Technol.* **132**, 39–48 (2015).
- [74] Lywood, W. J. and Twigg, M. V., "*Hydrogen production including a shift reaction process*", Patent EP0361648A1 (1990).
- [75] van Dijk, W. L., Niemantsverdriet, J. W., van der Kraan, A. M. and van der Baan, H. S., "*Effects of Manganese Oxide and Sulphate on the Olefin Selectivity of Iron Catalysts in the Fischer Tropsch Reaction*", *Appl. Catal.* **2**, 273–288 (1982).
- [76] Zhou, X., Ji, J., Wang, D., Duan, X., Qian, G., Chen, D. and Zhou, X., "*Hierarchical structured α -Al₂O₃ supported S-promoted Fe catalysts for direct conversion of syngas to lower olefins*", *Chem. Commun.* **51**, 8853–8856 (2015).
- [77] Madon, R. J. and Shaw, H., "*Effect of Sulfur on the Fischer-Tropsch Synthesis*", *Catal. Rev.* **15**, 69–106 (1977).
- [78] Förtsch, D., Pabst, K. and Groß-Hardt, E., "*The product distribution in Fischer-Tropsch synthesis: An extension of the ASF model to describe common deviations*", *Chem. Eng. Sci.* **138**, 333–346 (2015).
- [79] Berry, T. F., Ames, R. N. and Snow, R. B., "*Influence of Impurities and Role of Iron Carbides in Deposition of Carbon from Carbon Monoxide*", *J. Am. Ceram. Soc.* **39**, 308–318 (1956).

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Chapter 6

Combined In-situ X-Ray Powder Diffractometry/Raman Spectroscopy of Iron Carbide and Carbon Species Evolution in Fe(-Na- S)/ α -Al₂O₃ Catalysts during Fischer-Tropsch Synthesis

A Na-S promoted Fe-based catalyst converts a H₂:CO gas mixture into hydrocarbons with enriched C₂-C₄ olefin content in high-temperature (320-375°C) Fischer-Tropsch Synthesis (FTS) reaction. Above 300°C, the carbon depositing Boudouard reaction competes with the FTS reaction for the reactant CO. With a combined in-situ X-Ray Powder Diffractometry (XRPD)/Raman Spectroscopy set-up the simultaneous evolution of Fe_xO_y/α-Fe/Fe_xC and carbon species has been monitored during 340°C, 10 bar FTS reaction. CO carburized, Na-S promoted and unpromoted Fe(-Na-S)/α-Al₂O₃ catalysts were employed. Fe phases were quantified with Rietveld Quantitative Phase Analysis (R-QPA) from the XRPD patterns. The Raman D- and G-bands were analyzed for their relative intensities, bandwidths, and positions, and compared to reference carbon materials. Amorphous carbon with C sp³ and C sp² in chain-like ordering evolved towards Carbon Nanofiber (CNF)-type structures during FTS reaction. Na-S promotion and initial CO carburization ≥340°C led to increased cyclic 6-fold C sp² species. Preliminary carbon deposits on catalysts decreased the initial fast Raman band intensity increase, while Na-S promotion increased steady period band intensity growth. The carbon species evolution was unaffected by specific Fe carbides or carbide-to-carbide transitions. Na-S promotion aided in reduction of Fe₃O₄ by (H₂:)CO to carbon depositing Fe carbides. The results add to understanding on Fe and carbon species evolution during high-temperature FTS reaction.

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6.1 INTRODUCTION

With Fischer-Tropsch Synthesis (FTS) reaction, a $\text{H}_2\text{:CO}$ gas mixture can be converted into valuable hydrocarbons.^{1,2,11,3-10} With the combination of high reaction temperature (320-375°C) and Na-S chemical promotion, the synthesized hydrocarbon product slate can be directed towards the formation of industrially valuable, short-chained ($\text{C}_2\text{-C}_4$), olefinic hydrocarbons.¹²⁻²²

However, for FTS reaction temperatures $\geq 300^\circ\text{C}$,^{2,23-25} the Boudouard reaction (i.e. CO disproportionation of CO into C and CO_2) also becomes active depositing catalyst deactivating inactive carbon on the catalyst material. The Boudouard therefore competes with the FTS reaction directly for the reactant CO.^{26,27} Regeneration and removal of the carbon deposits would be possible via catalyst hydrogenation $\geq 350^\circ\text{C}$.² However, because of catalyst material's fragmentation associated to the carbon deposition, especially with bulk Fe catalysts, the catalyst's lost mechanical stability cannot be remedied with simple hydrogenation treatments.^{2,28-30}

Under FTS reaction conditions, the Fe-based catalyst material forms various (near-)zerovalent Fe carbides. The Fe carbides are the CO dissociating active phases necessary for both the competing FTS and Boudouard reactions.^{19,27,31,32} The deposition of inactive carbon has been proposed to be associated to the presence of $\theta\text{-Fe}_3\text{C}$ (cementite),³³⁻³⁵ and/or to the transition of C-rich " ϵ -carbides" (i.e. $\epsilon\text{-Fe}_3\text{C}$ and/or $\eta\text{-Fe}_2\text{C}$, **Chapter 2**) to lesser C-containing $\chi\text{-Fe}_5\text{C}_2$ (the Hägg carbide) or $\theta\text{-Fe}_3\text{C}$.³⁶⁻³⁸

Elements from alkali metal group, most often as Na or K, are commonly added chemical promoters to Fe-based FTS reaction catalyst materials. These alkali promoters intrinsically increase the carbon deposition rate.^{2,23} Individually added S as a promoter, is commonly observed to decrease the overall carbon deposition on Fe-based catalyst materials.³⁹⁻⁴³ However, the addition of S to the FTS reaction catalyst also results in an overall decreased CO conversion, therefore necessarily decreasing the carbon deposition.⁴⁴ Decreased CO conversion can also lead to removal of reactor bed hotspots which can lead to observations of decreased carbon deposition.⁴⁵⁻⁴⁸ That is, individual S addition does not necessarily alter the C selectivity between the FTS and Boudouard reactions,⁴⁸ unlike the alkali promoters. When Na and S are added together as promoters, the combined Na-S promotion behaves "alkali-like" and the carbon deposition is effectively increased in the high-temperature FTS reaction in comparison to unpromoted catalyst materials.^{17,20}

The type of carbon formed, deactivating the FTS reaction catalyst material, is often described with loosely defined terms as "graphitic-like".^{34,38,49,50} or as an amorphous carbonaceous overlayer.⁵⁰⁻⁵² Furthermore, the formation of fibrous carbon species is possible under the FTS reaction conditions, in the presence of H_2 or other H containing

chemical species.^{37,53–55} The formation of carbon species has been proposed to be related to the transition of C-rich (“ ϵ ”) into C-poor (χ , θ) Fe carbide phases. The Fe carbide lattice ejected C-atoms have been proposed to be providing nucleation centers for the deactivating carbon formation.^{36–38} The carbon species are thought to evolve from initial polymeric carbon towards more ordered carbon structures.^{38,50}

X-Ray Powder Diffractometry (XRPD) is a suitable tool for characterizing the Fe carbide phases and is widely applied within the FTS reaction research field.^{4,25,29,33,34,36,56–60} Raman Spectroscopy is a technique capable of differentiating between “graphitic-like”, amorphous and fibrous carbon species.^{61–65} Both characterization methods can in principle also be applied under in-situ or operando conditions, thereby allowing probing of the changes in the Fe phases and carbon deposits formation during the FTS reaction. Previously, in-situ/operando Raman Spectroscopy approach has been applied e.g. to follow carbon deposit formation in propane dehydrogenation,^{66,67} and Co-based FTS reaction.⁶⁸

In this Chapter, we combine XRPD and Raman Spectroscopy in one experimental

Figure 6.1

Illustration and photos of the scientific approach applied in this Chapter. Photos of the used a) combined in-situ X-ray Powder Diffractometry (XRPD)/Raman Spectroscopy set-up, b) close-up on the reactor cell (*top panel*) with the measured reactor isothermal zone (*bottom panel*). With the set-up, both c) XRPD and Raman Spectroscopy can be performed in real-time, at reaction conditions relevant to catalysis research.

set-up for studying the transformation of the different Fe phases as well as the evolution of carbon species *in-situ* (i.e. as measured at the reaction conditions) (**Figure 6.1**). This is done with a set-up recently developed in our research group.⁶⁸ The catalyst materials under study are characterized under FTS reaction conditions of 340°C at 10 bar in a H₂:CO 2:1 gas mixture. The studied catalyst materials are supported Fe(-Na-S)/ α -Al₂O₃ catalysts, prepared with and without Na-S promotion. The catalysts have been prepared to contain preformed Fe carbides (i.e. ϵ -Fe₃C, η -Fe₂C, χ -Fe₅C₂ and/or θ -Fe₃C) via a CO carburization step or to contain α -Fe/Fe_xO_y phases via a H₂ reduction step. The details on the catalyst preparation and related characterization data of these catalyst materials can be found in **Chapter 3**. Rietveld Quantitative Phase Analysis (R-QPA) is used to quantify the collected XRPD data. The R-QPA derived Fe phase content changes and the Fe phases' crystallite diameters are qualitatively compared to simultaneous changes observed in the collected Raman spectra.

6.2 EXPERIMENTAL METHODS

6.2.1 Catalyst Preparation

The details on the catalyst synthesis and the applied catalyst treatments of CO carburization and H₂ reduction are described in detail in **Chapter 3**. In short, nominal 7 weight percent (wt-%) of Fe on α -alumina supported (Fe-(Na-S)/ α -Al₂O₃) catalyst materials, with or without Na-S promotion, were synthesized with the use of a Fe citrate precursor. Nominal promoter loadings of 0.29 wt-% for Na and 0.04 wt-% for S were used. The synthesized catalyst materials were calcined (500°C, 6 h), and reduced under H₂ (400°C, 5 h). The H₂ reduction step was followed by a CO carburization step at either 240°C, 340°C or 440°C, in order to prepare preformed Fe carbides in the catalyst materials. For comparison, only H₂ reduced catalyst materials were also prepared.

6.2.2 Catalyst Characterization

6.2.2.1 Details of the In-situ Reactor Cell

The (ex-situ) prepared catalyst materials were characterized under FTS reaction conditions using a modified in-situ XRPD plug flow capillary reactor cell (iKey).^{69–71} The cell was combined with high-temperature Raman Spectroscopy probe.⁶⁸

The iKey reactor cell unit employs two infrared (IR) heater blocks for heating the reactor capillary up to the reaction temperature (**Figure 6.1b**). The reaction temperature is measured with a thermocouple inserted inside the reactor capillary. The original reactor cell was modified by reversing the inlet for reactant gas flow in order to avoid hydrocarbon condensation on the thermocouple inserted inside the reactor

capillary. In addition, the IR heaters were covered with a custom-made stainless steel “chimney” in order to decrease the thermal radiance from the IR heater blocks measured with the Raman probe. Furthermore, the IR heater blocks were resistance matched in order to acquire a uniform isothermal heating zone. Reactor cell temperature calibration was performed under nominal input flow of 1 ml/min Ar and 1 ml/min He by moving the thermocouple inside the reactor capillary while keeping the power fed to the heater at set constant. The reactor isothermal zone was measured to be $340 \pm 1.4^\circ\text{C}$ over a distance of ≈ 11.0 mm. Further details on the used reactor cell type and the laboratory-based XRPD/Raman Spectroscopy set-up can be found from the cited references.^{68–71}

6.2.2.2 Catalytic Reaction

The catalyst materials were inserted to 1 000 μm (10 μm wall thickness) borosilicate capillaries. An undiluted catalyst bed of ≈ 11 mm (6.4–7.2 mg of catalyst material, 212–425 μm catalyst particle size), pinned in between quartz wool plugs, was used for each separate in-situ FTS reaction run. Prior to each run, the experimental set-up was leak tested at 100°C under 1:1 Ar:He (2 ml/min) flow with the loaded sample capillary in place. After the leak test, the capillary reactor pressure was set to 0.5 bar(g).

The FTS reactions were performed at 340°C , at 10 bar H₂:CO:He (2.0:1.0:0.33 volume ratio) total pressure. The nominal input gas flows to the in-situ reactor were 0.6 ml/min H₂, 0.3 ml/min CO and 0.1 ml/min He giving a gas hourly space velocity (GHSV, as total input gas flow per total reactor bed volume) of $\approx 7\,200\text{ h}^{-1}$. After the initial leak testing at 100°C , the reactor capillary was heated to 120°C ($10^\circ\text{C}/\text{min}$) and pressurized at 120°C to 10 bar total reaction pressure. The pressurizing was done with 5x the FTS reaction gas flows, within 1 h. After reaching the 10 bar reaction pressure, the reactor was heated to the reaction temperature of 340°C ($2^\circ\text{C}/\text{min}$). The 0 h Time-on-Stream (ToS) was taken as the moment when 340°C was reached and the FTS reaction was then subsequently ran for 72 h. After the 72 h FTS reaction, the reactor was cooled down to 100°C within 1 h under the set H₂:CO:He flow while simultaneously decreasing the reaction pressure to 0.5 bar(g) ($0.5\text{ bar}/\text{min}$). At 100°C , the input gas flow was switched to 1:1 Ar:He (2 ml/min) and the reactor was flushed under the inert gases. H₂, Ar and He gas purities were grade 5.0 (99.999 % pure) and for CO grade 2.5 (99.5 % pure), as supplied by Linde Gas Benelux.

During the FTS reactions, up- and downstream pressure gauges and a mass flow meter upstream of the reactor capillary were used to follow possible mass flow limitations in the reactor bed. No mass flow limitations were observed in any of the performed FTS reaction runs.

6.2.2.3 In-situ X-ray Powder Diffractometry

XRPD patterns were collected in-situ during the FTS reaction (340°C, 10 bar, H₂:CO:He) as well as in quasi-in-situ (at 100°C, 0.5 bar, Ar:He, i.e. “spent catalyst”) after the respective 72 h FTS reaction run. The initial “fresh catalyst” was measured also under 100°C (0.5 bar, Ar:He) after the initial leak testing step. For collecting the in-situ XRPD patterns, a Bruker D8 Discover instrument in Debye-Scherrer transmission (capillary) geometry with a Mo ($K_{\alpha 1}$ 0.709 Å) source was used, as in previous Chapters. At the beginning of each in-situ reaction run, the capillary was focused onto the X-ray beam (beam: $\approx 600 \times 15\,000$ μm , height $\times$ width) for maximum diffraction. The diffraction patterns were collected over a 2θ range of 5–39° with scan step size of 0.015°. For collecting the XRPD patterns before and after the FTS reaction (quasi-in-situ), 6 h total measurement time was used. For the in-situ measurements during the FTS reaction at 340°C and during the pressurizing and temperature ramp steps, 0.5 h total measurement time was used. The term X-ray Powder Diffractometry (XRPD) is used to refer to X-ray diffraction phenomena based characterization experiments that are done under powder diffraction conditions.⁷²

The R-QPA method was employed for quantifying the crystalline Fe phases in the collected XRPD patterns. The application of R-QPA fitting has been described in detail in **Chapter 3** and is applied within this Chapter in a similar manner, with few modifications in the applied fitting model. As the primary modification in the R-QPA fitting model, the lattice parameters for the support material $\alpha\text{-Al}_2\text{O}_3$ were also refined simultaneously – unlike in the previous Chapters – with the rest of the fitted phases. This was done in order to accommodate the thermal expansion of the materials lattices during the in-situ measurements at elevated temperature. The effects of crystal lattice thermal expansion,⁷³ reactor capillary deformation/displacement and sample material density changes in the capillary,⁷⁴ all affect the phases’ diffraction peak positions and thus the lattice parameters observed in the performed in-situ XRPD measurements. The changes to the lattice parameters for the fitted phases could not be decoupled from the mentioned experimental effects in the in-situ XRPD runs and the intrinsic phase lattice parameters could not be solved for the fitted phases. All refined lattice parameters were constrained to an arbitrary range with constraints from -0.01 Å to +0.05 Å from the literature values (for Fe carbides, **Chapter 3**). The R-QPA fitting models and constrain values were adjusted until the measured XRPD diffraction peak positions were satisfactorily accounted for. The literature and database sources for the crystal structures used in the R-QPA fitting models are given in **Chapter 3**.

As further differences to the applied fitting model, all measured XRPD pattern backgrounds were modelled with a 3rd order Chebyshev polynomial. Three independent Lorentzian peaks were used for fitting the amorphous content scattering

and/or diffraction contribution within the range ≈ 8 – $12^\circ 2\theta$.

Predetermined R-QPA fitting models were applied on the measured quasi- and in-situ measured XRPD patterns over the full XRPD measurement range using a batch mode with the Bruker TOPAS v5.0 software. The phases with <0.4 wt-% phase content and/or relative wt-% fitting errors ≥ 30 % were removed from the fitting models. The measured, background subtracted, XRPD patterns were aligned and normalized to the α -Al₂O₃ peak (0 2 4) at its nominal position of $23.515^\circ 2\theta$ (at Mo K α_1) at room temperature, for presenting the diffraction pattern heatmaps versus the FTS reaction ToS.

The R-QPA derived values from the in-situ XRPD runs are reported as 5-point median values of the data points obtained every 0.5 h and expressed with median's Standard Deviation (STD) as an error estimate. R-QPA derived values for the “fresh catalysts” and quasi-in-situ measured “spent catalysts” after the FTS reaction run are reported for each single (6 h) measurement with their respective R-QPA fitting errors as the error estimates.

6.2.2.4 In-situ Raman Spectroscopy

Simultaneously to the in-situ XRPD measurements, in-situ Raman Spectroscopy measurements were performed in order to follow the formation and further development of carbon species on the catalyst materials during the FTS reactions. A thermoelectrically cooled AvaRaman (Avantes) spectroscopy system with 50 mW 532 nm excitation laser, coupled with a high-temperature InPhotonics Raman probe with ≈ 200 μm measurement spot size at focus, was used. The spectrometer's spectral resolution was 6 cm^{-1} . At the start of each FTS reaction run, the Raman probe was focused on the catalyst bed using the α -Al₂O₃ peak at $\approx 4\,389\text{ cm}^{-1}$ (see e.g. RRUFF database #R040096 for reference). The dark spectrum corrected, in-situ Raman spectra were collected over a spectral range of ≈ 174 – $5\,685\text{ cm}^{-1}$. A single Raman spectrum was recorded every 10 min by averaging 600 scans with 1 s integration time.

Carbon Nanofibers (CNF, Pyrograf, PR-24-XT-LHT), graphite (Aldrich, 282863), Activated Carbon (AC, Alfa Aesar, Norit ROW 0.8 mm, L16334) and Carbon Nanotubes (CNT, Baytubes, C150 HP) were measured as reference carbon materials. The reference materials were measured at room temperature (600 scans with a 1 s integration time) using a stand-alone LaserQuantum MPC 6000 532 nm laser operated at 200 mW power. The same AvaRaman spectrometer and the high-temperature InPhotonics Raman probe were used to collect the carbon reference spectra as was used for the in-situ Raman Spectroscopy measurements.

The in-situ collected Raman spectra were corrected for (fluorescence) background with the use of the Asymmetric Least Squares Smoothing (ALSS) algorithm. The so-

Table 6.1

Overview of the used shorthand notation for catalyst materials used in this Chapter. The catalyst materials after the applied H₂ reduction or CO carburization catalyst treatments are discussed in more detail in *Chapter 3*.

Shorthand Notation	Catalyst Material Description
H ₂	H ₂ reduction at 400°C for 5 h, after the calcining step
240, 340, 440	CO carburization (at 1 atm) temperature in °C, after the reduction step
UP	Unpromoted Fe/ α -Al ₂ O ₃ catalyst
Na-S	Na-S promoted Fe-Na-S/ α -Al ₂ O ₃ catalyst
Carb.	Catalyst material after H ₂ reduction or CO carburization ("fresh catalyst")
Q-FTS	Catalyst material after 72 h 340°C, 10 bar in-situ FTS run, measured quasi-in-situ at 100°C (0.5 bar, 1:1 Ar:He) ("spent catalyst").

called D ($\approx 1350\text{ cm}^{-1}$) and G ($\approx 1600\text{ cm}^{-1}$) Raman bands were fitted with four peak shapes. Iterative peak fitting (Levenberg-Marquardt) algorithm was used to find the best fit to the measured spectra.

D-band was fitted with Lorentzian peak D₁ at $\approx 1320\text{ cm}^{-1}$ and Gaussian peaks D₃ at $\approx 1500\text{ cm}^{-1}$ and D₄ at $\approx 1220\text{ cm}^{-1}$. G-band was fitted with a single Gaussian peak shape. The data points that had $\geq 40\%$ relative error in the fitted peak area or width were filtered out. Peaks fitted for the D₃ and D₄ positions were constrained near their nominal locations during the iterative peak fitting process. This was done in order to avoid the tendency of the D₃ and D₄ peaks from shifting and nearly or fully overlapping with the D₁- and G-band positions. Thus, the D₃ peak was constrained to a range of $1465 - 1525\text{ cm}^{-1}$ and D₄ to a range of $1100 - 1230\text{ cm}^{-1}$ during the fitting process.

The obtained fitted peak positions were used to follow the D- and G-band peak position shifts during the FTS reaction. The peak intensities $I(D)$ (D-band) and $I(G)$ (G-band) in the measured in-situ Raman spectra were obtained from the locations defined by the fitted peak positions as 3-point median values. The fitted peak widths were used to estimate the measured D- and G-band widths as peak Full Width at Half Maximums (FWHMs). The collected data points obtained every 10 mins were averaged to 12-point median values and are presented with their corresponding STDs as the error estimates.

For each in-situ Raman measurement run, the obtained Raman spectra were normalized to the, background corrected, maximum peak intensity of the Raman G-band within 0-72 h ToS. The measured carbon reference materials were normalized to the, background corrected, maximum of their respective Raman G-bands, and fitted with four individual peaks akin to the measured data.

6.3 RESULTS AND DISCUSSION

A combined in-situ XRD/Raman Spectroscopy set-up has been used to monitor the

changes taking place in the carbon species and Fe carbide phases formed during the FTS reaction (340°C, 10 bar, H₂:CO:He 2.0:1.0:0.33, GHSV 7 200 h⁻¹). This methodology has been applied on both unpromoted Fe/ α -Al₂O₃ (shorthand *UP*) and the Na-S promoted Fe-Na-S/ α -Al₂O₃ (*Na-S*) catalyst materials.

By applying a H₂ reduction and CO carburization treatments, the relative amounts and types of preformed Fe carbides and/or α -Fe/Fe_xO_y phases were varied in the starting catalyst materials. The shorthand notation of 240, 340 or 440 is used to refer to the applied CO carburization temperature (in °C). Shorthand notation *H₂* is used for the only H₂ reduced catalyst materials. The shorthand notation of *Carb.* (i.e. “fresh catalyst”)

Figure 6.2

X-ray Powder Diffractometry (XRPD) results for UP H₂ (Fe/ α -Al₂O₃) catalyst material during 72 h Fischer-Tropsch Synthesis (FTS) reaction. A) Heatmap of aligned and background corrected, in-situ collected XRPD patterns. B) Measured and Rietveld method calculated XRPD patterns at -3 h, 5 h and 70 h Time-on-Stream (ToS). Some characteristic peak positions for the Fe phases are indicated with markers. C) The crystalline Fe phase composition of catalyst and D) Fe phases average crystallite sizes during the 72 h FTS reaction. The measurements before (Carb.) and quasi-in-situ (Q-FTS) after the FTS reaction run are included for comparison. FTS conditions: 340°C, 10 bar, H₂:CO:He 2.0:1.0:0.33 v/v, $\approx$ 7 200 h⁻¹.

is used collectively for the catalyst characterizations done before the FTS reaction runs. *Q-FTS* notation is used for characterizations done after the FTS reaction runs (i.e. “spent catalyst”), as measured quasi-in-situ. The used shorthand notation, within the Chapter, for the catalyst materials is summarized in **Table 6.1**. Details of the catalyst material preparation and the related characterization data can be found in **Chapter 3**, while their catalytic performance in the FTS reaction is described in **Chapter 4**.

6.3.1 In-situ X-ray Powder Diffraction

The results for different in-situ XRPD reaction runs are given in **Figures 6.2-6.9** for the

Figure 6.3

X-ray Powder Diffraction (XRPD) results for Na-S H_2 (Fe-Na-S/ $\alpha\text{-Al}_2\text{O}_3$) catalyst material during 72 h Fischer-Tropsch Synthesis (FTS) reaction. A) Heatmap of aligned and background corrected, in-situ collected XRPD patterns. B) Measured and Rietveld method calculated XRPD patterns at -3 h, 5 h and 70 h Time-on-Stream (ToS). Some characteristic peak positions for the Fe phases are indicated with markers. C) The crystalline Fe phase composition of catalyst and D) Fe phases average crystallite sizes during the 72 h FTS reaction. The measurements before (Carb.) and quasi-in-situ (Q-FTS) after the FTS reaction run are included for comparison. FTS conditions: 340°C, 10 bar, $\text{H}_2\text{:CO:He}$ 2.0:1.0:0.33 v/v, $\approx 7\,200\text{ h}^{-1}$.

