Niobia-Supported Metal Catalysts for Synthesis Gas Conversion

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Niobia-Supported Metal Catalysts for Synthesis Gas Conversion

Niobia-gedragen metaalkatalysatoren voor synthesesegasconversie
(met een samenvatting in het Nederlands)

Proefschrift

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1

General Introduction

Human development is strongly intertwined with access to energy. In order to fulfil the enhancement in technology and life quality standards of a growing population, the global energy demand has been increasing^{1–3}. Particularly during the last decades, the rapid development has resulted in an unprecedented rise in energy consumption, tripling from 200 to 600 EJ/year in the last 50 years and projected to steadily increase^{3,4} (figure 1A). Consequently, to meet the current and future energy demand, affordable, accessible and sustainable sources of energy are fundamental^{5,6}.

Despite the significant growth of alternative energy sources, oil and gas are foreseen to remain crucial energy providers^{7–10} (figure 1A). Liquid fuels in particular prevail as source of energy due to their high energy density, easiness in handling and a well-established production and delivery infrastructure¹¹. These qualities are critical for various applications, but notoriously important for the transportation sector and the main consumer of liquid fuels (figure 1B). In fact, liquid fuels constitute 94% of the energy source for the transport industry and although it is projected to decrease, around 85% is predicted by 2040³. This high demand for transportation fuels has stimulated research towards efficient fuel production and a diversification of their sources, preferably towards renewable ones^{7,12,13}.

Figure 1.1 **a**, Global energy consumption and its main sources during the last five decades and a projection for the upcoming ones. **b**, Oil consumed in barrels per day (1 oil barrel ≈ 159 m³) by different sectors in recent years and an estimation for the following years, in green the sectors related to the transportation industry. Reproduced from reference 3.

Production of liquid fuels and chemicals from synthesis gas, a mixture of carbon monoxide and hydrogen to which carbon dioxide might be added, has gained ample interest due to the versatility of the process and the feasibility to generate ultra-clean fuels. On the one hand, synthesis gas can be obtained via gasification of numerous carbon-based feedstocks such as biomass, methane-rich gases, coal and even waste materials^{13–15}. This enables the decentralization of fuel production and a shift towards renewable resources. In fact, recent implementation of processes for the production of liquid fuels such as gas-to-

liquids (GTL) and coal-to-liquids (CTL), which rely on the conversion of synthesis gas, have materialized as a result of the shale gas revolution in the USA and the demand for alternative use of coal in China^{16–18}. On the other hand, the variety of possible products that can be selectively obtained from synthesis gas makes it an attractive resource for the chemical and energy industries. Synthesis gas can be directly or indirectly (e.g. via methanol) transformed to alcohols, long-chain hydrocarbons, olefins and aromatics, which constitute a large portion of industrial bulk chemicals and precursors for synthetic fuels^{19–21}. This successful transformation to desired products relies largely on solid catalysts^{19,22}.

Nowadays, due to their good performance and accessibility the main catalysts used are based on late transition metals (Fe, Co, Ni and Cu), either in bulk or supported. Iron in carbidic form is employed in the production of hydrocarbons with a high olefin content, it also shows high water-gas-shift activity which can be exploited to balance the H₂ to CO ratio in CO-rich synthesis gas from coal or biomass^{23,24}. Cobalt-based catalysts are used in the production of long-chain hydrocarbons (C₅₊), and contrary to iron, it shows low water-gas-shift activity so H₂-rich synthesis gas is preferred²². Cobalt-based catalysts therefore find application in the GTL process, in which the C₅₊ products are subsequently upgraded to liquid fuels. Conversion of synthesis gas based on Fe or Co catalysts is commonly known as Fischer-Tropsch (FT) synthesis reaction. Nickel has a high hydrogenation activity, and together with the reaction conditions needed to avoid the formation of volatile nickel carbonyls, it shows high selectivity towards methane, which can be used in the purification of H₂ from CO^{25–27}. Finally, copper-based catalysts typically in combination with zinc oxide are highly selective for the synthesis of methanol and therefore widely used in industry²⁸. Moreover, the product spectrum derived from synthesis gas can be expanded besides these products, for instance by combining these primary hydrogenation functions with a second catalyst (e.g. a solid acid) and produce alcohols, ethers, branched hydrocarbons and aromatics^{29–33}.

Besides the nature of the metal, the size of the metal particles matters. Metals in the nanoscale size offer a larger number of surface sites per unit mass. Simultaneously however, the reactivity of the surface sites is also modified which can affect their catalytic performance. In synthesis gas conversion, the nanoparticle size of late transition metals can have a significant influence on their overall performance^{34–40}. Therefore, a strategy to control the nanoparticles size is to immobilize them on a support to enhance their stability and control their spatial distribution⁴¹. For this, porous materials with mechanical stability are typically employed as support matrix for metal nanoparticles. Moreover, supports in catalysis have to withstand harsh environments commonly comprising high temperatures, pressures and reactive media. A large family of materials that can fulfil these characteristics are refractory oxides (e.g. SiO₂, TiO₂, Al₂O₃, CeO₂, etc.) and have therefore been extensively employed as support⁴².

Niobia (Nb₂O₅) is a transition metal oxide with various polymorphs, rich redox chemistry and acidic properties. It has attracted interest in catalysis as support material or as a promotor for various reactions^{43,44}. For FT synthesis, niobia-supported cobalt catalysts have proven particularly interesting due to their notably high selectivity towards long-chain hydrocarbons and great activity per unit weight of cobalt^{45,46}. Niobia being a reducible sup-

port, the origin of the enhanced FT performance has partially to do with the Lewis acidity of the material and the strong metal-support interaction (SMSI) effect^{47,48}. SMSI occurs for nanoparticles of late transition metals supported on reducible oxides^{49,50}. During reductive conditions, the support at the periphery of the nanoparticles can be partially reduced and forms suboxides (e.g. NbO_x). This suboxides can migrate onto the surface of the metal particles. With a partial surface coverage, the mild Lewis acidic character of the suboxides can promote the intrinsic FT catalytic activity and C_{5+} selectivity.

Niobium-based materials can present both Lewis and Brønsted acid sites. For example, $\text{Nb}_2\text{O}_5 \cdot n\text{H}_2\text{O}$ and NbOPO_4 have shown exceptional performance for various acid-catalysed reactions⁴⁴. Contrary to many solid acids, these materials are capable of maintaining high catalytic activity and stability when water is involved^{51,52}. Therefore, niobium-based solid acids are promising components as stable catalysts for hydration and dehydration reactions. In synthesis gas conversion, solid acids can serve as dimethyl ether (DME) synthesis catalyst by combining a methanol synthesis functionality. Overall, niobium-based materials have shown great potential in the conversion of synthesis gas to hydrocarbons, either as support material or promoter in FT and DME synthesis catalysts. Further research into these materials might increase our tools for the effective conversion of synthesis gas and allow us to find new applications.

The aim of this thesis is to explore and understand different strategies to enhance the catalytic performance, either in terms of activity, selectivity and/or stability, of niobium-based catalyst employed in the conversion of synthesis gas. Previous research carried out in the group on cobalt catalysts supported on niobia⁵³ set a strong base for the work presented here. Based on those insights, we focus on $\text{Co/Nb}_2\text{O}_5$, $\text{Ni/Nb}_2\text{O}_5$ and $\text{CoNi/Nb}_2\text{O}_5$ systems for FT and $\text{Nb}_2\text{O}_5 \cdot n\text{H}_2\text{O}$ and NbOPO_4 as solid acids in combination with a methanol synthesis catalyst for the direct synthesis of DME. Starting in **chapter 2** we review recent literature on metal-support interactions and tuning strategies which serves as an introduction to the field of supported metal nanoparticles and the tools to modify their catalytic performance. In addition to creating a critical overview of the field, the effect of modifying metal-support interactions on catalysis is quantified by systematically reporting the productivity enhancements obtained in C1-chemistry.

Thereafter, chapters 3 to 5 focus on niobia used as support for cobalt and bimetallic cobalt-nickel catalysts for the Fischer-Tropsch (FT) reaction. In **chapter 3** the importance of crystal phase, porosity and cobalt loading in $\text{Co/Nb}_2\text{O}_5$ is highlighted. Additionally, a carbon-templated crystallization method was carried out to overcome the limited porosity of crystalline niobia and allow higher Co loadings. The resulting crystalline niobia partially preserved the porosity of the precursor niobium oxide hydrate. With a higher Co loading, the catalyst-weight normalized FT activity increased without sacrificing C_{5+} selectivity. **Chapter 4** describes a method and a related mechanism to tune the coverage of metal nanoparticles by SMSI-species and the resulting catalytic activity. This was achieved by reduction-oxidation-reduction pre-treatments of cobalt catalysts supported on reducible metal oxides, i.e. Nb_2O_5 and TiO_2 . The positive effects of this treatment resulted in enhanced accessible cobalt surface area and proportional increase in FT activity. In **chapter 5**, we gradually

changed the composition of the metal nanoparticles from Co to Ni. We observed that when supported on reducible metal oxides, i.e. Nb_2O_5 , TiO_2 , bimetallic Co-Ni nanoparticles displayed enhanced FT activities and high C_{5+} selectivities, phenomenon not observed when supported on $\alpha\text{-Al}_2\text{O}_3$, a non-reducible metal oxide. Characterization pointed to a cobalt enrichment of the nanoparticles surfaces and a weaker adsorption of CO on Co-Ni supported on reducible oxides, modifying the FT mechanism.

Chapters 6 and 7 explore alternative catalytic applications of niobium-based materials for the conversion of synthesis gas. **Chapter 6** presents the change in reactivity of nickel nanoparticles when supported on niobia and the effect of different reduction temperatures to obtain stable Ni/ Nb_2O_5 for the hydrogenation of carbon monoxide. Here, the formation of niobium suboxides and their partial coverage of the nickel particles after high temperature reduction limited the formation of nickel carbonyl and slow down particle growth. Although this also led to a decrease in nickel-normalized catalytic activity, stable catalytic performance was gained in return. For **Chapter 7** we exploited the acidic character of hydrated niobium pentoxide and niobium phosphate as dehydration materials in the direct synthesis of DME from synthesis gas. In combination with a copper-based methanol synthesis catalyst, the niobium-based solid acids proved active and selective in the production of DME. Particularly the high volume-based activity of these materials and their water-tolerant acid sites makes them promising components for DME production.

Finally, conclusions of the work presented in this thesis and an outlook for future research are given in **chapter 8**.

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2 Control of Metal-Support Interactions in Heterogeneous Catalysts to Enhance Activity and Selectivity

Metal nanoparticles stabilised on a support material catalyse many major industrial reactions. Metal-support interaction (MSI) in these nanomaterials can have a substantial influence on the catalysis, making MSI modulation one of the few tools to enhance catalytic performance. This topic has received much attention in recent years, however, a systematic rationalisation of the field is lacking due to the great diversity in catalysts, reactions and MSI modification strategies. In this review, we cover and categorise the recent progress in MSI tuning strategies to enhance catalytic performance for various reactions. Furthermore, we quantify the productivity enhancements resulting from MSI control that have been achieved in C1 chemistry in recent years. Our analysis shows that up to 15-fold productivity enhancement has been achieved and that MSI is most impactful for metal nanoparticles smaller than 4 nm. These findings demonstrate the importance of MSI to improve performance in catalysis.

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Figure 2.1 Schematic representation of main metal-support interactions and their tuning strategies. The five main phenomena of metal-support interactions are depicted in **a**. The approaches for tuning such interactions are illustrated in **b** and divided after the different stages of catalyst modification, i.e., via solely the support or the nanoparticle or via treatments on the metal-support composite material.

2.1 Introduction

Metal nanoparticles are the key functional component in various nanotechnological applications, owing to the unique properties that arise from their size, shape and composition^{1,2}. Consequently, several strategies have been developed to design and control these properties. A key strategy is to immobilise nanoparticles on a support to enhance their stability and control their spatial distribution^{3,4}. However, supports are typically not inert and the interaction with nanoparticles gives rise to new interface phenomena. Such metal-support interaction (MSI) may have a profound impact on the resulting performance of the metal nanoparticles^{5,6}. Hence, strategies for controlling these interactions to optimise performance are highly desirable.

In heterogeneous catalysis, MSI affects the catalytic performance and its regulation thus provides options for catalyst design. Recently, the topic has gained much attention as judged by the increasing number of reports on the subject and substantial progress has been made in methodology to tune metal-support interactions with the aim to improve the performance of supported metal catalysts. Because of the great diversity in MSI tuning approaches, catalytic systems and reactions, a systematic and critical overview would be helpful to determine the most effective tuning strategies for real working catalysts.

This review starts with a brief introduction covering the relevant concepts of MSI phenomena and the following sections discuss the latest reports on MSI tuning strategies for catalysis, systematically arranged after the different stages of catalyst modification. Several interesting reviews have already been published in the field of MSI^{7–10}. In comparison, we have reviewed the literature published since 2015 on tuning interactions between metals and supports to improve catalytic performance, covering mainly 3D catalysts containing metal nanoparticles or clusters under industrially relevant conditions. For a general discussion, we provide a quantitative analysis of the scale of performance enhancement that has been reported in the past years. To quantify the effects of MSI modulation on catalytic performance, we focus on intrinsic activity and selectivity as performance descriptors and less on stability. Although highly relevant from an application point of view, activity enhancement due to changes in metal dispersion (increased metal specific surface area) are not covered here. Relative scaling factors are obtained by comparing the productivities of tuned and reference catalysts in C1 chemistry, which allow us to point out the most successful tuning strategies and opportunities in this field.

2.2 Metal-support interactions

Impact on catalysis originates from interactions between metal nanoparticles and their supporting matrix (Figure 2.1a). Typical metal-support phenomena relate to charge transfer, the interfacial perimeter, nanoparticle morphology, chemical composition and strong metal-support interaction (SMSI). These phenomena are often entangled and some will have a stronger influence than others, depending on the catalyst and the reaction.

Charge transfer. The interface between a metal NP and the support can give rise to a rearrangement of electrons within both materials⁵. Redistribution of electrons with noticeable effects is limited to a couple of atomic layers at the interface and might be accompanied in some cases by a change in oxidation state of the metal atoms from the NP or of the support's metal ions^{11,12}. The magnitude and direction of the charge transfer is driven by differences in the Fermi level of the metal NP and the support, ultimately seeking equilibration of the electron chemical potentials. The metallic character of the NPs enables electron mobility, however their size is relevant in the nanometer regime, since the smaller the NP the more localised are its electronic states. Several characteristics of the support are important for charge transfer, such as its conductivity, reducibility, exposed crystal planes, morphology and occurrence of defects^{13,14}.

Interfacial perimeter. Interface sites at the perimeter of the NP are a unique environment given that they are in direct contact with the NP, the support and the reactants, facilitating synchronised reactions^{15,16}. Furthermore, it has been shown that upon charge transfer, atoms at the perimeter favour the accumulation of excess charges¹⁷. All this can significantly enhance adsorption and reactions of molecules at the perimeter^{18,19}. Additionally, close proximity of the nanoparticle to different functionalities or defects at the surface of the support (e.g., oxygen vacancies, hydroxyl groups, Lewis acids or bases) might also aid local sequential reactions or stabilise transition states of reactants or products^{20,21}.

Spillover via the interfacial perimeter can occur as well. This initiates with the activation of a reactant on one surface, typically on the metal NP, which is then transferred to the other surface, e.g., the support. Note that this second surface does not activate the reactants itself under the same conditions. The most studied spillover is for H and to a lesser extent O or other molecules (e.g., CO, -OCH₃, etc.). Spillover from the support to the metal nanoparticle can also occur, referred sometimes as reverse spillover^{22–24}. The nature of the support is crucial for spillover; whereas hydrogen spillover on reducible supports occurs fast and at relative large distances, it has been shown to proceed ten orders of magnitude slower on non-reducible supports and is restricted to short distances²⁵.

NP morphology. The shape and crystal structure of nanoparticles have a strong influence on their catalytic performance, considering that different shapes expose certain facets and these facets can have favourable or unfavourable configurations of atoms^{26,27}. The adhesion energy at the metal-support interface affects the shape of the nanoparticles^{26,28}. In general, supports with stronger adhesion result in particles with more faceted and sometimes raft-like shapes²⁹. A trend observed for metal oxide supports suggests that adhesion energies increase with increasing heat of formation of the most stable oxide of the metal³⁰ and by decreasing the metal NP's size³¹. Besides NP shape, high adhesion energy will also reduce the mobility of the NPs and hence their tendency to grow^{6,32}.

The equilibrium shape of a metal NP is often determined by minimisation of its total surface free energy. Contact with the support can lower the surface energy of certain NP's planes, favouring some shapes over others. The surface energy of a metal can also change under reaction conditions upon adsorption of a gas, where the change in its surface energy tends to affect the contact surface area with the NP and hence modifies the NP's shape^{33,34}. Moreover, a misfit between the lattices of the support and the nanoparticle can generate strain and defects, modifying the morphology of the NP³⁵. Additionally, the effect of lattice mismatching is more pronounced for smaller metal nanoparticles, as observed for gold nanoparticles smaller than 3 nm supported on titania³⁶.

Chemical composition. A solid state reaction can take place between metal NPs and the support resulting in the formation of new phases. Exchange of species is possible in both directions, usually coupled with a redox process, with oxidation of the metal atoms from the nanoparticle or reduction of metal ions from the support. This phenomenon has ambivalent consequences, since the resulting species can both lower or enhance catalytic per-

formance. On the one hand, formation of inactive phases such as mixed metal oxides (e.g., metal aluminates) at the expense of active metal sites has been recognised for long time as a prominent deactivation process^{37,38}. On the other hand, formation of highly active intermetallic nanoparticles is also possible by reduction of metal or metalloid ions from the support to incorporate into the metal NP. This phenomenon has recently attracted significant attention and is sometimes referred as reactive metal-support interaction (RMSI)³⁹. The pre-deposited metal nanoparticles aid in the activation of the support. Upon high temperatures and reductive conditions, the former cations from the support can migrate to the nanoparticle. This can be facilitated by doping the support or employing 2D supports. The strategy has been effectively applied to incorporate difficult-to-reduce metals or metalloids (e.g., Si, Al, V, Ti, Nb, etc.) into late transition metal NPs, resulting in novel catalytic systems⁴⁰.

The local composition of alloyed metal nanoparticles can be affected by interacting with the support, where re-arrangement of the components in an alloyed nanoparticle is driven by preferential interaction of one of its elements with the support at the interface⁴¹. This can lead to compositional rearrangements different from the initially uniform composition, such as core-shell or segregated sub-cluster structures, affecting the synergy of the metals and hence their catalytic performance^{42,43}.

Strong metal-support interaction. The term strong metal-support interaction (SMSI) refers to metal NP coverage by suboxides, which are generated from the support under reducing conditions^{44,45}. The phenomenon is driven by minimisation of the high surface energy of the metal NP by mobile support suboxide species. High surface energy metals that are capable of activating hydrogen are prone to encapsulation and reducible supports are necessary to generate the suboxide species. The suboxides covering the nanoparticle consist of a few atomic layers with probably amorphous character and possess dynamic structures under different gas atmospheres as shown in the case of titanium and iron oxide^{46–48}. Extensive coverage of the NP is detrimental for the catalytic performance due to blockage of active sites. However, these suboxides can change the (local) electronic structure of the metal surface and act as Lewis acids, thereby promoting the activation of reactants and improve the catalytic performance⁴⁹.

