GENERAL INTRODUCTION
Catalysis

A catalyst can be described as a substance that increases the rate of a reaction without being consumed itself and that often permits reactions to take place more effectively or under milder conditions. Catalysis, although probably not recognized as such, has been used for thousands of years in the production of wine [1]. Compared to that, industrial production of chemicals using catalysts started rather late, just a few hundred years ago [2]. The concept of ‘catalysis’ was discovered in 1835 and the operation of a catalytic force in chemical reactions was mentioned for the first time [3]. Since that time both the scientific insight in the functioning of catalysts and their industrial use has grown tremendously. Nowadays catalysts have a large impact on society, as they are used for the efficient and clean production of many valuable consumer products.

The catalysts studied most often are heterogeneous catalysts in which catalyst and reactants/products are in a different phase. These catalysts generally consist of very small particles of an active phase, e.g. a metal oxide, deposited on oxidic support materials. The main role of the support is the anchoring of the catalytically active particles and thus the prevention of sintering during activation and operation. Generally, small amounts of promoting elements are added to enhance activity, selectivity or stability. In the Fischer-Tropsch synthesis supported cobalt, iron or ruthenium catalysts are used, promoted with a range of other elements.

History of the Fischer-Tropsch synthesis

The Fischer-Tropsch (FT) process is named after Franz Fischer and Hans Tropsch (figure 1) who discovered in 1923 that synthesis gas (CO/H₂) can be converted over a catalyst into hydrocarbons and water [4-6]. Using the FT process liquid transportation

![Figure 1. Franz Fischer (left) and Hans Tropsch (right).](image)
fuels of superior quality can be produced from other carbon sources than crude oil. This was of strategic importance for Germany before World War II as the country had virtually no oil supply, but availed of abundant coal reserves and wanted to be energy independent. Together with the coal hydrogenation process of Bergius, the FT synthesis could be used to ensure a supply of liquid fuels [7-9]. Already in 1935 Ruhrrchemie started the commercial application of the FT process and constructed the first out of nine plants. The maximum production of the fuels peaked in 1944 at 4.1 million barrels per year [7]. The FT plants were operated at atmospheric or at medium pressure (5-15 bar) and a cobalt catalyst was used. In the standard catalyst the mineral Kieselguhr (mainly SiO₂) was used as support material which was loaded with 31 wt% cobalt [8]. The addition of thoria (1.6 wt%) and magnesia (2.6 wt%) was found to be crucial to shift the product distribution towards the desired heavier hydrocarbons and to protect the catalyst against impurities [8]. After World War II the production of synthetic fuels was no longer economically viable and all plants were dismantled [9].

Although the German plants ceased to operate in 1945, interest in the FT process continued as reserves of crude oil were thought at that time to be rather limited [10,11]. However, after the discovery of the huge oil fields in the Middle East around 1955, the oil price sharply decreased and most research activities were abandoned. Only in South Africa scientific and industrial interest remained. In that country with large reserves of very cheap coal, the government wanted to become energy independent — as was the case in pre-war Germany — and stimulated the development of an own FT industry. The Sasol Company constructed several large FT plants from 1955 onwards and is currently the largest player in the synthetic fuel industry. In the seventies of the last century the oil embargo by major oil producing countries and the forecasts about fading oil reserves renewed global interest in the FT process. Oil companies like Shell, ExxonMobil, Gulf/Chevron and Statoil started research programs and all have now their own position defended with a patents portfolio [12].

Prospects of the Fischer-Tropsch synthesis

The current interest in the FT synthesis is driven by several factors: environmental demands, changes in fossil energy reserves, geopolitical reasons and the high oil prices. The environmental constraints are present at the site of oil recovery where the flaring of associated natural gas has to be reduced as much as possible [11]. Using the FT synthesis this natural gas can be converted into liquid fuels that don’t contain any sulfur or nitrogen (Gas-to-Liquids, GtL). These ultra clean FT fuels can be blended in traditional fuels to
help it meet strict fuel specifications. Changes in the estimation of fossil energy reserves are the second driver for interest in the FT synthesis. The currently known reserves of natural gas outnumber that of crude oil, but are often located too far from the markets. The conversion of gas to liquids enables their transport and adds economical value. Also geopolitical aspects are important for the current interest in the FT reaction. Using the FT process transportation fuels can be obtained from other carbon sources than crude oil, like coal (GtL) and also biomass (BtL) thus lowering the dependency on the oil exporting countries. The last driver for current interest in the FT synthesis is the oil price at values above 20$/barrel, which makes the production of synthetic fuels economically viable.