Figure 6.4

X-ray Powder Diffraction (XRPD) results for UP 240 (Fe/ α -Al₂O₃) catalyst material during 72 h Fischer-Tropsch Synthesis (FTS) reaction. A) Heatmap of aligned and background corrected, in-situ collected XRPD patterns. B) Measured and Rietveld method calculated XRPD patterns at -3 h, 5 h and 70 h Time-on-Stream (ToS). Some characteristic peak positions for the Fe phases are indicated with markers. C) The crystalline Fe phase composition of catalyst and D) Fe phases average crystallite sizes during the 72 h FTS reaction. The measurements before (Carb.) and quasi-in-situ (Q-FTS) after the FTS reaction run are included for comparison. FTS conditions: 340°C, 10 bar, H₂:CO:He 2.0:1.0:0.33 v/v, $\approx$ 7 200 h⁻¹.

studied UP and Na-S catalyst materials. In the figures, the aligned and background corrected in-situ collected XRPD patterns during the FTS reactions are given as heatmaps (**Figures 6.2a-6.9a**) as well as individual diffraction patterns at start of the FTS reaction at -3 h (120°C, H₂:CO), 5 h and 70 h ToS (340°C, H₂:CO) (**Figures 6.2b-6.9b**). Markers on characteristic Fe phase diffraction positions in have been added to the diffraction pattern containing figures.

For each of the individual diffraction patterns, the corresponding Rietveld method calculated patterns are also included in the figures (**Figures 6.2b-6.9b**). The most intense and sharp diffraction peaks in the individual diffraction patterns in the figures

Figure 6.5

X-ray Powder Diffraction (XRPD) results for Na-S 240 ($\text{Fe-Na-S}/\alpha\text{-Al}_2\text{O}_3$) catalyst material during 72 h Fischer-Tropsch Synthesis (FTS) reaction. A) Heatmap of aligned and background corrected, in-situ collected XRPD patterns. B) Measured and Rietveld method calculated XRPD patterns at -3 h, 5 h and 70 h Time-on-Stream (ToS). Some characteristic peak positions for the Fe phases are indicated with markers. C) The crystalline Fe phase composition of catalyst and D) Fe phases average crystallite sizes during the 72 h FTS reaction. The measurements before (Carb.) and quasi-in-situ (Q-FTS) after the FTS reaction run are included for comparison. FTS conditions: 340°C, 10 bar, $\text{H}_2\text{:CO:He}$ 2.0:1.0:0.33 v/v, $\approx 7\,200\text{ h}^{-1}$.

(e.g. at 19.58° and 27.13° 2θ) originate from the support $\alpha\text{-Al}_2\text{O}_3$, a phase of which diffraction markers are excluded for convenience.

The Fe carbide phases observed in the FTS reaction related research have been identified as $\varepsilon\text{-Fe}_3\text{C}$ $P6_322$ (182), $\eta\text{-Fe}_2\text{C}$ $Pnnm$ (58), $\chi\text{-Fe}_5\text{C}_2$ $C2/c$ (15) (the Hägg carbide), $\theta\text{-Fe}_3\text{C}$ $Pnma$ (62) (cementite) and $\theta\text{-Fe}_7\text{C}_3$ $Pnma$ (62) (Eckström-Adcock Carbide) on basis of the literature in **Chapter 2**. For all of the performed Rietveld method fittings (i.e. R-QPA) on the quasi- and in-situ measured XRPD patterns, the previously identified Fe carbide crystal structures give very good calculated fits (**Figures 6.2b-6.9b**).

Despite the Fe oxide phase being fitted with a Fe₃O₄ crystal structure, similar overall R-QPA fits could have been archived with ferrihydrite crystal structures.⁷⁵ The Rietveld method calculated Fe phase patterns have been given and discussed in detail in the previous Chapters and are omitted here.

Background corrected R-values (R_{wp}) representing the difference between the Rietveld calculated and measured XRPD patterns are given in **Figure 6.10**.⁷⁶ The R-QPA derived elemental Fe contents from the in-situ XRPD patterns stay close, yet are somewhat higher (≈ 6.8 -8.0 wt-%) (**Figure 6.11**), than the expected ≈ 6.5 -6.6 wt-% of elemental Fe for each catalyst material (**Chapter 3**).

Figure 6.6

X-ray Powder Diffractometry (XRPD) results for UP 340 (Fe/ α -Al₂O₃) catalyst material during 72 h Fischer-Tropsch Synthesis (FTS) reaction. A) Heatmap of aligned and background corrected, in-situ collected XRPD patterns. B) Measured and Rietveld method calculated XRPD patterns at -3 h, 5 h and 70 h Time-on-Stream (ToS). Some characteristic peak positions for the Fe phases are indicated with markers. C) The crystalline Fe phase composition of catalyst and D) Fe phases average crystallite sizes during the 72 h FTS reaction. The measurements before (Carb.) and quasi-in-situ (Q-FTS) after the FTS reaction run are included for comparison. FTS conditions: 340°C, 10 bar, H₂:CO:He 2.0:1.0:0.33 v/v, ≈ 7 200 h⁻¹.

The main contribution on the varying elemental Fe content originates, likely, from the varying accuracy of the fitted background polynomial. This alters the absolute quantity of the fitted crystalline material area and thus the derived elemental Fe wt-%s. Both, the R-values and the R-QPA derived elemental Fe contents, indicate very good and consistent R-QPA results in between the performed in-situ reaction runs.

6.3.1.1 Fe Phase Rietveld Quantitative Phase Analysis Quantification Changes

For both UP and Na-S H_2 catalyst materials, upon reaching the 0 h ToS when the FTS

Figure 6.7

X-ray Powder Diffraction (XRPD) results for Na-S 340 ($Fe-Na-S/\alpha-Al_2O_3$) catalyst material during 72 h Fischer-Tropsch Synthesis (FTS) reaction. A) Heatmap of aligned and background corrected, in-situ collected XRPD patterns. B) Measured and Rietveld method calculated XRPD patterns at -3 h, 5 h and 70 h Time-on-Stream (ToS). Some characteristic peak positions for the Fe phases are indicated with markers. C) The crystalline Fe phase composition of catalyst and D) Fe phases average crystallite sizes during the 72 h FTS reaction. The measurements before (Carb.) and quasi-in-situ (Q-FTS) after the FTS reaction run are included for comparison. FTS conditions: 340°C, 10 bar, $H_2:CO:He$ 2.0:1.0:0.33 v/v, $\approx 7\ 200\ h^{-1}$.

Figure 6.8

X-ray Powder Diffraction (XRPD) results for UP 440 (Fe/ α -Al₂O₃) catalyst material during 72 h Fischer-Tropsch Synthesis (FTS) reaction. A) Heatmap of aligned and background corrected, in-situ collected XRPD patterns. B) Measured and Rietveld method calculated XRPD patterns at -3 h, 5 h and 70 h Time-on-Stream (ToS). Some characteristic peak positions for the Fe phases are indicated with markers. C) The crystalline Fe phase composition of catalyst and D) Fe phases average crystallite sizes during the 72 h FTS reaction. The measurements before (Carb.) and quasi-in-situ (Q-FTS) after the FTS reaction run are included for comparison. FTS conditions: 340°C, 10 bar, H₂:CO:He 2.0:1.0:0.33 v/v, $\approx 7\ 200\ \text{h}^{-1}$.

reaction temperature of 340°C is reached, the majority of the initially present α -Fe/Fe_xO_y phases transforms into the temperature's most stable Fe carbide phase of χ -Fe₅C₂ (**Figures 6.2c** and **6.3c**).^{29,36,77–84} Without the added Na-S promotion, the transition of α -Fe/Fe_xO_y phases to χ -Fe₅C₂ takes longer in comparison to the unpromoted catalyst materials. Indeed, at 0 h ToS: for the Na-S H₂ catalyst material the χ -Fe₅C₂ phase already accounts for $\approx 81 \pm 7\%$ of the Fe phases (**Figure 6.3c**), while for the UP H₂ catalyst material only $\approx 56 \pm 15\%$ of the χ -Fe₅C₂ phase is present (**Figure 6.2c**).

This can be explained by an observed alkali effect, i.e. Na(-S) aiding in the reduction of Fe oxides at $\leq 300^\circ\text{C}$ by CO.^{56,85,86} In the Na-S H₂ catalyst materials the Fe oxidation

Figure 6.9

X-ray Powder Diffraction (XRPD) results for Na-S 440 (Fe-Na-S/ α -Al₂O₃) catalyst material during 72 h Fischer-Tropsch Synthesis (FTS) reaction. A) Heatmap of aligned and background corrected, in-situ collected XRPD patterns. B) Measured and Rietveld method calculated XRPD patterns at -3 h, 5 h and 70 h Time-on-Stream (ToS). Some characteristic peak positions for the Fe phases are indicated with markers. C) The crystalline Fe phase composition of catalyst and D) Fe phases average crystallite sizes during the 72 h FTS reaction. The measurements before (Carb.) and quasi-in-situ (Q-FTS) after the FTS reaction run are included for comparison. FTS conditions: 340°C, 10 bar, H₂:CO:He 2.0:1.0:0.33 v/v, $\approx$ 7 200 h⁻¹.

shell is removed more efficiently by CO in the presence of Na(-S) promotion during the temperature ramp ($\approx$ 2-0 h ToS) to 340°C, than with the unpromoted UP H₂ catalyst materials. The Fe oxides, which are present as Fe particle shell and/or core, are reduced into α -Fe and subsequently converted into the χ -Fe₅C₂ phase by CO. Regardless of the Na-S promotion, the transition of α -Fe to Fe carbides in the presence of CO with temperatures $\geq$ 200-250°C is very fast.^{36,83,87-89} and not the limiting step in the Fe carbide formation.⁹⁰

As a discrepancy to the previous results described in **Chapter 4**, during the in-situ XRPD run within this Chapter: no η -Fe₂C phase is observed for the Na-S H₂ catalyst

Figure 6.10

Background corrected R-values (R_{wp}) for a) UP (Fe/ α -Al₂O₃) and b) Na-S (Fe-Na-S/ α -Al₂O₃) H₂, 240, 340 and 440 catalyst materials. Values during the in-situ Fischer-Tropsch Synthesis (FTS) runs versus Time-on-Stream (ToS) and for the catalysts measured before (Carb.) and quasi-in-situ after the reaction run (Q-FTS).

material. Previously, after the 72 h FTS (340°C, H₂:CO:He 2.0:1.0:0.33, GHSV $\approx$ 5 000 h⁻¹) reaction run in **Chapter 4**, $\approx$ 27 % η -Fe₂C phase contribution in the R-QPA quantifications was observed for the Na-S H₂ (FTS) catalyst. The presence of “ ϵ -carbides” (i.e. ϵ -Fe₃C/ η -Fe₂C phases) is generally increased in Fe-based FTS catalyst materials after the FTS reaction with added alkali elements as K or Na.^{4,56,91,92}

As discussed in more detail in **Chapter 3**, the η -Fe₂C phase does not form $\geq$ 300°C but can be stable up to $\approx$ 340°C if it is formed and present prior to the FTS reaction. When comparing the UP and Na-S 240 catalyst materials with the initial presence of Fe carbides as the ϵ -Fe₃C and η -Fe₂C phases in the Carb. catalyst materials, the presence of Na-S promotion further stabilizes the η -Fe₂C phase during the FTS reaction run. For the Na-S 240 Q-FTS measurement, 50 ± 1 % of the η -Fe₂C phase is quantified (**Figure 6.4c**) after the FTS reaction run in comparison to 13 ± 1 % of the phase in UP 240 Q-FTS catalyst material (**Figure 6.5c**).

Thus, altogether, the results for the H₂ and 240 catalyst materials suggest that for an observable Na(-S) stabilization effect of the η -Fe₂C phase in the FTS reaction: the ϵ -Fe₃C/ η -Fe₂C phases need to be present prior to the start of the FTS reaction. Without Na(-S) promotion, significantly lesser amount of the initial ϵ -Fe₃C/ η -Fe₂C phases are stabilized as the η -Fe₂C phase during the high-temperature FTS reaction.

Rather interestingly, the requirement for a priori presence of the ϵ -Fe₃C/ η -Fe₂C phases for the η -Fe₂C phase stability in the FTS reaction is comparable to the stability behavior of “ ϵ -iron (carbo)nitrides”.⁹³ These Fe (carbo-)nitrides have crystal structures closely related to the ϵ -Fe₃C/ η -Fe₂C phases.^{94–99} The precise, fundamental reasons for

Figure 6.11

The Rietveld Quantitative Phase Analysis (R-QPA) derived elemental Fe wt-%'s for a) UP ($\text{Fe}/\alpha\text{-Al}_2\text{O}_3$) and b) Na-S ($\text{Fe-Na-S}/\alpha\text{-Al}_2\text{O}_3$) H_2 , 240, 340 and 440 catalyst materials. Values during the in-situ Fischer-Tropsch Synthesis (FTS) runs versus Time-on-Stream (ToS) and for the catalysts measured before (Carb.) and quasi-in-situ after the reaction run (Q-FTS).

the increased stability behavior with the added Na(-S) promotion in the FTS reaction with crystal structures corresponding to the $\eta\text{-Fe}_2\text{C}$ and “ ϵ -iron (carbo)nitrides” phases would make an interesting topic for a further study. The $\epsilon\text{-Fe}_3\text{C}$ phase was not stable in the FTS reaction (**Figures 6.4c** and **6.5c**), regardless of the Na-S promotion.

Besides the stabilization of the $\eta\text{-Fe}_2\text{C}$ phase by the Na-S promotion addition in the Na-S 240 catalyst materials, the catalysts Fe_3O_4 content is also reduced during the FTS reaction. A steady Fe_3O_4 fraction of $\approx 20\%$ is quantified for the UP 240 catalyst (**Figure 6.4c**) while for the Na-S 240 catalyst material (**Figure 6.5c**) only $\approx 8\%$ of Fe_3O_4 is observed after the start of the FTS reaction. This difference in the Fe oxide content is visible (at $\approx 27.5^\circ 2\theta$) in the in-situ collected XRPD patterns (**Figures 6.4a** and **6.5a**). The added alkali has been observed to reduce the Fe oxide content in Fe-based catalyst materials during the FTS reaction also in the literature,^{91,92} in agreement with the results for the Na-S 240 catalyst material.

Rather counter-intuitively, Na-S promotion increases the Fe oxide content in the Na-S 240 Carb. catalyst materials after the CO carburization (i.e. in the fresh catalysts), as is evident by comparing the R-QPA quantifications in **Figures 6.4c** and **6.5c**. This effect presumably originates from the Na-S promotion induced increased Fe phase affinity towards O atoms from the CO dissociation during the CO carburization step with short treatment time (**Chapter 3**).

Despite the Na-S 240 catalyst behaving as expected, i.e. Na-S promotion decreasing Fe_3O_4 content during the FTS reaction, why both UP and Na-S 240 catalyst materials show the presence of Fe_3O_4 *at all* during the in-situ XRPD runs, is odd. Any of the UP H_2 ,

340 or 440 (**Figures 6.2c, 6.6c and 6.8c**), or Na-S H₂, 340 or 440 (**Figures 6.3c, 6.7c and 6.9c**) catalysts *do not* show a significant presence or stabilization of the Fe₃O₄ phase. Furthermore, in **Chapter 4**, neither of the UP or Na-S 240 (FTS) catalyst materials characterized ex-situ after their FTS reaction runs showed any presence of the Fe₃O₄ phase. Perhaps, the ϵ -Fe₃C/ η -Fe₂C phases might be more susceptible towards Fe carbide reoxidation by CO₂ and H₂O,^{2,29,100–102} than the other Fe phases. Furthermore, undiluted reactor beds were used with the in-situ XRPD runs in contrast to the SiC diluted reactor beds used in **Chapter 4** during the FTS reaction runs. Possibly, the catalyst bed dilution with inert SiC, allows easier removal of the CO₂ and H₂O, in that way preventing the Fe phases oxidation.

With respect to the phase changes in the UP and Na-S 340 and 440 catalyst materials during their respective FTS reaction runs, only minor changes take place in contrast to the initial Carb. catalyst materials (**Figures 6.6c–6.9c**). Small amount of Fe₃O₄ ($\approx 7\%$) is present in the Na-S 340 catalyst material during the first 10 h ToS of the FTS reaction. For the UP 340 catalyst material, no Fe oxide is quantified. For Na-S 240 catalyst material, the Na-S promotion aided in the Fe₃O₄ reduction during the FTS reaction. However, when comparing the UP 340 and Na-S 340 catalysts materials, only the Na-S 340 catalyst shows the presence of the Fe oxides (**Figures 6.6c and 6.7c**). Thus, giving the opposite result as would be expected based on the discussion in earlier paragraphs.

A possible explanation could be the initially higher carbon deposition with the Na-S 340 than with the UP 340 catalyst materials during the initial CO carburization to prepare the catalyst (**Chapter 3**). The deposited carbon could be responsible for mass transfer limitations on the Na-S 340 catalyst material inhibiting the reduction of the initial Fe₃O₄ during the FTS reaction. Furthermore, Na-S 340 catalyst material gave significantly higher CO conversion than the UP 340 catalyst during the FTS reaction (**Chapter 4**). Therefore, Fe phases' reoxidation by H₂O may also play a role resulting in the presence of Fe₃O₄ in the Na-S 340 catalyst material, together with the undiluted reactor bed used for the in-situ XRPD runs.

For the UP and Na-S 440 catalyst materials, the effect of Na-S promotion is to aid the transformation of the θ -Fe₃C phase into χ -Fe₅C₂, which is the most stable Fe carbide at 340°C, during the FTS reaction (**Figures 6.8c and 6.9c**). With the Na-S 440 catalyst material, the θ -Fe₃C phase content steadily decreases with increasing χ -Fe₅C₂ contribution (**Figure 6.9c**).

6.3.1.2 Changes in Fe Phases' Crystallite Diameters

The in-situ XRPD observations for the R-QPA derived Fe phases' crystallite (volume-weighted) mean diameters follow the Fe phase quantities in the FTS reaction. The increasing phase quantity in general translates to increasing Fe phase crystallite

diameters, as more of the phase is present, thus allowing formation of larger crystallites. The Fe crystallite diameter evolutions are plotted in **Figures 6.2d-6.9d** for the studied catalyst materials.

Additionally, the presence of Na-S promotion favors the formation of larger Fe carbide crystallites for the H₂, 240 and 340 catalyst materials, while for the 440 catalyst materials the situation is mixed. The Na-S H₂, 240 and 340 catalyst materials show Fe carbide crystallite growth within the first ≈ 10 h ToS in comparison to their UP catalyst counterparts (**Figures 6.2d-6.7d**). This could be associated to Fe particle growth, which has been observed to take place within the first hours of the FTS reaction when Na-S promotion is added to the catalyst.²⁰ In **Chapter 4**, Transmission Electron Microscopy (TEM) results derived Fe particle growth could be observed for the Na-S 240 and Na-S 340 catalyst materials after the FTS reaction run in comparison to the respective UP catalyst materials, but not for the Na-S H₂ catalyst material.

However, as discussed in more detail in **Chapter 4**, when comparing ex-situ obtained results for the R-QPA and TEM, the Fe phase crystallite diameters did not conclusively follow the TEM-based Fe particle trends after the FTS reaction. In general, *Fe crystallite growth does not necessitate Fe particle growth*, as the measurables are different.¹⁰³ Thus, definitive conclusions whether Fe particle growth takes place cannot be made solely on the basis of the in-situ XRPD derived R-QPA crystallite diameter results. Whatever the fundamental origins are, the Na-S promotion causes increased Fe carbide crystallite mean diameters and the increase takes place within the first ≈ 10 h ToS of the FTS reaction.

The peculiar effect of Na-S promotion decreasing the θ -Fe₃C phase stability is also observed in the changes of the θ -Fe₃C phase's crystallite diameters between the UP and Na-S 440 catalyst materials (**Figures 6.8d** and **6.9d**). The added Na-S promotion induces slowly decreasing θ -Fe₃C crystallite mean diameters while increasing both, the χ -Fe₅C₂ content (**Figure 6.9c**), and its crystallite mean diameter (**Figure 6.9d**).

The large crystallite mean diameters with large STDs for the ϵ -Fe₃C and η -Fe₂C phases at around ≈ 0 h ToS are due to correlations between the ϵ -Fe₃C, η -Fe₂C and α -Al₂O₃ lattice parameters. During the temperature ramp $\lesssim 0$ h ToS, the ϵ -Fe₃C and η -Fe₂C crystal structures tend to fit the sharp α -Al₂O₃ diffraction peak (1 1 3) at $\approx 19.58^\circ 2\theta$, giving rise to very large crystallite mean diameters with large STDs. After the steady FTS reaction temperature is reached and/or the ϵ -Fe₃C phase consumed $\gtrsim 3$ h ToS, no correlation exists anymore with the η -Fe₂C and α -Al₂O₃ phases and η -Fe₂C crystallite mean diameters become consistent again (**Figures 6.4** and **6.5**).

Summarizing the results so far, as based on the R-QPA results derived from the in-situ XRPD runs, the Na-S promotion has the effects of:

- i) To stabilize the η -Fe₂C phase if ϵ -Fe₃C and/or η -Fe₂C phases are present in the initial catalyst at the start of the FTS reaction (Na-S H₂ versus Na-S 240);
- ii) to decrease Fe₃O₄ content (UP 240 versus Na-S 240);
- iii) to destabilize θ -Fe₃C phase during the FTS reaction (UP 440 versus Na-S 440); and also
- iv) Fe carbide crystallite mean diameters grow larger within the first 10 h ToS (excluding the θ -Fe₃C in Na-S 440 catalyst material) in comparison to the respective UP catalysts.

6.3.2 In-situ Raman Spectroscopy

Simultaneously to the in-situ XRPD data collection, in-situ Raman Spectroscopy

Figure 6.12

In-situ Raman Spectroscopy of H₂ catalysts during the 72 h Fischer-Tropsch Synthesis (FTS) reaction. 3D plot of background corrected and normalized Raman spectra a) for UP H₂ and c) for Na-S H₂ (Fe(-Na-S)/ α -Al₂O₃) catalysts. Corresponding heatmaps of the Raman spectra b) for UP H₂ and d) Na-S H₂. D- ($\approx$ 1 350 cm⁻¹) and G-bands ($\approx$ 1 600 cm⁻¹) are marked to the heatmaps (D, G). FTS conditions: 340°C, 10 bar, H₂:CO:He 2.0:1.0:0.33 v/v, $\approx$ 7 200 h⁻¹.

Figure 6.13

In-situ Raman Spectroscopy of 240 catalyst materials during the 72 h Fischer-Tropsch Synthesis (FTS) reaction. 3D plot of background corrected and normalized Raman spectra a) for UP 240 and c) for Na-S 240 (Fe(-Na-S)/ α -Al₂O₃) catalysts. Corresponding heatmaps of the Raman spectra b) for UP 240 and d) Na-S 240. D- (≈ 1350 cm⁻¹) and G-bands (≈ 1600 cm⁻¹) are marked to the heatmaps (D, G). FTS conditions: 340°C, 10 bar, H₂:CO:He 2.0:1.0:0.33 v/v, ≈ 7200 h⁻¹.

measurements were performed over the duration of the 72 h FTS reactions. With FTS reaction temperatures above $\approx 300^\circ\text{C}$, the Boudouard reaction deposits carbon from CO on the FTS reaction catalyst materials.^{2,23–25} In the spectra, bands with Raman shifts of ≈ 1350 cm⁻¹ (D-band) and ≈ 1600 cm⁻¹ (G-band) originate from carbon species.^{61–65,104} These bands can be used to follow the carbon deposition process during the course of the FTS reaction.

The in-situ collected, background corrected and normalized Raman spectra of the studied catalyst materials are given as 3D plots and heatmaps in **Figures 6.12–6.15**. The in-situ Raman spectra are shown over the Raman shift range 800–2000 cm⁻¹ showing the evolution of the D- and G-bands during the 72 h ToS in the FTS reaction.

The deviations in the in-situ collected Raman spectra in **Figure 6.12c–d** with the Na-

Figure 6.14

In-situ Raman Spectroscopy of 340 catalyst materials during the 72 h Fischer-Tropsch Synthesis (FTS) reaction. 3D plot of background corrected and normalized Raman spectra a) for UP 340 and c) for Na-S 340 (Fe(-Na-S)/ α -Al₂O₃) catalysts. Corresponding heatmaps of the Raman spectra b) for UP 340 and d) Na-S 340. D- (≈ 1350 cm⁻¹) and G-bands (≈ 1600 cm⁻¹) are marked to the heatmaps (D, G). FTS conditions: 340°C, 10 bar, H₂:CO:He 2.0:1.0:0.33 v/v, ≈ 7200 h⁻¹.

S H₂ catalyst material originate from a very high fluorescence background during the FTS reaction run. From the FTS reaction ≈ 0 h ToS onwards until ≈ 60 h ToS, high spectral background caused very high collected counts in the Raman spectrometer. This caused formation of artifacts with spectral period of $\approx 198 \pm 6$ cm⁻¹ together with the demanding background correction. Origins of the high spectral background for the run are unclear, but were only repeated in a significantly lesser degree with the run Na-S 240 (**Figure 6.13c-d**), and not with the other FTS reaction runs.