2.2.1 Modification of metal-support interactions

The aforementioned MSI phenomena can have a major impact on the catalytic performance. Therefore, modification of MSI can be employed as a tool for the design of catalytic systems with enhanced performance. Several synthetic strategies for the control of the MSI have been reported, which can be classified according to changes to the catalyst's components before and after assembly of the composite material (Figure 2.1b). Through this distinction, we aim to emphasise the similarities within one strategy, when applied to different families of catalysts, supports and reactions. In the coming section we start by discussing reports targeting modification mainly of the support, divided into strategies involving support composition, morphology, doping and surface modifications. Thereafter,

strategies that focus on nanoparticle modifications are discussed, particularly changes in NP's size and composition. Lastly, we cover the approaches to tune MSI on the as-prepared catalyst by use of a treatment. The identified treatments include thermal, reducing agent, reduction-oxidation cycles, overlayer deposition and adsorbate-mediated treatments.

2.3 Support

The first approach to tune the metal-support interactions is through a judicious choice of support characteristics. The support provides numerous opportunities for changing its structure and surface composition, making it one of the most employed handles to tune MSI. In this section, we will discuss modifications of supports prior to deposition of NPs. Support tuning strategies after NP loading are classified as a post-synthesis treatment and will be discussed in the Treatment section.

Support composition. The first point of consideration is the chemical composition of the support, as that partially defines the starting point for MSI. The discussion of support composition involves comparisons between different types of supports as well as between different chemical compositions of related support compounds. Examples of support properties impacting MSI include the surface composition of the support (such as extent of hydroxylation), the electronic structure of the support (especially important for electro- or photocatalysis), ion mobility (e.g., formation of oxygen vacancies or cation diffusion), reactivity of the support, and the possibility to segregate cations to form intermetallic compounds.

Several recent publications investigated the role of the support in the catalytic oxidation of CO by Au NPs. Saavedra et al.⁵⁰ studied in detail the origin of lower CO oxidation activity at room temperature of Au NP supported on Al_2O_3 compared to TiO_2 . They concluded that activity was to a large extent determined by competitive adsorption of water (promoting) and carbonates (poisoning) on the support and active metal sites. The role of the support was mainly to supply adsorbed water to the Au NPs. This was more efficient on TiO_2 , given that carbonates bind stronger to Al_2O_3 than to TiO_2 and they propose that oxygen vacancies do not participate significantly in the catalysis. Contrary, Wang et al.^{51,52} reported that oxygen vacancies are generated in TiO_2 and that these vacancies are mainly responsible for the modified catalytic activity. The vacancies caused overall electron donation to the Au NPs, making these NP negatively charged. The charge donation resulted in strongly modified CO adsorption strength and lower intrinsic activity at 80 °C. Interestingly, the TOF could be enhanced by one order of magnitude by re-oxidation of the catalyst, which reduced the amount of oxygen vacancies. One possibility for these two different explanations of the same catalytic system could be the different pre-treatment or reaction conditions, such as reaction temperature (RT vs. 80 °C), feed composition (1 vs 20 % O_2), or dilution with inert SiC. For example, it has been reported that the mechanism of CO oxidation changes with reaction temperature⁵².

The activity for benzyl alcohol oxidation followed the opposite trend as for CO oxidation with the intrinsic activity decreasing in the order $\text{Au}/\text{Al}_2\text{O}_3 > \text{Au}/\text{SiO}_2 > \text{Au}/\text{TiO}_2 > \text{Au}/$

ZnO⁵³ (Figure 2.2a). Charge transfer occurred to a different extent from various supports to Au NPs of 2-4 nm size and correlated inversely with the electron donation capacity of the support. Hydride transfer from the alcohol to Au was argued to be the rate determining in this case and would account for lower activity of more negatively charged Au NP.

In photocatalysis, a semiconductor support's bandgap of appropriate size and position facilitates light absorption and transfer of the generated charge to or from metal NPs performing catalysis. The activity of Rh/TiO₂ in steam reforming of methane was already 13 times higher than that of Rh/SiO₂ and Rh/ZrO₂ in dark conditions and the activity of Rh/TiO₂ was enhanced further nearly 3 times when exposed to light (Figure 2.2b)⁵⁴. However, the opposite has been observed as well; Pt/Ta₂O₅ was more active than Pt/TiO₂ for 2-propanol oxidation to acetone, because hot electrons generated on the Pt NPs were not transferred to the support and hence drove the catalysis on the Pt NPs⁵⁵. XPS analysis indicated that the Pt phase was more negatively charged on Ta₂O₅ than on other supports. Similar considerations also apply to electrocatalysis. The activity of Pt NPs for electrocatalytic reduction of oxygen was significantly enhanced when a mixture of boron carbide and graphite was used as support instead of pure graphite and it was argued that this was solely an electronic effect⁵⁶.

Perovskites are a class of metal oxides with the general formula ABO₃ in which a large variety of metal ions can be incorporated in the A- and B-sites of their crystal structures. Some of these ions can be extracted from the perovskite lattice upon reduction to form nanoparticles. This approach has received great attention for electrochemical systems⁵⁷ mainly due to the beneficial conductive properties of perovskites for electrodes. However, this approach has been employed to a lesser extent for catalysis due to the resulting low metal loading and limitation to easy-to-reduce metal ions, such as noble metals. Recently, non-stoichiometric perovskites with A-site deficiency extended the range of metal ions capable of forming nanoparticles to more difficult to reduce metal ions (e.g., Ti⁴⁺, Fe^{2+/3+}, Mn^{2+/3+}, Ni²⁺)^{58,59}. The resulting nanoparticles resisted the harsh conditions of methane reforming due to partial embedding in the support, avoiding the formation of carbon fibres at the periphery of the nanoparticles. Formation of alloyed nanoparticles is also possible by use of this strategy. Alloyed Pt₃Ni nanoparticles obtained from La_{0.9}Mn_{0.9}Pt_{0.075}Ni_{0.025}O_x perovskite have shown high activity for the electrocatalytic oxygen reduction reaction⁶⁰. The strong connection with the conductive perovskite, uniform NP distribution and small NP size for the obtained particles were beneficial to the measured activity.

The disadvantage, however, of using perovskites to form nanoparticles in catalysis is the low specific surface area of these compounds, due to the high temperatures needed to synthesise the perovskites. Progress has been achieved in fabricating high surface area perovskites by templating methods, however the challenge remains with the high temperatures needed to form the metal nanoparticles, which usually leads to collapse of the pore structure of the perovskites⁶¹.

Support morphology. Various allotropes or morphologies can exist for one type of support. We will discuss these two properties together, because they are often interrelated and exert

Figure 2.2 MSI tuning strategies involving modification of the support composition and morphology. **a**, TOF for benzyl alcohol selective oxidation plotted against the work function of the supports, which is the inverse of the support's electron-donating ability to gold NPs. Multiple work function values were obtained for some supports, because these values were calculated for individual support crystal facets (ref. 53). **b**, Methane steam reforming activity expressed as H₂ production rate for Rh NPs supported on SiO₂, ZrO₂ and TiO₂ with and without exposure to visible light (ref. 54). **c**, Use of different ceria morphologies (cubes or octahedra) as support for gold NPs and their effect on CO oxidation (ref. 70).

a combined effect. For example, the crystal structure and morphology of the support jointly determine the facets that are exposed at the surface of the support and thereby regulate the local environment for the metal nanoparticles. In this section, we will highlight some recent examples of how the crystal structure of metal oxides can direct NP shape and SMSI, and how shaped support particles can expose special surface sites or confine NPs.

The crystal structure of metal oxides can affect the NPs deposited onto it by directing the shape of the metal NPs. For example, when Pd/Al₂O₃ (α , γ , and θ) catalysts were investigated for methane oxidation, the crystal structure of the support affected the shape of Pd NPs, with more distorted NP on γ -Al₂O₃ and more regularly shaped and faceted NP on α - and θ -Al₂O₃⁶². The shape of the NP together with NP size determined the number of step sites, which could be correlated with intrinsic activity. The presence of pentacoordinate Al³⁺-sites on the surface of γ -Al₂O₃, as observed by NMR, and their absence in α - and θ -Al₂O₃ were proposed to distort the NP shape and increase the TOF of 7.5 nm NP from 0.1 to 0.6 s⁻¹. A similar effect was observed for Pt NPs on γ -Al₂O₃ and CeO₂³⁵. Especially on CeO₂, the authors were able to show that epitaxial NP growth, dictated by the support crystal structure, directed the shape of the NPs and caused strain. From theoretical investigations,

the predicted intrinsic activity for CO oxidation varied between $2 \cdot 10^{-3}$ and $5 \cdot 10^{-3} \text{ s}^{-1}$ with the occurrence of specific Pt surface sites, related to the shape and strain of these NPs.

In addition, one crystal structure can be more susceptible to partial reduction and SMSI. In the case of TiO_2 -supported Ru-promoted cobalt catalysts for the Fischer-Tropsch synthesis⁶³ and rhodium catalysts for steam reforming of propane⁶⁴, suboxide coverage was more extensive on TiO_2 in the anatase phase than in the rutile phase. In both cases, the overall activity of the catalysts was higher on rutile, because of fewer blockages of active sites by the TiO_x species. Furthermore, the specific surface area of the TiO_2 -anatase support was shown to also influence the extent of SMSI and activity on Ru-Co/ TiO_2 catalysts for the Fischer-Tropsch synthesis⁶⁵ and Ru/ TiO_2 catalysts for CO methanation⁶⁶. The cobalt-weight-based activity decreased for both catalysts with increasing specific surface area of the support, again because of a larger number of blocked sites. The TOF was, however, not affected by the support specific surface area. In this case, the anatase supports with higher surface area displayed a higher concentration of defects, as inferred from Raman spectroscopy, and this probably led to more facile formation of TiO_x species during reduction.

The shape of the support, i.e., the exposed crystal facets, also influence the catalytic performance through MSI. The activity of Pt/ TiO_2 for methanol oxidation⁶⁷, Co/ CeO_2 and Ru/ CeO_2 for ammonia synthesis^{68,69} and Au/ CeO_2 (Figure 2.2c) and Au/ ZnO for CO oxidation^{70,71} showed large differences depending on the facets on which the metal NPs were situated. The facets were controlled by synthesising nanostructured support particles of controlled shapes. The reason for the modified catalytic performance varied, however, from facilitated reactant/intermediate binding and charge transfer (Pt/ TiO_2), enhanced support reduction (Co and Ru on CeO_2) to the occurrence of more vacancies (Au on CeO_2 and ZnO). For Au/ ZnO , the vacancies allowed Au to replace Zn in the ZnO crystal lattice and promote a Mars-van Krevelen mechanism through the formation of Au-O-AuZn bonds, which are broken easier than Au-O-Zn bonds. This led to a remarkable 150 times increase in specific activity that was amplified using a very low activity reference catalyst (see Appendix A, entry 6).

One- and two-dimensional supports can give rise to confinement or exposure of special sites on the support surface. For example, Zhu et al.⁷² demonstrated enhanced CO oxidation activity for Pt NPs supported on boron nitride nanosheets. The NPs associated to B-vacancies displayed lower electron density while N-vacancies donated electron density to Pt-NPs. Since the N-vacancies were the main Pt-binding sites, the Pt NPs were electron rich compared to those supported on bulk boron nitride, which contained less vacancies. This enhanced O_2 adsorption and increased CO oxidation activity from 30 to 70 % conversion at 47 °C. Similarly, the selectivity towards CH_4 of Ni NPs on planar siloxenes in CO_2 hydrogenation was 90 % when the NPs were confined in the interior of the siloxenes structures and 53 % when the Ni NPs were located on the exterior of the support⁷³. In this case, confinement tuned the balance between the formate and the CO intermediate reaction pathway. Another example is confinement of Pt NPs in the interior of carbon nanotubes (CNT), which reduced NP size and prevented oxidation of Pt⁷⁴. This kept the metal in the active state and increased toluene oxidation activity from 4 to 27 $\mu\text{mol} \cdot \text{g}_{\text{Pt}}^{-1} \cdot \text{s}^{-1}$ at 140 °C compared to NPs located on the exterior surface of the CNT.

Two-dimensional early transition metal carbides present weaker metal-carbon bonds, due to their dimensionality, compared to bonds in traditional metal oxides or metal carbides. This results in increased chemical reactivity of the metal ions and facilitating RMSI. A two-dimensional niobium carbide Nb_2CT_x (where T accounts for various elements/groups) has been used as support for platinum nanoparticles and applied for the water-gas shift reaction⁷⁵. The two-dimensionality of this carbide material aided in the formation of a Pt–Nb surface alloy by H_2 reduction at 350 °C. Furthermore, the removal of functional groups (T) such as –OH, –O and –F, exposed terminal niobium sites which were identified as interfaces for H_2O activation. These exposed niobium atoms in contact with the Pt–Nb surface alloy showed strong affinities for H_2O or OH, as indicated by the WGS kinetics. However, this catalyst showed a similar reaction rate of $\sim 1.5 \cdot 10^{-2} \text{ mol}_{\text{H}_2} \cdot \text{mol}_{\text{Pt}}^{-1} \cdot \text{s}^{-1}$ as a Pt/ Al_2O_3 reference catalyst. The same research group has employed this material, platinum supported on niobium carbide (Pt/ Nb_2CT_x), as well as platinum supported on titanium carbide (Pt/ $\text{Ti}_3\text{C}_2\text{T}_x$) as catalysts for dehydrogenation of light alkanes⁷⁶. In this case, PtTi (Pt_3Ti) or Pt–Nb (Pt_3Nb) alloy formation increased selectivity towards propene from 60 to ~ 95 % at 15 % conversion through facilitating olefin desorption, which prevented secondary reactions.

The amount of literature on tuning MSI via support morphology for electro- or photo-catalysis is limited. This can be rationalised by considering that this strategy often concerns metal oxides with limited conductivity. One exception is the work by Shi et al.⁷⁷ on Au NPs supported on disordered TiO_2 rich in oxygen vacancies, i.e., black titania. They found that the presence of intermediate energy levels within the band gap enhanced trapping of hot plasmonic electrons from gold and increased the photocurrent densities from 126 to 280 $\mu\text{A} \cdot \text{cm}^{-1}$ with respect to Au on regular white TiO_2 , making photocatalytic water splitting more efficient.

Doping. Doping of supports with elements of different valency mainly serves to regulate the electronic structure of the support (and metal NP) and typically results in enhanced or reduced electron donating properties.

Doping of carbons is an active field, especially for electrochemical applications such as batteries and supercapacitors and metal-free catalysis. When used as a support material for metallic nanoparticles, carbon can be doped with a variety of heteroatoms of which N has been most investigated. For a more comprehensive overview of how this strategy can be applied to obtain the desired reactivities, we refer to a recent review⁷⁸. Here, we will cover the basics and highlight two studies which we believe illustrate the concept and possibilities.

N-doping is often reported to increase the support-metal nanoparticle binding strength and therefore leads to smaller NPs and higher stabilities⁷⁹. Incorporating N in a carbon matrix can have various effects on its electronic structure, depending on the position of incorporation (e.g., pyrrolic, pyridinic or graphitic). Ning et al.⁸⁰ investigated the electronic effect of different N species interacting with Pt nanoparticles of 2–4 nm and found that pyridinic N acted as an electron acceptor and graphitic N functioned as an electron donor for the Pt nanoparticles. The electron-enriched Pt NPs (in contact with graphitic N) gave the highest activity in electro-oxidation reactions of glycerol and formic acid. The high

activity was partially related to an increased rate of CO removal, which otherwise poisons the catalyst. On the other hand, the electron-deficient Pt NPs (in contact with pyridinic N) showed the highest activity in ammonia borane hydrolysis. For both the electron-rich and -deficient NPs, the modified electronic structure was proposed to tune the Pt-reactant bonds, thereby optimising reactant activation.

The application of carbon nitride with a stoichiometry of C_2N can be considered one of the most extreme cases of N-doping of a support⁸¹. These materials have a higher standard electrochemical potential than gold and are therefore termed noble carbons⁸². This means that even gold is electron deficient, when supported on C_2N , resulting in active materials for ammonia synthesis via electrocatalytic reduction of nitrogen⁸³. The positive effect of the C_2N support on catalysis was more pronounced when gold was dispersed as single atoms compared to nanoparticles, because of maximal MSI in the case of atomically dispersed metal.

Doping of a magnesium aluminate spinel support with Fe was investigated to improve the performance of a supported Ni catalyst for dry reforming of methane⁸⁴. During the reduction process, Ni catalysed the reduction of Fe from the support most probably via H-spillover and, as a result, up to 50 % Fe was extracted from the support and an Ni-Fe alloy was formed at the NP surface. At an Fe/Ni ratio of ~ 10 , carbon (coke) formation was inhibited. Interestingly, doping (Fe incorporated in the spinel) was more effective than surface modification (Fe on the surface of spinel), demonstrating the importance of the residual Fe ions left in the spinel structure of the $MgFe_xAl_{2-x}O$ support.

Doping $\gamma-Al_2O_3$ with Mg^{2+} ions prior to introduction of Ni partially prevented undesired mixed metal oxide formation during dry reforming of methane⁸⁵. This left more metallic Ni surface area available for catalysis and reduced deactivation. In addition, coke formation was suppressed, although that was mainly ascribed to the presence of small (~ 2 nm) Ni particles. Recently, a related study on Ni-based catalysts for dry methane reforming was conducted, focusing on doping the Al_2O_3 with La^{3+} ions⁸⁶. The addition of La^{3+} had several effects on catalysis, such as increased activity at La^{3+} loadings between 2 and 10 wt.% and decreased selectivity towards coke formation, resulting in increasing stability with La^{3+} content. The positive influence of La^{3+} was ascribed to the introduction of basic sites and stronger MSI. It is quite possible that doping with Mg^{2+} and La^{3+} affects catalytic performance via the same mechanisms, as both form basic oxides, which may counteract the typically acidic nature of $\gamma-Al_2O_3$.

Adding cationic or anionic dopants to reducible supports such as TiO_2 can increase their conductivity, making them more attractive supports for electrocatalysis. When both type of dopants were applied simultaneously, more charge transfer to 3 nm Pt NPs was observed⁸⁷. This resulted in 3 to 5 times higher Pt mass specific activity in electrocatalytic oxygen reduction than obtained with only one dopant (Figure 2.3a). Similarly, an increase in charge transfer from Fe^{3+} -doped ZnO to Pt NPs reportedly led to a 5-fold increase in TOF in CO oxidation⁸⁸. Other examples of dopants that affect oxygen vacancies or charge transfer in reducible supports examples are available as well^{89–91}. Furthermore, Schumann et al.⁹² found that dopants can stabilise the metal oxide by changing their reducibility. Trivalent dopants

Figure 2.3 MSI tuning strategies based on doping and surface modification of the support. **a**, Chart comparing the electrochemical performance in the oxygen reduction reaction of Pt on various single- and dual-doped titania supports and schematic representation of the degree of charge transfer from the support to the Pt NPs depending on the kind of doping, as depicted by the thickness of the arrows (ref. 87). **b**, XPS spectra of Pt 4f for Pt supported on carbon nanotubes (CNT) with various pre-treatments: pristine (Pt/CNT), oxidised (Pt/oCNT), ammonia treated (Pt/L-NCNT) or high nitrogen content (Pt/H-NCNT). The spectra show changes in the oxidation state of Pt depending on the CNT surface modification (ref. 98). **c**, Cobalt-normalised activities at pseudo-steady state for the Fischer-Tropsch synthesis reaction as a function of the acid–base character of the metal oxide surface layer inferred from the UV–vis band shift of a probe molecule (η) due to charge transfer (ref. 104).