Nowadays, Sasol and Shell commercially operate the Fischer-Tropsch process with a combined production of 0.2 million barrels per day [11]. Although this seems to be a lot, it is rather a small amount compared to the plans announced by Shell, Sasol, ExxonMobil and ConocoPhilips to build natural gas-based FT plants in Qatar with a total capacity of 0.8 million barrels per day in 2011 [13]. Apart from these huge projects in Qatar the construction of smaller plants in Australia, China, Nigeria and other countries is considered. This shows that the Fischer-Tropsch process more than 70 years after its introduction is of growing importance.

Key parameters of FT catalysts

The FT process can be performed on cobalt, iron and ruthenium catalysts. Ruthenium catalysts are reported to be the most active ones, but due to the very limited ruthenium reserves they cannot be used on a commercial scale. FT catalysts based on iron are very cheap, but not very active, and as they can be active in the water-gas shift reaction, they are mainly attractive for coal-based FT plants. Cobalt catalysts are well known for their activity and stability and they are the catalysts of choice for natural gas based FT plants. Currently, most research is dedicated to these catalysts and also this thesis will focus on cobalt catalysts, supported on carbon nanofibers.

In the FT reaction CO and H$_2$ are converted on the cobalt surface into water and hydrocarbons. In the generally accepted mechanism both CO and H$_2$ dissociate on the surface and oxygen is removed by reaction with hydrogen to water. Subsequently, carbon becomes partially hydrogenated, which is followed by a polymerization reaction resulting in hydrocarbon chains [14]. These chains can be terminated by either hydrogen addition, forming paraffins or by hydrogen abstraction forming olefins. In this way hydrocarbons with different chain lengths result. The chain growth probability ($\alpha$) is a key parameter in FT synthesis and a value between 0.9 and 1 is desired in order to limit the formation of
light hydrocarbons. Next to the $\alpha$ value generally the weight selectivities towards methane ($C_1$) and towards products with a chain length of 5 and higher ($C_{5+}$) are mentioned. Low methane selectivity and high $C_{5+}$ selectivity are preferred in order to minimize gas recycling. Besides the catalyst selectivity, the activity of the catalyst is an important issue. Activities are generally reported as activities normalized to the weight of cobalt in the catalyst (Cobalt Time Yield, CTY) or as specific activities normalized to the number of cobalt surface atoms in the catalyst (turn-over frequency, TOF).

**Cobalt particle size effects in FT catalysis**

More than 70 years of FT research has brought tremendous improvement in catalyst activity and stability [12]. A rational strategy in the quest for even more active catalysts is to improve the cobalt dispersion by decreasing the average cobalt particle size. In this way the available cobalt surface area per unit of weight is increased and a higher cobalt time yield can be expected. Most FT catalysts have a rather low cobalt dispersion with average cobalt particle sizes of about 20 nm and consequently 95% of the cobalt atoms are not located at the surface and hence are catalytically inactive [12]. If catalysts could be prepared with an average cobalt particle size of 5 nm this would result in a four times more efficient use of cobalt. As cobalt is not a cheap metal, a 75% reduction of cobalt usage for commercial FT catalysts would significantly decrease their costs. However, although the preparation of catalysts with smaller cobalt particle sizes is possible, these catalysts are often not as active as expected from the higher surface area, as it is reported that the TOF decreases for particles smaller than ~10 nm. The phenomenon of lower TOF values for smaller particles has been referred to as the cobalt particle size effect [15].

For cobalt particles larger than 10 nm the particle size effect seems to be absent. The most conclusive studies in this range have been performed by Iglesia et al. who showed that in the range of 9-200 nm the TOF was not systematically influenced by the cobalt particle size [16-18]. The absence of the cobalt particle size effect for catalysts with particles larger than 10 nm has been confirmed by several other authors [19-21]. However, going to catalysts with even smaller particle sizes the results reported in literature are more scattered. Some groups observed lower activities for smaller cobalt particles [15,22-30], while others reported the opposite [31-34]. This confusion is mainly caused by problems to synthesize fully reduced small cobalt particles on oxidic support materials. CoO can react with these supports both during synthesis and during the reduction treatment resulting in mixed compounds like CoAl$_2$O$_4$, CoSiO$_3$ or CoTiO$_3$. These mixed compounds require far too high reduction temperatures to extract the metal,
so in this way cobalt metal is lost, resulting in catalysts with lower activity. Moreover, the formation of mixed compounds has been observed also during FT operation even further lowering the activity [35,36]. Small particles have a relative large specific surface area and are therefore more susceptible for reaction with the support, resulting in a lower degree of reduction of cobalt in the reduced catalysts. This explanation for the lower activity of small cobalt particles supported on oxidic support materials is referred to as a secondary particle size effect [33]. In contrast to this are primary particle size effects not caused by the support material but by the particle size dependent exposure of specific active cobalt sites [37].