The in-situ collected Raman Spectroscopy data is not quantitative without a proper use of an internal standard. Inherently, the intensity of the Raman spectra is dependent on the focus of the incident excitation laser on the catalyst material, thereby causing variations in the absolute amount of collected Raman scattered photons. Thus, the

Figure 6.15

In-situ Raman Spectroscopy of 440 catalyst materials during the 72 h Fischer-Tropsch Synthesis (FTS) reaction. 3D plot of background corrected and normalized Raman spectra a) for UP 440 and c) for Na-S 440 (Fe(-Na-S)/ α -Al₂O₃) catalysts. Corresponding heatmaps of the Raman spectra b) for UP 440 and d) Na-S 440. D- (≈ 1350 cm⁻¹) and G-bands (≈ 1600 cm⁻¹) are marked to the heatmaps (D, G). FTS conditions: 340°C, 10 bar, H₂:CO:He 2.0:1.0:0.33 v/v, ≈ 7200 h⁻¹.

quantity of deposited carbon is not comparable between the different FTS reaction runs with the applied experimental approach.

In addition, any carbon species present in the Carb. catalyst materials at the beginning of the FTS reaction runs decreased the collected Raman D- and G-band intensities. During the catalyst preparation, Na-S 340 Carb. and UP and Na-S 440 Carb. catalyst materials deposited carbon during the CO carburization step (**Chapter 3**). This can be observed in overall decreased non-normalized Raman band intensities (data not shown), and thus as decreased signal-to-noise ratios in the normalized Raman spectra in **Figures 6.14c-d** and **6.15**. On the Counts per Second (CPS) scale with the background corrected data, the highest G-band intensity was collected for the Na-S 240 (≈ 0.055 CPS) and lowest for the Na-S 440 (≈ 0.023 CPS) catalyst material.

Notwithstanding the above considerations, a qualitative discussion on the in-situ Raman spectra is possible by normalizing the observed Raman intensities to the maximum of (e.g.) the G-band within each respective FTS reaction run. By following the relative band intensity ratio $I(D)/I(G)$ and the spectral positions for the D- and G-bands, information on the type and ToS dependent evolution of the carbon species can be followed,⁶⁴ over the course of the FTS reaction.

The observable Raman shifts with the visible wavelength (i.e. 532 nm) laser excitation originate from differences in the polarizability of the π -bonding in the carbon-containing compounds. Long range polarizable C sp² π -bonds give rise to the Raman D- and G-bands while C sp³ σ -bonds polarize poorly, being weakly or non-Raman active with a visible light wavelength excitation laser.⁶⁴ The G-band is due to cyclic and/or chain structures with C sp² while the D-band originates from the presence of disorder/defects in the cyclic C sp² arrangements.^{61,63–65} The differences in C sp² and C sp³ bond polarization and thus in observed Raman activity is another reason why quantitative carbon deposition is hard to determine with Raman Spectroscopy.

Both the D- and G-bands are present in all of the in-situ Raman spectra in **Figures 6.12-6.15**. This points towards formation of C sp² containing carbon species with disordered structures,⁶⁵ within the FTS reaction runs.

6.3.2.1 Temporal Changes in the D- and G-band Intensities and Positions

In the **Figures 6.16-6.19** are given the evolution of D- and G-band intensities as determined from the measured in-situ Raman spectra versus the FTS reaction ToS. The corresponding, measured $I(D)/I(G)$ band intensity ratios are also included in the figures.

A. D- and G-band Intensities and $I(D)/I(G)$ Ratios

First, an interesting yet expected difference can be observed between the UP and Na-S H₂ catalyst materials on how their D- and G-band intensities develop as a function of the FTS reaction ToS. With UP H₂ catalyst material, the initial D- and G-bands only appear after an onset period of $\approx$ 5-7 h ToS, while with the Na-S H₂ catalyst material the G-band appears at $\approx$ 0 h ToS (**Figure 6.16c-d**). This behavior matches with the in-situ XRPD results.

As the carbon depositing Boudouard reaction requires CO dissociation (i.e. CO disproportionation to C and CO₂),^{26,27} first the Fe₃O₄ phase need to be converted into (near-)zerovalent Fe carbides capable of dissociating CO.^{19,31,105} Without Na-S, the Fe₃O₄ to χ -Fe₅C₂ conversion is slower under H₂:CO (**Figures 6.2c** and **6.3c**), resulting in the onset period for the D- and G-band formation with the UP H₂ catalyst material (**Figure 6.16c**). This effect also explains literature observations of lower initial deposition of carbon with unpromoted Fe-based catalyst materials with respect to Na-

Figure 6.16

Analysis of changes in D- and G-band intensities as derived from in-situ collected Raman spectra in H₂ catalyst materials during the 72 h Fischer-Tropsch Synthesis (FTS) reactions. Comparison of background corrected and normalized Raman spectra at 10 h and 70 h Time-on-Stream (ToS) for a) UP H₂ and b) Na-S H₂ (Fe(-Na-S)/ α -Al₂O₃) catalyst materials. Gray vertical dashed lines mark the Raman D- (≈ 1350 cm⁻¹) and G-band (≈ 1600 cm⁻¹) regions. Changes in the intensity of the G- and D-bands for c) UP H₂ and d) Na-S H₂, and the bands' intensity ratio I(D)/I(G) for e) UP and Na-S H₂ catalysts during 72 h FTS reaction.

S promoted ones.²⁰ However, it is worth to keep in mind the earlier mentioned fluorescence induced spectral deviations in the Raman spectra of the Na-S H₂ catalyst material which may skew the results. This especially at the early FTS reaction ToS.

For the UP and Na-S 240 and 340, and UP 440 catalyst materials, no differences in the G- and D-band appearance onset times are observed (**Figures 6.17c-d - 6.19c-d**), as these catalysts' majority phases are Fe carbides at the start of the FTS reactions (**Figures 6.4c-6.9c**).

With respect to the different Fe crystalline phases: the C atoms ejected during the transition of C-rich “ ϵ -carbides” (i.e. ϵ -Fe₃C and/or η -Fe₂C), to the lesser C containing Fe carbides (χ , θ) have been proposed to act as nucleation sites for carbon formation.³⁶⁻³⁸ As is experimentally shown for Fe carbides observable in the FTS reaction in **Chapter 3**,

Figure 6.17

Analysis of changes in D- and G-band intensities as derived from in-situ collected Raman spectra in 240 catalyst materials during the 72 h Fischer-Tropsch Synthesis (FTS) reactions. Comparison of background corrected and normalized Raman spectra at 10 h and 70 h Time-on-Stream (ToS) for a) UP 240 and b) Na-S 240 (Fe(-Na-S)/ α -Al₂O₃) catalyst materials. Gray vertical dashed lines mark the Raman D- (≈ 1350 cm⁻¹) and G-band (≈ 1600 cm⁻¹) regions. Changes in the intensity of the G- and D-bands for c) UP 240 and d) Na-S 240, and the bands' intensity ratio I(D)/I(G) for e) UP and Na-S H₂ 240 catalysts during 72 h FTS reaction.

the η -Fe₂C phase is C-rich while the ε -Fe₃C phase contains the least C atoms in the carbide's crystal lattice. Thus, transition of the η -Fe₂C phase to χ -Fe₅C₂ or θ -Fe₃C phases should correlate to changes in the Raman spectra. However, no direct correlation exists between any of the Fe carbide phases or carbide-to-carbide transitions observed in the in-situ XRPD (**Figures 6.2c-6.9c**) and the simultaneous in-situ Raman D- and G-band intensity evolutions (**Figures 6.12c-d - 6.15c-d**). This conclusion while excluding the mentioned Fe₃O₄ to Fe carbide transition.

The changes in the D- and G-band intensities derived from the in-situ collected Raman spectra have two regions of band intensity growth for the UP and Na-S H₂ and 240 catalyst materials (**Figures 6.16c-d** and **6.17c-d**). These can be divided to: i) within ≈ 10 -15 h ToS from the initial appearance of the D- and G-bands the intensity growth is

Figure 6.18

Analysis of changes in D- and G-band intensities as derived from in-situ collected Raman spectra in 340 catalyst materials during the 72 h Fischer-Tropsch Synthesis (FTS) reactions. Comparison of background corrected and normalized Raman spectra at 10 h and 70 h Time-on-Stream (ToS) for a) UP 340 and b) Na-S 340 (Fe(-Na-S)/ α -Al₂O₃) catalyst materials. Gray vertical dashed lines mark the Raman D- (≈ 1350 cm⁻¹) and G-band (≈ 1600 cm⁻¹) regions. Changes in the intensity of the G- and D-bands for c) UP 340 and d) Na-S 340, and the bands' intensity ratio I(D)/I(G) for e) UP and Na-S H₂ 340 catalysts during 72 h FTS reaction.

fast, and ii) after ≥ 20 h ToS the D- and G-bands intensities settle to a near steady values or to a lower rate of intensity growth. With the Na-S H₂ catalyst materials, the initial D- and G-band intensity growth is observed to be lesser which is, possibly, due to data analysis problems instigated by the high fluorescence background.

However, with Na-S promotion, the D- and G-band intensities continue growing after the initial fast growth period (≤ 15 h ToS), unlike with UP H₂ and 240 catalyst materials. The normalized, median G-band intensity increases with a rate of $\approx 4.7 \pm 0.3 \times 10^{-3}$ h⁻¹ for the Na-S H₂ and 240, and $\approx 1.9 \pm 0.7 \times 10^{-3}$ h⁻¹ for the UP H₂ and 240 catalyst materials over the ≈ 21 -70 h ToS period (**Figures 6.16c-d** and **6.17c-d**). That is, G-band intensities grow $\approx 2.5 \pm 0.9$ faster for the Na-S than for the respective UP H₂ and 240 catalyst materials.

Figure 6.19

Analysis of changes in D- and G-band intensities as derived from in-situ collected Raman spectra in 440 catalyst materials during the 72 h Fischer-Tropsch Synthesis (FTS) reactions. Comparison of background corrected and normalized Raman spectra at 10 h and 70 h Time-on-Stream (ToS) for a) UP 440 and b) Na-S 440 (Fe(-Na-S)/ α -Al₂O₃) catalyst materials. Gray vertical dashed lines mark the Raman D- (≈ 1350 cm⁻¹) and G-band (≈ 1600 cm⁻¹) regions. Changes in the intensity of the G- and D-bands for c) UP 440 and d) Na-S 440, and the bands' intensity ratio $I(D)/I(G)$ for e) UP and Na-S H₂ 440 catalysts during 72 h FTS reaction.

This would be expected as the Na-S catalyst materials have in overall significantly higher CO conversions than the UP catalyst materials have under the FTS reaction conditions applied here (**Chapter 4**). This leads to a higher possible rate of the Boudouard reaction.²⁶ The added alkali Na(-S) promotion also intrinsically increases the carbon deposition rate for the Fe-based catalyst materials.²

Nevertheless, the initial fast period (≤ 15 h ToS) of the D- and G-band intensity growth is present for both the UP and Na-S 240 catalyst materials regardless of the Na-S promotion. This suggests that non-Na-S promotion related phenomena are operative, perhaps such as the reactor bed heating by the exothermic FTS reaction.¹⁰⁶ A 10°C increase in the reactor bed temperature in the FTS reaction, increases the carbon deposition by ≈ 50 %.²

Figure 6.20

Comparison of in-situ (340°C, H₂/CO) at ≈ 70 h ToS, and quasi-in-situ (100°C, Ar/He) collected Raman spectra after the 72 h Fischer-Tropsch Synthesis (FTS) reaction. The spectra are compared for FTS reaction runs with a) UP 240 and b) Na-S 340 (Fe(-Na-S)/ α -Al₂O₃) catalyst materials.

Furthermore, similarly to the results in **Figures 6.16c-d** and **6.17c-d**, two-phase carbon deposition periods have been observed by Sancier, Isakson and Wise.¹⁰⁷ The initial fast rate growth deposition period was proposed to be due to the initial Fe carburization, which however is not supported by our results. The e.g. UP H₂ (as α -Fe/Fe_xO_y) and Na-S 240 (as $\approx 89\%$ Fe carbides at ≈ 0 h ToS) catalyst materials (**Figures 6.2c** and **6.5c**), behave in similar manner with regard to their D- and G-band intensities (**Figures 6.16c** and **6.17d**), regardless of their initial level of Fe carburization.

For the UP and Na-S 340 and 440 catalyst materials, with initial carbon deposits present from the CO carburizations applied in the catalyst preparation, the initial fast step (≤ 15 h ToS) of rapid D- and G-band intensity growth is absent (**Figures 6.18c-d** and **6.19c-d**). The UP 340 catalyst, with the least amount of initially deposited carbon within the group of UP and Na-S 340 and 440 catalyst materials, shows slight yet subdued initial fast Raman signal increase. Thus, either the initial carbon deposits i) dilute the catalyst bed with FTS inert carbon, allowing a more isothermal bed operation, ii) cover and deactivate the supported Fe particles i.e. decrease the CO conversion and/or iii) hide the Fe surface, where the Boudouard reaction takes place, from the Raman probe. That is, the Raman inactive carbon species formed during CO carburization should be different from Raman active carbon species formed during the FTS reaction. This will be discussed more later on.

All of the above listed phenomena would effectively decrease the observable Raman signal from the carbon deposition during the FTS reaction. Which explanation is the most correct, cannot be deduced from the results.

For all of the FTS reaction runs, the $I(D)/I(G)$ band intensity ratios are within range ≈ 1.0 -0.7 (**Figures 6.16e - 6.19e**). As exceptions, the Na-S 340 and 440 catalyst materials show initially higher >1.0 $I(D)/I(G)$ ratios (**Figures 6.18e and 6.19e**), due to poor data quality (**Figures 6.14c-d and 6.15c-d**). At a different measurement spot, quasi-in-situ measured Raman spectrum and the $I(D)/I(G)$ ratio of the Na-S 340 catalyst material was comparable to the other FTS reaction runs (**Figure 6.20**).

Due to a hysteresis phenomenon, when carbon species evolve from tetrahedral C sp³ towards C sp² carbon species with more order, the interpretation of the $I(D)/I(G)$ band intensity ratios is not straight-forward.⁶⁴ Nevertheless, the measured Raman spectra with $I(D)/I(G) < 1.0$ can be assigned to carbon species with little crystal order and/or disordered structures, with diameters < 7 nm.⁶⁵ Decrease in the $I(D)$ intensity (i.e. $I(D)/I(G) < 1.0$), and increase in the D-bands width as will be discussed later, are signs of the presence of cyclic C sp² carbon species which have cyclic carbon *different* from cyclic 6-fold carbon structures. Increasing $I(D)/I(G) \gtrsim 1.0$ ratio in turn signifies the increasing presence of clustered 6-fold cyclic C sp² (i.e. aromatic) carbon structures,⁶⁴ in disordered carbon species.^{64,65}

B. D- and G-band Deconvolution, Peak Positions and Widths

The measured Raman D-band can be divided into sub-bands. Following the approach by Sadezky et al.,¹⁰⁴ the Raman D-band can further be divided into bands such as D₁ centered at ≈ 1320 cm⁻¹, D₂ at ≈ 1620 cm⁻¹, D₃ at ≈ 1500 cm⁻¹ and D₄ at ≈ 1220 cm⁻¹.

The G-band at ≈ 1590 cm⁻¹ is thought to correspond to the ring vibration of defect-free graphitic lattice (E_{2g}-symmetry). The D₁ position is believed to arise from disordered graphite lattice with A_{1g}-symmetry (e.g. in graphene layer edges). D₂ position in turn is assignable e.g. to graphite disorder with E_{2g}-symmetry in graphene surface layers. D₃ position is often associated to presence of amorphous carbon. Finally, D₄ position signals presence of disordered graphitic lattice with A_{1g}-symmetry (e.g. polyenes or ionic impurities).¹⁰⁴

Thus, by fitting the separate D₁₋₄- (and G-) band positions with individual peaks, additional information should in principle be obtainable from the collected in-situ Raman spectra. Our group has applied this approach earlier in operando experiments to study the formation of carbon species.⁶⁶⁻⁶⁸

For each of the in-situ measured Raman spectra multiple peaks were fitted. One peak for G-band at ≈ 1590 cm⁻¹ and three peaks to correspond the D₁ (≈ 1320 cm⁻¹), D₃ (≈ 1500 cm⁻¹) and D₄ (≈ 1220 cm⁻¹) positions. It was not possible to fit a peak for the D₂ (≈ 1620 cm⁻¹) position. Lack of sub-band peak for the D₂ position can be taken as

Figure 6.21

Peak fitting of the in-situ collected Raman spectra during the 72 h Fischer-Tropsch Synthesis (FTS) reaction with the H₂ catalysts. The measured Raman spectra at -3 h, 5 h and 70 h Time-on-Stream (ToS) with fitted G, D₁, D₃ and D₄ peaks for a) UP H₂ and b) Na-S H₂ (Fe(-Na-S)/ α -Al₂O₃) catalysts. Vertical gray lines mark the corresponding nominal Raman band positions, fitted peaks are indicated by their colored letters and the cumulative fit is in red. The peak D₁- and G-band widths over 72 h ToS in c) and positions in d) for UP and Na-S H₂ catalysts.

indication of poorly ordered graphite structure.⁶⁸

Moreover, the fitted peak relative area or width errors for the D₃ and D₄ peaks were only occasionally below the set filtering condition of 40 %. Therefore, no usable quantitative data could be collected for the D₃ or D₄ peaks. Therefore, in the following, the discussion is focused on the information collected from the fitted D₁- and G-bands, akin to what has been done earlier by our group.^{66,68} In principle, D₁- and G-bands provide sufficient information to identify the carbon species.¹⁰⁴

The general trends with shifts in the D₁- and G-band peak positions show similarities between the different FTS reaction runs (**Figures 6.21-6.24**). That is, i) G-band positions start (≈ 0 h ToS) at $>1\,600\text{ cm}^{-1}$ and shift $\lesssim 1\,600\text{ cm}^{-1}$, ii) the D₁-band positions start at $\approx 1\,350\text{ cm}^{-1}$ while shifting towards $\approx 1\,330\text{ cm}^{-1}$ by the time when ≈ 70 h ToS in the FTS reaction is reached. The Na-S promotion tends to iii) increase the initial (≈ 0 h ToS) G-band positions towards $\approx 1\,600\text{ cm}^{-1}$.

Figure 6.22

Peak fitting of the in-situ collected Raman spectra during the 72 h Fischer-Tropsch Synthesis (FTS) reaction with the 240 catalysts. The measured Raman spectra at -3 h, 5 h and 70 h Time-on-Stream (ToS) with fitted G, D₁, D₃ and D₄ peaks for a) UP 240 and b) Na-S 240 (Fe(-Na-S)/ α -Al₂O₃) catalysts. Vertical gray lines mark the corresponding nominal Raman band positions, fitted peaks are indicated by their colored letters and the cumulative fit is in red. The peak D₁- and G-band widths over 72 h ToS in e) and positions in d) for UP and Na-S 240 catalysts.

The initial, high ($>1\,600\text{ cm}^{-1}$) G-band Raman shifts are due to olefinic, chain-like carbon species with C sp² and (tetrahedral) C sp³ amorphous carbon structures.^{64,108} The high ($\geq 1\,350\text{ cm}^{-1}$) initial position for the D₁-band originates from the presence of amorphous carbon.⁶³ For both the D₁- and G-bands, the shifts towards lower wavenumbers during the FTS reactions (i.e. D₁-band $\rightarrow \approx 1\,330\text{ cm}^{-1}$ and G-band $\rightarrow \approx 1\,600\text{ cm}^{-1}$), signify a transition towards an increasing C sp² content in relation to C sp³. Also, more cyclic, rather than chain-like, carbon species form.⁶⁴

The general trends in the D₁- and G-band peak widths (FWHM) evolution also suggest increasing carbon species ordering processes during the FTS reaction (**Figures 6.21c-6.24c**). Decreasing D₁ and G-band peak widths have been associated to increasing graphitization and ordering of the carbon species.^{66,68}

The G-band widths decrease from initial $>100\text{ cm}^{-1}$ at ≈ 0 -10 h ToS towards 70-80 cm⁻¹ at ≈ 70 h ToS for all of the studied catalyst materials (**Figures 6.21c - 6.24c**).

Figure 6.23

Peak fitting of the in-situ collected Raman spectra during the 72 h Fischer-Tropsch Synthesis (FTS) reaction with the 340 catalysts. The measured Raman spectra at -3 h, 5 h and 70 h Time-on-Stream (ToS) with fitted G, D₁, D₃ and D₄ peaks for a) UP 340 and b) Na-S 340 ($\text{Fe}(-\text{Na-S})/\alpha\text{-Al}_2\text{O}_3$) catalysts. Vertical gray lines mark the corresponding nominal Raman band positions, fitted peaks are indicated by their colored letters and the cumulative fit is in red. The peak D₁- and G-band widths over 72 h ToS in e) and positions in d) for UP and Na-S 340 catalysts.

This G-band width decrease thus can be associated to a carbon species *ordering* processes during the FTS reaction ToS.

For the D₁-band width evolution the situation is mixed. With UP and Na-S H₂ and 240 catalysts the D₁-band decreases (from $\geq 200 \text{ cm}^{-1}$ to $\approx 160\text{-}180 \text{ cm}^{-1}$), while for the UP and Na-S 340 and 440 catalysts the D₁-band increases (from $\approx 100 \text{ cm}^{-1}$ to $\approx 140\text{-}160 \text{ cm}^{-1}$) during the FTS reaction (**Figures 6.23c** and **6.24c**). The D₁-band width decrease is associated to the carbon species ordering process.^{66,68} The UP and Na-S 340 and 440 catalysts have initial carbon deposits from the CO carburization. Also, for these catalysts the initial $I(D)/I(G)$ ratios are higher is a sign of increased initial presence of C sp² in cyclic 6-fold ordered carbon rings, as was discussed earlier. Thus, the D₁-band width increase for the UP and Na-S 340 and 440 catalyst materials can be explained by formation of cyclic C sp², non-6-fold cyclic carbon structures during the FTS reaction.⁶⁴ This is in-line with the previous discussion on the $I(D)/I(G)$ ratios for the UP and Na-S

Figure 6.24

Peak fitting of the in-situ collected Raman spectra during the 72 h Fischer-Tropsch Synthesis (FTS) reaction with the 440 catalysts. The measured Raman spectra at -3 h, 5 h and 70 h Time-on-Stream (ToS) with fitted G, D₁, D₃ and D₄ peaks for a) UP 440 and b) Na-S 440 (Fe(-Na-S)/ α -Al₂O₃) catalysts. Vertical gray lines mark the corresponding nominal Raman band positions, fitted peaks are indicated by their colored letters and the cumulative fit is in red. The peak D₁- and G-band widths over 72 h ToS in e) and positions in d) for UP and Na-S 440 catalysts.

340 and 440 catalyst.

Summarizing the general trends for the carbon species evolution for the catalyst materials under study during the FTS reaction runs: the carbon species evolve from, tetrahedral C sp³ with C sp² in chain-like structured amorphous carbon species towards carbon materials with varying cyclic - *but non-6* - fold order with features <7 nm in diameter. The trend of increasing ordering of the carbon species is in-line with previous studies for carbon deposits formation during the FTS reaction.⁵⁰

6.3.2.2 Comparison to Carbon Reference Materials

Further identification of the carbon species formed during the FTS reactions can be done by comparing the in-situ collected Raman spectra at $\approx$ 70 h ToS to (ex-situ) measured carbon reference materials of graphite, Carbon Nanotubes (CNT), Carbon Nanofibers (CNF) and Activated Carbon (AC).

Figure 6.25

Comparison of in-situ collected Raman spectrum of UP 340 (Fe/ α -Al₂O₃) catalyst material at ≈ 70 h Time-on-Stream (ToS) of Fischer-Tropsch Synthesis (FTS) reaction with ex-situ measured carbon reference materials. Comparison of the Raman spectrum obtained on the catalyst material to a) graphite, b) Carbon Nanotube (CNT), c) Carbon Nanofiber (CNF) and d) Activated Carbon (AC) carbon reference materials.

Saturated and unsaturated long-chained hydrocarbons i.e. waxes, can also give observable Raman spectra,¹⁰⁸ and can be produced in the FTS reaction. However, the collected Raman spectra do not show any particular resemblance to Raman spectra from wax samples.¹⁰⁸ With the used (532 nm) visible wavelength excitation laser the structural majority C sp³ σ -bonds in hydrocarbons polarize poorly and do not give strong Raman signal,⁶⁴ even if present. Thus, it is unlikely that any hydrocarbon wax species contribute in any significant manner to the collected Raman spectra.

As examples, in **Figure 6.25** the ex-situ collected Raman spectra for the carbon reference materials are compared to the in-situ collected Raman spectrum for the UP 340 catalyst material at ≈ 70 h ToS. The other catalyst materials gave comparable Raman spectra to the UP 340 catalyst at ≈ 70 h ToS (**Figures 6.21a-b - 6.24a-b**).

The in-situ measured median values, at ≈ 70 h ToS, for D₁- and G-band peak

Table 6.2

In-situ Raman Spectroscopy derived median D₁- and G-band values at ≈ 70 h Time-on-Stream (ToS) of the Fischer-Tropsch Synthesis (FTS) reaction runs for the studied UP and Na-S (Fe(-Na-S)/ α -Al₂O₃) catalyst materials. Reference carbon materials measured ex-situ at room temperature.