(Al³⁺, Ga³⁺) increased the conductivity of the support and activity in reverse water-gas shift and methanol synthesis, whereas divalent Mg²⁺ lowered the activity.

Surface modification. We distinguish two types of surface modification: introduction of functional groups and (complete) coating of the surface with another phase up to the point that the surface properties are completely dictated by the coating material.

Oxygen- or nitrogen-containing functional groups are often introduced on carbon supports as a way to regulate MSI. The basic concept is that these functionalities act as anchoring sites for the metal NPs. That just anchoring NPs is not a complete picture was recognised for example by two groups working on surface functionalisation of CNT as support for Co catalysts for the Fischer-Tropsch synthesis^{93–95}. Eschemann et al.⁹⁵ reported substantially higher TOF for Co supported on pristine carbon nanotubes (CNT) compared to surface-oxidised CNT. The authors proposed an increased fraction of more active hcp Co on pristine CNT as the cause of these differences. This hypothesis can be strengthened by earlier literature, as Co was previously shown to form of an hcp phase on graphite (0001)⁹⁶.

In addition, several other studies showed that the role of functional groups was not limited to anchoring of NPs in hydrogenation^{97,98} and oxidation⁹⁹ of organic compounds. Charge transfer between the functionalised support and noble metal nanoparticles substantially altered catalytic performance (Figure 2.3b).

Metal oxides can also be functionalised to facilitate metal NP binding using, e.g., amine or thiol groups to anchor metal NPs to a support. These functional groups can affect the activity and selectivity of catalysts supported on irreducible oxides^{100,101}, but this is not very common. Often the functional groups do not change the intrinsic activity of the catalysts and rather facilitate binding to the support and can impart greater stability to the catalysts¹⁰².

Surface coating can be applied to the support via precursor decomposition (glucose, organometallic precursors, etc.) or atomic-layer deposition. For example, coating the surface of a nanostructured In_2O_3 with carbon made this support more suitable for photocatalytic CO_2 reduction using Pt as the metal¹⁰³. The Pt NPs were the catalytically active sites and the carbon increased absorption of visible light through lowering of the bandgap, lowered electron-hole recombination, suppressed H_2 production from protons, and facilitated CO_2 adsorption. Through all these support functions, the production rate of CO increased from 27 to 127 $\mu\text{mol}_{\text{CO}}\cdot\text{h}^{-1}$ and the production of methane increased from 4 to 28 $\mu\text{mol}_{\text{CH}_4}\cdot\text{h}^{-1}$. It should be noted that (electronic) interactions between In_2O_3 and C were present, so the composite material displayed the combined properties of both materials.

Prieto et al. utilised coatings to isolate the intrinsic properties of different metal oxide supports from other factors such as support morphology and verified the effect of these properties on the performance of Ru-promoted Co catalysts¹⁰⁴. The authors found a correlation between the Lewis acidity of the metal oxide surface layer and the catalytic activity and selectivity in the Fischer-Tropsch synthesis (Figure 2.3c). These studies show that a surface layer can be applied to effectively replace the surface properties of the original support with that of the coating.

2.4 Metal nanoparticles

The second category of MSI tuning focusses mainly on the metal NPs. Of the three stages for MSI tuning (support, metal NP, treatment), this is least reported yet it does provide interesting opportunities. In this section, we will discuss recent examples of how modification of the size or composition of the nanoparticles affects MSI and hence catalytic performance.

Size. MSI can have a strong influence on the size of metal NPs, clusters and single atoms during catalysis and we refer to a recent review for a detailed discussion on this topic¹⁰⁵. Focussing on metal NPs, the vast majority of literature on MSI tuning deals with NPs <5 nm. Most probably because the effect of the support on the metal NPs is attenuated for larger NPs because of reduced impact of charge transfer and relatively less metallic surface area in intimate contact with the support, i.e., less interface sites. NP size has the most pronounced

Figure 2.4 MSI tuning strategies involving alterations to the metal nanoparticle size or composition. **a**, Average charge per Pt atom to the ceria support as a function of the Pt particle size (ref. 106). **b**, Schematic representation of the balance between charge transfer and H-spillover for Ru of different sizes (atoms, 1 nm nanoclusters and 4 nm nanoparticles) supported on ceria and its effect on the TOF in CO_2 methanation (ref. 107). **c**, HAADF images and model reconstruction showing Rh segregation to the TiO_2 support for a reduced AuRh/ TiO_2 sample and the energy scheme for two binding configurations of AuRh clusters to TiO_2 derived from DFT. Calculations point to Rh segregation to the support as the most favourable configuration (ref.110).

influence on purely electronic MSI effects, which are short range, as Lykhach et al.¹⁰⁶ showed for 1.0-1.5 nm Pt NPs with a partial positive charge of 0.11 per Pt atom in Pt/ CeO_2 catalyst (Figure 2.4a). They observed using resonant photoemission spectroscopy on 2D model systems that the partial positive charge per Pt atom decayed for larger particles. Furthermore, the overall charge transfer was limited by the support (17 % surface Ce^{3+} seems the limit for CeO_2 reduction). The need for small NPs to induce effective electronic MSI is also reflected in literature where most reports on catalytic performance relate to particles smaller than 5 nm (Figure 2.7b). Conversely, this also means that it is unlikely that electronic MSI plays a significant role in large (>2 nm) NPs, unless the NPs are encapsulated by the support in which case charge transfer could still occur to all surface sites.

Guo et al.¹⁰⁷ investigated the effect of Ru NP size on the performance of Ru/ CeO_2 in CO_2 hydrogenation varying between single atoms, 1 nm clusters and 4 nm NP. With increasing NP size, the electronic MSI interaction decreased which facilitated CO_2 activation and increased reactivity (Figure 2.4b). At the same time, H-spillover increased with NP size, hindering H_2O removal and decreasing activity. Competition between both effects makes the 1 nm clusters (intermediate size) the most active system with a TOF about 50 % higher

than single atoms and one order of magnitude higher than NPs. Interestingly, the selectivity to CH_4 was 100 % for all sizes. This is in contradiction to a recent report by Yan et al.¹⁰⁸, who observed a Ru NP size-dependent selectivity in CO_2 hydrogenation on $\gamma\text{-Al}_2\text{O}_3$. CO formation via reverse WGS was favoured for Ru clusters while the selectivity shifted to CH_4 for larger NPs. One possible explanation for the different observations could be the nature of the supports that were employed (CeO_2 and $\gamma\text{-Al}_2\text{O}_3$), because the support was involved in the reaction in both cases. Notably, in Ru/ $\gamma\text{-Al}_2\text{O}_3$, the interface oxygen (Ru-O-Al) was shown via isotope labelling to exchange oxygen atoms with CO_2 during the reaction.

Composition. The metal distribution in an NP depends to a large extent on the strength of the bonds between the metal atoms and between metal atoms and support. Theoretical calculations¹⁰⁹ on Au-Rh and Pd-Ir nanoparticles supported on titania showed that the surface binding strength of Rh or Ir atoms to $\text{TiO}_2(110)$ is greater than for Pd or Au to the support, due to stronger Rh-O or Ir-O interactions than Au-O or Pd-O. Therefore, Rh or Ir segregated towards TiO_2 . This has been experimentally observed for Au-Rh nanoparticles supported on titania nanorods¹¹⁰ (Figure 2.4c) and employed for tetralin hydrogenation in the presence of H_2S ¹¹¹. The Au/Rh/ TiO_2 stacking configuration had a detrimental effect on the initial hydrogenation activity. Eventually, Au/Rh/ TiO_2 was more stable due to the stabilising effect of gold against H_2S poisoning of Rh. Likewise, a segregation of iridium from Au-Ir nanoparticles towards TiO_2 has been experimentally observed, resulting in higher resistance towards sintering than Au/ TiO_2 during thermal treatments¹¹².

For Au-Cu on Al_2O_3 and SiO_2 the NPs de-alloyed under oxidising conditions on both supports to form Au NPs and a CuO_x phase. However, on Al_2O_3 , CuO_x formed separate patches on the support, which prevented the creation of active Au- CuO_x interfacial sites present on SiO_2 ¹¹³. Consequently, Au- CuO/SiO_2 approached 100 % CO conversion while Au- $\text{CuO}/\text{Al}_2\text{O}_3$ converted 11 % of the CO at 150 °C.

Seemala et al.¹¹⁴ studied Cu-Ni nanoparticles supported on either θ -alumina or titania and observed TiO_2 -induced metal segregation upon reduction using H_2 , during which Cu enriched the NP surface while Ni segregated to the NP-support interface. This arrangement was explained by a stronger interaction between nickel and titania than copper and titania. The Cu-Ni/ TiO_2 catalyst showed high activity in furfural hydrodeoxygenation, high selectivity to methyl furan and good recyclability, outperforming the Cu-Ni supported on alumina and the titania-supported monometallic catalysts. A similar phenomenon was observed in the case of Ni-Pt supported on mesoporous silica (SBA-15)¹¹⁵. Here, a strong nickel-support interaction, most likely generated during metal precursor deposition on silica at basic conditions, led to the formation of a Pt-rich (Pt_3Ni) intermetallic compound thus favouring the formation of active Pt-Ni bonds rather than Ni-Ni. This in turn increased the selectivity of CO_2 reduction to CO instead of CH_4 , as the latter product is typical for Ni-based catalysts.

Divins et al.¹¹⁶ showed that ceria as support influenced the oxidation state and metal arrangement of Rh-Pd nanoparticles under different atmospheres using NAP-XPS at 0.05 mbar. Upon reduction at 573 K, Rh-Pd/ CeO_2 and non-supported Rh-Pd nanoparticles showed segregation of palladium to the surface. However, at conditions close to eth-

anol steam reforming the metals in the non-supported nanoparticles re-arranged back to a uniform distribution, whereas the CeO_2 -supported ones maintained the Pd-rich surface. Because the Rh- CeO_2 interaction was stronger, the core-shell structure was maintained. Furthermore, the CeO_2 -supported nanoparticles presented higher oxidation states, especially at the outermost layers due to H_2O activation at the CeO_2 surface. The high H_2 selectivity of the supported catalyst, compared to the non-supported nanoparticles, was derived from promotion of WGS and methane steam reforming.

Gubó et al.¹¹⁷ showed that an increase of the relative Au concentration in Au-Pd nanoparticles supported on rutile TiO_2 prevented the encapsulation of the nanoparticles by TiO_x . The nanoparticles formed a bimetallic core with an Au enriched shell and became less prone to SMSI due to the lower surface free energy of Au.

Organic ligands coordinated to the surface of metal NPs can affect MSI, e.g. by acting as a carbon-precursor. Zhan et al.¹¹⁸ placed pre-formed Au colloids, capped with oleylamine ligands, on TiO_2 . The ligands were decomposed using an N_2 treatment to form a carbon shell, which protected Au NPs from sintering. The higher overall CO oxidation activity of the N_2 -treated sample was ascribed to smaller NP size. Gao et al.¹¹⁹ co-impregnated a nickel precursor and ligands on SiO_2 and obtained different NP sizes and stability during dry reforming, depending on the ligands (oleic acid, oleylamine or a mixture of both). The smaller NP size led to doubling of the CH_4 conversion, while the surface-specific activity remained unchanged ($\sim 2.5 \text{ s}^{-1}$).

2.5 Treatments

We define treatments as any action to modify MSI that is performed on the metal-support composite material prior to catalysis. This has mainly been investigated in the context of tuning MSI of metals with reducible supports, i.e., SMSI.

Thermal treatment. Tang et al. investigated MSI for various group 11 metals on TiO_2 and for Au supported on various reducible oxidic supports¹²⁰. They observed that metal NP overgrowth under reducing conditions started at 200 °C and was most pronounced at 400–500 °C. The overgrowth blocked the accessible metallic surface area and thereby quenched the reactivity for CO oxidation, in line with earlier literature on group 8–10 metals on reducible oxides. Furthermore, a simultaneous charge transfer from the support to Au was observed by XPS, resulting in an electron rich Au phase. These effects could be reversed and the reactivity could be restored by an oxidative treatment at 400 °C. Interestingly, the same authors also observed similar effects for Au NPs supported on a phosphate hydroxyapatite, yet with the reverse response to oxidising and reducing conditions¹²¹; now oxidation at 300 °C and higher resulted in the support encapsulating the Au NPs and lowering the CO oxidation activity, which could be reversed by a reductive treatment at 500 °C. It was recently suggested that loss of OH groups at high temperature gave rise to this type of interaction and the phenomenon was also observed on group 10 metals supported on ZnO-nanorods¹²². Wang et al.¹²³ even avoided the necessity for reducing or oxidising atmospheres altogether

by exploiting the thermally-induced transition of a layered double hydroxide to the corresponding oxide in an inert atmosphere, possibly also caused by loss of OH groups. This induced a similar encapsulation of Au NPs with lowered CO oxidation activity.

Changes in activity and product selectivities during CO hydrogenation using Ni/Nb₂O₅ were reported after different reduction temperatures (250–450 °C) and related to SMSI effects¹²⁴. An intermediate reduction temperature (350 °C) showed the highest activity ($3.9 \cdot 10^{-5} \text{ mol}_{\text{CO}} \cdot \text{g}_{\text{Ni}}^{-1} \cdot \text{s}^{-1}$) and C₅₊-selectivity (55 wt.%). Lower reduction temperature resulted in severe deactivation due to particle growth via nickel tetracarbonyl formation and a lower final activity ($2.2 \cdot 10^{-5} \text{ mol}_{\text{CO}} \cdot \text{g}_{\text{Ni}}^{-1} \cdot \text{s}^{-1}$). On the other hand, a higher reduction temperature (450 °C) displayed stable performance but with a medium activity ($2.7 \cdot 10^{-5} \text{ mol}_{\text{CO}} \cdot \text{g}_{\text{Ni}}^{-1} \cdot \text{s}^{-1}$) and a selectivity shift to shorter hydrocarbon products, probably due to blockage of active sites by NbO_x suboxides. Similarly, in the case of Ni/TiO₂ catalysts for WGS, the coverage of Ni nanoparticles by TiO_x could be tuned via reduction temperatures between 400 and 600 °C¹²⁵ (Figure 2.5a). The metal-support interface was maximised by starting from an NiTi-layered double hydroxide precursor. Charge transfer to interfacial Ni, coverage of Ni NP by suboxides and the number of oxygen vacancies in TiO_x all increased with higher reduction temperature. Moderate MSI after reduction at 450 °C showed the highest catalytic activity with a TOF of 3.8 s⁻¹, about two times more active than after reduction at 400, 500 or 600 °C. The high activity was attributed to the interplay between interfacial Ni^{δ-} and oxygen vacancies. In the case of Pd/TiO₂ catalysts, the reduction temperature affected the coverage of Pd NPs by TiO_x species⁴⁸ (Figure 2.5b), and the amount of oxygen vacancies in Pd/TiO₂ used for formaldehyde oxidation¹²⁶. When reduced at 450 °C, more oxygen vacancies were generated, which in turn aided O₂ activation and H₂O dissociation to form OH groups and increased the formaldehyde oxidation activity 7.5-fold. These species directly decomposed formaldehyde without the slow formation of CO as intermediate, as observed after reduction at 300 °C.

An intermetallic nickel silicide catalyst obtained by reacting a nickel complex with silica via pyrolysis at high temperatures has been shown to be highly active for chemoselective hydrogenation of a wide variety of compounds (e.g., nitroarenes, carbonyls, nitriles, N-heterocycles and unsaturated carbon–carbon bonds)¹²⁷. The researchers found that the formation of this versatile catalyst strongly depended on the pyrolysis temperature, the nitrogen-doped carbon species from the ligand for Si–O bond reduction and the silica specific surface area. A pyrolysis temperature of 600 °C resulted in metallic nickel supported on silica and upon increasing the pyrolysis temperature to 800 °C a Ni₁₇Si₃ phase was observed. The most active catalyst was obtained at 1000 °C with silicon-enriched phases Ni₃₁Si₁₂ and Ni₂Si. Additionally, coverage of metal nanoparticles by support suboxides generated at elevated temperature can steer hydrogenation selectivity, as summarised before¹²⁸.

Reducing agent. The extent of MSI and in particular partial support reduction to form suboxides and oxygen vacancies depend on the overall severity of the reduction treatment. In 2014, Rui et al.¹²⁹ reported that the SMSI state in Pt/TiO₂ could be induced at room temperature during a liquid phase reduction process using NaBH₄ or formaldehyde as reducing

Figure 2.5 MSI tuning strategies involving treatments of supported metal catalysts based on temperature, reducing agent or reduction-oxidation cycles. **a**, The influence of reduction temperature of Ni@TiO_x on the Ti^{3+} to Ti^{4+} ratio and WGS reaction rate (ref. 125). **b**, In-situ observation of a TiO_x overlayer on a Pd NP under reducing conditions at 5 vol.% H_2 in Ar, 1 bar, 250 and 500 °C (ref. 48). **c**, Support reduction using different reducing agents (C_3H_6 , H_2 or CO) for Pt/CeO_2 in temperature-programmed experiments, as deduced from the fraction of Ce^{3+} obtained by Ce L3-edge XANES spectra (ref. 131). **d**, Schematic representation of a reduction-oxidation-reduction (ROR) treatment of cobalt supported on reducible supports. **e**, The effect of different oxidation (O) temperatures in the ROR procedure on the hydrogen uptake in chemisorption experiments and Fischer-Tropsch synthesis activity of Co/TiO_2 (green hexagons), $\text{Co/Nb}_2\text{O}_5$ (red diamonds) and $\text{Co/Al}_2\text{O}_3$ (violet triangles). Singly reduced samples are indicated by open symbols (ref. 133).

agent. The SMSI state, characterised by suppressed CO chemisorption, negatively charged Pt NPs, and oxygen vacancies formation, was beneficial for toluene oxidation activity, which decreased in the order $\text{NaBH}_4 > \text{formaldehyde} > \text{H}_2$. Furthermore, the MSI effect was stronger on anatase than on rutile or P25, again highlighting the importance of the support morphology as previously discussed.

Few systematic studies focusing on the effect of the reducing agent on MSI have been published in the meantime. A recent example includes the use of reducing agents with different reduction strengths to determine the rate of Pt-precursor reduction, which in turn regulated the association of NPs to different types of N-functionalities in N-doped carbon nanotubes (see Doping section)⁸⁰. As a second recent example, Gänzler et al.^{130,131} showed that the CO oxidation activity of Pt NPs supported on a CeO₂/Al₂O₃ composite support strongly varied as a function of the reducing agent, following the order CO > H₂ > C₃H₆ (Figure 2.5c). The effect of the reducing agent was ascribed to its ability to partially reduce the support. Additionally, MSI and catalytic performance could be further tuned by reduction-oxidation cycles (see next section).