In order to study the influence of cobalt particle size on the FT reaction without the interference of the effects caused by the support material, inert carbon supports could be beneficial. Preliminary studies report on the use of activated carbon support materials [15,31,32]. Activated carbon often contains impurities as well as micropores with limited accessibility. Therefore, we decided to fundamentally study cobalt particle size effects using the pure and well-defined carbon nanofibers (CNF) as a support material. CNF is a new graphitic support with an attractive meso- and macroporous structure and with potential in many (catalytic) applications [38,39]. In figure 2, a TEM image of a fiber is shown in which the individual graphitic planes are visible. The fibers are interwoven, see the SEM image in figure 3, resulting in strong macroscopic bodies that are easy to handle and only contain meso- and macropores between the fibers.

CNF is not only a very suitable support to study cobalt particle size effects in FT catalysis, but it also provides a way to study promotion effects without interference of the support material. Promoters that are added to enhance selectivity towards C\text{5+} products are most often metal oxides. Therefore, it can be understood that the oxidic support

\begin{figure}[h]
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\includegraphics[width=0.4\textwidth]{TEM_image.png}
\caption{TEM image of CNF.}
\end{figure}

\begin{figure}[h]
\centering
\includegraphics[width=0.4\textwidth]{SEM_image.png}
\caption{SEM image of CNF showing the open structure at the surface of a particle.}
\end{figure}
materials also increase selectivity towards longer chains, thus acting as a promoter itself [40,41]. In this way promotion effects induced by a support could mask the effect of the added promoter. Furthermore, the added promoter is stabilized on the oxidic support and is therefore at best not only present in contact with the cobalt metal, but also separately on the support surface, resulting in less pronounced promoting effects. On CNF the support does not promote the selectivity and, moreover, the inert support does not stabilize the added metal oxides, so it can be expected that promoter effects on CNF will be more pronounced as compared to studies using traditional oxidic supports.

Scope and outline of this thesis

Aim of the work described in this thesis is to investigate carbon nanofibers as support for the Fischer-Tropsch reaction both in the study of the influence of cobalt particle size on catalytic performance and in the study of promoter effects. Since use of well-defined systems is crucial, special care has been given to the preparation and characterization of the catalysts.

In chapter 2 the preparation of highly loaded cobalt catalysts on CNF and on \( \text{SiO}_2 \) using homogeneous deposition precipitation (HDP) is studied. It is shown that with the traditionally applied HDP method, which uses urea hydrolysis to achieve a slow and homogeneous pH increase, catalysts with unsatisfactory cobalt dispersions are obtained. An alternative HDP method in which ammonia evaporation is used to achieve a slow and homogeneous pH decrease is developed, which results in better-dispersed catalysts. In chapter 3 the synthesis and characterization of Co/CNF catalysts with average cobalt particle sizes varying from 2.6 to 27 nm is described. It is shown that the catalysts have quite narrow cobalt particle size distributions and are fully metallic after an \textit{in situ} reduction treatment. Using catalytic data obtained at atmospheric pressure the pronounced influence of the cobalt particle size in the FT reaction is shown for catalysts with cobalt sizes smaller than 6 nm. At industrially relevant pressure (35 bar) the cobalt particle size turned out to be even more critical for performance than at atmospheric pressure. X-ray absorption spectroscopy results show that the observed cobalt particle size effects cannot be explained by the presence of bulk or surface oxides, or by classical structure sensitivity. It is argued that lower catalytic performances activities are caused by CO-induced, non-classical structure sensitivity of cobalt particles. In chapter 4 our study on the preparation and catalytic performance of MnO promoted Co/CNF catalysts is presented. It is demonstrated that the promoter is only present associated with the cobalt phase and not separately on the support, both in the dried and in the reduced samples.
Moreover, it is proven that the addition of minor amounts of the promoter results in increased activities and selectivities in catalytic tests at 1 bar, while in experiments at 20 bar the TOF increased largely whereas the selectivity increased only slightly. In chapter 5 it is shown that the inner tubes of carbon nanofibers are opened during the activation treatment (oxidation in boiling HNO₃) and are now accessible, resulting in the deposition of metal particles inside the fibers. It is shown that the weight fraction of metal deposited in the inner tube is related to the fraction of surface area or pore volume related with this tube. Finally, in chapter 6 a summary of the results of the previous chapters is given. In this chapter also some concluding remarks and suggestions for further research are presented.

References