Catalyst		D ₁ -band		G-band		I(D)/I(G) (-)
		Position (cm ⁻¹)	FWHM (cm ⁻¹)	Position (cm ⁻¹)	FWHM (cm ⁻¹)	
H ₂	UP	1 332 $\pm$ 1	162 $\pm$ 5	1 599 $\pm$ 0	69 $\pm$ 3	0.76 $\pm$ 0.05
	Na-S	1 346 $\pm$ 2	172 $\pm$ 7	1 600 $\pm$ 0	67 $\pm$ 1	0.66 $\pm$ 0.06
240	UP	1 334 $\pm$ 0	183 $\pm$ 9	1 597 $\pm$ 0	71 $\pm$ 2	0.73 $\pm$ 0.05
	Na-S	1 334 $\pm$ 0	176 $\pm$ 9	1 598 $\pm$ 0	71 $\pm$ 2	0.72 $\pm$ 0.04
340	UP	1 331 $\pm$ 0	157 $\pm$ 5	1 598 $\pm$ 0	68 $\pm$ 2	0.77 $\pm$ 0.05
	Na-S	1 346 $\pm$ 0	137 $\pm$ 9	1 597 $\pm$ 0	79 $\pm$ 6	0.89 $\pm$ 0.11
440	UP	1 332 $\pm$ 0	155 $\pm$ 8	1 599 $\pm$ 0	73 $\pm$ 5	0.82 $\pm$ 0.07
	Na-S	1 342 $\pm$ 0	140 $\pm$ 17	1 599 $\pm$ 0	71 $\pm$ 4	0.85 $\pm$ 0.10
Reference materials	Graphite	1 334	113	1 565	39	0.37
	CNF	1 338	111	1 571	89	0.86
	AC	1 328	143	1 584	97	1.31
	CNT	1 333	86	1 576	91	1.36

FWHM = Full Width at Half Maximum (of fitted peak), CNF = Carbon Nanotubes, AC = Activated Carbon, CNT = Carbon Nanotubes.

positions, related peak widths as FWHMs and $I(D)/I(G)$ ratios are given in **Table 6.2** with the corresponding values for the carbon reference materials.

By comparing the in-situ collected Raman spectrum for the UP 340 catalyst at ≈ 70 h ToS, the most comparable carbon reference spectrum is the one of CNF (**Figure 6.25**). Both the D₁-band position and $I(D)/I(G)$ ratio are very similar to the reference CNF material. However, the G-band position is at a higher wavenumber ($\approx 1\,598\text{ cm}^{-1}$ versus $\approx 1\,571\text{ cm}^{-1}$) and the D₁-band width is also wider in the measured spectrum for the catalyst material than for the reference CNF material. The G-band position is more akin to the G-band position with that of the AC reference carbon material (**Figure 6.25**).

The higher width of the measured D₁-band can be explained by a wider variety of carbon ring sizes whilst the G-band shift towards higher wavenumber would suggest the increased presence of C sp² in chain-like carbon species or clustering,⁶⁴ than is present in the reference CNF material.

For the measured catalyst materials, the Na-S 340 and Na-S 440 catalysts show in addition an increase in their D₁-band intensities in comparison to the rest of the catalyst materials at ≈ 70 h ToS (**Figures 6.18e** and **6.19e**). The D₁-band intensity increase i.e. increase in the $I(D)/I(G)$ ratio, is due to the increased presence of clustered cyclic 6-fold C sp² carbon species.⁶⁴

Summarizing the discussion on carbon species evolution: during the FTS reaction

under the applied reaction conditions, the carbon species formed resemble most closely the CNF reference carbon material. With added Na-S promotion in comparison to the respective UP catalyst materials: i) for H₂ and 240 catalyst materials, the carbon species evolution starts with more C sp² in chain-like species; ii) more of the clustered 6-fold cyclic carbon species for 340 and 440 catalyst materials are present; and iii) the Fe₃O₄ phases are reduced more efficiently by CO, removing the onset time for appearance of the carbon species between the Na-S H₂ and UP H₂ catalyst materials.

It is noteworthy to mention that the CNF materials contain “graphite-like” planes in their fiber structure.^{37,53} Thus assigning a Fe-based FTS reaction catalyst’s deactivation to be due to “graphitic” carbon overlayers over the active Fe carbides should be done with care, and with clear distinction to a possible presence of CNF materials. CNF materials grow away from the catalyst surface,^{35,109} which is a significantly different phenomena than a carbon overlayer formation over the Fe surface.¹⁰⁹

Finally, the carbon species formed under CO carburization and under H₂:CO during the FTS reaction are different. No significant or only weak Raman D- and G-bands were observed for the initial carbon containing UP and Na-S 340 and 440 catalyst materials at the beginning of the FTS reactions. Rather, the D₁- and G-bands appear and grow during the FTS reaction (**Figures 6.14** and **6.15**). As based on the observations in literature, under pure CO encapsulating carbon species form while in the presence of H₂:CO, growth of filamentous carbon takes place.^{35,37,54,55,109,110} This is in agreement with the results, i.e. the initial carbon deposits due to the CO carburization are formed with C sp³ structures which are Raman inactive with the used (532 nm) visible wavelength excitation laser.⁶⁴ The formation of CNF-like carbon species with Raman active C sp² structures takes place under the applied FTS conditions in the presence of H₂:CO,³⁷ explaining the rise of the in-situ collected Raman spectra for the studied catalyst materials (**Figures 6.12-6.15**).

6.4 CONCLUSIONS

We have studied supported Fe(-Na-S)/α-Al₂O₃ catalyst materials, with and without Na-S promotion. Ex-situ CO carburizations at various temperatures (240-440°C) were applied to prepare preformed Fe carbides, or only H₂ reduction was applied for preparing α-Fe/Fe oxide mixtures on the catalysts. The catalyst materials were characterized in-situ during 72 h FTS reaction (340°C, 10 bar H₂:CO:He 2.0:1.0:0.33 v/v, GHSV ≈ 7 200 h⁻¹). The in-situ characterization was performed using a combined XRPD/Raman Spectroscopy set-up. The collected XRPD patterns were quantified with the use of R-QPA.

Out of the prepared Fe carbides, namely: ε-Fe₃C *P6₃22* (182), η-Fe₂C *Pnnm* (58), χ-

Fe₅C₂ *C2/c* (15) (the Hägg carbide) and, θ -Fe₃C *Pnma* (62) (cementite), the χ -Fe₅C₂ phase was the most stable under the used FTS reaction temperature. Hence, the χ -Fe₅C₂ phase formed preferentially. Furthermore, the Na-S promotion altered the Fe oxides and carbide phases' properties by:

- i) *stabilizing* the η -Fe₂C phase, *but only if* either ε -Fe₃C and/or η -Fe₂C phase was present in the initial catalyst,
- ii) *destabilizing* the θ -Fe₃C phase and aiding in its transition to χ -Fe₅C₂,
- iii) increasing the reducibility of Fe₃O₄ phase by (H₂:)CO,
- iv) decreasing the Fe₃O₄ content during the FTS reaction for catalyst with initial Fe carbide phases as ε -Fe₃C and/or η -Fe₂C; and also by
- v) inducing Fe crystallite growth for the Fe carbides within the ≤ 15 h ToS, with the exception of the θ -Fe₃C phase, for which the crystallite diameters decreased.

Irrespective to the Na-S promotion, no significant presence of the Fe₃O₄ phase for catalyst materials with α -Fe/Fe_xO_y, χ -Fe₅C₂ or θ -Fe₃C as the reaction starting materials were observed during the FTS reactions.

Carbon deposition via the Boudouard reaction was observed via in-situ Raman Spectroscopy. The carbon deposition did not correlate with any specific Fe carbide phase or carbide-to-carbide transition. However, with H₂ reduced catalysts, the initial carbon deposition did not start before the Fe₃O₄ phase, a phase incapable of CO dissociation, was reduced to Fe carbides.

For the catalyst materials with insignificant initial carbon deposits i.e. H₂ reduced or $< 300^\circ\text{C}$ CO carburized catalysts, the Raman D- and G-band intensity growth during the FTS reaction could be divided into two periods: i) an initial fast (≤ 10 -15 h ToS), and ii) a steady or lesser (≥ 15 h ToS) intensity growth period. The initial fast growth period was present regardless of the Na-S promotion. However, after reaching the steady growth period Na-S promotion induced a higher rate of the Raman D- and G-band intensity growth (for the G-band $\approx 2.5 \pm 0.9$ faster) in comparison to the unpromoted catalyst materials. For catalysts with carbon deposits from CO carburization $\geq 340^\circ\text{C}$, the initial fast growth period was absent, regardless of the Na-S promotion. Possibly, an initial non-isothermal bed operation could explain the initial fast D- and G-band intensity gain within ≤ 10 -15 h ToS.

The carbon species formed during catalyst preparation CO carburizations were weakly/non-Raman active with the used (532 nm) visible wavelength excitation laser i.e. mainly made of structures with C sp³. Under H₂:CO during the FTS reaction more ordered CNF-like phases with C sp² formed resulting in increased Raman signal

intensity. During the FTS reactions, the carbon species evolved from amorphous carbon species, with structures containing both tetrahedral C sp³ and C sp² in chain-like ordering, towards more ordered carbon materials with their structures containing C sp² in varying non-6-fold cyclic order. The formed carbon materials had feature sizes <7 nm in diameter.

In comparison to the measured carbon reference materials, the catalysts' Raman spectra at ≈70 h ToS compared best to a CNF reference material. The catalyst materials contained higher amounts of C sp² in chain-like structures and a wider variety of non-6-fold carbon rings than were present in the measured reference CNF material.

Na-S promotion affected the FTS reaction formed carbon species by: i) increasing the initial C sp² content in chain-like carbon structures, and ii) increasing 6-fold cyclic carbon species for catalyst materials with the initial CO carburization ≥340°C.

As most of the changes in the Fe phases and Raman spectra take place within the first ≤15 h ToS with the used Fe-based catalyst materials, the initial catalyst changes would be an interesting further research topic for the continued application of the combined in-situ XRPD/Raman Spectroscopy approach.

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6.6 REFERENCES

- [1] Mittasch, A. and Schneider, C., "*Producing Compounds Containing Carbon and Hydrogen*", Patent US1201850A (1916).
- [2] Dry, M. E., "*The Fischer-Tropsch Synthesis*" in *Catalysis - Science and Technology* (eds. Anderson, J. R. & Boudart, M.) **1**, 159–256 (Springer-Verlag, Berlin, 1981).
- [3] Dry, M. E., "*FT catalysts*" in *Fischer-Tropsch Technology* (eds. Steynberg, A. P. & Dry, M. E.) **152**, 533–600 (Elsevier, Amsterdam, 2004).
- [4] Dictor, R. and Bell, A. T., "*Fischer-Tropsch synthesis over reduced and unreduced iron oxide catalysts*", *J. Catal.* **97**, 121–136 (1986).
- [5] Todic, B., Nowicki, L., Nikacevic, N. and Bukur, D. B., "*Fischer-Tropsch synthesis product selectivity over an industrial iron-based catalyst: Effect of process conditions*", *Catal. Today* **261**, 28–39 (2016).
- [6] van der Laan, G. P. and Beenackers, A. A. C. M., "*Kinetics and Selectivity of the Fischer-Tropsch Synthesis: A Literature Review*", *Catal. Rev.* **41**, 255–318 (1999).
- [7] dos Santos, R. G. and Alencar, A. C., "*Biomass-derived syngas production via gasification process and*

- its catalytic conversion into fuels by Fischer Tropsch synthesis: A review", *Int. J. Hydrogen Energy* (2019). DOI:10.1016/j.ijhydene.2019.07.133
- [8] Kirchner, J., Baysal, Z. and Kureti, S., "Activity and Structural Changes of Fe-based Catalysts during CO₂ Hydrogenation towards CH₄ – A Mini Review", *ChemCatChem* **12**, 981–988 (2020).
 - [9] Mahmoudi, H., Mahmoudi, M., Doustdar, O., Jahangiri, H., Tsolakis, A., Gu, S. and Lech Wyszynski, M., "A review of Fischer Tropsch synthesis process, mechanism, surface chemistry and catalyst formulation", *Biofuels Eng.* **2**, 11–31 (2017).
 - [10] Molino, A., Larocca, V., Chianese, S. and Musmarra, D., "Biofuels Production by Biomass Gasification: A Review", *Energies* **11**, 811 (2018).
 - [11] Muleja, A. A., Gorimbo, J. and Masuku, C. M., "Effect of Co-Feeding Inorganic and Organic Molecules in the Fe and Co Catalyzed Fischer–Tropsch Synthesis: A Review", *Catalysts* **9**, 746 (2019).
 - [12] Torres Galvis, H. M. and de Jong, K. P., "Catalysts for Production of Lower Olefins from Synthesis Gas: A Review", *ACS Catal.* **3**, 2130–2149 (2013).
 - [13] Torres Galvis, H. M., Bitter, J. H., Khare, C. B., Ruitenbeek, M., Dugulan, A. I. and de Jong, K. P., "Supported Iron Nanoparticles as Catalysts for Sustainable Production of Lower Olefins", *Science* **335**, 835–838 (2012).
 - [14] Myddleton, W. W., "Improvements Relating to the Catalytic Synthesis of Hydrocarbon Oils from Gaseous Mixtures of Carbon Monoxide and Hydrogen", Patent GB509325A (1939).
 - [15] Torres Galvis, H. M., Bitter, J. H., Davidian, T., Ruitenbeek, M., Dugulan, A. I. and de Jong, K. P., "Iron Particle Size Effects for Direct Production of Lower Olefins from Synthesis Gas", *J. Am. Chem. Soc.* **134**, 16207–16215 (2012).
 - [16] Torres Galvis, H. M., Koeken, A. C. J., Bitter, J. H., Davidian, T., Ruitenbeek, M., Dugulan, A. I. and De Jong, K. P., "Effect of precursor on the catalytic performance of supported iron catalysts for the Fischer-Tropsch synthesis of lower olefins", *Catal. Today* **215**, 95–102 (2013).
 - [17] Torres Galvis, H. M., Koeken, A. C. J., Bitter, J. H., Davidian, T., Ruitenbeek, M., Dugulan, A. I. and de Jong, K. P., "Effects of sodium and sulfur on catalytic performance of supported iron catalysts for the Fischer–Tropsch synthesis of lower olefins", *J. Catal.* **303**, 22–30 (2013).
 - [18] Botes, G. F., Bromfield, T. C., Coetzer, R. L. J., Crous, R., Gibson, P. and Ferreira, A. C., "Development of a chemical selective iron Fischer Tropsch catalyst", *Catal. Today* **275**, 40–48 (2016).
 - [19] Xie, J., Yang, J., Dugulan, A. I., Holmen, A., Chen, D., De Jong, K. P. and Louwerse, M. J., "Size and Promoter Effects in Supported Iron Fischer-Tropsch Catalysts: Insights from Experiment and Theory", *ACS Catal.* **6**, 3147–3157 (2016).
 - [20] Xie, J., Torres Galvis, H. M., Koeken, A. C. J., Kirilin, A., Dugulan, A. I., Ruitenbeek, M. and de Jong, K. P., "Size and Promoter Effects on Stability of Carbon-Nanofiber-Supported Iron-Based Fischer–Tropsch Catalysts", *ACS Catal.* **6**, 4017–4024 (2016).
 - [21] Crous, R., Bromfield, T. C. and Booyens, S., "Olefin Selective FT Catalyst Composition and Preparation Thereof", Patent WO2010066386A1 (2010).
 - [22] Johnson, J. Y., "Improvements in the Manufacture and Production of Unsaturated Hydrocarbons of Low Boiling Point", Patent GB322284A (1929).
 - [23] Dry, M. E., Shingles, T. and van H. Botha, C. S., "Factors influencing the formation of carbon on iron Fischer-Tropsch catalysts I. The influence of promoters", *J. Catal.* **17**, 341–346 (1970).
 - [24] Dry, M. E., Shingles, T., Boshoff, L. J. and van H. Botha, C. S., "Factors influencing the formation of carbon on iron Fischer-Tropsch catalysts. II. The effect of temperature and of gases and vapors present during Fischer-Tropsch synthesis", *J. Catal.* **17**, 347–354 (1970).
 - [25] Cohn, E. M., Bean, E. H., Mentser, M., Hofer, L. J. E., Pontello, A., Peebles, W. C. and Jack, K. H., "The

- carburization of iron oxide with carbon monoxide: Modifications of Hägg iron carbide", *J. Appl. Chem.* **5**, 418–425 (1955).
- [26] Bartholomew, C. H., "Mechanisms of catalyst deactivation", *Appl. Catal. A Gen.* **212**, 17–60 (2001).
- [27] Niemantsverdriet, J. W. and van der Kraan, A. M., "On the time-dependent behavior of iron catalysts in Fischer-Tropsch synthesis", *J. Catal.* **72**, 385–388 (1981).
- [28] Dry, M. E., "The Fischer-Tropsch process: 1950–2000", *Catal. Today* **71**, 227–241 (2002).
- [29] Shultz, J. F., Hall, W. K., Seligman, B. and Anderson, R. B., "Studies of the Fischer-Tropsch Synthesis. XIV. Hägg Carbide as Catalysts", *J. Am. Chem. Soc.* **77**, 213–221 (1955).
- [30] Steynberg, A. P., Espinoza, R. L., Jager, B. and Vosloo, A. C., "High temperature Fischer-Tropsch synthesis in commercial practice", *Appl. Catal. A Gen.* **186**, 41–54 (1999).
- [31] Benziger, J. and Madix, R. J., "The effects of carbon, oxygen, sulfur and potassium adlayers on CO and H₂ adsorption on Fe(100)", *Surf. Sci.* **94**, 119–153 (1980).
- [32] Le Caër, G., Dubois, J. M., Pijolat, M., Perrichon, V. and Bussière, P., "Characterization by Moessbauer Spectroscopy of Iron Carbides Formed by Fischer-Tropsch Synthesis", *J. Phys. Chem.* **86**, 4799–4808 (1982).
- [33] de Smit, E., Beale, A. M., Nikitenko, S. and Weckhuysen, B. M., "Local and long range order in promoted iron-based Fischer-Tropsch catalysts: A combined in situ X-ray absorption spectroscopy/wide angle X-ray scattering study", *J. Catal.* **262**, 244–256 (2009).
- [34] de Smit, E., Cinquini, F., Beale, A. M., Safonova, O. V., van Beek, W., Sautet, P. and Weckhuysen, B. M., "Stability and Reactivity of ϵ - χ - θ Iron Carbide Catalyst Phases in Fischer-Tropsch Synthesis: Controlling μ_c ", *J. Am. Chem. Soc.* **132**, 14928–14941 (2010).
- [35] Mazzucco, S., Wang, Y., Tanase, M., Picher, M., Li, K., Wu, Z., Irle, S. and Sharma, R., "Direct evidence of active and inactive phases of Fe catalyst nanoparticles for carbon nanotube formation", *J. Catal.* **319**, 54–60 (2014).
- [36] Jung, H. and Thomson, W. J., "Dynamic X-ray diffraction study of an unsupported iron catalyst in Fischer-Tropsch synthesis", *J. Catal.* **134**, 654–667 (1992).
- [37] Kock, A. J. H. M., de Bokx, P. K., Boellaard, E., Klop, W. and Geus, J. W., "The formation of filamentous carbon on iron and nickel catalysts II. Mechanism", *J. Catal.* **96**, 468–480 (1985).
- [38] Eliason, S. A. and Bartholomew, C. H., "Reaction and deactivation kinetics for Fischer-Tropsch synthesis on unpromoted and potassium-promoted iron catalysts", *Appl. Catal. A Gen.* **186**, 229–243 (1999).
- [39] Schneider, A. and Inden, G., "Carbon diffusion in cementite (Fe₃C) and Hägg carbide (Fe₅C₂)", *Calphad* **31**, 141–147 (2007).
- [40] Moszyński, D., Grabke, H. J. and Schneider, A., "Effect of sulphur on the formation of graphite at the surface of carburized iron", *Surf. Interface Anal.* **34**, 380–383 (2002).
- [41] Olsson, R. G. and Turkdogan, E. T., "Catalytic effect of iron on decomposition of carbon monoxide: II. Effect of additions of H₂, H₂O, CO₂, SO₂ and H₂S", *Metall. Trans.* **5**, 21–26 (1974).
- [42] Arabczyk, W., Moszyński, D., Narkiewicz, U., Pelka, R. and Podsiadły, M., "Poisoning of iron catalyst by sulfur", *Catal. Today* **124**, 43–48 (2007).
- [43] Berry, T. F., Ames, R. N. and Snow, R. B., "Influence of Impurities and Role of Iron Carbides in Deposition of Carbon from Carbon Monoxide", *J. Am. Ceram. Soc.* **39**, 308–318 (1956).
- [44] Xu, J.-D., Chang, Z.-Y., Zhu, K.-T., Weng, X.-F., Weng, W.-Z., Zheng, Y.-P., Huang, C.-J. and Wan, H.-L., "Effect of sulfur on α -Al₂O₃-supported iron catalyst for Fischer-Tropsch synthesis", *Appl. Catal. A Gen.* **514**, 103–113 (2016).

- [45] Zhou, X., Ji, J., Wang, D., Duan, X., Qian, G., Chen, D. and Zhou, X., "Hierarchical structured α -Al₂O₃ supported S-promoted Fe catalysts for direct conversion of syngas to lower olefins", *Chem. Commun.* **51**, 8853–8856 (2015).
- [46] Dalla Betta, R. A., Piken, A. G. and Shelef, M., "Heterogeneous methanation: Steady-state rate of CO hydrogenation on supported ruthenium, nickel and rhenium", *J. Catal.* **40**, 173–183 (1975).
- [47] van Dijk, W. L., Niemantsverdriet, J. W., van dar Kraan, A. M. and van der Baan, H. S., "Effects of Manganese Oxide and Sulphate on the Olefin Selectivity of Iron Catalysts in the Fischer Tropsch Reaction", *Appl. Catal.* **2**, 273–288 (1982).
- [48] Madon, R. J. and Shaw, H., "Effect of Sulfur on the Fischer-Tropsch Synthesis", *Catal. Rev.* **15**, 69–106 (1977).
- [49] Herranz, T., Rojas, S., Pérez-Alonso, F. J., Ojeda, M., Terreros, P. and Fierro, J. L. G., "Genesis of iron carbides and their role in the synthesis of hydrocarbons from synthesis gas", *J. Catal.* **243**, 199–211 (2006).
- [50] Xu, J. and Bartholomew, C. H., "Temperature-Programmed Hydrogenation (TPH) and in Situ Mössbauer Spectroscopy Studies of Carbonaceous Species on Silica-Supported Iron Fischer-Tropsch Catalysts", *J. Phys. Chem. B* **109**, 2392–2403 (2005).
- [51] Hamilton, N. G., Warringham, R., Silverwood, I. P., Kapitán, J., Hecht, L., Webb, P. B., Tooze, R. P., Zhou, W., Frost, C. D., Parker, S. F. and Lennon, D., "The application of inelastic neutron scattering to investigate CO hydrogenation over an iron Fischer-Tropsch synthesis catalyst", *J. Catal.* **312**, 221–231 (2014).
- [52] Ning, W., Koizumi, N., Chang, H., Mochizuki, T., Itoh, T. and Yamada, M., "Phase transformation of unpromoted and promoted Fe catalysts and the formation of carbonaceous compounds during Fischer-Tropsch synthesis reaction", *Appl. Catal. A Gen.* **312**, 35–44 (2006).
- [53] Nolan, P. E., Lynch, D. C. and Cutler, A. H., "Carbon Deposition and Hydrocarbon Formation on Group VIII Metal Catalysts", *J. Phys. Chem. B* **102**, 4165–4175 (1998).
- [54] Boellaard, E., de Bokx, P. K., Kock, A. J. H. M. and Geus, J. W., "The formation of filamentous carbon on iron and nickel catalysts III. Morphology", *J. Catal.* **96**, 481–490 (1985).
- [55] de Bokx, P. K., Kock, A. J. H. M., Boellaard, E., Klop, W. and Geus, J. W., "The formation of filamentous carbon on iron and nickel catalysts. I. Thermodynamics", *J. Catal.* **96**, 454–467 (1985).
- [56] O'Brien, R. J., Xu, L., Milburn, D. R., Li, Y.-X., Klabunde, K. J. and Davis, B. H., "Fischer-Tropsch synthesis: Impact of potassium and zirconium promoters on the activity and structure of an ultrafine iron oxide catalyst", *Top. Catal.* **2**, 1–15 (1995).
- [57] Bukur, D. B., Okabe, K., Rosynek, M. P., Li, C. P., Wang, D. J., Rao, K. R. P. M. and Huffman, G. P., "Activation Studies with a Precipitated Iron Catalyst for Fischer-Tropsch Synthesis. I. Characterization Studies", *Journal of Catalysis* **155**, 353–365 (1995).
- [58] Datye, A. K., Jin, Y., Mansker, L. D., Motjope, R. T., Dlamini, T. H. and Coville, N. J., "The nature of the active phase in iron Fischer-Tropsch catalysts" in *Studies in Surface Science and Catalysis* **130**, 1139–1144 (2000).
- [59] Mansker, L. D., Jin, Y., Bukur, D. B. and Datye, A. K., "Characterization of slurry phase iron catalysts for Fischer-Tropsch synthesis", *Appl. Catal. A Gen.* **186**, 277–296 (1999).
- [60] McCartney, J. T., Hofer, L. J. E., Seligman, B., Lecky, J. A., Peebles, W. C. and Anderson, R. B., "Electron and X-Ray Diffraction Studies of Iron Fischer-Tropsch Catalysts", *J. Phys. Chem.* **57**, 730–736 (1953).
- [61] Wang, Y., Alsmeyer, D. C. and McCreery, R. L., "Raman spectroscopy of carbon materials: structural basis of observed spectra", *Chem. Mater.* **2**, 557–563 (1990).
- [62] Wang, Y., Serrano, S. and Santiago-Avilés, J. J., "Raman characterization of carbon nanofibers prepared using electrospinning", **138**, 423–427 (2003).