Reduction-oxidation cycles. Reduction-oxidation (RO) cycles have been intensively investigated, mainly to regulate the metal NP size through re-dispersion, but also to affect MSI in various ways. Here, we will highlight several possibilities of RO for MSI tuning that were recently published.

Besides different reducing agents, Gänzler et al.^{130,131} applied RO cycles on a CO oxidation catalyst consisting of Pt/CeO₂/Al₂O₃ in order to control both the Pt NP size and oxidation state, which in turn affected the reduction of CeO₂ support. Metallic Pt NPs were necessary to reduce CeO₂ at low temperature and the support had a crucial role in CO oxidation, as discussed before. 1.4 nm Pt NPs were identified as the optimal size, because at this size most interfacial sites were available while maintaining the Pt NPs in the active metallic state. Further RO cycles induced Pt NP growth and reduced the CO oxidation activity.

Alternatively, Freakley et al.¹³² employed the reduction step of an RO cycle on a Pd-Sn/TiO₂ catalyst to selectively modify small Pd NPs that otherwise gave rise to side reactions. Surprisingly, the NPs were not covered by TiO_x species, but by SnO_x species, as evidenced by STEM-EELS and similarly with a Pd-Sn system supported on irreducible SiO₂. The final oxidation step was necessary to generate Pd²⁺ ions on the larger NPs, which were less active for side reactions than metallic Pd. The investigated reaction was the direct synthesis of H₂O₂ from O₂ and H₂ and the selectivity is a balance between H₂O₂ production rate (hydrogenation of O₂) and H₂O₂ decomposition rate. By covering the small NPs and having a Pd²⁺ containing surface on the larger NPs, the H₂O₂ decomposition was almost completely suppressed, resulting in hydrogen selectivities towards H₂O₂ of 95 %.

It is well established that the SMSI state is typically generated under reducing conditions and that the SMSI state can be reversed by an oxidative treatment⁴⁸. In an earlier publication¹³³, we applied this principle to enhance the FT activity of Co/TiO₂ and Co/Nb₂O₅ catalysts via a reduction-oxidation-reduction (ROR) process (Figure 2.5d). The first reduction at 350 °C fully reduced the cobalt oxide to metallic cobalt and simultaneously induced the SMSI state. Oxidation at 200 °C modified the suboxides, but did not oxidise the cobalt fully to Co₃O₄. Consequently, the second reduction could be performed at 220 °C only, which resulted in less suboxide coverage and hence twice the accessible metallic surface area, as compared to the samples reduced at 350 °C. The FT activity increased proportionally to the metallic surface area, implying that the number of active sites increased and that the TOF

and thus the nature of the active sites remained unchanged.

Overlayer deposition. As-prepared catalysts containing NPs on a support can be covered with an overlayer of another compound and its most basic function is to stabilise the NPs via immobilisation, as was the case for a carbon¹³⁴ and SiO_2 ¹³⁵ overlayer. In addition, in a 2D model study, a Pt(111) surface was covered with a thin layer of TiO_x to mimic an SMSI state¹³⁶. Compared to the clean Pt(111) surface, the TiO_x species increased CO oxidation activity and the effect was assigned to the formation of interfacial perimeter sites. Furthermore, Weng et al.¹³⁷ deposited SiO_2 over $\text{Pt}/\text{Al}_2\text{O}_3$ and observed the formation of Brønsted acid Si-O-Al sites. The SiO_2 overlayer decreased activity in cinnamaldehyde hydrogenation, possibly via site blockage by SiO_2 , while at the same time, selectivity towards cinnamyl alcohol increased from 25-30 % to 85 %.

Overlayers can also be applied to create specific interfacial sites, such as Cu-ZrO_2 in a Cu/SiO_2 catalyst¹³⁸. These interface sites enhanced the intrinsic activity for ethyl acetate formation from ethanol and for methanol synthesis from CO_2 by one order of magnitude. Furthermore, Moon et al.¹³⁹ applied an overlayer of various reducible oxides to a Pt/SiO_2 cat-

Figure 2.6 MSI tuning strategies involving overlayer deposition and adsorbate-mediated treatments of supported metal catalysts. **a**, Schematic representation of the effect of a silica overlayer on a copper phyllosilicate-based catalyst and the activation of dimethyl oxalate (DMO). The chart shows DMO conversion and ethylene glycol (EG) selectivity for the catalyst with and without silica overlayer (ref. 144). **b**, In-situ STEM observation of SMSI in Rh/TiO_2 after a treatment in H_2 at 550°C which induced a TiO_x bilayer (SMSI overlayer) and after treatment in $20\text{CO}_2:2\text{H}_2$ at 250°C which induced an amorphous TiO_x overlayer (A-SMSI overlayer). Production rates of CH_4 (red) and CO (grey) are shown on the chart for Rh supported on alumina or titania after H_2 or $20\text{CO}_2:2\text{H}_2$ treatments (ref. 145).

alyst and investigated its effect on CO oxidation. The activity followed the order $\text{TiO}_2 > \text{CeO}_2 > \text{Pt/SiO}_2 > \text{Ta}_2\text{O}_5 \approx \text{Nb}_2\text{O}_5$ and the increased activity was mainly ascribed to the formation of interfacial perimeter sites between Pt and the TiO_2 or CeO_2 overlayer. In addition, the overlayer made the catalyst more resistant towards sintering of Pt NP at elevated temperature.

Yang et al.¹⁴⁰ prepared Rh/ SiO_2 catalysts covered with TiO_2 or Al_2O_3 and applied these for CO hydrogenation. The Al_2O_3 overlayer decreased the activity through site blockage. The TiO_2 overlayer, on the other hand, increased the intrinsic activity and selectivity towards C_{5+} alkanes and alkenes, while the selectivity towards higher alcohols remained unchanged. Its catalytic performance was similar to that of Rh NPs on TiO_2 -coated SiO_2 , showing either that coverage of the NPs themselves was irrelevant for catalysis or that the system was dynamic and reached the same (SMSI) state during catalysis. The latter option can be rationalised considering that overlayer deposition can be used to create artificial support suboxide coverage on NPs, thereby mimicking an SMSI state¹⁴¹.

Treatment of Au/ TiO_2 with TiCl_3 at room temperature resulted in the formation of a TiO_x overlayer on Au, similar to SMSI. The TiO_x overlayer increased the activity of the catalyst for CO oxidation (0.68 vs. 0.26 $\text{mol}_{\text{CO}} \cdot \text{mol}_{\text{Au}}^{-1} \cdot \text{s}^{-1}$) and brought about stability to the gold nanoparticles. The Au- TiO_x interface was identified as the active site for oxygen activation, most likely due to oxygen vacancies, which were then regenerated after reaction with CO. The suboxides, however, also donated electrons to Au resulting in Au^δ and decreasing CO adsorption. An oxidative pre-treatment increased the activity of the catalyst by removing the excess electrons in Au, enhancing CO adsorption¹⁴².

Copper phyllosilicates have been employed as precursor for the formation of silica-supported metal nanoparticles upon reduction in H_2 , leading to high Cu loadings (~40–50 wt.%) with uniform distribution and particle size. The role of the generated Cu- SiO_2 interface in these materials has been exploited, for example, in the decomposition of methanol to hydrogen and dimethoxymethane in the liquid phase¹⁴³, where Cu^+ and Cu-O-Si moieties were necessary for the activity and high selectivity of the catalyst. The copper-silica interface (Cu-O- SiO_x) was recently further optimised by use of a mesoporous silica layer coating the copper phyllosilicate prior H_2 activation¹⁴⁴ (Figure 2.6a). In ester hydrogenation, the bare Cu/ SiO_2 obtained from copper phyllosilicate gave a TOF of $6.4 \cdot 10^{-3} \text{ s}^{-1}$ and a selectivity to ethylene glycol of 23 %, whereas the performance of Cu/ SiO_2 with a mesoporous silica layer increased with a TOF of $11.4 \cdot 10^{-3} \text{ s}^{-1}$ and a selectivity to ethylene glycol of 96 %. The Cu-O- SiO_x interface was shown to stabilise the transition state of the ester (in this case dimethyl oxalate) and to activate H_2 in a heterolytic way forming Cu-H^δ and SiO-H^δ , as previously discussed for H_2 activation with nanosised non-reducible supports.

Adsorbate-mediated MSI. MSI can be tuned by adsorbing specific compounds prior to inducing the MSI state. So far, this strategy has been limited to reducible supports, because the adsorbates mainly affect the coverage of the metal NPs by support suboxides. Matsubu et al.¹⁴⁵ recently reported this strategy for the first time. They investigated Rh/ TiO_2 catalysts for CO_2 hydrogenation and found that a treatment in 20 % CO_2 , 2 % H_2 , 78 % He atmosphere at 250 °C caused the formation of HCOx adsorbates on the Rh NPs. In the untreated

Figure 2.7 Enhancement of catalytic performance in C1 chemistry achieved through control of MSI in recent years. **a**, Relative differences in productivity of a desired compound for the different MSI tuning strategies grouped by general strategy (support, nanoparticle and treatment) and with different symbols indicating the main MSI phenomenon affected. Tuning strategies by modifications on the support or post-synthetic treatments have been mostly explored. **b**, Productivity enhancement factor as a function of metal particle size of the optimal catalyst, separated on the main MSI phenomenon affected by tuning. The grey-blue area is added as a guide to the eye and indicates the domain in which the NP size brought about the strongest productivity enhancement.

Rh/TiO₂ sample, a crystalline SMSI overlayer, which contained Ti³⁺-ions, formed during reduction at 550 °C, whereas the adsorbate-mediated SMSI state, induced at only 250 °C, led to an amorphous overlayer containing both Ti³⁺- and Ti⁴⁺-ions (Figure 2.6b). In the adsorbate-mediated case, the support suboxides as well as the adsorbates can interact with the active sites. By covering the Rh NPs with an adsorbate-mediated SMSI overlayer, which was more stable under reaction conditions, it was possible to steer the catalyst selectivity from mainly CH₄ producing (on Rh NPs) to mainly CO producing (on single Rh atoms). Rh NPs were thus more affected by the adsorbate-mediated SMSI overlayer than the single Rh atoms.

Interestingly, a similar 20 % CO₂/2 % H₂ pre-treatment was used by Wang et al.¹⁴⁶ for Cu/CeO₂ catalysts for WGS. However, they mainly used the adsorbate-mediated SMSI

strategy to prevent sintering of the Cu NPs and the effect on intrinsic activity was modest, although also some charge transfer from the support to the Cu NPs was inferred from XPS. This shows that the effect of such a treatment is highly dependent on the interplay between metal, support and reaction.

2.6 Discussion

We analysed the literature to quantify the enhancement of catalytic performance that was achieved in recent years through MSI modifications. We limited the analysis largely to C1 chemistry, i.e., catalytic reactions involving CO, CH₄, CO₂ or methanol as the main reactant. The performance of tuned catalysts was benchmarked against a reference catalyst reported in the same paper and therefore investigated under the same conditions. Consequently, an enhancement factor for the tuned catalyst over the reference one was obtained. This approach provides a measure for the efficiency of the various MSI tuning strategies and facilitates comparison between different papers reporting a wide variety of reactions, conditions and units.

The rate of formation (productivity) of desirable products, i.e., the product of total activity and selectivity, was taken as a measure for catalytic performance. Productivity was used because this shows the combined effect of activity and selectivity changes and hence provides a more complete picture of the effect of MSI tuning than either parameter alone. Turnover frequencies or specific activities were preferred over conversions as activity descriptors, because these provide more information about intrinsic catalytic activities. Furthermore, selectivities are not relevant for certain reactions such as CO oxidation reactions. For these systems, 100 % selectivity is assumed and productivity enhancement is essentially determined by activity differences. All analysed catalytic data and references can be found in Appendix A Table A1.

Figure 2.7a shows the productivity enhancement as a function of the different MSI tuning methods. Relative productivity enhancements up to a factor of ~15 have been obtained using various tuning methods, irrespective of which catalyst component is altered. Support modifications were effective in altering all MSI phenomena with substantial increase of the corresponding productivity. Particularly, selection of a certain support composition¹¹³ or adding dopants to the support⁸⁵ strongly improved the performance due to changes in the overall catalyst chemical composition. Treatments on the as-synthesized catalysts to tune the MSI have also proven beneficial to enhance their performance, most effort has focused on modifying the SMSI effect from which induction of this phenomenon on Au nanoparticles by thermal treatment¹²⁰ and use of overlayer deposition of transition metal oxides^{139,140} led to significant catalytic enhancement. Reports involving strategies based on NP modifications to affect MSI were fewer, however an approach leading to substantially increased performance involved changing NP size which in turn improved the interfacial contribution for CO₂ hydrogenation of a Ru/CeO₂ catalyst¹⁰⁷.

For the enhancement of selectivity, the largest increase was reported for a treatment to modify MSI in catalysts for CO₂ hydrogenation (78 %), where preferential blockage of

small Rh NPs or single atoms leads to a strong shift in selectivity from CH_4 towards CO ¹⁴⁵. However, the strong increase in selectivity was accompanied by a decrease in activity, leading to a productivity enhancement factor of 3.2. Besides this example, selectivity increases of 20-30 % are occasionally reported for various reactions. Furthermore, CO oxidation and reduction reactions were investigated most; 22 studies focused on CO oxidation and 11 on CO reduction reactions out of 50 papers analysed.

The enhancement of productivity can be correlated with metal particle size of the catalyst after MSI tuning (Figure 2.7b, dataset divided on the main MSI phenomenon that was affected). In general, the efficiency of MSI tuning rapidly decayed with increasing particle size and the highest enhancements were obtained for metal particles smaller than 4 nm through modification of any MSI phenomenon. The majority of studies focused on catalysts with particle sizes in the <4 nm size range. For metal particles that are larger than 4 nm, the gain in productivity as a result of MSI tuning is modest in most cases, although a few exceptions were reported. Furthermore, for these larger particles, SMSI was most often the dominant phenomenon, implying that SMSI is less affected by metal nanoparticle size. This can be rationalised by the support covering the NP and thus being in contact with a large fraction of the metal surface, regardless of particle size in the range described here.

When considering many types of catalysis, it became apparent that mainly late transition metals, starting from group 10, were involved when charge transfer between metal and support played a role in the catalysis. As for the supports, charge transfer with the metal required either conductive supports (e.g., graphite), or semi conductive supports (reducible metal oxides), often modified by dopants to increase conductivity further. Insulators (irreducible oxides) require dopants or functionalisation for charge transfer to occur on a noticeable scale¹⁰¹. This can be explained by a mismatch in band positions between insulating supports and the nanoparticles, i.e., the valence band of the insulator being too low in energy to affect the electronic properties of the metal NP.

Another observation is that the work on MSI modifications for electro- and photocatalysis is limited. On one hand, this might be ascribed to early development of the role MSI in these fields of catalysis and on the other hand, the range of applicable supports/metals might be more limited¹⁴⁷. Nevertheless, we believe that the development of MSI tuning methods could be worthwhile for these applications.

Overall, MSI can improve catalytic performance roughly by one order of magnitude under industrially relevant conditions. This effect may seem modest compared to, for example, a difference of four orders of magnitude in CO hydrogenation activity that is obtained with various metals from groups 8-10 in the periodic table¹⁴⁸. However, often the selection of the metal is fixed by selectivity considerations and MSI modification is one of the few effective tools for designing and enhancing catalyst performance. In addition, these results show that supports are more than merely an inert structural matrix and that their chemical properties can be applied to substantially improve catalytic performance.

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3 Crystalline Niobia with Tailored Porosity as Support for Cobalt Catalysts for the Fischer–Tropsch Synthesis

Structure and catalytic performance of niobia-supported cobalt catalysts were studied based on crystal phase, porosity and cobalt loading. Crystalline niobia as support proved to be a prerequisite to obtain highly active and selective Co/niobia Fischer–Tropsch catalysts, whereas amorphous niobia showed minimal activity. Crystallization changed the porous morphology of $\text{Nb}_2\text{O}_5 \cdot n\text{H}_2\text{O}$ resulting in a dense material with low specific pore volume and specific surface area. Multiple impregnations on crystalline Nb_2O_5 were necessary to achieve cobalt loadings higher than 6 wt.%; this led to larger cobalt particles, diminished interaction of cobalt with niobia and therefore decreased activity per unit weight of cobalt and C_{5+} selectivity. Carbon deposition via sucrose pyrolysis was employed in order to partly maintain the porosity during crystallization. The obtained porous crystalline niobia was used as support for cobalt catalysts with higher metal loadings. STEM-EDX mapping characterization of the catalysts provided unique information for this kind of materials, e.g. cobalt distribution and particle size. The catalysts showed high cobalt-normalized catalytic activity and C_{5+} selectivity for the Fischer–Tropsch synthesis under industrially relevant conditions. Moreover, higher cobalt loadings led to an increased catalyst-weight normalized catalytic activity.

Hernández Mejía, C., den Otter, J. H., Weber, J. L. & de Jong, K. P. Crystalline niobia with tailored porosity as support for cobalt catalysts for the Fischer–Tropsch synthesis. *Appl. Catal., A* **548**, 143–149 (2017).

3.1 Introduction

Fischer–Tropsch synthesis involves the transformation of synthesis gas (a mixture of H_2 and CO) to chemicals and ultra-clean fuels. Particularly, cobalt-based catalysts are industrially relevant for the production of long-chain hydrocarbons (C_{5+}). These catalysts offer high selectivity, activity and stability, especially when promoted with noble metals and/or transition metal oxides¹. Since the first reports by Schmal and coworkers^{2–4}, cobalt supported on niobia (Nb_2O_5) has gained considerable interest due to its notably high selectivity towards C_{5+} . Furthermore, the Co/ Nb_2O_5 system shows great activity per unit weight of cobalt and markedly increases turnover frequencies upon noble metal promotion^{5–8}.

Niobia as support has been reported to be effective for cobalt Fischer–Tropsch catalysts solely in the crystalline form. Generally, this crystalline niobia has a very low specific pore structure compared to typical Fischer–Tropsch supports (e.g. SiO_2 and $\gamma-Al_2O_3$), limiting the application of high metal loadings. Therefore, crystalline niobia with higher porosity would allow higher cobalt loadings and dispersion. Several methods have been reported for the synthesis of porous Nb_2O_5 ⁹. However, despite the higher porosity obtained, most of these methods have basic disadvantages to be applied in large-scale support synthesis. Expensive and highly reactive precursors were involved^{10–12} (e.g. $NbCl_5$, $Nb(OEt)_5$, copolymers) or the resulting Nb_2O_5 had low crystallinity and high acidity^{13–14}. In order to be used as Fischer–Tropsch support material, where large quantities are necessary, a simple and efficient method is required. Contrary to the common Nb_2O_5 crystalline form, amorphous niobium oxide hydrate ($Nb_2O_5 \cdot nH_2O$) has a mesoporous structure with relatively high specific pore volume and specific surface area. However, due to its acidic properties, niobium oxide hydrate is reactive towards cobalt salts during catalyst preparation, leading to formation of inactive species for Fischer–Tropsch synthesis. Niobium oxide hydrate can be effectively used as precursor for niobia via thermal crystallization at temperatures greater than 500 °C as has been shown by Schmal and co-workers^{2–4}. This thermal treatment however decreases considerably porosity and specific surface area.

Here we report the influence of niobia crystal phase, porosity and cobalt loading on the catalysts' structure and performance in Fischer–Tropsch synthesis. Sucrose impregnation, polymerization and pyrolysis over the niobium oxide hydrate surface was employed in order to maintain the porosity during crystallization. This facile method resulted in a crystalline niobia material which preserved a great fraction of the mesoporous structure of the niobium oxide hydrate. The material was used as support to prepare cobalt catalysts and tested for the Fischer–Tropsch synthesis. These catalysts showed high cobalt-specific catalytic activity and good C_{5+} selectivity, furthermore due to the higher cobalt loading the catalyst weight-based activity was markedly higher.

3.2 Experimental

Synthesis. Niobium oxide hydrate ($Nb_2O_5 \cdot nH_2O$, HY-340, AD/4465) was obtained from Companhia Brasileira de Metalurgia e Mineração – CBMM. Thermal treatment of niobium

oxide hydrate was performed in stagnant air, air flow or N₂ flow.

Mesoporous crystalline niobia (Nb₂O₅-MC): The support was prepared starting from niobium oxide hydrate (Nb₂O₅•*n*H₂O, HY-340, AD/4465, 75 - 150 μm), which was firstly dried under dynamic vacuum. Thereafter it was impregnated with a sucrose aqueous solution (0.25 g·cm⁻³), using equal amounts of sucrose and Nb₂O₅•*n*H₂O (m/m).

In order to polymerize and pyrolyze the sucrose, the impregnated niobium oxide hydrate was heated in a tubular furnace under N₂ flow at 150 °C for 2 h (5 °C·min⁻¹). The sample was then heated to 600 °C for 2 h (20 °C·min⁻¹) under N₂ flow. The obtained sample, a black uniform powder, was left to cool down to room temperature. Finally, the carbon was burned off at 400 °C for 4 h (5 °C·min⁻¹) in 30 vol.% O₂/N₂ flow.

The cobalt catalysts were prepared using incipient wetness impregnation of niobium oxide hydrate calcined at temperatures between 120 °C and 600 °C or Nb₂O₅-MC. Prior to impregnation the supports (75 – 150 μm grains) were dried under vacuum at 80 °C for 1 h. The impregnation was performed with aqueous solution of Co(NO₃)₂•6H₂O (Acros, 99 %), where the concentration depended on the pore volume of the support used and the target metal loading. Multiple impregnations were necessary to achieve Co loadings larger than 6 wt.% for niobia with low specific pore volume. In the next step, the catalysts were dried for 12 h at 60 °C in stagnant air and subsequently calcined for 2 h at 350 °C (3 °C·min⁻¹) in a fixed bed reactor under N₂ flow. Metal loadings were defined as the mass of metallic cobalt per gram of reduced catalyst.

Characterization. Powder X-ray diffractograms were measured using a Bruker-AXS D2 Phaser X-ray diffractometer, Co-Kα radiation (λ = 1.789 Å). For calcined catalysts Co₃O₄ crystallite size was calculated using the Scherrer equation (k = 0.9) to the (311) diffraction line at 2θ = 43.0° or (220) diffraction line at 2θ = 36.5°. In situ XRD was measured using a Bruker-AXS D8 Advance X-ray diffractometer, Co-Kα radiation (λ = 1.789 Å). The sample was heated to 350 °C (2 h, 5 °C·min⁻¹) in 25 vol% H₂/He. A micromeritics TriStar 3000 apparatus was used to perform N₂-physisorption at -196 °C. Prior to analysis the sample was dried at either at 120 or 200 °C for 16 h in N₂ flow. Specific surface area was calculated using the BET theory for p/p₀ = 0.06 – 0.25. The pore size distribution was determined using the BJH theory applied to the adsorption branch. The specific mesopore volume was calculated using single point at p/p₀ = 0.98. Thermogravimetric analysis was performed using a TGA Q50 equipment, around 20 mg of sample were placed in a platinum crucible under 60 cm³·min⁻¹ air flow and heated until 400 °C (15 °C·min⁻¹) for 4 h thereafter heated until 1000 °C (15 °C·min⁻¹), 40 cm³·min⁻¹ N₂ flow was used as reference. Temperature programmed reduction (TPR) analyses were performed using a Micromeritics Autochem 2990 instrument, where 100 mg sample were dried at 120 °C for 1 h in Ar flow followed by reduction from room temperature up to 1000 °C (10 °C·min⁻¹) in a 5 vol% H₂/Ar flow. Bright field transmission electron microscopy (TEM) imaging was performed using a Tecnai 12 operated at 120 kV. Scanning transmission electron microscopy (STEM-EDX) images were acquired with a Philips Tecnai-20 FEG (200 kV) microscope equipped with an energy dispersive X-ray (EDX) and high-angle annular dark-field (HAADF) detector.

Catalytic testing. Low pressure catalytic testing was performed in a quartz glass plug-flow reactor, typically loaded with 15–20 mg catalyst (38–150 μm) diluted with 200 mg SiC. Typically, the catalysts were reduced in situ at 350 $^{\circ}\text{C}$ (5 $^{\circ}\text{C}\cdot\text{min}^{-1}$, 2h) in a 20/40 $\text{cm}^3\cdot\text{min}^{-1}$ H_2/Ar flow. Fischer-Tropsch catalysis was performed at 220 $^{\circ}\text{C}$, 1 bar, $\text{H}_2/\text{CO} = 2.0$ v/v, GHSV = 24000 - 48000 h^{-1} , CO conversion < 5 %. C1–C18 products were analyzed by online gas chromatography (Varian 430 GC, CP sil-5 column). Activity and selectivities were reported after at least 40 hours on stream. High pressure catalytic testing was performed using an Avantium Flowrence 16 parallel, continuous flow, fixed bed reactor system. Typically, 100 mg catalyst (38–150 μm) were diluted with 300 mg SiC and loaded in a stainless-steel reactor. The catalysts were reduced in situ at atmospheric pressure in a 25 vol% H_2/He flow, for 8 h at 350 $^{\circ}\text{C}$ (heating rate of 1 $^{\circ}\text{C}\cdot\text{min}^{-1}$). Thereafter, reactors were cooled down to 180 $^{\circ}\text{C}$ and the gas stream was switched to synthesis gas, $\text{H}_2/\text{CO} = 2.0$ v/v, GHSV 4500 h^{-1} . Reactors were pressurized to 20 bar and subsequently heated to reaction temperature 220 $^{\circ}\text{C}$ (1 $^{\circ}\text{C}\cdot\text{min}^{-1}$), CO conversion was maintained at 15–25 %. Products up to C9 were analyzed using online gas chromatography. GHSV was defined as total gas flow divided by the catalyst volume.

3.3 Results and discussion

3.3.1 Niobium oxide hydrate thermal treatment

Niobium oxide hydrate was characterized by powder X-ray diffraction (XRD) and N_2 -physisorption after the different thermal treatments. Niobium oxide hydrate remained amorphous after stagnant air calcination in a muffle oven up to 400 $^{\circ}\text{C}$ (Figure 3.1a). Crystallization started after calcination at 500 $^{\circ}\text{C}$, transforming the material into low-crystalline pseudo-hexagonal Nb_2O_5 TT-phase. Calcination at temperatures above 600 $^{\circ}\text{C}$ led to the orthorhombic Nb_2O_5 T-phase, as indicated by the splitting of the peaks at $2\theta = 33^{\circ}$ and 42° . Monoclinic Nb_2O_5 phase was observed after calcination at 900 $^{\circ}\text{C}$ ^{15–17}.

Increase in calcination temperature changed as well the niobia morphology (Figure 3.1b). Niobium oxide hydrate after drying at 120 $^{\circ}\text{C}$ had a BET specific surface area

Figure 3.1 a, X-ray diffractograms for niobium oxide hydrate calcined in stagnant air at 400, 500, 700 and 900 $^{\circ}\text{C}$. b, change in specific surface area (black circles) and specific pore volume (red squares) of niobium oxide hydrate upon temperature increase.

and specific mesopore volume of $173 \text{ m}^2\cdot\text{g}^{-1}$ and $0.19 \text{ cm}^3\cdot\text{g}^{-1}$ respectively, as determined by N_2 -physisorption. Upon increasing calcination temperature these values decreased. In particular, after crystallization at 600°C the specific surface dropped to $9 \text{ m}^2\cdot\text{g}^{-1}$ and the specific mesopore volume to $0.05 \text{ cm}^3\cdot\text{g}^{-1}$.

The porosity of niobium oxide hydrate after drying at 120°C consisted mainly of 2–5 nm mesopores as indicated by the hysteresis at $p/p_0 = 0.4\text{--}0.7$ (Figure 3.2) and TEM images (Appendix B: Figure B1), these mesopores were maintained up to 400°C . After crystallization at 600°C most of the mesopores had collapsed and only hysteresis at $p/p_0 = 0.9$ was observed, indicative for larger pores ($> 50 \text{ nm}$). These macropores originated from the Nb_2O_5 interparticle space. Table 3.1 summarizes the characterization results for the different materials.

Figure 3.2 N_2 -physisorption isotherms (a) and pore size distributions (b) for niobium oxide hydrate treated in the temperature range 120 to 600°C .

3.3.2 Modified niobia crystallization

Stagnant air, air flow or N_2 flow were used during niobia crystallization at 600°C to study the effect of different gas atmospheres and hydrodynamics. For all cases, pseudo-hexagonal niobia TT-phase was obtained with BET specific surface areas of $22\text{--}25 \text{ m}^2\cdot\text{g}^{-1}$ (Table 3.1). Calcination in stagnant air led to a higher specific mesopore volume ($0.11 \text{ cm}^3\cdot\text{g}^{-1}$) than after calcination in N_2 or air flow ($0.06 \text{ cm}^3\cdot\text{g}^{-1}$).

In order to inhibit porosity loss during crystallization, the niobium oxide hydrate pores were filled with sucrose as carbon precursor prior thermal treatment. Niobium oxide hydrate was impregnated with a sucrose solution, which polymerized by the acidic properties of the oxide and thermal treatment at 150°C . After pyrolysis and crystallization at 600°C , the obtained black powder showed the pseudo-hexagonal Nb_2O_5 TT-phase (Figure 3.3a) and a decrease in specific mesopore volume ($0.08 \text{ cm}^3\cdot\text{g}^{-1}$) which might indicate a blockage of the niobia pores by carbon. Thermogravimetric analysis (TGA) in air of this material shows most of the weight loss after 4 h at 400°C (Appendix B: Figure B2), indicating that carbon can be effectively removed under these conditions. After carbon was burned off the obtained crystalline material has a mesopore volume of $0.16 \text{ cm}^3\cdot\text{g}^{-1}$ with a specific surface area of $56 \text{ m}^2\cdot\text{g}^{-1}$. Figure 3.3b shows the pore size distribution of niobium oxide hydrate

Table 3.1 Summary of the characterization results (XRD and N₂-physisorption) for niobia after the different treatments.

Crystallization conditions	Crystal phase	Specific Surface Area (m ² ·g ⁻¹)	Specific Mesopore Volume (cm ³ ·g ⁻¹)	Pore Diameter (nm)
Niobium oxide hydrate thermal treatment				
120 °C, stagnant air, muffle oven	amorphous	173	0.19	2-5
400 °C, stagnant air, muffle oven	amorphous	86	0.12	2-7
600 °C, stagnant air, muffle oven	pseudo-hexagonal TT	9	0.05	> 50
700 °C, stagnant air, muffle oven	hexagonal T	6	0.01	> 50
900 °C, stagnant air, muffle oven	monoclinic H	1	<0.01	> 50
Modified niobia crystallization				
600 °C, stagnant air, quartz reactor	pseudo-hexagonal TT	25	0.11	5-60
600 °C, air flow, quartz reactor	pseudo-hexagonal TT	22	0.06	5-25
600 °C, N ₂ flow, quartz reactor	pseudo-hexagonal TT	22	0.06	5-25
Nb ₂ O ₅ -MC	pseudo-hexagonal TT	56	0.16	2-12

Figure 3.3 **a**, X-ray diffractograms for the niobium oxide hydrate (red), low pore volume niobia (brown), niobia after sucrose pyrolysis (grey) and mesoporous niobia (pink). **b**, Pore size distribution for the initial material (niobium oxide hydrate, red) and the crystalline materials: Nb₂O₅ calcined at 600 °C (brown) and Nb₂O₅-MC (pink).

dried at 120 °C, crystallized at 600 °C and the mesoporous crystalline niobia (Nb₂O₅-MC). Despite the template used not all of the mesopores from niobium oxide hydrate could be maintained during the treatment; however, their collapse was retarded compared to normal crystallization at 600 °C. Dark field STEM images of these two crystalline materials are shown in figure 3.4. Clearly the niobia crystallized at 600 °C without template has a dense structure whereas for Nb₂O₅-MC a more porous structure is observed.

Figure 3.4 Dark field STEM images of the crystalline materials: **a**, dense Nb_2O_5 obtained by calcination at 600 °C and **b**, porous Nb_2O_5 -MC obtained by sucrose impregnation, pyrolysis and calcination

3.3.3 Cobalt deposition

Deposition of cobalt on the support was performed by incipient wetness impregnation method. Niobium oxide hydrate calcined at 120 °C or 600 °C was used as support and deposition of cobalt was performed by single or multiple impregnation (4 – 21 wt.%) followed by drying and calcination at 350 °C. XRD showed no crystalline cobalt species up to 10 wt.% independently of the support used, i.e. amorphous or crystalline niobia. Co_3O_4 was observed only on the calcined samples with >13 wt.% Co (Figure 3.5). Furthermore, samples supported on crystalline niobia were reduced in situ (25 vol.% H_2/He , 350 °C) and still no cobalt species were observed for the low loadings (Figure 3.5b). This indicates that for low cobalt loadings poorly crystalline cobalt species, very small crystallite sizes or Co-Nb oxide species were formed independently of the niobia pretreatment, in line with previous reports¹⁸.

Figure 3.5 X-ray diffractograms of the calcined cobalt catalysts supported on (a) amorphous niobium oxide hydrate or (b) crystalline niobia pretreated at 600 °C. The symbols indicate diffraction peaks corresponding to Co_3O_4 (★), Nb_2O_5 T-phase (◆) and Co^0 (●).

The support used, amorphous or crystalline niobia, had a strong impact on the reduction of the cobalt species as shown by the temperature programmed reduction profiles (Figure 3.6). The reduction on crystalline niobia proceeded in two steps as previously reported: from Co_3O_4 to CoO and from CoO to metallic Co ^{18–20}. The reduction temperature is significantly lower if compared with γ -alumina- or silica-supported cobalt catalysts, therefore reduction can be effectively performed at temperatures lower than 400 °C without noble metal promotion. In contrast, cobalt supported on amorphous $\text{Nb}_2\text{O}_5 \cdot n\text{H}_2\text{O}$ showed no distinctive reduction peaks until temperatures greater than 450 °C (Figure 3.6). A continuous H_2 consumption is observed throughout temperature increase, attributed to reduction of the support. This different reduction profile can be attributed to a stronger interaction between cobalt and niobium oxide hydrate. Most likely no Co_3O_4 was formed after impregnation and calcination but rather Co-Nb oxide species which cannot be easily reduced.

The mesoporous crystalline niobia ($\text{Nb}_2\text{O}_5\text{-MC}$) was used as support for 6 and 10 wt.% Co, prepared by incipient wetness impregnation. Due to the larger specific pore volume of $\text{Nb}_2\text{O}_5\text{-MC}$, a higher metal loading could be achieved in a single impregnation step. In general, characterization of niobia-supported catalysts using TEM in the dark or bright

Figure 3.6 Temperature programmed reduction profiles for two catalysts after impregnation, drying and calcination: 5 wt.% cobalt supported on crystalline niobia (treated at 600 °C, brown line) and 10 wt.% cobalt supported on amorphous niobium oxide hydrate (treated at 120 °C, red dashed line).

field has the challenge of phase distinction between Co_3O_4 and $\text{Nb}_2\text{O}_5\text{-MC}$ due to their similar electron density. Therefore, electron microscopy combined with EDX mapping is an important and powerful technique for the characterization of this kind of materials. Figure 3.7 shows the STEM-EDX mapping images of the $\text{Nb}_2\text{O}_5\text{-MC}$ -supported catalysts and for comparison purposes a 6 wt.% Co supported on pretreated Nb_2O_5 at 600 °C. STEM-EDX mapping images were taken after reduction at 350 °C and passivation. A comparison of the $\text{Nb}_2\text{O}_5\text{-MC}$ -supported catalysts (Figure 3.7 a and b) shows that the 6 wt.% Co catalyst had smaller particles (9.7 ± 3.3) than the 10 wt.% Co (13.9 ± 6.5), which is expected for higher metal loadings. Still these two catalysts show a smaller particle size if compared to the one supported on the dense niobia calcined at 600 °C (15.6 ± 4.3 , Figure 3.7 c and d). The porous morphology of $\text{Nb}_2\text{O}_5\text{-MC}$ is suggested to restrict particle growth during reduction.

Figure 3.7 STEM-EDX mapping images of cobalt catalysts after reduction and passivation. Cobalt is shown in red and the support in grey. **a**, Nb₂O₅-MC supported catalysts with 6 wt.% Co and **b**, 10 wt.% Co. **c**, 6 wt.% Co catalyst supported on niobia pretreated at 600 °C. **d**, Histogram from the particle size measurement.

3.3.4 Catalytic performance

Prepared catalysts were investigated for the Fischer–Tropsch reaction at 1 bar, 220 °C and H₂/CO = 2 to obtain activity and selectivity data (Table 3.2). 5 wt.% Co supported on crystalline niobia (pretreated at 600 °C) was reduced prior to reaction conditions at 350 °C, cobalt-weight normalized activity (Cobalt-Time-Yield, CTY = $3 \cdot 10^{-5} \text{ mol}_{\text{CO}} \text{g}_{\text{Co}}^{-1} \text{s}^{-1}$) and C₅₊ selectivity (~70 wt.%) were observed after 40 h on stream similar to results observed previously for promoted Co/SiO₂ catalysts²¹. Reduction at 500 °C prior to reaction led to 10 times decrease in CTY. Since niobia is a reducible support, SMSI effects by reducing at higher temperatures are expected and have been observed previously by Silva et al.³. Catalysts supported on amorphous niobium oxide hydrate showed low catalytic activity (Table 3.2), this might be due to formation of irreducible cobalt species on this support as shown by TPR. Encapsulation of cobalt in the mesopores (2-5 nm) of this material during catalyst preparation or catalytic testing might have also led to inaccessibility of the active sites. The amorphous form of niobia appears too reactive thereby inhibiting activation of cobalt for the Fischer–Tropsch reaction and thus crystalline niobia is required to obtain active cobalt catalysts.