- [63] Shimodaira, N. and Masui, A., "Raman spectroscopic investigations of activated carbon materials", *J. Appl. Phys.* **92**, 902–909 (2002).
- [64] Ferrari, A. C. and Robertson, J., "Interpretation of Raman spectra of disordered and amorphous carbon", *Phys. Rev. B* **61**, 14095–14107 (2000).
- [65] Escribano, R., Sloan, J. J., Siddique, N., Sze, N. and Dudev, T., "Raman spectroscopy of carbon-containing particles", *Vib. Spectrosc.* **26**, 179–186 (2001).
- [66] Sattler, J. J. H. B., Beale, A. M. and Weckhuysen, B. M., "Operando Raman Spectroscopy Study on the Deactivation of Pt/Al₂O₃ and Pt-Sn/Al₂O₃ Propane Dehydrogenation Catalysts", *Phys. Chem. Chem. Phys.* **15**, 12095 (2013).
- [67] Sattler, J. J. H. B., Mens, A. M. and Weckhuysen, B. M., "Real-Time Quantitative Operando Raman Spectroscopy of a CrO_x/Al₂O₃ Propane Dehydrogenation Catalyst in a Pilot-Scale Reactor", *ChemCatChem* **6**, 3139–3145 (2014).
- [68] Cats, K. H. and Weckhuysen, B. M., "Combined Operando X-ray Diffraction/Raman Spectroscopy of Catalytic Solids in the Laboratory: The Co/TiO₂ Fischer-Tropsch Synthesis Catalyst Showcase", *ChemCatChem* **8**, 1531–1542 (2016).
- [69] Fischer, N. and Claeys, M., "Phase changes studied under in situ conditions - A novel cell", *Catal. Today* **275**, 149–154 (2016).
- [70] Centre for Catalysis Research - University of Cape Town, "iKey in-situ XRD Cell", Available at: <http://www.catcentre.uct.ac.za/cat/ikey-products/xrd-cell> (Accessed: March 2020).
- [71] Bare, S. R., Yang, N., Kelly, S. D., Mickelson, G. E. and Modica, F. S., "Design and operation of a high pressure reaction cell for in situ X-ray absorption spectroscopy", *Catal. Today* **126**, 18–26 (2007).
- [72] Jenkins, R. and Snyder, R. L., "Introduction to X-ray Powder Diffraction", *Introduction to X-ray Powder Diffraction* **138** (John Wiley & Sons, Inc., Hoboken, NJ, USA, 1996).
- [73] Wood, I. G., Vočadlo, L., Knight, K. S., Dobson, D. P., Marshall, W. G., Price, G. D. and Brodholt, J., "Thermal expansion and crystal structure of cementite, Fe₃C, between 4 and 600 K determined by time-of-flight neutron powder diffraction", *J. Appl. Crystallogr.* **37**, 82–90 (2004).
- [74] Sabine, T. M., Hunter, B. A., Sabine, W. R. and Ball, C. J., "Analytical Expressions for the Transmission Factor and Peak Shift in Absorbing Cylindrical Specimens", *J. Appl. Crystallogr.* **31**, 47–51 (1998).
- [75] Michel, F. M., Ehm, L., Antao, S. M., Lee, P. L., Chupas, P. J., Liu, G., Strongin, D. R., Schoonen, M. A. A., Phillips, B. L. and Parise, J. B., "The Structure of Ferrihydrite, a Nanocrystalline Material", *Science* **316**, 1726–1729 (2007).
- [76] Toby, B. H., "R factors in Rietveld analysis: How good is good enough?", *Powder Diffr.* **21**, 67–70 (2006).
- [77] Nagakura, S., "Study of Metallic Carbides by Electron Diffraction Part III. Iron Carbides", *J. Phys. Soc. Japan* **14**, 186–195 (1959).
- [78] Amelse, J. A., Grynkewich, G., Butt, J. B. and Schwartz, L. H., "Moessbauer spectroscopic study of passivated small particles of iron and iron carbide", *J. Phys. Chem.* **85**, 2484–2488 (1981).
- [79] Jiang, F., Zhang, M., Liu, B., Xu, Y. and Liu, X., "Insights into the influence of support and potassium or sulfur promoter on iron-based Fischer-Tropsch synthesis: understanding the control of catalytic activity, selectivity to lower olefins, and catalyst deactivation", *Catal. Sci. Technol.* **7**, 1245–1265 (2017).
- [80] Raupp, G. B. and Delgass, W. N., "Mössbauer Investigation of Supported Fe and FeNi Catalysts II. Carbides Formed by Fischer-Tropsch Synthesis", *J. Catal.* **58**, 348–360 (1979).
- [81] Tau, L. M., Borcar, S., Bianchi, D. and Bennett, C. O., "Investigation of supported iron Fischer-Tropsch synthesis catalysts by Mössbauer spectroscopy", *J. Catal.* **87**, 36–54 (1984).

- [82] du Plessis, H. E., de Villiers, J. P. R., Kruger, G. J., Steuwer, A. and Brunelli, M., "*Rietveld and pair distribution function study of Hägg carbide using synchrotron X-ray diffraction*", *J. Synchrotron Radiat.* **18**, 266–271 (2011).
- [83] Hofer, L. J. E., "*Nature of the carbides of iron*", *U.S. Bureau of Mines Bulletin* **631** (1966). Available at: <http://www.onemine.org/document/abstract.cfm?docid=186163&title=Nature-Of-The-Carbides-Of-Iron> (Accessed: February 2014).
- [84] Riedel, T., Schulz, H., Schaub, G., Jun, K.-W., Hwang, J.-S. and Lee, K.-W., "*Fischer-Tropsch on Iron with H₂/CO and H₂/CO₂ as Synthesis Gases: The Episodes of Formation of the Fischer-Tropsch Regime and Construction of the Catalyst*", *Top. Catal.* **26**, 41–54 (2003).
- [85] Berry, F. J. and Smith, M. R., "*A Mössbauer investigation of iron-containing catalysts prepared at low temperatures and active for carbon monoxide hydrogenation*", *J. Chem. Soc. Faraday Trans. 1 Phys. Chem. Condens. Phases* **85**, 467–477 (1989).
- [86] Ribeiro, M. C., Jacobs, G., Davis, B. H., Cronauer, D. C., Kropf, A. J. and Marshall, C. L., "*Fischer-Tropsch Synthesis: An In-Situ TPR-EXAFS/XANES Investigation of the Influence of Group I Alkali Promoters on the Local Atomic and Electronic Structure of Carburized Iron/Silica Catalysts*", *J. Phys. Chem. C* **114**, 7895–7903 (2010).
- [87] Manes, M., Damick, A. D., Mentser, M., Cohn, E. M. and Hofer, L. J. E., "*Hexagonal Iron Carbide as an Intermediate in the Carbiding of Iron Fischer-Tropsch Catalysts*", *J. Am. Chem. Soc.* **74**, 6207–6209 (1952).
- [88] Boellaard, E., van der Kraan, A. M. and Geus, J. W., "*Behaviour of a cyanide-derived Fe/Al₂O₃ catalyst during Fischer-Tropsch synthesis*", *Appl. Catal. A Gen.* **147**, 229–245 (1996).
- [89] Pijolat, M., Perrichon, V. and Bussière, P., "*Study of the carburization of an iron catalyst during the Fischer-Tropsch synthesis: Influence on its catalytic activity*", *J. Catal.* **107**, 82–91 (1987).
- [90] Butt, J. B., "*Carbide phases on iron-based Fischer-Tropsch synthesis catalysts part II: Some reaction studies*", *Catal. Lett.* **7**, 83–106 (1990).
- [91] Pendyala, V. R. R., Graham, U. M., Jacobs, G., Hamdeh, H. H. and Davis, B. H., "*Fischer-Tropsch Synthesis: Deactivation as a Function of Potassium Promoter Loading for Precipitated Iron Catalyst*", *Catal. Lett.* **144**, 1704–1716 (2014).
- [92] An, X., Wu, B., Wan, H.-J., Li, T.-Z., Tao, Z.-C., Xiang, H.-W. and Li, Y.-W., "*Comparative study of iron-based Fischer-Tropsch synthesis catalyst promoted with potassium or sodium*", *Catal. Commun.* **8**, 1957–1962 (2007).
- [93] Shultz, J. F., Abelson, M., Shaw, L. and Anderson, R. B., "*Fischer-Tropsch Synthesis. Nitrides and Carbonitrides of Iron as Catalysts*", *Ind. Eng. Chem.* **49**, 2055–2060 (1957).
- [94] Niewa, R., Rau, D., Wosylus, A., Meier, K., Hanfland, M., Wessel, M., Dronskowski, R., Dzivenko, D. A., Riedel, R. and Schwarz, U., "*High-Pressure, High-Temperature Single-Crystal Growth, Ab initio Electronic Structure Calculations, and Equation of State of ϵ -Fe₃N_{1+x}*", *Chem. Mater.* **21**, 392–398 (2009).
- [95] Leineweber, A., Shang, S., Liu, Z.-K., Widenmeyer, M. and Niewa, R., "*Crystal structure determination of Hägg carbide, χ -Fe₅C₂ by first-principles calculations and Rietveld refinement*", *Zeitschrift für Krist.* **227**, 207–220 (2012).
- [96] Jack, K. H., "*The iron-nitrogen system: the crystal structures of ϵ -phase iron nitrides*", *Acta Crystallogr.* **5**, 404–411 (1952).
- [97] Rechenbach, D. and Jacobs, H., "*Structure determination of ζ -Fe₂N by neutron and synchrotron powder diffraction*", *J. Alloys Compd.* **235**, 15–22 (1996).
- [98] Jacobs, H., Rechenbach, D. and Zachwieja, U., "*Structure determination of γ' -Fe₄N and ϵ -Fe₃N*", *J. Alloys Compd.* **227**, 10–17 (1995).

- [99] Nagakura, S. and Tanehashi, K., "Electronic Structure of Iron Nitrides Studied by Electron Diffraction. II. ϵ -Fe₂N and ζ -Fe₂N", *J. Phys. Soc. Japan* **25**, 840–846 (1968).
- [100] O'Brien, R. J., Xu, L., Spicer, R. L. and Davis, B. H., "Activation Study of Precipitated Iron Fischer-Tropsch Catalysts", *Energy & Fuels* **10**, 921–926 (1996).
- [101] Shultz, J. F., Abelson, M., Stein, K. C. and Anderson, R. B., "Studies of the Fischer-Tropsch Synthesis. XVIII. Influence of Catalyst Geometry on Synthesis on Iron Catalysts", *J. Phys. Chem.* **63**, 496–500 (1959).
- [102] Anderson, R. B., Hofer, L. J. E., Cohn, E. M. and Seligman, B., "Studies of the Fischer—Tropsch Synthesis. IX. Phase Changes of Iron Catalysts in the Synthesis", *J. Am. Chem. Soc.* **73**, 944–946 (1951).
- [103] Matyi, R. J., Schwartz, L. H. and Butt, J. B., "Particle Size, Particle Size Distribution, and Related Measurements of Supported Metal Catalysts", *Catal. Rev.* **29**, 41–99 (1987).
- [104] Sadezky, A., Muckenhuber, H., Grothe, H., Niessner, R. and Pöschl, U., "Raman Microspectroscopy of Soot and Related Carbonaceous Materials: Spectral Analysis and Structural Information", *Carbon* **43**, 1731–1742 (2005).
- [105] Ratnasamy, C. and Wagner, J. P., "Water Gas Shift Catalysis", *Catal. Rev.* **51**, 325–440 (2009).
- [106] Podgurski, H. H., Kummer, J. T., DeWitt, T. W. and Emmett, P. H., "Preparation, Stability and Adsorptive Properties of the Carbides of Iron", *J. Am. Chem. Soc.* **72**, 5382–5388 (1950).
- [107] Sancier, K. M., Isakson, W. E. and Wise, H., "Carburization Studies of Iron Fischer-Tropsch Catalysts" in *Hydrocarbon Synthesis from Carbon Monoxide and Hydrogen* (eds. Kugler, E. L. & Steffgen, F. W.) **178**, 129–145 (American Chemical Society, Washington, 1979).
- [108] Edwards, H. G. M. and Falk, M. J. P., "Fourier-transform Raman spectroscopic study of unsaturated and saturated waxes", *Spectrochim. Acta Part A Mol. Biomol. Spectrosc.* **53**, 2685–2694 (1997).
- [109] Nolan, P. E., Lynch, D. C. and Cutler, A. H., "Catalytic disproportionation of CO in the absence of hydrogen: Encapsulating shell carbon formation", *Carbon* **32**, 477–483 (1994).
- [110] Alstrup, I., Tavares, M. T., Bernardo, C. A., Sørensen, O. and Rostrup-Nielsen, J. R., "Carbon formation on nickel and nickel-copper alloy catalysts", *Mater. Corros.* **49**, 367–372 (1998).

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Chapter 7

Summary and Future Perspectives

Currently, hydrocarbons are used in the vast majority of modern industrial processes leading to the production of transportation fuels, plastics, coatings and other materials. In the foreseeable future the current primary source for these hydrocarbons, namely crude oil from Earth's crust, will be depleted and new alternatives as a source for hydrocarbons will be required. The industrial Fischer-Tropsch Process (FTP) is capable of converting a carbon-containing feedstock, such as natural gas, coal, biomass or municipal waste, into a variety of product hydrocarbons. The heterogeneously catalyzed Fischer-Tropsch Synthesis (FTS) reaction is employed in the FTP for converting a mixture of carbon monoxide (CO) and hydrogen (H₂), better known as synthesis gas or syngas, into synthetic crude, which is further refined to the hydrocarbon products. In this PhD Dissertation, we have studied the FTS reaction using iron (Fe)-based, sodium (Na)-sulphur (S) promoted or unpromoted supported Fe(-Na-S)/ α -Al₂O₃ catalyst materials. The main focus of this Dissertation has been on the characterization of the active phases of the catalyst materials catalyzing the FTS reaction, namely the in-depth characterization of Fe carbides. X-ray Diffraction (XRD) was applied as the primary characterization technique and the collected data were quantified with Rietveld Quantitative Phase Analysis (R-QPA). Fe carbide identification, formation conditions and their subtypes, as defined by carbide's lattice parameters, were investigated. This PhD Dissertation defines the effects that the promotion of Na and S has on the Fe carbide formation and the carbides properties in the FTS reaction.

Figure 7.1

Overview of the overall Fischer-Tropsch Process (FTP) applying the Fischer-Tropsch Synthesis (FTS) reaction in the industrial process of converting carbon-containing feedstock into refined hydrocarbon products. The general FTP steps are a) Feedstock-to-Syngas, Syngas-to-Syncrude and Syncrude-to-Products. The input feedstock b) largely defines the CO₂ footprint of the overall FTP, as the c) FTS reaction consumes the reaction reactant syngas H₂:CO in ratio of ≈ 2 in the Syngas-to-Syncrude FTP step. With feedstocks other than natural gas, the effective syngas H₂:CO ratio is < 2 and H₂ needs to be produced and added to the FTP, raising the total CO₂ footprint. Waste = Municipal waste, Coal = Average of different coal types, Biomass = Switchgrass, HC = hydrocarbons.

7.1 SUMMARY

Despite that the catalytic conversion of a mixture of H₂ and CO, also known as synthesis gas or syngas, into hydrocarbons is already known for more than 100 years, a lot remains to be learned. This catalytic reaction is called the Fischer-Tropsch Synthesis (FTS). At the heart of the FTS reaction with Iron (Fe)-based catalyst materials are the Fe carbides, which are considered to be the active phases in this reaction. The main motivation for conducting the research work in this PhD Dissertation has been to learn more on the behavior and formation of the different Fe carbide phases and how they are affected by adding Sodium (Na) and Sulphur (S) as chemical promoters. In the following, the work conducted within this PhD Dissertation is summarized, highlighting the main conclusions from this research work.

Figure 7.2

A simplified summary of the reaction pathways for C from input CO in a Fe-based Fischer-Tropsch Synthesis (FTS) catalyst particle. The input CO + H₂ gives originally a reductive environment (Red). For C from CO dissociation the pathways to react are: (1) with α-Fe to form Fe_xC, (2) with H to form hydrocarbons, (3) with C to form inactive carbon. Without CO dissociation: The C pathway (4) may reduce Fe_xO_y to α-Fe, while releasing CO₂. Removal of O atoms from CO as H₂O or CO₂ gradually leads to an oxidative environment (Ox) towards the core of the catalyst particle, and the outlet of a fixed bed reactor. If the FTS active Fe_xC phase is oxidized to Fe₃O₄, pathway (5) may convert H₂O + CO to CO₂ + H₂ via the Water-gas Shift (WGS) reaction.

Chapter 1 – The history and motivations on the application of the overall industrial Fischer-Tropsch Process (FTP) was briefly introduced. In the FTP, a carbon-containing input feedstock is converted into refined hydrocarbon products. The FTP steps discussed were (**Figure 7.1**): *Feedstock-to-Syngas*, *Syngas-to-Syncrude* and *Syncrude-to-Products*. The catalyzed FTS reaction itself is employed in the *Syngas-to-Syncrude* process step for converting syngas into a mixture of various hydrocarbons and their derivatives (syncrude).

The CO₂ footprint of the overall FTP depends in a large part on the input feedstock. The CO₂ footprint increases in the following order: natural gas < communal waste < coal < biomass. Due to its lack of impurities, natural gas can be directly converted into ready-to-use syngas with H₂:CO ratio ≈ 2, satisfying the required FTS reaction stoichiometry. With the other feedstocks, which contain heteroatoms (mainly Nitrogen (N), Oxygen (O) and Sulphur (S)) as impurities, the effective attainable H₂:CO ratio is <2. Therefore, cheap and environmentally sourced H₂ needs to be added to the FTP for these feedstocks to be able to compete with the natural gas-based FTP environmentally. The used FTP feedstock is also important from an economic perspective. Producing the purified syngas for use in the FTS reaction takes ≈ 0-70 % of the total capital costs in a

coal-based FTP, while the corresponding costs for natural gas-based FTP are $\approx 30\text{-}50\%$.

Chapter 2 – The heterogeneous catalysis of the FTS reaction with Fe-based catalyst materials was reviewed. Topics, such as the common catalyst compositions, the various chemical reactions taking place and the possible reaction pathways for C from input CO in a Fe-based FTS reaction catalyst, were discussed. The C possible pathways in the FTS reaction are summarized in **Figure 7.2**. Furthermore, the effects of the various FTS reaction condition parameters on the hydrocarbon and Carbon (C) pathway selectivities were reviewed. The effects of parameters, such as the reaction temperature, input $\text{H}_2\text{:CO}$ ratio, gas space velocity and reaction total pressure, were discussed. As the specific topics of this PhD Dissertation: the effects arising from the added chemical Na-S promotion in the Fe-based FTS reaction and the identification of the Fe carbide phases, encountered in the field of FTS catalysis, were discussed.

The Na-S promotion in the FTS reaction has the effects of i) decreasing the selectivity towards methane (CH_4) to a lower value than predicted by the Anderson-Schulz-Flory (ASF) distribution, ii) a lesser increase in the hydrocarbon chain length (i.e. α -value) in comparison if only alkaline metal (i.e., Na) is added, iii) an increased selectivity towards olefins, and iv) an overall increasing CO conversion. These selectivity effects resemble alkaline metals (e.g., K or Na) only promotion effects in the FTS reaction. However, the unique feature of the promotion by Na and S is its ability to decrease the CH_4 selectivity to a value lower than predicted by the ASF-distribution. This special feature is not attainable without the added S.

The Fe carbides, observable in the field of FTS catalysis, with their corresponding crystal structures are:

- hexagonal $\epsilon\text{-Fe}_3\text{C}$ $P6_322$ (182),
- orthorhombic $\eta\text{-Fe}_2\text{C}$ $Pnnm$ (58),
- monoclinic $\chi\text{-Fe}_5\text{C}_2$ $C2/c$ (15) (the Hägg carbide),
- orthorhombic $\theta\text{-Fe}_3\text{C}$ $Pnma$ (62) (cementite), and
- orthorhombic $\theta\text{-Fe}_7\text{C}_3$ $Pnma$ (62) (the Eckström-Adcock carbide).

The formation of the Fe carbides is dependent on the temperature where the zerovalent $\alpha\text{-Fe}$ is exposed to a C atom source. The expected thermal stability and formation temperature ranges for the Fe carbides are $\epsilon\text{-Fe}_3\text{C}$ ($100\text{-}265^\circ\text{C}$) < $\eta\text{-Fe}_2\text{C}$ ($160\text{-}340^\circ\text{C}$) < $\chi\text{-Fe}_5\text{C}_2$ ($240\text{-}350^\circ\text{C}$) < $\theta\text{-Fe}_3\text{C}$ ($310\text{-}600^\circ\text{C}$) as based on the literature data.

The formation of the $\theta\text{-Fe}_7\text{C}_3$ phase does not follow the same route as for the rest of the Fe carbides. Although, despite rather extreme reaction conditions have often been cited as requirements for the formation of the $\theta\text{-Fe}_7\text{C}_3$ phase, it may also form under

Figure 7.3

Fe carbide formation regions (*hatched fill*) as temperature versus treatment exposure time as based on the available experimental literature data (*non-cross*) and this PhD Dissertation (*cross*). Arrows: Maximum thermal stability with preformed Fe carbides for (A) η -Fe₂C and (B) θ -Fe₃C. The θ -Fe₇C₃ Pnma (62) formation temperatures are excluded as its formation follows a different, not solely temperature dependent, route. Each of the Fe carbides were assigned with their precise crystal structures, on the basis of literature.

relatively mild FTS reaction conditions. Observations of the θ -Fe₇C₃ phase forming at $\approx 340^\circ\text{C}$ under mild reaction conditions have been made in the literature. It was speculated that the θ -Fe₇C₃ phase formation could be related to the presence of CO₂ under Fe carburizing conditions.

Chapter 3 – In this first experimental research Chapter of this PhD Dissertation, the identification and formation temperatures of the Fe carbides in the field of FTS catalysis were experimentally probed. Especially, the effect of the Na-S promotion on the Fe carbide formation process was studied. The study was performed by carburizing H₂ pre-reduced supported Fe(-Na-S)/ α -Al₂O₃ catalyst materials, with and without the added Na-S promotion, with CO within carburization temperatures of 240–440°C. In this way prepared Fe carbides were then characterized by using ex-situ X-ray Diffraction (XRD) with Rietveld Quantitative Phase Analysis (R-QPA). The obtained R-QPA results were compared to the corresponding data, obtained with ex-situ Mössbauer Absorption Spectroscopy (MAS), on the same, carburized, catalyst materials.

With this characterization methods at hand, it was possible to confirm the identification of the Fe carbides, their crystal structures and the unified nomenclature for the XRD and MAS techniques, as assigned in **Chapter 2**. Relative C atom contents, non-equivalent Fe position ratios and their corresponding MAS hyperfine fields were

assigned for the Fe carbides from the experimental data.

Together with the obtained experimental results and literature, the Fe carbide thermal stability ranges were refined to be at 5 h treatment time (**Figure 7.3**):

$$\begin{array}{ccccccc} \epsilon\text{-Fe}_3\text{C} & < & \eta\text{-Fe}_2\text{C} & < & \chi\text{-Fe}_5\text{C}_2 & < & \theta\text{-Fe}_3\text{C} \\ 100\text{-}265^\circ\text{C} & & 160\text{-}300^\circ\text{C} & & 240\text{-}420^\circ\text{C} & & 350\text{-}500^\circ\text{C} \end{array}$$

The $\eta\text{-Fe}_2\text{C}$ phase may, however, be stable up to 340°C in case if it is first formed at a lower temperature ($\leq 300^\circ\text{C}$) and after that it has been exposed to a higher temperature. This was explained by comparing the experimental results to the literature observations. The $\theta\text{-Fe}_3\text{C}$ phase decomposition into C and $\alpha\text{-Fe}$ may require a temperature as high as 600°C if the carbide phase is covered by an oxide shell, as was also explained on the basis of literature observations.

Some amounts of the $\theta\text{-Fe}_7\text{C}_3$ phase were formed if a $\text{Fe}(-\text{Na-S})/\alpha\text{-Al}_2\text{O}_3$ catalyst material – with or without Na-S promotion – was carburized at 25 bar CO pressure at 340°C , directly *after a catalyst calcining* step without first reducing it from $\alpha\text{-Fe}_2\text{O}_3$ to $\alpha\text{-Fe}$. In addition, with direct carburization of the $\alpha\text{-Fe}_2\text{O}_3$ phase, a distinctively distorted form of the $\chi\text{-Fe}_5\text{C}_2$ phase was formed. Its distorted crystal lattice parameters deviated clearly from the $\chi\text{-Fe}_5\text{C}_2$ phase formed from the H_2 pre-reduced catalysts with $\alpha\text{-Fe}$ as the carburization precursor.