Catalysts prepared by multiple impregnations showed a decrease in CTY and C₅₊ selectivity by increasing the cobalt loading (Figure 3.8). Considering the low specific surface area of the support, small interparticle distance at higher cobalt loadings can lead to parti-

Table 3.2 Summary of the catalytic results for the Fischer–Tropsch reaction at 1 or 20 bar, 220 °C and $H_2/CO = 2$

Support ^a	Number of Impregnations	Co loading (wt.%)	Cobalt-Time-Yield ^b ($10^{-5} \text{ mol}_{\text{Co}} \text{ g}_{\text{Co}}^{-1} \text{ s}^{-1}$)	C_{5+} selectivity (wt.%)
Amorphous $Nb_2O_5 \cdot nH_2O$ (120 °C)	2	10	< 0.3	45
Amorphous $Nb_2O_5 \cdot nH_2O$ (400 °C)	1	5	0.5	49
	1	5	3.0	70
	2	10	2.5	64
Crystalline Nb_2O_5 (600 °C)	3	15	2.2	60
	4	17	1.5	55
	4	21	2.1	42
	1	6	4.5 (20 bar)	80 (20 bar)
	1	6	4.2 (20 bar) 2.1 (1 bar)	80 (20 bar) 64 (1 bar)
Nb_2O_5 -MC	1	10	3.7 (20 bar) 2.0 (1 bar)	81 (20 bar) 65 (1 bar)

a. In brackets the calcination temperature of the support

b. Catalysts tested at 20 bar are indicated and the value reported is after 100h TOS, if not indicated catalysts were tested at 1 bar and 40h TOS.

cle growth and sintering. In a similar way, larger particles lead to a decreased Co- Nb_2O_5 interface, where the chain growth probability is larger, therefore decreasing the C_{5+} selectivity⁵.

Nb_2O_5 -MC supported catalysts were tested both at 1 and at 20 bar, 220 °C and $H_2/CO = 2$. Results are shown on table 3.2. For comparison purposes, a 6 wt.% cobalt catalyst with niobia treated at 600 °C as support was also tested at high pressure. The catalytic activity normalized per catalyst weight (Weight Time Yield, WTY) tested at 20 bar is shown in figure 3.9a. Clearly the 10 wt.% Co/ Nb_2O_5 -MC catalyst (red triangles) outperforms the 6 wt.% Co catalysts because of the higher metal content. The 6 wt.% Co/ Nb_2O_5 -MC catalyst (pink circles) shows a slightly lower WTY than the 6 wt.% Co/ Nb_2O_5 (pretreated at 600 °C, brown squares) at the initial hours of the experiment, however after 70 hours on stream its steady deactivation lead to the same activity as the Nb_2O_5 -MC supported catalyst. Figure 3.9b shows the CTY through time on stream, the three catalysts reach virtually the same value after 100 hours on stream. The catalyst supported on Nb_2O_5 treated at 600 °C shows a more pronounced deactivation throughout time compared with the Nb_2O_5 -MC supported catalysts. One of the main causes of deactivation for cobalt Fischer–Tropsch catalysts is particle sintering. It is possible to think that the porous structure of the Nb_2O_5 -MC support has retarded the cobalt particles from sintering, leading to more stable catalysts during long time on stream. In contrast, the flat surface of Nb_2O_5 treated at 600 °C allows particle growth and decrease in catalytic activity with time. The three catalysts showed a similar C_{5+} selectivity of ~80 % during the catalytic experiments (Appendix B: Table B1).

Figure 3.8 Cobalt-weight normalized activity (CTY) and C_{5+} selectivity for the Fischer–Tropsch reaction (1 bar, 220 °C and $\text{H}_2/\text{CO} = 2$). Cobalt was deposited by multiple impregnations (loadings ≥ 10 wt.%) on crystalline niobia pretreated at 600 °C.

Figure 3.9 Catalytic activity up to 100 hours on stream for Co supported on crystalline niobia (20 bar, 220 °C and $\text{H}_2/\text{CO} = 2$). **a**, Activity normalized per catalyst weight (Weight Time Yield, WTY) and **b**, activity per unit weight of cobalt (Cobalt Time Yield, CTY).

3.4 Conclusions

The pore structure of amorphous niobium oxide hydrate was determined to be intricate with 2–5 nm mesopores giving rise to high specific surface and pore volume. Collapse of this pore structure during thermal treatment led to a drastic decrease in specific surface area and specific mesopore volume. For the synthesis of active cobalt Fischer–Tropsch catalysts, niobia crystallization at temperatures above 400 °C prior to cobalt deposition was found necessary to allow formation of reducible cobalt oxide species. Consequently, no activity was observed for the Fischer–Tropsch synthesis using amorphous niobia as support. Contrastingly, cobalt supported on crystalline niobia prepared by impregnation and reduced at 350 °C prior reaction conditions showed remarkably high activity per unit weight of cobalt and C_{5+} selectivity, previously only observed for promoted Co catalysts. Higher reduction temperature (500 °C) significantly decreased the catalyst activity, probably due to coverage of the cobalt surface sites due to SMSI effects. The maximum cobalt loading achievable

in a single impregnation was 6 wt. % by using crystalline niobia as support. A decrease in activity per unit weight of cobalt was observed by increasing the cobalt loading using multiple impregnations, due to formation of larger cobalt particles and decreased interaction of cobalt with the support. Additionally, this decreased cobalt-support interaction suppressed the beneficial effect of niobia on C_{5+} selectivity. A facile carbon deposition method was used to restrict the collapse of the niobium oxide hydrate porous structure during crystallization. The carbon on the surface acted as structural template at the high temperatures needed to obtain crystalline niobia. The resulting crystalline niobia displayed an important fraction of the mesopores from the niobium oxide hydrate. The porous niobia was used as support to prepare cobalt catalysts and further tested in industrially relevant conditions for the Fischer–Tropsch synthesis. These catalysts proved to be highly active and selective. The porous structure allowed higher cobalt loadings leading to an increased weight-normalized catalytic activity. Furthermore, this porosity prevented the cobalt particles from sintering, resulting in very stable catalysts. STEM-EDX mapping characterization made possible to determine cobalt particle size and distribution in the catalysts, this technique demonstrated to be a powerful tool to study systems where phase distinction between its components is difficult due to similar electron density.

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4 Activity Enhancement of Cobalt Catalysts by Tuning Metal-Support Interactions

Interactions between metal nanoparticles and support materials can strongly influence the performance of catalysts. In particular, reducible oxidic supports can form sub-oxides that can decorate metal nanoparticles and enhance catalytic performance or block active sites. Therefore, tuning this metal-support interaction is essential for catalyst design. Here, we investigate reduction-oxidation-reduction (ROR) treatments as a method to affect metal-support interactions and related catalytic performance. Controlled oxidation of pre-reduced cobalt on reducible (TiO_2 and Nb_2O_5) and irreducible ($\alpha\text{-Al}_2\text{O}_3$) supports leads to the formation of hollow cobalt oxide particles. The second reduction results in a twofold increase in cobalt surface area only on reducible oxides and proportionally enhances the cobalt-based catalytic activity during Fischer-Tropsch synthesis at industrially relevant conditions. Such activities are usually only obtained by noble metal promotion of cobalt catalysts. ROR proves an effective approach to tune the interaction between metallic nanoparticles and reducible oxidic supports, leading to improved catalytic performance.

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4.1 Introduction

Metal particles catalyze major chemical processes, including the synthesis of bulk chemicals and transportation fuels^{1–4}. The catalytic reactions that are involved occur mainly at the metal surface. Therefore, the surface-to-volume ratio of these particles is typically maximized through nanosizing, leading to an adequate exposure of the active sites and efficient utilization of the metal^{5,6}. Supports play a critical role in stabilizing the reactive nanoparticles but also in generating new interphase phenomena, such as electron transfer or shape rearrangement^{7–9}. These phenomena can have ambivalent consequences for the catalytic performance such as promoting activity and selectivity or blocking active sites, which decreases the catalyst efficiency.

A renowned example of support effects occurs when reducible metal oxide supports (TiO_2 , Nb_2O_5 , CeO_2 , etc.) are partially reduced by hydrogen spillover from the metal nanoparticle¹⁰, i.e. the so-called strong metal-support interaction (SMSI)^{11,12}. As a result, suboxide species are generated from the support and these may migrate onto the metal nanoparticles surface^{13–16}. In the case of cobalt catalysts for the Fischer-Tropsch (FT) synthesis, i.e. the conversion of synthesis gas (H_2/CO) into ultra clean fuels and chemicals, the effect of SMSI is twofold. On one hand, the cobalt catalysts benefit from the mildly Lewis acidic character of the suboxide species, as it increases the intrinsic activity (turnover frequency, TOF) and selectivity towards C_{5+} products^{17,18}. The increased TOF is believed to originate from the interface between the metal and suboxide where the CO-dissociation rate is enhanced^{19–21}. On the other hand, the catalytic activity can be lowered by a dense overlayer of suboxide species that block the access to the active sites¹⁴. The interplay between promotion of the catalytic performance and blockage of active sites is not clear and control over the metal-support interactions may thus provide an opportunity to increase the number of accessible, promoted active sites.

The SMSI state can be reversed by oxidative treatments. However, this reversibility has been mainly studied for noble metals, while reports of base metals are scarce^{12,22–24}. Soled et al.²⁵ studied the impact of SMSI on H_2 -chemisorption for cobalt nanoparticles supported on titania. The H_2 -uptake was initially suppressed because of site blockage but increased significantly after a reduction-oxidation-reduction (ROR) treatment. This brought H_2 -chemisorption and TEM and XRD results into closer agreement, but the effect of ROR on the structure of the cobalt particles as well as its implications for catalysis remained unclear. Besides reversal of the SMSI state, ROR has been applied to regenerate deactivated catalysts through re-dispersion of the active metal^{26–29}. The work on catalyst regeneration focused, however, on cobalt catalysts supported on irreducible oxides, such as Al_2O_3 and SiO_2 , in which SMSI effects do not play a role.

In this work, we investigate the possibility to tune the metal-support interactions of cobalt supported on reducible metal oxides via reduction-oxidation-reduction treatments with the aim to enhance the catalytic activity in the Fischer-Tropsch synthesis. To this end, Co/TiO_2 and $\text{Co}/\text{Nb}_2\text{O}_5$ are synthesized and subjected to ROR treatments. Co on irreducible $\alpha\text{-Al}_2\text{O}_3$ is prepared for comparison. After the first reduction, oxidation above 100 °C

leads to the formation of hollow cobalt oxide particles. Upon re-reduction, the H_2 -uptake doubles for the reducible metal oxides due to optimization of the SMSI state and not by cobalt re-dispersion, while the H_2 -uptake decreases for $\alpha\text{-Al}_2\text{O}_3$. The modified metal-support interaction on reducible supports drastically enhances the catalytic activity under industrially relevant FT conditions, effectively doubling the number of available active sites without changing their TOF. Modulation of the metal-support interaction via ROR is thus a promising strategy to boost the catalytic performance and to greatly improve the efficiency of metal catalysts supported on reducible oxides.

4.2 Experimental

Synthesis. The samples were synthesized by incipient wetness impregnation using aqueous cobalt nitrate solutions. The precursor solutions were prepared by dissolving appropriate amounts of cobalt nitrate hexahydrate (99+ %, Acros Organics) in Milli-Q water to obtain 6 wt.% cobalt loading on each catalyst. The supports, TiO_2 (P25, Evonik, SA_{BET} : $50 \text{ m}^2\cdot\text{g}^{-1}$, PV: $0.30 \text{ cm}^3\cdot\text{g}^{-1}$), Nb_2O_5 (pseudo-hexagonal TT-phase, CBMM, SA_{BET} : $9 \text{ m}^2\cdot\text{g}^{-1}$, PV: $0.06 \text{ cm}^3\cdot\text{g}^{-1}$) and $\alpha\text{-Al}_2\text{O}_3$ (BASF, SA_{BET} : $7 \text{ m}^2\cdot\text{g}^{-1}$, PV: $0.02 \text{ cm}^3\cdot\text{g}^{-1}$), were sieved to a grain size of 75-150 μm . Nb_2O_5 was obtained from amorphous niobium oxide hydrate (HY-340, AD/4465, CBMM) by calcination in a muffle oven at 600 $^\circ\text{C}$ for 4 h.

For a typical impregnation, 2 g of support was pre-dried at 80 $^\circ\text{C}$ for 1 h under vacuum. Just before the impregnation, the vacuum was released and a pore filling amount of precursor solution was added dropwise to the support under magnetic and manual stirring. In the case of Co/TiO_2 , 2 g of sample was dried and heat treated in fluidized bed mode in a U-shaped glass reactor following a previously reported procedure³⁰. The sample was first dried at 80 $^\circ\text{C}$ for 2 h and heat treated directly afterwards at 250 $^\circ\text{C}$ for 2 h. Both steps were performed in $1 \text{ L}\cdot\text{min}^{-1}$ N_2 upward flow with a heating ramp of 2 $^\circ\text{C}\cdot\text{min}^{-1}$. $\text{Co}/\text{Nb}_2\text{O}_5$ and $\text{Co}/\alpha\text{-Al}_2\text{O}_3$ catalysts were dried for 12 h at 60 $^\circ\text{C}$ overnight in stagnant air and subsequently calcined in a fixed bed reactor under N_2 flow ($1 \text{ L}\cdot\text{min}^{-1}$) at 350 $^\circ\text{C}$ for 2 h with a heating ramp of 3 $^\circ\text{C}\cdot\text{min}^{-1}$. Multiple batches of 2 g were mixed to obtain a substantial amount of sample. The obtained samples were pressed and sieved to a grain size of 75-150 μm .

Ex situ reduction-oxidation (RO) treatments were performed in U-shaped glass reactors. To this end, batches of 500 mg were first reduced at 350 $^\circ\text{C}$ for 2 h (2 $^\circ\text{C}\cdot\text{min}^{-1}$) in $120 \text{ mL}\cdot\text{min}^{-1}$ of 25 vol.% H_2 in N_2 and subsequently cooled to 100 $^\circ\text{C}$. At this point, the reactor was flushed with N_2 and cooled down further to 30 $^\circ\text{C}$. The oxidation step followed directly after the reduction and was performed in $95 \text{ mL}\cdot\text{min}^{-1}$ of 5 vol.% O_2 in N_2 at various temperatures up to 400 $^\circ\text{C}$ for 2 h with a 2 $^\circ\text{C}\cdot\text{min}^{-1}$ heating ramp.

Characterization. Scanning transmission electron microscopy combined with high-angle annular dark-field (STEM-HAADF) and energy-dispersive X-ray spectroscopy (EDX) analyses were performed on an FEI Talos F200X. This microscope was equipped with a high-brightness field emission gun (X-FEG) and a Super-X G2 EDX detector and operated at 200 kV. The EM samples were prepared by suspending the samples in 2-propanol (>99.9 %, Sig-

ma-Aldrich) using sonication and dropcasting the suspension on a carbon-coated Cu grid (200 mesh). The cobalt particle size was determined using the iTEM software and at least 200 particles were analyzed. The reduced and passivated samples were corrected for a 3 nm CoO layer and the particle surface averaged diameters ($D[3,2]$) were calculated.

H₂-chemisorption was measured on a Micromeritics ASAP 2020C using ~200 mg of sample. The catalysts were reduced in pure H₂ prior to the measurement. The pristine samples were reduced for 2 h (1 °C·min⁻¹) at 350 °C, while the RO-samples were reduced at 220 °C. After reduction, the samples were evacuated, cooled to 150 °C and analyzed at that temperature. The metallic surface area and average particle diameter were calculated assuming a cobalt cross-sectional area of 0.0662 nm², an H/Co stoichiometry of 1 and spherical cobalt particles³¹.

Inductively coupled plasma-optical emission spectroscopy (ICP-OES) was performed on a SPECTRO ARCOS. The samples were prepared by extraction of cobalt using aqua regia.

Temperature-programmed reduction (TPR) profiles were measured using a Micromeritics Autochem 2920, equipped with a TCD detector. Typically, 100 mg sample was reduced up to 1000 °C with 5 °C·min⁻¹ in a flow of 5 vol.% H₂ in Ar. To determine the degree of reduction, the samples were first reduced in the TPR setup in a flow of pure H₂ for 2 h at 350 °C or 220 °C depending of the stage in the ROR treatment and then, the TPR profile was recorded from 50 to 800 °C in a flow of 5 vol.% H₂ in Ar. The cobalt that had not been reduced was quantified from the areas of the peaks between 250 and 700 °C.

Fischer-Tropsch synthesis. The catalytic performance was measured using an Avantium Flowrence 16 parallel reactor setup. Stainless steel reactors (ID = 2 mm) were loaded with 75-100 mg of catalyst (75-150 µm) and diluted with 100 mg SiC (212-425 µm). Prior to reaction, the catalysts were reduced in situ for 8 h (1 °C·min⁻¹) in 25 vol.% H₂ in He at 1 bar. The pristine samples were reduced at 350 °C, while the RO-samples were reduced at 220 °C. After reduction, the temperature was lowered to 180 °C (3 °C·min⁻¹) and the pressure was increased to 20 bar under H₂ flow. Finally, synthesis gas with H₂/CO = 2 V/V (5 vol.% He as internal standard) was introduced and the temperature was raised to 220 °C with 1 °C·min⁻¹. The product stream was analyzed online with an Agilent 7890A GC. The hydrocarbon products were analyzed on an Agilent J&W PoraBOND Q column connected to an FID. The permanent gasses were separated on a ShinCarbon ST column and quantified using a TCD.

The activity of the catalysts was expressed as CO conversion, cobalt time yield (CTY) and turnover frequency (TOF). The CO conversion was defined according to equation 1, CTY according to equation 2 and TOF according to equation 3:

$$X_{CO} = (F_{CO,in} - F_{CO,out}) \cdot F_{CO,in}^{-1} \quad (\text{Equation 1})$$

$$CTY = F_{CO,in} \cdot X_{CO} \cdot V_m^{-1} \cdot m_{Co}^{-1} \quad (\text{Equation 2})$$

$$TOF = CTY \cdot N_A \cdot d_{Co} \cdot SA_{Co}^{-1} \quad (\text{Equation 3})$$

In these equations, X_{CO} is the CO conversion, $F_{CO,in}$ is the flow of CO into the reactor and $F_{CO,out}$ is the flow of CO in the product stream. V_m denotes the molar volume, m_{Co} the mass of cobalt in the reactor, N_A is the Avogadro constant, d_{Co} the cross-sectional area of a cobalt atom (0.0662 nm² according to ref. 31) and SA_{Co} is the cobalt specific surface area as obtained by H₂-chemisorption.

The selectivity towards light hydrocarbon products with carbon number n (with $1 \leq n \leq 4$) was calculated as in equation 4 and the selectivity towards the heavier fraction ($n \geq 5$) as in equation 5

$$S_{C1-C4} = F_{Cn} \cdot n \cdot (F_{CO,in} \cdot X_{CO})^{-1} \quad (\text{Equation 4})$$

$$S_{C5+} = 1 - S_{C1-C4} \quad (\text{Equation 5})$$

In this case, S_{Cn} represents the selectivity towards hydrocarbon product of a specific carbon number and F_{Cn} is the flow of the corresponding hydrocarbon product.