The Na-S promotion did not affect the formation of the Fe carbides from the $\alpha\text{-Fe}$ phase in the H_2 pre-reduced catalyst materials. However, as explained with comparisons to the literature, alkaline promoters increase the reducibility of Fe oxides by CO at low reduction temperatures ($\approx 270^\circ\text{C}$). Thus, the presence of alkaline metal increases the availability of the $\alpha\text{-Fe}$ phase and its subsequent carburization by CO with Fe oxide carburization starting materials. This alkaline effect accounts for the occasionally observed increase in the Fe-based catalysts' carburization levels in literature, when the carburization process is started with a Fe oxide.

Some Na-S promotion effects in the CO carburization of the reduced $\alpha\text{-Fe}/\alpha\text{-Al}_2\text{O}_3$ catalyst materials were also observed. The observations are: i) increase in Fe oxidation, presumably by O from the CO dissociation acting as oxidation agent, with short, low temperature CO carburization treatments ($\leq 290^\circ\text{C}$, ≤ 3 h), ii) decreased crystallite diameter of the $\theta\text{-Fe}_3\text{C}$ phase formed after CO treatment at 440°C , and iii) increased rate of carbon deposition from CO at $\geq 340^\circ\text{C}$ via the Boudouard reaction. However, the increased carbon deposition rate diminished at 390°C and disappeared when reaching the CO carburization temperature of 440°C , in comparison to the carbon deposition on the respective unpromoted $\text{Fe}/\alpha\text{-Al}_2\text{O}_3$ catalyst materials.

Chapter 4 – The effect of added Na-S promotion on the performance and stability of

the various Fe carbides in the FTS reaction was studied. The supported Fe(-Na-S)/ α - Al_2O_3 catalyst materials, prepared in **Chapter 3**, with preformed Fe carbides or only H_2 reduced catalysts, with or without Na-S promotion, were used for this purpose. The catalyst materials were tested in a 72 h FTS reaction (340°C , 10 bar H_2 :CO:He 2.0:1.0:0.33 v/v, GHSV $\approx 5\,000\text{ h}^{-1}$) to evaluate their catalytic performances. The catalysts were characterized *after* the FTS reaction by using XRD with R-QPA. The obtained results were compared to the R-QPA results from **Chapter 3** *before* the FTS reaction.

The Fe carbide phases of η - Fe_2C *Pnnm* (58), χ - Fe_5C_2 *C2/c* (15), θ - Fe_3C *Pnma* (62) and θ - Fe_7C_3 *Pnma* (62) were observed in the catalysts. The ε - Fe_3C *P6₃22* (182) phase was not stable in the FTS reaction and was not present in any of the studied catalyst materials after the FTS reaction. By comparing the lattice parameters of the Fe carbides, the η - Fe_2C and χ - Fe_5C_2 phases were further divided into carbide subtypes with their typical formation conditions as:

χ - Fe_5C_2

- Type I** After CO carburization, or FTS *without* Na-S promotion,
- Type II** After FTS *with* Na-S promotion,
- Type III** After CO carburization of Fe oxide (α - Fe_2O_3), the subtype is stable in FTS *regardless* of the Na-S promotion,

η - Fe_2C

- Type I** After CO carburization, or FTS *without* Na-S promotion,
- Type II** After FTS *with* Na-S promotion,
- Type III** After martensite tempering at 120°C . *Not observed in FTS.*

Most interestingly, the distinctively distorted χ - Fe_5C_2 phase (i.e. Type III) prevailed unchanged in the FTS reaction. No Fe carbide subtypes could be assigned for the θ - Fe_3C or θ - Fe_7C_3 phases.

The addition of the Na-S promotion affected the Fe carbides in the FTS reaction by i) causing a maximum of $\approx 0.02\text{ \AA}$ anisotropic changes in the crystal lattice parameters for the η - Fe_2C and χ - Fe_5C_2 phases (i.e. subtypes Type II), ii) the η - Fe_2C phase was *stabilized*, while iii) the θ - Fe_3C phase was *destabilized*, in comparison to the respective phases in the unpromoted catalyst materials. The stability of the θ - Fe_7C_3 phase in the FTS reaction was not affected by the Na-S promotion (**Figure 7.4**).

With respect to the catalysts' FTS reaction performance, the Na-S promotion had the general effects of i) increased CO conversion, ii) $\approx +10\%$ increased C_2 - C_4 selectivity with significantly suppressed CH_4 selectivity below the ASF expectations, iii) increased olefin content and iv) increased α -value, in comparison to the respective unpromoted catalyst

Figure 7.4

Overview of Na-S promotion dependent Fe carbide phase stabilities, as compared before (Carb.) and after 72 h Fischer-Tropsch Synthesis (FTS) reaction. Rietveld Quantitative Phase Analysis (R-QPA)-based Fe phase fractions for a) unpromoted (UP) and b) Na-S promoted (Na-S) Fe(-Na-S)/α-Al₂O₃ catalyst materials. Na-S promotion **A** stabilizes η-Fe₂C, **B** destabilizes θ-Fe₃C and **C** does not affect the stability of the θ-Fe₇C₃ phase in the FTS reaction. FTS conditions: 340°C, 10 bar, H₂:CO:He 2.0:1.0:0.33 v/v, ~5 000 h⁻¹.

materials. However, as adverse FTS reaction effects, with the Na-S promotion i) CO₂ selectivity increased significantly from ~16 % to ~38-43 % and ii) the fraction of CO converted to FTS reaction produced hydrocarbons dropped to ~0.42-0.47 with respect to the unpromoted catalyst materials.

Furthermore, the Usage Ratios H₂:CO decreased from ~1.8-2.3 to ~0.7-0.8 with the added Na-S promotion as a sign of increased, CO₂ releasing, Boudouard and/or Water-gas Shift (WGS) reactions consuming the input CO. No WGS reaction active Fe₃O₄ was present in any of the catalyst materials after the FTS reaction. Therefore, the Na(-S) promotion was discussed to provide the directly active reaction sites for the possible WGS reaction.

Nevertheless, despite the lost C pathway selectivity towards CO conversion to hydrocarbons: ~4.4 times more hydrocarbons were still converted from CO per unit of time with the most active Na-S promoted catalyst in comparison to the most active unpromoted catalyst material.

When the FTS reaction activity results were contrasted to the R-QPA quantification results, no direct correlation between the FTS reaction activity and any of the bulk Fe carbide phases could be made. That is, any specific Fe carbide was not more active in the FTS reaction than any other of the studied carbides. However, in terms of hydrocarbon product selectivities, some cautious correlations could be assigned. It was observed that i) the θ -Fe₃C phase mildly ($\approx +5\%$) increased the hydrocarbon product slate paraffin content. In combination with the Na-S promotion: ii) the η -Fe₂C Type II and χ -Fe₅C₂ Type II were present in the high olefin and low CH₄ selective FTS catalyst materials, and iii) the χ -Fe₅C₂ Type III might increase the olefin selectivity more than the χ -Fe₅C₂ Type II does, when combined with the Na-S promotion.

Any conclusions on the role of the θ -Fe₇C₃ phase in the FTS reaction could not be drawn, as the phase was present in too minor phase quantities in the studied FTS reaction catalyst materials.

Chapter 5 – The combined effects of the total FTS reaction pressure, Na-S promotion and the catalysts' H₂ reduction prior to the FTS reaction were studied. The main aim of the work was to follow the effects of the aforementioned parameters on the formation of Fe carbides and their subtypes, and to correlate this information on Fe carbide phases to the FTS reaction performance of the catalyst materials. Thus, supported Fe(-Na-S)/ α -Al₂O₃ catalyst materials, with and without Na-S promotion, were prepared for this study. The catalysts were either calcined only or subsequently to calcining also H₂ reduced, before the catalytic performance testing in the FTS reaction. The FTS reactions were separately ran for 72 h at either 3, 10 or 20 bar total reaction pressure (340°C, H₂:CO:He 1.0:1.0:0.2 v/v, GHSV $\approx 5\,500\text{ h}^{-1}$). XRD patterns were collected ex-situ for each of the studied catalyst materials after the FTS reaction runs and were quantified using R-QPA.

After the FTS reactions, the Fe carbide phases identified in the catalyst materials were η -Fe₂C *Pnnm* (58), χ -Fe₅C₂ *C2/c* (15) and/or θ -Fe₇C₃ *Pnma* (62). For all of the studied catalyst materials the χ -Fe₅C₂ phase was quantified as the most abundant. The Na-S promotion had the FTS reaction pressure dependent effects on the Fe carbide formation of i) inducing the appearance of the η -Fe₂C phase with ≥ 10 bar FTS reaction pressure, ii) whereas the calcined only catalyst materials favored the η -Fe₂C phase formation more than the H₂ reduced catalyst, and iii) also inducing formation of minor amounts of the θ -Fe₇C₃ phase in the calcined only catalyst after the 20 bar FTS reaction.

In relation to the FTS reaction pressure and the added Na-S promotion, the carbide subtypes form as follows:

χ -Fe₅C₂

Type I

Without Na-S promotion regardless of reaction pressure, or

- Type II** with 3 bar FTS reaction pressure *regardless* of Na-S promotion,
Type III *With* Na-S promotion, and ≥ 10 bar FTS reaction pressure,
 Fe oxide ($\alpha\text{-Fe}_2\text{O}_3$) i.e. calcined only catalyst as the FTS starting material *regardless* of the Na-S promotion or the FTS reaction pressure,
 $\eta\text{-Fe}_2\text{C}$
Type II *With* Na-S promotion, and ≥ 10 bar FTS reaction pressure.

The performance of the catalyst materials depended on the reaction pressure, which could be altered by the presence of Na and S as promoters. Whether the catalyst was only calcined or also H_2 reduced, had a lesser influence on the catalytic performance.

Figure 7.5

Overview of the effects of Fischer-Tropsch Synthesis (FTS) reaction pressure, Na-S promotion and catalyst H_2 pre-reduction on unpromoted (UP) and Na-S promoted (Na-S) $\text{Fe}(-\text{Na-S})/\alpha\text{-Al}_2\text{O}_3$ catalyst materials in a 72 h FTS reaction for different pressures (3, 10, 20 bar). The catalyst materials were exposed to the FTS reaction directly after calcining (Calcin.) or H_2 reduced prior to the reaction (H_2). The FTS activity as a) Fe Time Yields (FTYs) show 10 bar pressure threshold for Na-S and 20 bar threshold for UP catalyst materials for boosted FTY. The FTY boost b) correlates to the Fe carbide subtypes (I, II, III) with transition of $\chi\text{-Fe}_5\text{C}_2$ Type I to II and the presence of $\chi\text{-Fe}_5\text{C}_2$ Type III with Na-S promotion. At 10 bar FTS reaction pressure c) the $\text{C}_2\text{H}_4/\text{C}_2\text{H}_6$ ratio is increased with the Calcin. catalysts, regardless of the Na-S promotion. This correlates with the presence of $\chi\text{-Fe}_5\text{C}_2$ Type III. FTS conditions: 340°C , 3, 10 or 20 bar, $\text{H}_2:\text{CO}:\text{He}$ 1.0:1.0:0.2 v/v, $\approx 5\,500\text{ h}^{-1}$.

The Na-S promotion combined with a 10 bar FTS reaction pressure threshold, had the effects that: i) catalysts showed a significant boost in the Fe Time Yields (FTYs), ii) Usage Ratio $H_2:CO$, CO converted to hydrocarbons and hydrocarbon selectivities became reaction pressure independent, and iii) the selectivity towards CO_2 was increased significantly. These FTS reaction performance changes correlated with Na-S induced transition of $\chi-Fe_5C_2$ Type I to Type II, and to the presence of $\chi-Fe_5C_2$ Type III with Na-S promotion. For unpromoted catalysts, a 20 bar FTS reaction pressure threshold was required for attaining similar FTS reaction catalysis effects as were observed with the Na-S promoted catalyst materials with ≥ 10 bar reaction pressure. For these changes in the unpromoted catalysts, $\chi-Fe_5C_2$ Type I and unpromoted Type III were present as the $\chi-Fe_5C_2$ phase subtypes.

With 3 bar reaction pressure, none of the studied catalyst materials showed significant FTYs regardless of the Na-S promotion. The presence of $\eta-Fe_2C$ Type II did not correlate with any of the FTS reactions' catalytic performance - activity or selectivity - indicators, as was deduced on the basis of the R-QPA quantified Fe phase fractions.

Regardless of the Na-S promotion, when calcined only catalyst materials were used in the FTS reaction: i) the C_2H_4/C_2H_6 ratio was increased with 10 bar FTS reaction pressure and ii) the overall FTYs were decreased with 20 bar reaction pressure in comparison to the H_2 reduced catalysts. The increased C_2H_4/C_2H_6 ratio was associated to the presence of $\chi-Fe_5C_2$ Type III, independently of the Na-S promotion, with 10 bar reaction pressure. In other words, the $\chi-Fe_5C_2$ Type III phase correlated with a decreased hydrogenation ability of the catalyst material. Decreased FTYs in turn correlated with the presence of the Fe_3O_4 phase, in the calcined only, 20 bar FTS catalysts. The Fe_3O_4 likely originated from carbon deposition induced mass transfer limitations inhibiting the reduction of the initial $\alpha-Fe_2O_3/(\alpha-Al_2O_3)$ phase by $H_2:CO$ during the FTS reaction. An overview of the discussed FTS reaction performance effects is given in **Figure 7.5**.

Chapter 6 – In this final research Chapter, the main aim was to study the effect of the Na-S promotion on the simultaneous Fe carbide phase changes and carbon deposition *during* the FTS reaction. This was done by using in-situ characterization methods. More specifically, a combined XRD/Raman spectroscopy set-up was employed. The supported $Fe(-Na-S)/\alpha-Al_2O_3$ catalyst materials, prepared in **Chapter 3**, with preformed Fe carbides or only H_2 reduced catalysts, with or without Na-S promotion, were used. The catalysts were characterized in-situ with XRD/Raman spectroscopy during a 72 h FTS reaction ($340^\circ C$, 10 bar $H_2:CO:He$ 2.0:1.0:0.33 v/v, GHSV $\approx 7\,200\,h^{-1}$). The in-situ collected XRD patterns were quantified with the use of R-QPA. The Raman spectra were evaluated for the carbon species by following the

Figure 7.6

Summary of simultaneous in-situ X-ray Powder Diffraction (XRPD)/Raman spectroscopy results during the Fischer-Tropsch Synthesis (FTS) reaction on unpromoted (UP) and Na-S promoted (Na-S) Fe-(Na-S)/ α -Al₂O₃ catalyst materials without initial carbon deposits. The intensities of the D and G Raman bands a) initially grow fast within Time-on-Stream (ToS) ≤ 15 h, and for ToS ≥ 15 h ToS the growth remains faster with the Na-S catalysts. Rietveld Quantitative Phase Analysis (R-QPA)-based Fe phase fractions change b) as the χ -Fe₅C₂ phase preferentially forms during the FTS reaction at 340°C, but the Na-S promotion significantly stabilizes the η -Fe₂C phase. If present, Na-S promotion destabilizes the θ -Fe₃C and Fe₃O₄ phases. The formed carbon species c) compare closely to Carbon Nanofiber (CNF) reference carbon material at ToS 70 h, for both UP and Na-S catalysts. *FTS conditions:* 340°C, 10 bar, H₂:CO:He 2.0:1.0:0.33 v/v, ≈ 7 200 h⁻¹.

intensities of the D (≈ 1 350 cm⁻¹) and G (≈ 1 600 cm⁻¹) Raman bands. An overview of the most significant results from this study is given in **Figure 7.6**.

The Na-S promotion altered the Fe oxide and carbide phases' properties by:

- stabilizing* the η -Fe₂C phase, *but only if* either ϵ -Fe₃C and/or η -Fe₂C was present in the initial catalyst,
- destabilizing* the θ -Fe₃C phase and aiding in its transition to χ -Fe₅C₂,
- increasing the reducibility of Fe₃O₄ phase by (H₂:CO),
- decreasing the Fe₃O₄ content during the FTS reaction on the catalysts; and also by
- inducing Fe crystallite growth for the Fe carbides within the ≤ 15 h Time-on-

Stream (ToS) period. The θ -Fe₃C phase turned out to be an exception to this, as for the phase the crystallite diameters decreased with Na-S promotion.

The carbon deposition on the catalyst materials did not correlate with any specific Fe carbide phase or carbide-to-carbide transition. With H₂ reduced catalysts, the carbon deposition did not start before the Fe₃O₄ phase, a phase incapable for CO dissociation, was reduced.

With catalyst materials with insignificant initial carbon deposits i.e. with H₂ reduced or <300°C CO carburized catalysts, the increase of the D and G Raman bands during the FTS reaction could be divided into two periods: i) an initial fast (≤ 10 -15 h ToS), and ii) a steady or lesser (≥ 15 h ToS) intensity growth period. The initial fast growth period was present regardless of the Na-S promotion. However, after reaching the steady growth period Na-S promotion induced a higher rate of intensity growth of the D and G Raman bands (for the G-band $\approx 2.7 \pm 0.2$ faster) in comparison to the unpromoted catalyst materials. For catalysts with initial carbon deposits from CO carburization $\geq 340^\circ\text{C}$, the initial fast growth period was absent, regardless of the Na-S promotion. Possibly, an initial non-isothermal bed operation could have explained by the initial fast D- and G-band intensity gains within ≤ 10 -15 h ToS for the catalyst materials without initial carbon deposits.

The carbon species formed during catalyst preparation CO carburizations were weakly Raman active with the used (532 nm) visible wavelength excitation laser. That is, they were mainly made of carbon structures with C sp³ with a band gap above the energy available from the visible wavelength excitation laser. Under H₂:CO during the FTS reaction, more ordered CNF-like phases with C sp² formed, which led to an increased Raman signal intensity. During the FTS reactions, the carbon species evolved from amorphous carbon species, with structures containing both tetrahedral C sp³ and C sp² in chain-like ordering, towards more ordered carbon materials with their structures containing C sp² in varying non-6-fold cyclic order with feature sizes <7 nm in diameter.

In comparison to the measured carbon reference materials, the catalysts' Raman spectra at ≈ 70 h ToS compared best to a Carbon Nanofiber (CNF) reference material. However, the catalyst materials contained possibly a higher amount of C sp² in chain-like structures (G-band blue shift to higher cm⁻¹) and a wider variety of non-6-fold carbon rings (wider D-band peak) than in the reference CNF material (**Figure 7.6c**).

Na-S promotion affected the FTS reaction formed carbon species by: i) increasing the initial C sp² content in chain-like carbon structures, and ii) increasing 6-fold cyclic carbon species for catalyst materials with the initial CO carburization temperature $\geq 340^\circ\text{C}$.

7.2 FUTURE PERSPECTIVES

As invariably tends to happen with any research, new scientific questions arise at the same pace as the old ones are answered. In the following, few of the most interesting future research topics arising from the work conducted in this PhD Dissertation are briefly discussed.

Comparison of ϵ -Fe₃C and η -Fe₂C to ϵ -Fe₃N and ζ -Fe₂N. As was highlighted in the **Chapter 3**, the Fe carbide ϵ -Fe₃C and η -Fe₂C phases' crystal structures are closely related to the ϵ -Fe₃N and ζ -Fe₂N Fe nitrides' structures, respectively. A comparative study on the behavior and the FTS reaction performance of the ϵ -Fe₃C and η -Fe₂C in comparison to the Fe₃N and ζ -Fe₂N phases, with and without the Na-S promotion, would make an interesting study. Especially, it would be worth finding out whether the ζ -Fe₂N phase can be stabilized in the FTS reaction with Na-S promotion in the same way as was observed for the η -Fe₂C phase. The Fe nitride phases are usually not stable under carburizing conditions but rather convert into Fe carbonitrides.¹⁻³ Fe nitride-based catalyst materials have been observed to be selective toward olefin production in the FTS reaction.³

Formation of the θ -Fe₇C₃ Phase. Although some minor amounts of the θ -Fe₇C₃ phase was formed in the studies, described in the research Chapters of this Dissertation, more effort is still needed on studying the phase's formation behavior under the FTS reaction relevant conditions. As was speculated in **Chapter 3**, the θ -Fe₇C₃ phase's formation under carburizing conditions might be dependent on the presence of CO₂ during the carburization process. A systematic probing on the effect of carburizing CO₂:CO gas mixtures on the θ -Fe₇C₃ phase's formation from Fe-based materials should be conducted in the future. This would aid in determining the FTS reaction role and properties of this still vastly understudied Fe carbide.

Fe Carbide Subtypes' Crystal Structures. In **Chapter 4** the η -Fe₂C and the χ -Fe₅C₂ phases were divided into distinct subtypes based on their distinctively different lattice parameter a . However, the precise structural origins of the crystal lattice changes for the resulting carbide subtypes could not be answered within the scope of this PhD Dissertation. In the future, more detailed probing of the crystal structure differences in the Fe carbide subtypes should be performed with the use of a monochromatic X-ray source. In addition, probing of whether the Na-S promotion induced subtype formations are truly due to the Na(-S) promoters entering the Fe carbide lattices or something else, could be investigated using Neutron Diffraction (ND).

Furthermore, in **Chapter 5**, the presence of the χ -Fe₅C₂ Type III phase was correlated with a decreased hydrogenation ability in the FTS reaction. That is, the χ -Fe₅C₂ Type III increased the catalyst material's FTS hydrocarbon selectivity towards the

production of olefins. The presence of χ -Fe₅C₂ Type III would also explain similar selectivity results obtained in literature.^{4,5} This effect, neither, was not explained with any fundamental insight in the Chapter. How and why the χ -Fe₅C₂ Type III favors the olefin formation in comparison to the other Fe carbide subtypes would make an interesting study by performing Density Functional Theory (DFT) calculations.

7.3 REFERENCES

- [1] Jack, K. H., "Binary and Ternary Interstitial Alloys III. The Iron-Carbon System: The Characterization of a New Iron Carbide", *Proc. R. Soc. A Math. Phys. Eng. Sci.* **195**, 56–61 (1948).
- [2] Jack, K. H., "Binary and Ternary Interstitial Alloys. II. The Iron-Carbon-Nitrogen System", *Proc. R. Soc. A Math. Phys. Eng. Sci.* **195**, 41–55 (1948).
- [3] Butt, J. B., "Carbide phases on iron-based Fischer-Tropsch synthesis catalysts part II: Some reaction studies", *Catal. Lett.* **7**, 83–106 (1990).
- [4] Bukur, D. B., Nowicki, L., Manne, R. K. and Lang, X. S., "Activation Studies with a Precipitated Iron Catalyst for Fischer-Tropsch Synthesis II. Reaction Studies", *J. Catal.* **155**, 366–375 (1995).
- [5] Wezendonk, T. A. et al., "Controlled formation of iron carbides and their performance in Fischer-Tropsch synthesis", *J. Catal.* **362**, 106–117 (2018).

Chapter 8

Nederlandse Samenvatting en Toekomstperspectieven

Momenteel worden koolwaterstoffen gebruikt in het overgrote deel van moderne industriële processen, die leiden tot de productie van brandstoffen, kunststoffen, coatings en andere materialen. In de nabije toekomst zal de huidige primaire bron voor deze koolwaterstoffen, namelijk ruwe olie uit de aardkorst, opraken en zullen nieuwe alternatieven als bron voor koolwaterstoffen nodig zijn. Het industriële Fischer-Tropsch-proces (FTP) is in staat om een koolstofhoudende grondstof, zoals aardgas, steenkool, biomassa of gemeentelijk afval, om te zetten in een verscheidenheid aan koolwaterstofproducten. De heterogeen gekatalyseerde Fischer-Tropsch synthese (FTS)-reactie wordt gebruikt in het FTP voor het omzetten van een synthesesegasmengsel van $\text{CO} + \text{H}_2$ in synthetische ruwe olie, die verder wordt gezuiverd tot de uiteindelijke koolwaterstofproducten. In dit proefschrift hebben we de FTS-reactie bestudeerd met behulp van Fe-gebaseerde, wel of niet met Na-S gepromote, ondersteunde $\text{Fe}(-\text{Na-S})/\alpha\text{-Al}_2\text{O}_3$ -katalysatormaterialen. De focus van deze dissertatie lag voornamelijk op de karakterisering van de actieve fasen van de FTS-reactie katalysatoren: de Fe-carbiden. Röntgenpoederdiffractometrie (XRPD) werd toegepast als de primaire karakteriseringstechniek en de verzamelde gegevens werden gekwantificeerd met Rietveld kwantitatieve fase-analyse (R-QPA). Identificatie van Fe-carbide, vormingsomstandigheden en hun subtypen, zoals gedefinieerd door de roosterparameters van carbide, werden onderzocht. Dit proefschrift specificeert de effecten, die Na-S-promotor heeft op de Fe-carbidevorming en de carbide-eigenschappen in de FTS-reactie.