4.3 Results and discussion

4.3.1 Reduction

Cobalt particles supported on reducible oxides TiO₂ and Nb₂O₅, and on irreducible oxide α -Al₂O₃ were prepared by incipient wetness impregnation followed by drying and thermal treatment. The nominal cobalt loading was 6 wt.% and experimentally determined loadings are given in Table C1 (Appendix C). H₂-chemisorption analysis was performed on the pristine samples, which were reduced at 350 °C prior to the measurement (referred to as R-samples). After H₂-chemisorption, the samples were passivated by exposure to air at room temperature and subsequently analyzed using scanning transmission electron micros-

Table 4.1 The results of cobalt particle size analyses using STEM-EDX and H₂-chemisorption for the pristine samples after reduction at 350 °C (R-samples) and the samples after reduction at 350 °C, oxidation at 200 °C and reduction at 220 °C (RO200R-samples).

Sample	Particle diameter D[3,2] ^a ± standard deviation (nm)	Theoretical H ₂ -uptake ^a ($\mu\text{mol}_{\text{H}_2} \cdot \text{g}_{\text{Co}}^{-1}$)	Experimental H ₂ -uptake ^b ($\mu\text{mol}_{\text{H}_2} \cdot \text{g}_{\text{Co}}^{-1}$)
R-samples			
R-TiO ₂	11 ± 3.4	787	341
R-Nb ₂ O ₅	19 ± 10	437	265
R-Al ₂ O ₃	13 ± 6.5	666	631
RO200R-samples			
RO200R-TiO ₂	10 ± 3.8	865	783
RO200R-Nb ₂ O ₅	18 ± 7.9	470	657
RO200R-Al ₂ O ₃	21 ± 11	412	499

a. Derived from STEM-EDX

b. Derived from H₂-chemisorption

Figure 4.1 Electron microscopy images of the samples upon reduction-oxidation-reduction treatments. STEM-EDX mapping of Co/TiO₂, Co/Nb₂O₅ and Co/ α -Al₂O₃ at various stages of the ROR treatment. Co is depicted in yellow, Ti in blue, Nb in red and Al in violet. **a, b, c**, Samples after reduction at 350 °C and passivation (R-Samples); **d, e, f**, samples after reduction at 350 °C and oxidation at 200 °C (RO200-samples); **g, h, i**, samples after reduction at 350 °C, oxidation at 200 °C and reduction at 220 °C (RO200R-samples) and passivation. The scale bar corresponds to 100 nm. Additional electron microscopy results for these samples can be found in Appendix C: Figures 1-3.

copy-energy-dispersive X-ray spectroscopy (STEM-EDX, Figure 4.1a-c). The cobalt particles were rather uniformly distributed over TiO₂ and Nb₂O₅ while the spatial distribution was more heterogeneous on α -Al₂O₃.

H₂-chemisorption and STEM-EDX results for the R-samples are given in Table 4.1. The theoretical H₂-uptake was calculated for cobalt particles using the surface-average particle diameter derived from STEM-EDX images. This theoretical value was compared to the experimental uptake measured by H₂-chemisorption. In the case of R-TiO₂ and R-Nb₂O₅, a substantial discrepancy in H₂-uptake was observed between both methodologies. This is explained by partial coverage of the metallic cobalt surface by suboxide species leading to suppressed uptake in the H₂-chemisorption measurement. It is important to note that the total amount of suboxide species is probably low, because no overlays could be detected

with STEM-EDX nor with in situ TEM of $\text{Co}/\text{Nb}_2\text{O}_5$ under reducing conditions in a previous study³². No large discrepancy between the theoretical and experimental H_2 -uptake of $\text{R-Al}_2\text{O}_3$ was observed, because suboxides were not formed.

4.3.2 Reduction-oxidation

After the first reduction treatment at 350 °C, the R-samples were subjected to an oxidative treatment at temperatures varying between 30 °C and 400 °C (referred to as RO30- to RO400-samples). The temperature-programmed reduction (TPR) profiles of pristine $\text{Co}_3\text{O}_4/\text{Nb}_2\text{O}_5$ and RO30- Nb_2O_5 to RO400- Nb_2O_5 are shown in Figure 4.2a. The pristine sample displayed two-step, consecutive reduction from Co_3O_4 to CoO (280-300 °C) and from CoO to Co (300-400 °C). Samples that had been reduced and oxidized at temperatures up to 100 °C showed only one sharp reduction peak at 230 °C corresponding to the reduction of CoO . Therefore, the second reduction of these samples can be performed at substantially lower temperature than the first one. Based on the amount of consumed H_2 , we found that some metallic cobalt was still present on those samples, probably as a metallic core covered by a CoO layer. Further increasing the oxidation temperature to 150 °C led to broadening of the narrow peak (RO150- Nb_2O_5) and eventually resulted in a two-step reduction profile, associated with the formation of Co_3O_4 during oxidation (RO200- Nb_2O_5). Upon oxidation at 400 °C, the reduction profile resembled that of the pristine $\text{Co}_3\text{O}_4/\text{Nb}_2\text{O}_5$ sample.

The RO-samples were characterized by STEM-EDX mapping. Samples oxidized at

Figure 4.2 The effect of the oxidation temperature on the structure of $\text{Co}/\text{Nb}_2\text{O}_5$. **a**, Temperature-programmed reduction profiles, **b**, schematic illustration and **c**, STEM-EDX images of $\text{Co}/\text{Nb}_2\text{O}_5$ after reduction and oxidation at various temperatures (30-400 °C). Co is depicted in yellow, Nb in red. The scale bar corresponds to 100 nm.

low temperatures appeared unchanged (Figure 4.2b,c). However, at oxidation temperatures of 200 °C, hollow cobalt oxide particles were observed (Figure 4.1d-f). The formation of these hollow particles was ascribed to the Kirkendall effect^{33–35}. During oxidation, an initial oxide layer forms around the metallic particle and at higher temperature, the smaller Co^{2+} or Co^{3+} cations diffuse outwards through the oxide layer faster than the larger O^{2-} anions diffuse inwards, forming shells of cobalt oxide leaving behind empty cores. At an oxidation temperature of 400 °C, the hollow cobalt oxide particles got distorted and agglomerated.

4.3.3 Reduction-oxidation-reduction

The samples after an ROR cycle were characterized by H_2 -chemisorption (Figure 4.3a). The second reduction of the ROR treatment was performed at 220 °C, whereas the R-samples had been reduced at 350 °C. For the reducible oxides, the H_2 -uptake significantly increased at oxidation temperatures above 100 °C. In the case of TiO_2 , it changed from $341 \mu\text{mol}_{\text{H}_2} \cdot \text{g}_{\text{Co}}^{-1}$ for R-TiO₂ to $783 \mu\text{mol}_{\text{H}_2} \cdot \text{g}_{\text{Co}}^{-1}$ for RO200R-TiO₂. Similarly, for Nb_2O_5 it increased from $265 \mu\text{mol}_{\text{H}_2} \cdot \text{g}_{\text{Co}}^{-1}$ for R-Nb₂O₅ to $657 \mu\text{mol}_{\text{H}_2} \cdot \text{g}_{\text{Co}}^{-1}$ for RO200R-Nb₂O₅. On $\alpha\text{-Al}_2\text{O}_3$ however, a substantial decrease of H_2 -uptake was observed after ROR treatments. The degree of reduction (DOR) was determined by TPR directly after the last reduction for all R- and RO200R-samples and for RO400R-Nb₂O₅ (Appendix C: Figure C4 and Table C2). The DOR for the R-samples was 97–98 % and decreased slightly to 84–95 % after ROR. Because these changes were minor, the H_2 -chemisorption results were not corrected for the DOR.

The particle sizes of the RO200R-samples were investigated using STEM-EDX (Figure 4.1g-i). The spatial distribution of the particles over the supports was not markedly different from that in the R-samples (Figure 4.1a-c). Furthermore, the average size of the cobalt particles was similar to that of the R-samples, despite the significantly different values obtained by H_2 -chemisorption (Figure 4.3b-d, Table 4.1). In fact, the theoretical H_2 -uptake now approached the values of the experimental H_2 -uptake.

On TiO_2 , the increase in H_2 -uptake with a similar average particle size implied that ROR did not induce substantial re-dispersion of cobalt. Rather, the ROR treatment resulted in a higher fraction of accessible metallic cobalt surface through a decrease of the surface coverage by suboxide species (Figure 4.3e). On Nb_2O_5 , however, the situation is more complex, because the experimental H_2 -uptake after ROR was higher than the theoretical one. The additional H_2 -uptake could be rationalized in two ways. First, re-dispersion of few large cobalt particles could have formed small particles, which would be undetectable by STEM-EDX. Second, hydrogen could have spilled over to Nb_2O_5 , in line with the fact that Nb_2O_5 has been proven to facilitate hydrogen storage^{36,37}. On $\alpha\text{-Al}_2\text{O}_3$, the same Kirkendall behavior occurred at oxidation temperatures above 100 °C (Figure 4.1f), but here the H_2 -uptake decreased on all ROR-samples due to particle growth.

ROR has been reported to regenerate deactivated catalysts through re-dispersion of the active metal via the Kirkendall effect^{26–29}. However, the work on catalyst regeneration focused on cobalt catalysts supported on irreducible oxides, such as Al_2O_3 and SiO_2 , in which SMSI effects do not play a role. Furthermore, we ascribe the absence of net re-dispersion

Figure 4.3 The effect of ROR treatments on the exposed cobalt surface area and particle size. **a**, Hydrogen uptake for Co/TiO₂ (blue squares), Co/Nb₂O₅ (red circles) and Co/ α -Al₂O₃ (violet triangles) after various reduction-oxidation-reduction treatments, as determined by H₂-chemisorption. The results of the pristine samples after reduction at 350 °C (open symbols) are included at 0 on the x-axis. **b,c,d**, Particle size distributions of cobalt supported on TiO₂, Nb₂O₅ and α -Al₂O₃, respectively, after reduction at 350 °C (open bars) and after reduction at 350 °C followed by oxidation at 200 °C and reduction at 220 °C (solid filled bars), as determined by STEM-EDX. **e**, Schematic illustration of the effect of the ROR treatment on cobalt supported on reducible oxides.

in our samples to different initial cobalt particle sizes. The particles in our R-TiO₂ (11 nm) and R-Al₂O₃ (13 nm) were substantially smaller than those reported in literature (22 nm)²⁹. According to Sadasivan et al.³⁸, only cobalt particles above a certain critical size give rise to re-dispersion upon ROR treatments.

The trends observed with H₂-chemisorption for the reducible oxides can be understood based on the previously discussed results. The Kirkendall effect was most likely key in tuning the SMSI during ROR, because at oxidation temperatures up to 100 °C, where this effect was not observed, the increase in H₂-uptake was minor. The H₂-uptake only increased significantly when the Kirkendall effect took place. On the other side of the optimum, at an oxidation temperature of 400 °C, the high temperature induced particle growth from 10 up to 15 nm for RO400R-TiO₂, as determined using STEM-EDX (Appendix C: Figure C5). This

reduced the metallic surface area and counteracted the positive effect of the ROR treatment on the SMSI.

Further indications for the optimization of SMSI effects through ROR were found when the second reduction was performed at a higher temperature (Figure 4.4). The H_2 -uptake decreased for the RO200R-TiO₂ and RO200R-Nb₂O₅ samples with increasing reduction temperature. At 350 °C, the H_2 -uptake values returned to the values of the initial R-samples that were reduced once. Apparently, the mild temperature of the second reduction was essential to keep the concentration or mobility of the suboxide species low, while it was sufficiently high to reduce cobalt oxide to metallic cobalt. Additionally, the H_2 -uptakes of the R-samples at reduction temperatures of 220 and 350 °C were comparable. The substantial increase in H_2 -uptake for the RO200R-samples was thus not merely caused by reduction at lower temperature. In contrast, the H_2 -uptake of the Co/ α -Al₂O₃ catalysts increased slightly at higher reduction temperatures.

Figure 4.4 The influence of the temperature of the second reduction on the exposed cobalt surface area. **a**, Hydrogen uptake as a function of the second reduction temperature. Dashed bars correspond to the pristine samples after reduction at 220 or 350 °C and solid filled bars correspond to the samples after reduction at 350 °C followed by oxidation at 200 °C and reduction at 220 or 350 °C. **b**, Schematic illustration of the effect of the reduction temperature on catalysts supported on reducible oxides.

4.3.3 Fischer-Tropsch synthesis

The catalytic activity of Co/TiO₂ and Co/Nb₂O₅ in FT after ROR followed the same trend as H_2 -chemisorption, i.e. increased activity with the optimum at 200 °C (Figure 4.5a). Notably, the activity doubled on TiO₂ and Nb₂O₅ as a result of the RO200R treatment and the enhancement was stable over at least 100 h time-on-stream (Appendix C: Figure 6). As expected, the activity of Co/ α -Al₂O₃ was not enhanced, indicating that the positive effect of the ROR treatment was specific for catalysts supported on reducible oxides. The C₅₊-selectivity for all catalysts was 85-89 % and did not change significantly as a result of the ROR

Figure 4.5 The effect of the ROR treatment on the catalytic activity in the Fischer-Tropsch synthesis. FT was performed at 20 bar, 220 $^{\circ}\text{C}$, $\text{H}_2/\text{CO} = 2 \text{ V/V}$, GHSV = 1000–13000 h^{-1} , time-on-stream = 90–100 h, CO conv. = 15–34 % (TiO_2), 17–25 % (Nb_2O_5), 8–12 % (Al_2O_3). **a**, Cobalt-weight-based catalytic activity of Co/TiO_2 (blue squares), $\text{Co}/\text{Nb}_2\text{O}_5$ (red circles) and $\text{Co}/\text{Al}_2\text{O}_3$ (violet triangles) after various reduction-oxidation-reduction treatments. The activity of the pristine samples after reduction at 350 $^{\circ}\text{C}$ (R-samples, open symbols) is included at 0 on the x-axis. **b**, Cobalt-weight-based activity as a function of H_2 -uptake for the R-samples (open symbols) and the samples after reduction at 350 $^{\circ}\text{C}$ followed by oxidation between 30–400 $^{\circ}\text{C}$ and reduction at either 220 $^{\circ}\text{C}$ (filled symbols) or at 250 $^{\circ}\text{C}$ (dashed symbols); values for the turnover frequencies (TOF) have been calculated from the slopes of the lines.

treatments (Appendix C: Table C3).

The observed cobalt-weight-based activities of RO200R- TiO_2 ($16 \cdot 10^{-5} \text{ mol}_{\text{CO}} \cdot \text{g}_{\text{Co}}^{-1} \cdot \text{s}^{-1}$) and RO200R- Nb_2O_5 ($8.9 \cdot 10^{-5} \text{ mol}_{\text{CO}} \cdot \text{g}_{\text{Co}}^{-1} \cdot \text{s}^{-1}$) are exceptionally high. Compared to literature^{18,32,39–43}, activities in this range are normally only achieved by promoting a cobalt-based catalyst with noble metals (Appendix C: Figure C7). Tuning of the metal-support interactions by ROR or other pretreatments might thus provide an attractive alternative to promotion with expensive and scarce noble metals.

The ROR treatments increased the catalytic activity of Co/TiO_2 and $\text{Co}/\text{Nb}_2\text{O}_5$ with respect to the R-samples. The increase in activity was proportional to the H_2 -uptake (Figure 4.5b), indicating that the surface-specific activity or turnover frequency (TOF, based on activity and H_2 -chemisorption data) was constant and more surface sites with identical characteristics became available. The opposite was observed with irreducible $\alpha\text{-Al}_2\text{O}_3$, where the activity decreased after ROR and less surface sites were available albeit at constant TOF. Clearly, the TOF was support-dependent and increased in the order $\alpha\text{-Al}_2\text{O}_3 < \text{Nb}_2\text{O}_5 < \text{TiO}_2$.

The high TOF values for the reducible oxides show that Co surface sites were promoted by TiO_x or NbO_x in the R- and ROR-samples. In addition, the TOF was independent of ROR, meaning that ROR did not change the nature of the promoted active sites. Therefore, the enhanced cobalt-weight-based activity of Co/TiO_2 and $\text{Co}/\text{Nb}_2\text{O}_5$ implied that the number of promoted active sites increased as a result of ROR. Furthermore, the effect of the second reduction temperature on the activity is included as well in Figure 4.5b for $\text{Co}/\text{Nb}_2\text{O}_5$. Reduction at 250 $^{\circ}\text{C}$ gave only a moderate increase in H_2 -chemisorption and a corresponding increase in activity, while reduction at 220 $^{\circ}\text{C}$ doubled the H_2 -uptake and activity.

Although the TOF of cobalt catalysts has been reported to be support independent^{39,44}, recent publications have shown that the promoting effect of the support can be

substantial^{17,18,21,32}. This promoting effect on the TOF has been related to the Lewis acidity of the metal oxide: an increase in acidity leads to an increase in TOF^{17,18}. The Lewis acid character of oxidic materials originates from exposed metal centers⁴⁵, meaning that the structural arrangement and oxidation state of the ions will determine their acid strength⁴⁶. Jeong et al.⁴⁷ have recently reported an acidity scale based on the intramolecular charge transfer energy between organic molecules and several metal oxides (Appendix C: Table C4). The values reported for the supports used in our work do predict higher TOF for TiO₂ and Nb₂O₅ compared to Al₂O₃, but the comparison between TiO₂ and Nb₂O₅ requires further analysis. As mentioned before, Lewis acidity depends on the oxidation state of the cation, thus values for lower oxidation states in suboxides (e.g. Ti³⁺, Nb⁴⁺ or Nb³⁺) gain importance for reducible metal oxides as shown in the work of Boffa et al.^{21,48}. Because the oxidation state and structural arrangement of the relevant suboxides are not completely established, the formal Lewis acidity remains uncertain.

4.4 Conclusions

In summary, reduction-oxidation-reduction (ROR) treatments were investigated as a tool to tune metal-support interactions in supported cobalt catalysts to improve their performance in the Fischer-Tropsch synthesis. Reduction of cobalt oxide supported on reducible (TiO₂ and Nb₂O₅) and irreducible (α -Al₂O₃) oxides followed by controlled oxidation led to hollow cobalt oxide particles via the Kirkendall effect. A second reduction resulted in a twofold increase in H₂-uptake for the TiO₂- and Nb₂O₅-supported samples and a decrease for the α -Al₂O₃-supported sample. This effect was attributed to modulation of the metal-support interactions rather than re-dispersion of the cobalt phase. The modified metal-support interactions greatly increased the catalytic activity in the Fischer-Tropsch synthesis, as the activity doubled on TiO₂ and Nb₂O₅ and decreased slightly on α -Al₂O₃. This increased activity was caused by more accessible cobalt surface sites as revealed by the constant turnover frequency, while preserving the full promotional effect of the TiO_x or NbO_x species. The more efficient utilization of the cobalt and support interphase led to exceptionally active catalysts. Tailoring of metal-support interactions via ROR treatments is thus an effective method to improve the activity of metal catalysts supported on reducible oxides.