Figuur 8.1

Overzicht van het volledige Fischer-Tropsch-proces (FTP), die de Fischer-Tropsch synthese (FTS)-reactie toepast in het industriële proces van de omzetting van koolstofhoudende grondstoffen in geraffineerde koolwaterstofproducten. De algemene FTP-stappen zijn a) Grondstof naar Syngas, Syngas naar Synruwe Olie en Synruwe Olie naar Producten. De grondstof b) bepaalt grotendeels de CO₂-voetafdruk van de algehele FTP, aangezien de c) FTS-reactie een syngas H₂:CO in een verhouding van ≈2 in de Syngas-naar-Synruwe Olie FTP-stap verbruikt. Met andere grondstoffen dan aardgas moet de effectieve syngas H₂:CO-verhouding <2 en H₂ worden geproduceerd en toegevoegd aan de FTP, waardoor de totale CO₂-voetafdruk toeneemt. Afval = Gemeentelijk afval, Steenkool = Gemiddelde van verschillende kolentypen, Biomassa = vingergras, HC = koolwaterstoffen.

8.1 SAMENVATTING

Ondanks dat de katalytische omzetting van een H₂ + CO mengsel in koolwaterstoffen met de Fischer-Tropsch synthese-reactie (FTS-reactie) al meer dan 100 jaar bekend is, valt er nog veel te leren. De Fe-carbiden, de actieve fasen in de reactie, vormen de basis van de FTS-reactie met Fe-gebaseerde katalysatormaterialen. De belangrijkste motivatie voor het uitvoeren van het onderzoek in dit proefschrift was om meer te leren over het gedrag en de vorming van de verschillende Fe-carbide fasen en hoe ze worden beïnvloed door de toegevoegde chemische Na-S-promotor. Hieronder volgt een samenvatting van het werk dat is uitgevoerd voor dit proefschrift, waarbij de belangrijkste conclusies worden belicht.

Hoofdstuk 1 - De geschiedenis over én motivaties voor de toepassing van het algehele industriële Fischer-Tropsch-proces (FTP) werden kort geïntroduceerd. In de FTP wordt een koolstofhoudende grondstof omgezet in geraffineerde koolwaterstofproducten. De FTP-stappen die werden besproken zijn (**Figuur 8.1**): *Grondstof naar Syngas, Syngas naar Synruwe Olie en Synruwe olie naar Producten*. De gekatalyseerde FTS-reactie wordt zelf gebruikt in de Syngas naar Synruwe Olie-processtap voor het omzetten van $H_2 + CO$ mengsel (syngas) naar een mengsel van verschillende koolwaterstoffen en hun derivaten (synruwe olie).

De CO_2 -voetafdruk van het algehele FTP hangt voor een groot deel af van de grondstof in de volgende volgorde: aardgas < gemeenschappelijk afval < steenkool < biomassa. Vanwege de zuiverheid kan aardgas direct worden omgezet in gebruiksklaar syngas met een $H_2:CO$ -verhouding ≈ 2 , dat voldoet aan de vereiste stoichiometrie van de FTS-reactie. Met de andere grondstoffen, die heteroatomen (voornamelijk N, O en S) als onzuiverheden bevatten, is de effectief haalbare $H_2:CO$ -verhouding minder dan 2. Daarom moet voor deze grondstoffen goedkoop en duurzaam geproduceerd H_2 aan de FTP worden toegevoegd om met aardgas gebaseerde FTP te kunnen concurreren. De gebruikte FTP-grondstof is ook belangrijk vanuit economisch perspectief. Het produceren van het gezuiverde syngas voor gebruik in de FTS-reactie bedraagt 60-70 % van de totale kapitaalkosten in een op steenkool gebaseerde FTP, terwijl dat voor de op aardgas gebaseerde FTP slechts 30-50 % is.

Hoofdstuk 2 - De heterogene katalyse van de FTS-reactie met Fe-gebaseerde katalysatormaterialen is besproken. Onderwerpen zoals de gangbare katalysatorsamenstellingen, de verschillende chemische reacties die plaatsvinden en de mogelijke reactietrajecten voor C van CO -input in een Fe-gebaseerde FTS-reactiekatalysator zijn de revue gepasseerd. De mogelijke C-routes in de FTS-reactie zijn samengevat in **Figuur 8.2**. Verder werden de effecten van de verschillende FTS-reactie-conditieparameters op de koolwaterstof- en C-route-selectiviteiten bekeken. De effecten van parameters, zoals reactietemperatuur, input $H_2:CO$ -verhouding, gasruimte-snelheid en totale reactiedruk, werden besproken. De specifieke onderwerpen van deze dissertatie zijn: i) de effecten die voortkomen uit de toegevoegde chemische Na-S-promotie in de Fe-gebaseerde FTS-reactie en ii) de identificatie van de Fe-carbidefasen die werden aangetroffen in het FTS-onderzoeksdomein.

De Na-S-promotie in de FTS-reactie heeft als effect i) het verlagen van de CH_4 -selectiviteit tot een lagere waarde dan voorspeld door de Anderson-Shulz-Flory-verdeling (ASF-verdeling), ii) minder toename in de koolwaterstofketenlengte (d.w.z., α -waarde) in vergelijking met wanneer alleen alkali wordt toegevoegd, iii) verhoogde

Figuur 8.2

Een vereenvoudigde samenvatting van de reactiepaden voor C uit CO-invoer in een katalysatordeeltje voor de Fe-gebaseerd Fischer-Tropsch synthese (FTS)-reactie. De invoer $\text{CO} + \text{H}_2$ geeft oorspronkelijk een reductieve omgeving (rood). Voor C van CO-dissociatie zijn de reactiepaden: (1) met $\alpha\text{-Fe}$ om Fe_xC te vormen, (2) met H om koolwaterstoffen te vormen, (3) met C om inactieve koolstof te vormen. Zonder CO-dissociatie: C-pad (4) kan Fe_xO_y reduceren tot $\alpha\text{-Fe}$ terwijl CO_2 vrijkomt. Verwijdering van O-atomen uit CO naar H_2O of CO_2 leidt geleidelijk tot een oxiderende omgeving (Ox) in de richting van de kern van het katalysatordeeltje en de uitlaat van een reactor met een vast bed. Als de actieve FTS-reactie Fe_xC geoxideerd is tot Fe_3O_4 , kan route (5) $\text{H}_2\text{O} + \text{CO}$ omzetten in $\text{CO}_2 + \text{H}_2$ via de water-gasverschuivingsreactie (WGS).

selectiviteit van alkenen, en iv) een algeheel verhoogde CO-omzetting. Deze selectiviteitseffecten lijken op promotie-effecten van alleen alkali (als K of Na) in de FTS-reactie. De unieke eigenschap van de Na-S-promotie is echter het vermogen om de CH_4 -selectiviteit te verlagen tot een lagere waarde dan voorspeld door de ASF-verdeling. Deze prestatie is niet haalbaar zonder de toegevoegde S.

De Fe-carbiden die waarneembaar zijn in het FTS-reactieonderzoeksveld met hun kristalstructuren zijn:

- hexagonal $\epsilon\text{-Fe}_3\text{C}$ $P6_322$ (182),
- orthorhombic $\eta\text{-Fe}_2\text{C}$ $Pnmm$ (58),
- monoclinic $\chi\text{-Fe}_5\text{C}_2$ $C2/c$ (15) (the Hägg carbide),
- orthorhombic $\theta\text{-Fe}_3\text{C}$ $Pnma$ (62) (cementite), and
- orthorhombic $\theta\text{-Fe}_7\text{C}_3$ $Pnma$ (62) (the Eckström-Adcock carbide).

De totstandkoming van de Fe-carbiden is afhankelijk van de temperatuur waarbij het nulwaardige $\alpha\text{-Fe}$ wordt blootgesteld aan een C-atoombron. De verwachte thermische

stabiliteit en vormingstemperatuur voor de Fe-carbiden zijn op basis van de literatuurgegevens: $\epsilon\text{-Fe}_3\text{C}$ (100-265°C) < $\eta\text{-Fe}_2\text{C}$ (160-340°C) < $\chi\text{-Fe}_5\text{C}_2$ (240-350°C) < $\theta\text{-Fe}_3\text{C}$ (310-600°C).

De totstandkoming van de $\theta\text{-Fe}_7\text{C}_3$ -fase verloopt niet op dezelfde manier als voor de rest van de carbiden van Fe. Ondanks dat nogal extreme reactieomstandigheden vaak worden genoemd als vereisten voor de vorming van de $\theta\text{-Fe}_7\text{C}_3$ -fase, kan deze zich ook vormen onder relatief milde FTS-reactieomstandigheden. Waarnemingen van de totstandkoming van de $\theta\text{-Fe}_7\text{C}_3$ -fase bij $\approx 340^\circ\text{C}$ onder milde reactieomstandigheden zijn gemaakt in de literatuur. Er is gespeculeerd dat de totstandkoming van de $\theta\text{-Fe}_7\text{C}_3$ -fase gerelateerd zou kunnen zijn aan de aanwezigheid van CO_2 onder Fe-carburiseringsomstandigheden.

Hoofdstuk 3 - In dit eerste experimentele hoofdstuk werden de identificatie- en vormingstemperaturen van de Fe-carbiden in het FTS-onderzoeksdomein onderzocht. Vooral het effect van de Na-S-promotie op het Fe-carbidevormingsproces werd bestudeerd. De studie werd uitgevoerd door het carboneren van H_2 -voorgereduceerde gedragen $\text{Fe}(-\text{Na-S})/\alpha\text{-Al}_2\text{O}_3$ -katalysatormaterialen, met en zonder de toegevoegde Na-S-promotie, met CO binnen carburisatietemperaturen van 240-440°C. Op deze manier bereide Fe-carbiden werden vervolgens gekarakteriseerd door ex-situ Röntgenpoederdiffractometrie (XRPD) te gebruiken met Rietveld kwantitatieve fase-analyse (R-QPA). De verkregen R-QPA-resultaten werden vergeleken met respectievelijke ex-situ Mössbauer absorptie spectroscopie (MAS)-karakterisatieresultaten op dezelfde, gecarburiseerde katalysatormaterialen.

Met deze benadering was het mogelijk om de identificatie van de Fe-carbiden, hun kristalstructuren en de uniforme nomenclatuur voor de XRPD- en MAS-technieken te bevestigen, zoals toegewezen in **Hoofdstuk 2**. Relatieve C-atomen, niet-equivalente Fe-positieverhoudingen en hun overeenkomstige MAS-hyperfijnvelden werden toegewezen voor de Fe-carbiden uit de experimentele gegevens.

Samen met de verkregen experimentele resultaten en literatuur werden de thermische stabiliteits-bereiken van de Fe-carbiden verfijnd om tot een behandelingstijd van 5 uur te komen (**Figuur 8.3**):

$$\begin{array}{ccccccc} \epsilon\text{-Fe}_3\text{C} & < & \eta\text{-Fe}_2\text{C} & < & \chi\text{-Fe}_5\text{C}_2 & < & \theta\text{-Fe}_3\text{C} \\ 100\text{-}265^\circ\text{C} & & 160\text{-}300^\circ\text{C} & & 240\text{-}420^\circ\text{C} & & 350\text{-}500^\circ\text{C} \end{array}$$

De $\eta\text{-Fe}_2\text{C}$ fase kan echter stabiel zijn tot 340°C in het geval dat het eerst wordt gevormd bij een lagere temperatuur ($\lesssim 30^\circ\text{C}$) en daarna wordt blootgesteld aan een hogere temperatuur. Door de experimentele resultaten te vergelijken met de literatuurobservaties kwamen we tot een verklaring. De ontleding van de $\theta\text{-Fe}_3\text{C}$ -fase

Figuur 8.3

Fe-carbide-vormingsgebieden (*gearceerd gedeelte*) voor temperatuur versus behandlingsbloomstellingstijd op basis van de beschikbare literatuurgegevens over experimenteel onderzoek (*niet-aangekruist*) en deze PhD-dissertatie (*aangekruist*). *Pijlen*: maximale thermische stabiliteit met voorgevormde Fe-carbiden voor (A) η -Fe₂C en (B) θ -Fe₃C. De θ -Fe₇C₃ *Pnma* (62) vormingstemperaturen zijn uitgesloten omdat de formatie ervan een andere, niet alleen temperatuurafhankelijke, route volgt. Elk van de Fe-carbiden kreeg, op basis van literatuur, hun exacte kristalstructuren toegewezen.

tot C en α -Fe kan een temperatuur van wel 600°C vereisen als de carbidefase wordt bedekt door een oxidatieschaal, zoals ook werd verklaard aan de hand van literatuurobservaties.

Sommige hoeveelheden van de θ -Fe₇C₃-fase werden gevormd wanneer een Fe(-Na-S)/ α -Al₂O₃-katalysatormateriaal - met of zonder Na-S-promotie - werd gecarburiseerd bij 25 bar CO-druk bij 340°C, direct ná een *katalysator-calcinatiestap* zonder deze eerst te reduceren van α -Fe₂O₃ tot α -Fe. Met directe carburisatie van de α -Fe₂O₃-fase, werd een duidelijk vervormde vorm van de χ -Fe₅C₂-fase gevormd. De vervormde kristalroosterparameters weken duidelijk af van de χ -Fe₅C₂-fase gevormd uit de H₂-voorgereduceerde katalysatoren met α -Fe als de carburisatie-precursor.

De Na-S-promotie had geen invloed op de vorming van de Fe-carbiden uit de α -Fe-fase in de H₂-voorgereduceerde katalysatormaterialen. Echter, zoals is uitgelegd middels vergelijkingen met de literatuur, verhogen alkali-promoters de reduceerbaarheid van Fe-oxiden door CO bij lage reductietemperaturen ($\approx 270^\circ\text{C}$). Oftewel, alkali verhoogt de beschikbaarheid van de α -Fe-fase en de daaropvolgende carburisering door CO met Fe-oxide carboneringsuitgangsmaterialen. Dit alkalische effect verklaart de van tijd tot tijd waargenomen toename van de carburiseringsniveaus van de op basis van Fe-gebaseerde katalysatoren in de literatuur, wanneer het

carburisatieproces wordt gestart met een Fe-oxide.

Sommige Na-S-promotie-effecten bij de CO-carburisatie van de gereduceerde α -Fe/ α -Al₂O₃-katalysatormaterialen werden ook waargenomen. De waarnemingen zijn: i) toename van de Fe-oxidatie, vermoedelijk door O van de CO-dissociatie die werkt als oxidatiemiddel, met korte CO-carburatiebehandelingen bij lage temperatuur ($\leq 290^\circ\text{C}$, ≤ 3 uur), ii) verminderde kristallietdiameter van de θ -Fe₃C-fase gevormd na CO-behandeling bij 440°C , en iii) verhoogde snelheid van koolstofafzetting uit CO bij $\geq 340^\circ\text{C}$ via de Boudouard-reactie. De verhoogde koolstofafzettingssnelheid nam echter af bij 390°C en verdween bij het bereiken van de CO-carburisatietemperatuur van 440°C , in vergelijking met de koolstofafzetting op de respectievelijke niet-gepromote Fe/ α -Al₂O₃-katalysatormaterialen.

Hoofdstuk 4 - Het effect van toegevoegde Na-S-promotie op de prestaties en stabiliteit van de verschillende Fe-carbiden in de FTS-reactie werd bestudeerd. De ondersteunde Fe(-Na-S)/ α -Al₂O₃-katalysatormaterialen bereid in **Hoofdstuk 3** met voorgevormde Fe-carbiden of alleen met H₂-gereduceerde katalysatoren, met of zonder Na-S-promotie, werden hiervoor gebruikt. De katalysatormaterialen werden getest in een 72 uur FTS-reactie (340°C , 10 bar H₂:CO:He 2.0:1.0:0.33 v/v, GHSV $\approx 5\,000\text{ h}^{-1}$) vanwege hun katalytische prestatie. De katalysatoren werden gekarakteriseerd ná de FTS-reactie door XRPD met R-QPA te gebruiken. De verkregen resultaten werden vergeleken met de R-QPA-resultaten vóór de FTS-reactie uit **Hoofdstuk 3**.

De Fe carbide-fasen van η -Fe₂C *Pnnm* (58), χ -Fe₅C₂ *C2/c* (15), θ -Fe₃C *Pnma* (62) en θ -Fe₇C₃ *Pnma* (62) werden waargenomen in de katalysatoren. De ε -Fe₃C *P6₃22* (182)-fase was niet stabiel in de FTS-reactie en was na de FTS-reactie in geen enkele van de bestudeerde katalysatormaterialen aanwezig.

Door de roosterparameters van de Fe-carbiden te vergelijken, werden de η -Fe₂C- en de χ -Fe₅C₂-fase verder onderverdeeld in carbide-subtypen met hun typische formaties zoals:

χ -Fe₅C₂

- Type I** Na CO-carburisatie, of FTS zónder Na-S promotie,
- Type II** Na FTS mét Na-S promotie,
- Type III** Na CO-carburisatie of Fe oxide (α -Fe₂O₃), het subtype is stabiel in FTS óngeacht de Na-S promotie,

η -Fe₂C

- Type I** Na CO-carburisatie, of FTS zónder Na-S promotie,
- Type II** Na FTS mét Na-S promotie,
- Type III** Na martensiet vermenging bij 120°C . *Niet geobserveerd in FTS.*

Figuur 8.4

Overzicht van Na-S-promotie-afhankelijke Fe-carbide-fasestabiliteit, zoals vergeleken vóór (Carb.) en na 72 uur Fischer-Tropsch synthese (FTS)-reactie. Rietveld kwantitatieve fase-analyse (R-QPA) gebaseerde Fe-fase fracties voor a) niet-gepromote (unpromoted, UP) en b) Na-S-gepromoot (Na-S) $\text{Fe}(-\text{Na-S})/\alpha\text{-Al}_2\text{O}_3$ katalysatormaterialen. Na-S-promotie **A** stabiliseert $\eta\text{-Fe}_2\text{C}$, **B** destabiliseert $\theta\text{-Fe}_3\text{C}$ en **C** heeft geen effect op de stabiliteit van de $\theta\text{-Fe}_7\text{C}_3$ -fase in de FTS-reactie. FTS-omstandigheden: 340°C , 10 bar, $\text{H}_2\text{:CO:He}$ 2.0:1.0:0.33 v/v, $\approx 5\,000\text{ h}^{-1}$.

Het meest interessante is dat de kenmerkend vervormde $\chi\text{-Fe}_5\text{C}_2$ -fase (d.w.z., Type III) onveranderd bleef in de FTS-reactie. Er konden geen Fe-carbide-subtypen worden toegewezen voor de $\theta\text{-Fe}_3\text{C}$ - of $\theta\text{-Fe}_7\text{C}_3$ -fasen.

De toevoeging van de Na-S-promotie had invloed op de Fe-carbiden in de FTS-reactie door i) het veroorzaakte anisotropische veranderingen met een maximum van $\approx 0,02\text{ \AA}$ in de kristalroosterparameters voor de $\eta\text{-Fe}_2\text{C}$ - en $\chi\text{-Fe}_5\text{C}_2$ -fasen (d.w.z., subtypen Type II), ii) de $\eta\text{-Fe}_2\text{C}$ -fase was *gestabiliseerd*, terwijl iii) de $\theta\text{-Fe}_3\text{C}$ -fase was *gedestabiliseerd*, in vergelijking met de respectievelijke fasen in de niet-gepromote katalysatormaterialen. De stabiliteit van de $\theta\text{-Fe}_7\text{C}_3$ -fase in de FTS-reactie werd niet beïnvloed door de Na-S-promotie (**Figuur 8.4**).

Met betrekking tot de FTS-reactieprestaties van de katalysator had de Na-S-promotie de algemene effecten van i) verhoogde CO-omzetting, ii) $\approx +10\%$ verhoogde $\text{C}_2\text{-C}_4$ -selectiviteit met aanzienlijk onderdrukte CH_4 -selectiviteit onder de ASF-

verwachtingen, iii) toegenomen alkeengehalte en iv) verhoogde α -waarde in vergelijking met de respectieve niet-gepromote katalysatormaterialen. Als nadelige FTS-reactie-effecten nam met de Na-S-promotie i) de CO_2 -selectiviteit significant toe van $\leq 16\%$ tot $\approx 38-43\%$ en ii) de hoeveelheid CO geconverteerd tot FTS-reactie-koolwaterstoffen daalde tot $\approx 0,42-0,47$ in relatie tot de niet-gepromote katalysatormaterialen.

Verder namen de gebruiksratio's $\text{H}_2:\text{CO}$ af van $\approx 1.8-2.3$ tot $\approx 0.7-0.8$ met de toegevoegde Na-S-promotie. Dit is een indicatie van CO_2 -vrijmakende, Boudouard-en/of Water-Gas Shift-reacties (WGS-reacties) die de ingevoerde CO verbruiken. Omdat er na de FTS-reactie in geen enkel van de katalysatormaterialen WGS-reactie-actieve Fe_3O_4 aanwezig was, werd de Na(-S)-promotie besproken om de direct actieve reactieplaatsen voor de mogelijke WGS-reactie te verschaffen.

Desalniettemin, ondanks de verloren C-route was er selectiviteit naar CO-omzetting in koolwaterstoffen: ≈ 4.4 keer meer koolwaterstoffen werden nog steeds omgezet van CO per tijdseenheid met de meest actieve Na-S gepromote katalysator in vergelijking met het meest actieve niet-gepromote katalysatormateriaal.

Toen de resultaten van de FTS-reactieactiviteit werden gecontrasteerd met de R-QPA-kwantificeringsresultaten, kon geen directe correlatie tussen de FTS-reactieactiviteit en een van de bulk Fe-carbidefasen worden gemaakt. Dat wil zeggen dat geen enkele Fe-carbide in de FTS-reactie actiever was dan elk andere bestudeerde Fe-carbide. In termen van selectiviteit van koolwaterstofproducten konden echter enkele voorzichtige correlaties worden toegewezen. Er werd waargenomen dat i) de $\theta\text{-Fe}_3\text{C}$ -fase ($\approx +5\%$) het paraffine-gehalte van het koolwaterstofproducttablet enigszins verhoogde. In combinatie met de Na-S-promotie: ii) de $\eta\text{-Fe}_2\text{C}$ Type II en $\chi\text{-Fe}_5\text{C}_2$ Type II waren aanwezig in de hoge alkeen- en lage CH_4 -selectieve FTS-katalysatormaterialen en iii) het $\chi\text{-Fe}_5\text{C}_2$ Type III zou, meer dan de $\chi\text{-Fe}_5\text{C}_2$ Type II, de alkeenselectiviteit kunnen verhogen wanneer het gecombineerd wordt met de Na-S-promotie.

Over de rol van de $\theta\text{-Fe}_7\text{C}_3$ -fase in de FTS-reactie konden geen conclusies getrokken worden, omdat de fase aanwezig was in te kleine fasehoeveelheden in de bestudeerde FTS-reactiekatalysatormaterialen.

Hoofdstuk 5 - De gecombineerde effecten van de totale FTS-reactiedruk, Na-S-promotie en de H_2 -reductie van de katalysator voorafgaand aan de FTS-reactie werden bestudeerd. Het hoofddoel was voornamelijk om de effecten van de bovengenoemde parameters op de Fe-carbiden en hun subtypevorming te volgen en deze informatie te correleren met de FTS-reactieprestaties van de katalysatormaterialen. Hiervoor werden ondersteunde Fe(-Na-S)/ $\alpha\text{-Al}_2\text{O}_3$ katalysatormaterialen, met en zonder Na-S-promotie, voor het onderzoek bereid. De katalysatoren werden ofwel alleen gecalcineerd of na calcinatie ook gereduceerd in H_2 , voorafgaand aan de prestatietesten

voor de katalysatoren in de FTS-reactie. De FTS-reacties werden afzonderlijk gedurende 72 uur uitgevoerd bij een totale reactiedruk van 3, 10 of 20 bar (340°C, H₂:CO:He 1.0:1.0:0.2 v/v, GHSV $\approx$ 5 500 h⁻¹). XRPD-patronen werden ex-situ verzameld voor elk van de bestudeerde katalysatormaterialen nadat de FTS-reactie werd uitgevoerd en werden gekwantificeerd met behulp van R-QPA.

Na de FTS-reacties waren de Fe-carbidefasen, die in de katalysatormaterialen werden geïdentificeerd, η -Fe₂C *Pnnm* (58), χ -Fe₅C₂ *C2/c* (15) en/of θ -Fe₇C₃ *Pnma* (62). Voor alle bestudeerde katalysatormaterialen werd de χ -Fe₅C₂-fase als de meest voorkomende gekwantificeerd. De Na-S-promotie had de volgende FTS-reactiedruk-afhankelijke effecten op de Fe-carbidevorming: i) het induceren van het verschijnen van de η -Fe₂C-fase bij ≥ 10 bar FTS-reactiedruk, terwijl de katalysatormaterialen die alleen gecalcineerd waren de η -Fe₂C-fasevorming meer begunstigden dan de H₂-gereduceerde katalysator, en ii) de vorming van minieme hoeveelheden van de θ -Fe₇C₃-fase na de FTS-reactie onder 20 bar in de katalysator die alleen gecalcineerd was.

Met betrekking tot de FTS-reactiedruk en de toegevoegde Na-S-promotie, vormen de carbide-subtypen zich als volgt:

χ -Fe₅C₂

Type I Zónder Na-S-promotie óngeacht reactiedruk of met 3 bar FTS-reactiedruk óngeacht Na-S-promotie,

Type II Mét Na-S-promotie en ≥ 10 bar FTS-reactiedruk,

Type III Fe-oxide (α -Fe₂O₃) d.w.z. alleen gecalcineerde katalysator als startmateriaal voor de FTS óngeacht de Na-S-promotie of de FTS-reactiedruk,

η -Fe₂C

Type II Mét Na-S-promotie en ≥ 10 bar FTS-reactiedruk.

De prestatieafhankelijkheid van de katalysator van de FTS-reactie op de reactiedruk werd voornamelijk veranderd door de Na-S-promotie. Het alleen calcineren van de katalysator en ook reduceren in H₂ hadden een kleinere invloed op de katalytische prestatie van het katalysatormateriaal.

De Na-S-promotie in combinatie met een FTS-reactiedrukdrempel van 10 bar had als effecten dat i) de katalysatoren een significante toename in de Fe-tijdsopbrengsten (FTY) vertoonden en ii) de gebruiksverhouding H₂:CO, CO omgezet in koolwaterstoffen en koolwaterstof selectiviteiten reactiedruk-onafhankelijk werden en iii) de CO₂-selectiviteit aanzienlijk verhoogd werd. Deze veranderingen in de FTS-reactieprestatie correleerden met Na-S-geïnduceerde overgang van χ -Fe₅C₂ Type I naar Type II, en met de aanwezigheid van χ -Fe₅C₂ Type III met Na-S-promotie. Voor niet-gepromote

Figuur 8.5

Belangrijkste observaties van de effecten van Fischer-Tropsch synthese (FTS)-reactiedruk, Na-S-promotie en katalysator H₂-pre-reductie op niet-gepromote (UP) en Na-S-gepromote (Na-S) Fe(-Na-S)/α-Al₂O₃ - katalysatormaterialen in een 72 uur durende FTS-reactie (3, 10, 20 bar). De katalysatormaterialen werden direct na calcineren (Calcin.) aan de FTS-reactie blootgesteld of werden in H₂ gereduceerd voorafgaand aan de reactie (H₂). De FTS-reactieactiviteit van de katalysatormaterialen als a) Fe-tijdsopbrengsten (FTY's) tonen een drempel van 10 bar voor Na-S en een drempel van 20 bar voor UP-katalysatormaterialen voor versterkte FTY. De FTY-verhoging b) correleert met de Fe-carbide-subtypen (I, II, III) met de overgang van χ-Fe₅C₂ Type I naar II en de aanwezigheid van χ-Fe₅C₂ Type III met Na-S-promotie. Bij een FTS-reactiedruk van 10 bar c) de C₂H₄/C₂H₆-verhouding wordt verhoogd met de Calcin. katalysatoren, ongeacht de Na-S-promotie. Dit komt overeen met de aanwezigheid van χ-Fe₅C₂ Type III. *FTS-omstandigheden*: 340°C, 3, 10 or 20 bar, H₂:CO:He 1.0:1.0:0.2 v/v, ≈5 500 h⁻¹.

katalysatoren was een reactiedrukdrempel van 20 bar FTS vereist voor het bereiken van vergelijkbare FTS-reactie-katalyse-effecten, zoals is waargenomen met de Na-S-gepromote katalysatormaterialen met ≥10 bar reactiedruk. Voor deze veranderingen in de niet-gepromote katalysatoren waren χ-Fe₅C₂ Type I en niet-gepromote Type III aanwezig als de χ-Fe₅C₂-fase-subtypen.

Met een reactiedruk van 3 bar vertoonde geen van de bestudeerde katalysatormaterialen significante FTY's ongeacht de Na-S-promotie. De aanwezigheid van η-Fe₂C Type II correleerde niet met de katalytische prestatie-indicatoren - activiteit of selectiviteit - van de FTS-reacties, zoals werd afgeleid van de door R-QPA

gekwantificeerde Fe-fasefracties.

Wanneer alleen gecalcineerde katalysatormaterialen gebruikt werden in de FTS-reactie, ongeacht de Na-S-promotie: i) werd de C_2H_4/C_2H_6 -verhouding verhoogd met 10 bar FTS reactiedruk en ii) werden de totale FTY's verlaagd bij 20 bar reactiedruk in vergelijking met de H_2 gereduceerde katalysatoren. De verhoogde C_2H_4/C_2H_6 -verhouding wordt geassocieerd met de aanwezigheid van $\chi\text{-Fe}_5C_2$ Type III, onafhankelijk van de Na-S-promotie, bij een reactiedruk van 10 bar. Dat wil zeggen, $\chi\text{-Fe}_5C_2$ Type III correleerde met het verminderde hydrogenatievermogen van katalysatormaterialen. Verminderde FTY's op hun beurt correleerden met de aanwezigheid van Fe_3O_4 in de alleen gecalcineerde, 20 bar FTS-katalysatoren. Het Fe_3O_4 is waarschijnlijk afkomstig van door koolstofdepositie geïnduceerde stoftransportbeperkingen die de reductie remmen van de initiële $\alpha\text{-Fe}_2O_3$ ($/\alpha\text{-Al}_2O_3$)-fase door $H_2:CO$ gedurende de FTS-reactie. Het overzicht van de besproken effecten van de FTS-reactieresultaten wordt gegeven in **Figuur 8.5**.

Hoofdstuk 6 - In dit hoofdstuk was het voornaamste doel om het effect van de Na-S-promotie op de gelijktijdige Fe-carbide faseveranderingen en koolstofdepositie tijdens de FTS-reactie, d.w.z. met in-situ karakteriseringsmethoden, te bestuderen. Hiertoe werd een gecombineerde XRPD/Raman-spectroscopie-opstelling gebruikt. De ondersteunde Fe(-Na-S)/ $\alpha\text{-Al}_2O_3$ -katalysatormaterialen bereid in **Hoofdstuk 3** met voorgevormde Fe-carbiden of alleen met H_2 gereduceerde katalysatoren, met of zonder Na-S-promotie, werden gebruikt. De katalysatoren werden in situ gekarakteriseerd met de XRPD/Raman-spectroscopie benadering tijdens een FTS-reactie van 72 uur ($340^\circ C$, 10 bar $H_2:CO:He$ 2.0:1.0:0.33 v/v, GHSV $\approx 7\,200\,h^{-1}$). De in-situ verzamelde XRPD patronen werden gekwantificeerd met behulp van R-QPA. De Raman-spectra werden beoordeeld op de koolstofsoorten door het volgen van de intensiteit van de D- ($\approx 1\,350\,cm^{-1}$) en G- ($\approx 1\,600\,cm^{-1}$) Raman-banden. Een overzicht van de belangrijkste resultaten wordt gegeven in **Figuur 8.6**.

De Na-S-promotie veranderde de eigenschappen van Fe-oxide en carbidefasen door:

- i) de $\eta\text{-Fe}_2C$ -fase te *stabiliseren*, maar alléén als $\varepsilon\text{-Fe}_3C$ en/of $\eta\text{-Fe}_2C$ in de initiële katalysator aanwezig was,
- ii) *destabilisatie* van de $\theta\text{-Fe}_3C$ -fase en het helpen ervan bij de overgang naar $\chi\text{-Fe}_5C_2$,
- iii) verhoging van de reduceerbaarheid van Fe_3O_4 -fase door $(H_2):CO$,
- iv) verlaging van het Fe_3O_4 -gehalte tijdens de FTS-reactie op de katalysatoren; en ook door
- v) het induceren van Fe-kristallietgroei voor de Fe-carbiden binnen de ≤ 15 uur tijd-op-stroom (ToS). De $\theta\text{-Fe}_3C$ -fase was hierop een uitzondering, aangezien

Figuur 8.6

Een samenvatting van simultane in-situ Röntgenpoederdiffractometrie (XRPD)/Raman-spectroscopieresultaten tijdens Fischer-Tropsch synthese (FTS)-reactie op niet-gepromote (UP) en Na-S-gepromote (Na-S) Fe-(Na-S)/ α -Al₂O₃-katalysatormaterialen zonder initiële koolstofafzettingen. Raman-spectra D- en G-band intensiteiten a) groeien aanvankelijk snel binnen tijd-op-stroom (ToS) ≤ 15 uur en ≥ 15 uur ToS-band intensiteitsgroei blijft sneller met de Na-S-katalysatoren. Op Rietveld kwantitatieve fase-analyse (R-QPA) gebaseerde Fe-fasefracties veranderen b) aangezien de χ -Fe₅C₂-fase bij voorkeur wordt gevormd tijdens de FTS-reactie bij 340°C, maar de Na-S-promotie stabiliseert de η -Fe₂C-fase significant. Indien aanwezig, destabiliseert Na-S-promotie de θ -Fe₃C- en Fe₃O₄-fasen. De gevormde koolstofsoorten c) lijken erg op een koolstof nanofiber (CNF) referentiekoolstofmateriaal bij ToS 70 uur, voor zowel UP- als Na-S-katalysatoren. FTS-omstandigheden: 340°C, 10 bar, H₂:CO:He 2.0:1.0:0.33 v/v, ≈ 7 200 h⁻¹.

voor de fase de kristallietdiameters afnamen met Na-S-promotie.

De koolstofafzetting op de katalysatormaterialen correleerde met geen enkele Fe-carbidefase of carbide-naar-carbide-overgang. Met H₂-gereduceerde katalysatoren startte de koolstofdepositie pas als de Fe₃O₄-fase, een fase die niet in staat is om CO-dissociatie uit te voeren, was gereduceerd.

Bij katalysatormaterialen met verwaarloosbare initiële koolstofafzettingen, d.w.z. met H₂-gereduceerde of $< 300^\circ\text{C}$ CO-gecarburiseerde katalysatoren, kon de intensiteitsgroei van de D- en G-banden in de Raman-spectra tijdens de FTS-reactie worden opgeknipt in twee perioden: i) een initiële snelle (≤ 10 -15 uur ToS), en ii) een

gestage of kleinere (≥ 15 uur ToS) intensiteitsgroeiperiode. De initiële snelle groeiperiode was aanwezig ongeacht de Na-S-promotie. Maar na het bereiken van de gestage groeiperiode wekte Na-S-promotie een hogere mate van groei op van de D- en G-bandintensiteit (voor de G-band $< 2,7 \pm 0,2$ sneller) in vergelijking met de niet-gepromote katalysatormaterialen. Voor katalysatoren met initiële koolstofafzettingen van CO-carburatie $\geq 340^\circ\text{C}$ was de initiële snelle groeiperiode afwezig, ongeacht de Na-S-promotie. Een mogelijke verklaring voor de initiële snelle D- en G-band intensiteitswinst binnen ≤ 10 -15 uur ToS voor de katalysatormaterialen zonder initiële koolstofafzettingen, zou een eerste niet-isotherme bedoperatie zijn.

De koolstofsoorten die gevormd zijn tijdens katalysatorbereiding-CO-carburaties waren licht Raman-actief met de gebruikte (532 nm) zichtbare golflengte laser. Met andere woorden, ze waren hoofdzakelijk gemaakt van koolstofstructuren met C sp^3 met een bandafstand boven de energie die beschikbaar is van de zichtbare golflengte-laser. Onder $\text{H}_2\text{:CO}$ tijdens de FTS-reactie vormden meer geordende CNF-achtige fasen met C sp^2 , wat leidde tot verhoogde Raman-signaalintensiteit. Tijdens de FTS-reacties evolueerden de koolstofsoorten van amorf koolstofsoorten, met structuren die zowel tetrahedrische C sp^3 als C sp^2 in ketenachtige ordening bevatten, naar meer geordende koolstofmaterialen met structuren die C sp^2 bevatten in variërende niet-zesvoudige cyclische volgorde met kenmerkende afmetingen < 7 nm in diameter.

In vergelijking met de gemeten koolstofreferentiematerialen waren de Raman-spectra van de katalysator bij ≈ 70 uur ToS het best te vergelijken met deze van een koolstof nanovezel (CNF) referentiemateriaal. De katalysatormaterialen bevatten echter mogelijk een hogere hoeveelheid C sp^2 in ketenachtige structuren (G-band blauwe verschuiving naar hogere cm^{-1}) en een grotere verscheidenheid aan niet-zesvoudige koolstofringen (bredere D-bandpiek) dan in het referentie CNF-materiaal (**Figuur 8.6c**).

Na-S-promotie beïnvloedde de door FTS-reactie gevormde koolstofsoorten door: i) het aanvankelijke C sp^2 -gehalte in ketenachtige koolstofstructuren te verhogen, en ii) het verhogen van zesvoudige cyclische koolstofsoorten voor katalysatormaterialen met de initiële CO-carburatie temperatuur $\geq 340^\circ\text{C}$.

8.2 TOEKOMSTPERSPECTIEVEN

Zoals bij elk onderzoek het geval is ontstaan nieuwe wetenschappelijke vragen in hetzelfde tempo als dat de oude worden beantwoord. Enkele van de meest interessante toekomstige onderzoeksthema's, die voortkomen uit het werk van dit proefschrift, worden hierna kort besproken.

Vergelijking van $\epsilon\text{-Fe}_3\text{C}$ en $\eta\text{-Fe}_2\text{C}$ tot $\epsilon\text{-Fe}_3\text{N}$ en $\zeta\text{-Fe}_2\text{N}$. Zoals kort in **Hoofdstuk 3**

werd benadrukt, zijn de kristalstructuren van Fe-carbide ε -Fe₃C en η -Fe₂C-fasen nauw verwant aan respectievelijk de structuren ε -Fe₃N en ζ -Fe₂N Fe-nitriden. Een vergelijkend onderzoek naar het gedrag en de FTS-reactieprestaties van ε -Fe₃C en η -Fe₂C in vergelijking met de Fe₃N- en ζ -Fe₂N-fasen, met en zonder de Na-S-promotie, zou een interessant onderzoek opleveren.

In het bijzonder zou het waardevol zijn om uit te vinden of de ζ -Fe₂N-fase kan worden gestabiliseerd in de FTS-reactie met Na-S-promotie op dezelfde manier als werd waargenomen voor de η -Fe₂C-fase. De Fe-nitridefasen zijn gewoonlijk niet stabiel onder carburiserende omstandigheden maar worden eerder omgezet in Fe-carbonitriden.¹⁻³ Er is waargenomen dat op Fe-nitride gebaseerde katalysatormaterialen selectief zijn richting alkeenproductie in de FTS-reactie.³

Vorming van de θ -Fe₇C₃-fase. Hoewel enkele kleine hoeveelheden van de θ -Fe₇C₃-fase werden gevormd in het onderzoek van deze dissertatie, is er nog meer inspanning nodig om het vormingsgedrag van de fase te bestuderen onder de FTS-reactie-relevante omstandigheden. Zoals in **Hoofdstuk 3** werd gespeculeerd, kan de vorming van de θ -Fe₇C₃-fase onder carburiserende omstandigheden afhankelijk zijn van de aanwezigheid van CO₂ tijdens het carburisatieproces. Een systematisch onderzoek naar het effect van carburiserende CO₂:CO-gasmengsels op de θ -Fe₇C₃-fase-vorming van op Fe-gebaseerde materialen zou in de toekomst moeten worden uitgevoerd. Dit zou helpen bij het bepalen van de rol van de FTS-reactie en de eigenschappen van dit nog steeds veel te weinig bestudeerde Fe-carbide.

Kristalstructuren van Fe Carbide Subtypen. De η -Fe₂C- en de χ -Fe₅C₂-fasen werden onderverdeeld in verschillende subtypen naar hun kenmerkend verschillende roosterparameter a 's in **Hoofdstuk 4**. Echter, de precieze kristalstructuuroorsprong van de roosterwijzigingen voor de uiteindelijke carbide-subtypen kon niet worden achterhaald binnen de reikwijdte van deze dissertatie. In de toekomst moet meer gedetailleerd onderzoek gedaan worden naar de fundamentele verschillen in kristalstructuur in de Fe-carbide-subtypen met behulp van een monochromatische röntgenbron. Daarnaast kan neutronenpoederdiffractie (NPD) ingezet worden om te achterhalen of de door Na-S-promotie geïnduceerde subtype-formaties echt het gevolg zijn van de Na(-S)-promotoren die de Fe-carbideroosters binnenkomen of van iets anders.

Verder werd in **Hoofdstuk 5** de associatie gemaakt van het χ -Fe₅C₂ Type III met katalysatormaterialen met verminderd hydrogeneringsvermogen in de FTS-reactie. Dat wil zeggen dat het χ -Fe₅C₂ Type III de FTS-koolwaterstofselectiviteit van het katalysatormateriaal naar de productie van alkenen verhoogde. De aanwezigheid van χ -Fe₅C₂ Type III zou ook de vergelijkbare selectiviteitsresultaten in de literatuur kunnen verklaren.^{4,5} In het hoofdstuk wordt dit effect niet voorzien van fundamenteel

inzicht. Hoe en waarom het χ -Fe₅C₂ Type III de alkeenvorming ten goede komt in vergelijking met de andere Fe-carbidesubtypen, zou een interessant onderzoek opleveren. Hierbij zou dan gebruik kunnen gemaakt worden van de dichtheid functionele theorie (DFT) berekeningenbenadering.

8.3 REFERENTIES

- [1] Jack, K. H., "Binary and Ternary Interstitial Alloys III. The Iron-Carbon System: The Characterization of a New Iron Carbide", *Proc. R. Soc. A Math. Phys. Eng. Sci.* **195**, 56–61 (1948).
- [2] Jack, K. H., "Binary and Ternary Interstitial Alloys. II. The Iron-Carbon-Nitrogen System", *Proc. R. Soc. A Math. Phys. Eng. Sci.* **195**, 41–55 (1948).
- [3] Butt, J. B., "Carbide phases on iron-based Fischer-Tropsch synthesis catalysts part II: Some reaction studies", *Catal. Lett.* **7**, 83–106 (1990).
- [4] Bukur, D. B., Nowicki, L., Manne, R. K. and Lang, X. S., "Activation Studies with a Precipitated Iron Catalyst for Fischer-Tropsch Synthesis II. Reaction Studies", *J. Catal.* **155**, 366–375 (1995).
- [5] Wezendonk, T. A., Sun, X., Dugulan, A. I., van Hoof, A. J. F., Hensen, E. J. M., Kapteijn, F. and Gascon, J., "Controlled formation of iron carbides and their performance in Fischer-Tropsch synthesis", *J. Catal.* **362**, 106–117 (2018).

List of Abbreviations

AC	Activated Carbon	FWHM	Full Width at Half Maximum
ALSS	Asymmetric Least Squares Smoothing	GC	Gas Chromatography
ASF	Anderson-Schulz-Flory	GHSV	Gas Hourly Space Velocity
BASF	Badische Anilin & Soda Fabrik	GTL	Gas-to-Liquids
BTL	Biomass-to-Liquids	HC	Hydrocarbons
CNF	Carbon Nanofiber	HTFT	High-temperature Fischer-Tropsch
CNT	Carbon Nanotube	ICDD-PDF	International Centre for Diffraction Data Powder Diffraction File
COD	Crystallography Open Database	ICP-OES	Inductively Coupled Plasma - Optical Emission Spectrophotometry
CPS	Counts per Second	IR	Infrared
CTL	Coal-to-Liquids	IWI	Incipient Wetness Impregnation
DFT	Density Functional Theory	JM	Johnson Matthey
ED	Electron Diffraction	LTFT	Low-temperature Fischer-Tropsch
ETEM	Environmental TEM	MAS	Mössbauer Absorption Spectroscopy
FEG	Field Emission Gun	MOF	Metal Organic Framework
FID	Flame Ionization Detector	MTH	Methanol-to-Hydrocarbons
FPA	Fundamental Parameters Approach	MTO	Methanol-to-Olefins
FTP	Fischer-Tropsch Process		
FTS	Fischer-Tropsch Synthesis		
FTY	Fe Time Yield		

List of Abbreviations

NBS-SRM	National Bureau of Standards - Standard Reference Material	STD	Standard Deviation
NNPC	Nigerian National Petroleum Corporation	TCD	Thermal Conductivity Detector
NPD	Neutron Powder Diffraction	TEM	Transmission Electron Microscopy
NWO	Nederlandse Organisatie voor Wetenschappelijk Onderzoek	TGA	Thermogravimetric Analysis
OX-ZEO	Oxide-Zeolite	TGA-MS	Thermogravimetric Analysis - Mass Spectrometry
PetroSA	South African national oil company	TM	Thermomagnetic
PSD	Position Sensitive Detector	ToS	Time-on-Stream
QP	Qatar Petroleum	TU Delft	Technische Universiteit Delft
R-QPA	Rietveld Quantitative Phase Analysis	UU	Universiteit Utrecht
R_{wp}	R-Weighted Pattern	WGS	Water-gas Shift
Sasol	Suid Afrikaanse Steenkool en Olie	Wt-%	Weight percent
SMR	Steam Methane Reforming	WTL	Waste-to-Liquids
SPM	Superparamagnetic	XRF	X-ray Fluorescence
		XRPD	X-ray Powder Diffractometry
		XTL	Anything-to-Liquids

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List of Publications and Presentations

PUBLICATIONS

- 2020 Paalanen, P. P. and Weckhuysen B. M., "*Carbon Pathways, Sodium-Sulfur Promotion and Identification of Iron Carbides in Iron-based Fischer-Tropsch Synthesis*", *ChemCatChem*, accepted article (2020).
- 2019 Xie, J., Paalanen, P. P., van Deelen, T. W., Weckhuysen, B. M., Louwerse, M. J. and de Jong, K. P., "*Promoted cobalt metal catalysts suitable for the production of lower olefins from natural gas*", *Nat. Commun.* **10**, 167 (2019).
- 2018 Falkenhagen, J. P., Maisonneuve, L., Paalanen, P. P., Coste, N., Malicki, N. and Weckhuysen, B. M., "Cobalt-Iron-Manganese Catalysts for the Conversion of End-of-Life-Tire-Derived Syngas into Light Terminal Olefins", *Chem. - A Eur. J.* **24**, 4597–4606 (2018).
- 2017 Marquez, C., Rivera-Torrente, M., Paalanen, P. P., Weckhuysen, B. M., Cirujano, F. G., de Vos, D. and de Baerdemaeker, T., "*Increasing the availability of active sites in Zn-Co double metal cyanides by dispersion onto a SiO₂ support*", *J. Catal.* **354**, 92–99 (2017).
- 2016 Kalirai, S., Paalanen, P. P., Wang, J., Meirer, F. and Weckhuysen, B. M., "Visualizing Dealumination of a Single Zeolite Domain in a Real-Life Catalytic Cracking Particle", *Angew. Chemie Int. Ed.* **55**, 11134–11138 (2016).
- Whiting, G. T., Chowdhury, A. D., Oord, R., Paalanen, P. P. and Weckhuysen, B. M., "The curious case of zeolite-clay/binder interactions and their consequences for catalyst preparation", *Faraday Discuss.* **188**, 369–386 (2016).
- 2014 Lezcano-Gonzalez, I., Deka, U., van der Bij, H. E., Paalanen, P. P., Arstad, B., Weckhuysen, B. M. and Beale, A. M., "*Chemical deactivation of Cu-*

*SSZ-13 ammonia selective catalytic reduction (NH₃-SCR) systems", *Appl. Catal. B Environ.* **154-155**, 339-349 (2014).*

- 2013 Paalanen, P. P., Weckhuysen, B. M. and Sankar, M., "Progress in controlling the size, composition and nanostructure of supported gold-palladium nanoparticles for catalytic applications", *Catal. Sci. Technol.* **3**, 2869 (2013).

PRESENTATIONS

- 2017 *Poster Presentation* - Paalanen, P. P., Bertram M., Velthoen, E. Z. M., Meirer, F. and Weckhuysen, B. M., "Pyridine-IR Spectroscopy Investigation on Na, S and Na-S Promotion Effect on a Fe/ α -Al₂O₃ Catalyst for FTO", The Netherlands Catalysis and Chemistry Conference XVIII, Noordwijkerhout, the Netherlands, March 2017.

Poster Presentation - Paalanen, P. P., Xie, J., de Jong, K. P., Meirer, F., and Weckhuysen, B. M., "Na-S Promoter Effect on the Formation of Fe Carbides in the Fischer-Tropsch-to-Olefins Reaction", 25th North American Meeting (NAM25) of the Catalysis Society, Denver, Colorado, United States of America, June 2017.

Curriculum Vitae

Pasi P. Paalanen was born in Otava, Mikkeli in Finland on February 27th 1985. Following the completion of the sports oriented high school in 2004, he moved on to complete his obligatory military service as well as to spent time working, and also travelling in Europe.

In 2007 he continued pursuing higher education, and began university studies in University of Jyväskylä in Finland. This included a year spent in an Erasmus student exchange program at the Warsaw University of Technology in Poland. He graduated in 2011 with a Bachelor's degree in physical chemistry, with minors in physics and mathematics.

Following this, further continuing with higher education, he then moved to Utrecht, the Netherlands in 2011 and began studies in the Nanomaterials: Chemistry and Physics Master's program at Utrecht University. After finishing the Master's degree in 2013, he embarked with his scientific career towards a PhD in Utrecht University in the Inorganic Catalysis and Chemistry group under de supervision of Professor Bert Weckhuysen. This endeavor has led to the work described in this PhD Dissertation.

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