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5 Cobalt-Nickel Nanoparticles Supported on Reducible Oxides as Fischer-Tropsch Catalysts

Efficient and more sustainable production of transportation fuels is key to fulfill the ever-increasing global demand. In order to achieve this, progress in the development of highly active and selective catalysts is fundamental. The combination of bimetallic nanoparticles and reactive support materials offers unique and complex interactions that can be exploited for improved catalyst performance. Here, we report on cobalt-nickel nanoparticles on reducible metal oxides as support material for enhanced performance in the Fischer-Tropsch synthesis. For this, different cobalt to nickel ratios (Ni/(Ni+Co): 0.0, 0.25, 0.50, 0.75 or 1.0 at/at) supported on reducible (TiO_2 and Nb_2O_5) or non-reducible ($\alpha\text{-Al}_2\text{O}_3$) oxides were studied. At 1 bar, Co-Ni nanoparticles supported on TiO_2 and Nb_2O_5 showed stable catalytic performance, high activities and remarkably high selectivities for long-chain hydrocarbons (C_{5+} , ~80 wt.%). In contrast, catalysts supported on $\alpha\text{-Al}_2\text{O}_3$ independently of the metal composition showed lower activities, high methane production and considerable deactivation throughout the experiment. At 20 bar, the combination of cobalt and nickel supported on reducible oxides allowed for 25 to 50 % cobalt substitution by nickel with increased Fischer-Tropsch activity and without sacrificing much C_{5+} selectivity. STEM-EDX and IR of adsorbed CO pointed to a cobalt enrichment of the nanoparticle's surface and a weaker adsorption of CO in Co-Ni supported on TiO_2 and Nb_2O_5 and not on $\alpha\text{-Al}_2\text{O}_3$, modifying the rate determining step and the catalytic performance. Overall, we show the strong effect and potential of reducible metal oxides as support materials for bimetallic nanoparticles for enhanced catalytic performance.

Hernández Mejía, C., van der Hoeven, J. E. S., de Jongh, P. E. & de Jong, K. P. Cobalt-nickel nanoparticles supported on reducible oxides as Fischer-Tropsch catalysts. *ACS Catal.* **10**, 7343–7354 (2020).

5.1 Introduction

The increasing demand for transportation fuels has stimulated the diversification of their sources and encouraged research towards efficient production^{1,2}. Liquid fuels in particular have been widely employed due to their high energy density and convenience to handle³. Fuels produced from processes such as gas-to-liquids (GTL) or coal-to-liquids (CTL) have emerged as an attractive alternative to the traditional fuels derived from crude oil. The GTL and CTL processes allow feedstock diversification and generate ultra-clean fuels. A crucial step in GTL and CTL is the catalytic transformation of synthesis gas (a mixture of carbon monoxide and hydrogen) to hydrocarbons, also known as the Fischer-Tropsch (FT) synthesis. The competitiveness of FT, and therefore the GTL and CTL processes, heavily rely on highly productive and stable catalysts. Finding materials with improved FT catalytic performance is highly desirable.

The FT synthesis is a complex reaction that is typically catalyzed by late-transition metals in the metallic or carbidic form. Current research has shown that the rate-controlling step in such catalytic surfaces need a balance between CO dissociation, water removal, chain growth and chain-growth termination for an optimal FT performance⁴⁻⁶. However, no single metal surface displays these characteristics concurrently⁴. Bimetallic systems hold potential to bring about unique catalytic properties distinct from those of the individual metals⁷⁻¹⁰.

Nowadays, cobalt-based FT catalysts are employed in GTL due to their selectivity towards long-chain hydrocarbons (C_{5+}), low water-gas-shift activity, stable performance and costs^{11,12}. Considering these characteristics, iron, nickel or copper are potential candidates to form bimetallic catalysts with cobalt. Taking into account the industrial FT conditions, that is temperatures between 200-250 °C and pressures 10-40 bar, CO dissociation on copper is not favored and thus Co-Cu systems can be employed for the synthesis of alcohols¹³⁻¹⁵. Iron under FT conditions often favors the formation of iron carbide that might lead to segregation in Co-Fe systems and loss of possible bimetallic synergy^{16,17}. Finally, nickel can readily dissociate CO and form stable Co-Ni alloys, making it an attractive option. However, the risks exist of lower C_{5+} selectivity due to high hydrogenation activity and concomitant methane production and decreased stability due to formation of volatile nickel tetracarbonyl¹⁸. Indeed, in most previous reports a compromise between activity and C_{5+} selectivity has been observed for Co-Ni-based FT catalysts, although a common feature has been the utilization of non-reducible supports, such as silica, alumina or zirconia¹⁹⁻²⁴. Early work of Arai et al.²⁵⁻²⁸ has shown that the nature of the support has important consequences for the FT performance of Co-Ni catalysts; they observed differences in catalytic performance from supports with contrasting electronegativities but similar performance of reducible and non-reducible supports.

The interaction between metal nanoparticles and the support has become a prominent tool in the design of catalysts with enhanced performance^{29,30}. For bimetallic nanoparticles, the interaction with the support can as well lead to various and usually complex phenomena that strongly affect their catalytic performance³¹⁻³⁵. The understanding of such interactions is often difficult. One of the phenomena that arises from the interaction of

mono- and bimetallic nanoparticles supported on reducible metal oxides (e.g. TiO_2 , Nb_2O_5 , CeO_2 , etc.) is the so-called strong metal-support interaction (SMSI)^{36,37}. This phenomenon takes place upon partial reduction of the support at the periphery of the metal nanoparticle, leading to the generation of mobile suboxide species (e.g. TiO_x , NbO_x) that partially cover the surface of the metal nanoparticle. In FT, reducible oxidic supports have a major influence on the catalyst performance^{38,39}. The mild Lewis acidity of the suboxides is known to promote the intrinsic surface-specific catalytic activity (turnover frequency, TOF) and selectivity towards C_{5+} products⁴⁰. The increased TOF is believed to originate at the interphase between the suboxides and the metal where an enhanced CO adsorption and rate of hydrogenation occurs^{41,42}. Tuning this interaction can lead for instance to cobalt-based catalysts with enhanced FT activities⁴³ and in the case of nickel-based catalysts, SMSI can be employed to suppress the formation of nickel tetracarbonyl and enhance the selectivity towards longer-hydrocarbons^{44,45}. Hence, improvement can be achieved by careful selection of the components in the Co-Ni catalytic system, particularly of the support material.

In this research, we investigated the effect of cobalt substitution by nickel on supported FT catalysts and the influence of the support nature on the catalytic behavior of the metals. Several characterization techniques, in particular IR spectroscopy of adsorbed CO, were employed to elucidate the effect of combining cobalt and nickel on the different supports. At 1 bar, the Co-Ni samples displayed increased activities and C_{5+} selectivities, up to doubling the activity compared to the monometallic catalysts. Contrastingly, $\alpha\text{-Al}_2\text{O}_3$ -supported catalysts had for all Co-Ni compositions lower metal-normalized activities and higher selectivities towards methane. Moreover, these catalysts deactivated severely throughout the experiment in contrast to the more stable TiO_2 - and Nb_2O_5 -supported catalysts. Increasing synthesis gas pressure to 20 bar benefited the activity and selectivity of the samples supported on reducible oxides with high cobalt content, and with similar C_{5+} selectivities as the monometallic cobalt-based catalysts. Reducible oxides used as support material strongly modified the reactivity of alloys, opening new possibilities for more efficient catalysts in general.

5.2 Experimental

Synthesis. Niobia (Nb_2O_5) and titania (TiO_2) were employed as reducible supports. Nb_2O_5 was obtained by crystallization of niobium oxide hydrate ($\text{Nb}_2\text{O}_5 \cdot n\text{H}_2\text{O}$, HY-340, AD/4465 provided by Companhia Brasileira de Metalurgia e Mineração – CBMM). Crystallization was carried out in stagnant air at 600 °C (5 °C·min⁻¹, 4 h). The obtained Nb_2O_5 had a pseudo-hexagonal TT-phase, a specific surface area of 9 m²·g⁻¹ and a specific mesopore volume of 0.05 cm³·g⁻¹. TiO_2 had a rutile phase, a specific surface area of 11 m²·g⁻¹ and a specific mesopore volume of 0.04 cm³·g⁻¹. Alpha-alumina ($\alpha\text{-Al}_2\text{O}_3$) was employed as non-reducible support and supplied by BASF in the form of extrudates. The $\alpha\text{-Al}_2\text{O}_3$ consisted of only alpha-phase with specific surface area of 7 m²·g⁻¹ and specific mesopore volume of 0.02 cm³·g⁻¹. Support materials were crushed and sieved (75 – 150 µm grains) prior to catalyst preparation.

The supported metal catalysts were prepared using the incipient wetness impreg-

nation method. First, 2.0 g of support material were dried under vacuum at 80 °C for 1 h, thereafter the impregnation was performed at room temperature with a 4.2 M aqueous solution with the appropriate cobalt-nickel ratio. The aqueous solutions were prepared using $\text{Ni}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$ (Acros, 99+%) and/or $\text{Co}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$ (Acros, 99+%) in Milli-Q water. After impregnation, the materials were dried at 60 °C ($5\text{ }^\circ\text{C}\cdot\text{min}^{-1}$, 2 h) in a fixed bed reactor under N_2 flow and subsequently calcined at 350 °C ($3\text{ }^\circ\text{C}\cdot\text{min}^{-1}$, 2 h). Metal loadings were defined as the total mass of metallic Ni and/or Co per gram of reduced catalyst, resulting in total metal loadings of 6 – 8 wt.% (Appendix D: Table D1). The total metal loading per support was chosen in order to maintain similar metal loadings per unit surface area within all the samples. In this way, the metal distribution over the different supports is expected to be similar. The metal composition is expressed as Ni/(Ni+Co) atomic ratio and the ratios studied were: 0.0, 0.25, 0.5, 0.75 and 1.0 at/at.

Characterization. Temperature programmed reduction (TPR) analyses were performed using a Micromeritics Autochem 2990 instrument, where typically 50 mg of sample (75 – 150 μm grains) were dried at 120 °C for 1 h in Ar flow followed by reduction from room temperature up to 600 °C ($5\text{ }^\circ\text{C}\cdot\text{min}^{-1}$) in a 5 vol.% H_2/Ar flow.

Bright field transmission electron microscopy (TEM) and dark field scanning transmission electron microscopy (STEM-EDX) images were acquired at a FEI Talos F200X microscope operated at 200 kV equipped with 4 energy dispersive X-ray (EDX) detectors, a high-angle annular dark-field (HAADF) and a bright field detector. The reduced and subsequently passivated samples for the microscopy analysis were prepared by suspending the catalysts in 2-propanol (>99.9 %, Sigma-Aldrich) using sonication and drop casting the suspension on a Cu TEM grid (200 mesh copper (100), Formvar/carbon film). The metal particle size measurements and Co-Ni distribution cross-section analyses were carried out using the ImageJ⁴⁶ software by analyzing at least 500 particles. Particle surface average diameters or Sauter mean ($D[3,2]$) were then calculated and corrected for a 2 nm oxide shell. The theoretical H_2 -uptake ($\mu\text{mol}_{\text{H}_2} \cdot \text{g}_{\text{Metal}}^{-1}$) was calculated by first obtaining the specific metallic surface area (SA_{metal} , $\text{m}^2 \cdot \text{g}_{\text{metal}}^{-1}$) from $D[3,2]$ (nm) from TEM and assuming hemispherical particles:

$$\text{SA}_{\text{metal}} = 6 \cdot (10^6 \rho \cdot 10^{-9} D[3,2])^{-1}$$

Where ρ is the density ($8.9\text{ g}\cdot\text{cm}^{-3}$) for cobalt and nickel. Then, assuming an average metal cross-sectional area of 0.0656 nm^2 , a metal to H stoichiometry of 1 and $N_A = 6.0221 \times 10^{23}\text{ mol}^{-1}$:

$$\text{Theoretical } \text{H}_2\text{-uptake} = \text{SA}_{\text{metal}} \cdot (2 \cdot N_A \cdot 10^{-18} \text{metal cross-section area})^{-1}$$

H_2 -chemisorption was measured on a Micromeritics ASAP 2020C using ~100 mg of sample. Prior to the measurement, the sample was reduced in pure H_2 at 350 °C ($5\text{ }^\circ\text{C}\cdot\text{min}^{-1}$, 2 h). The sample was then evacuated, cooled to 150 °C and H_2 -chemisorption was measured at that temperature. Inductively coupled plasma-optical emission spectroscopy (ICP-OES) was performed on a SPECTRO ARCOS in order to establish the cobalt to nickel ratio before

and after catalysis; samples were extracted using aqua regia.

Fourier transform infrared (FTIR) spectroscopy measurements were carried out in a PerkinElmer 2000 instrument, in a specially designed cell fitted with CaF_2 windows. Self-supported catalyst wafers were prepared by applying on a powdered sample a force of 4000 kg for 20 s, yielding a wafer of 1 cm diameter, and < 1 mm thickness. Before dosing CO , the wafer sample was placed in the FTIR cell and reduced using a flow of pure hydrogen at 350 °C ($5\text{ }^\circ\text{C}\cdot\text{min}^{-1}$, 2 h), then at the same temperature the hydrogen flow was stopped and evacuated to $\sim 10^{-5}$ mbar. Thereafter the sample was cooled down to 220 °C under dynamic vacuum and left for one hour. A 10 vol.% CO in He mixture was slowly introduced into the cell until the pressure reached $\sim 10^{-4}$ mbar and allowed to equilibrate for 5 minutes to collect the spectrum. CO/He mixture was slowly further introduced to reach various pressures up to 1 bar and spectra were measured at these different pressures after equilibration for 5 minutes before each measurement. For treatment of the data, the measured spectra were normalized by the total available metal sites per sample as obtained from H_2 -chemisorption. Areas resulting from the deconvolution in the bimetallic samples were normalized to the area of the corresponding monometallic sample.

Fischer-Tropsch synthesis. The low-pressure catalytic performance was assessed in a quartz glass plug-flow reactor, loaded with ~ 20 mg catalyst ($38 - 150\text{ }\mu\text{m}$) diluted with ~ 200 mg SiC ($212 - 425\text{ }\mu\text{m}$). Catalysts were reduced in situ at 350 °C ($5\text{ }^\circ\text{C}\cdot\text{min}^{-1}$, 2h) in an $\text{Ar/H}_2 = 2\text{ v/v}$ flow ($\text{GHSV} = 60000\text{ h}^{-1}$) at 1 bar. After reduction, the sample was cooled down to 220 °C and once the temperature was reached the gas composition was changed to synthesis gas ($\text{H}_2/\text{CO} = 2\text{ v/v}$, $\text{GHSV} = 20000\text{ h}^{-1}$) maintaining 1 bar total pressure. CO conversion was below 5 % and the reaction was carried out for 40 h. C1-C18 products were analyzed by online gas chromatography (Varian 430 GC, CP sil-5 column). After reaction, the synthesis gas flow was changed for argon and the reactor was cooled down to room temperature.

The high-pressure catalytic performance was measured using an Avantium Flowrence 16 parallel reactor setup. Stainless steel reactors ($\text{ID} = 2\text{ mm}$) were loaded with 50-100 mg of catalyst ($38 - 150\text{ }\mu\text{m}$) and diluted with 200 mg of SiC ($212 - 425\text{ }\mu\text{m}$). Prior to reaction, the catalysts were reduced in-situ at 350 °C ($1\text{ }^\circ\text{C}\cdot\text{min}^{-1}$, 8 h) in 25 vol.% H_2 in He at 1 bar. After reduction, the temperature was lowered to 220 °C, 240 °C or 260 °C ($3\text{ }^\circ\text{C}\cdot\text{min}^{-1}$) and the pressure was increased to 20 bar under H_2 flow. Synthesis gas ($\text{H}_2/\text{CO} = 2\text{ v/v}$, 5 vol.% He as internal standard) was then introduced. The product stream was analyzed online with an Agilent 7890A GC, hydrocarbon products were analyzed on an Agilent J&W PoraBOND Q column connected to an FID and the permanent gases were separated on a ShinCarbon ST column and quantified using a TCD.

5.3 Results and discussion

5.3.1 Catalysts characterization

After calcination, samples were characterized by temperature programmed reduction (TPR) under hydrogen flow and the corresponding reduction profiles are shown in

Figure 5.1. Samples containing only cobalt ($\text{Ni}/(\text{Ni}+\text{Co}) = 0.0$ at/at) show two distinctive H_2 -uptake peaks, the first one corresponds to the reduction of Co_3O_4 to CoO and the second one to the reduction of CoO to metallic cobalt. For the reducible supports (Figure 5.1a and b), the first reduction event appears at ~ 250 °C and the second one shows two overlapping peaks which finalize at temperatures around 400-500 °C. The alumina-supported sample shows a first reduction event at 225 °C and reduction is complete at 350 °C (Figure 5.1c). Partial replacement of cobalt with nickel ($\text{Ni}/(\text{Ni}+\text{Co}) = 0.25, 0.5$ and 0.75 at/at) shifted the reduction profiles to lower temperatures, which indicates an influence of the presence of nickel on the cobalt oxide reduction. This influence was more pronounced on the reducible supports than on the non-reducible support. The lowest reduction temperature for the supported cobalt-nickel oxides was observed for the $\text{Ni}/(\text{Ni}+\text{Co}) = 0.75$ at/at sample in the case of the reducible supports and 0.5 at/at for the non-reducible support. Moreover, the intensity of the first reduction step decreased gradually when increasing the cobalt substitution, likely due to the decreased amount of Co^{3+} species. Total substitution of cobalt by nickel ($\text{Ni}/(\text{Ni}+\text{Co}) = 1.0$ at/at) showed a slight increase of the temperatures in the reduction profile of nickel oxide to metallic nickel compared to the bimetallic samples.

Quantification from the reduction profiles revealed a decrease in the molar ratio of H_2 -consumption to metal loading upon replacement of cobalt with nickel (Appendix D: Table D1). For the three supports, monometallic cobalt samples had an H_2/Co molar ratio of 1.4, closely corresponding to a 1.3 ratio expected for the full reduction of Co_3O_4 to metallic Co, and monometallic nickel samples had an H_2/Ni molar ratio of 1.0, which corresponds to the reduction of NiO to Ni. The bimetallic samples showed intermediate values, indicative of a mix of Co^{3+} , Co^{2+} and Ni^{2+} species. Overall, the mixed cobalt and nickel oxides formed after co-impregnation and subsequent calcination displayed lower reduction temperatures than the monometallic samples, particularly in the case of the samples supported on reducible oxides.

Figure 5.1 Temperature Programmed Reduction (TPR) profiles of the Co-Ni oxide samples supported on niobia (a), titania (b) or α -alumina (c). The metal composition $\text{Ni}/(\text{Ni}+\text{Co})$ at/at is indicated for each profile.

Based on the TPR results, samples were treated under hydrogen flow at 350 °C to reduce the cobalt and nickel oxides to the metallic form and thereafter H₂-chemisorption measurements were carried out. Hydrogen uptake results indicate that gradual replacement of cobalt with nickel increased the adsorption of hydrogen (Table 5.1), suggesting an increased metal dispersion over the support. The effect seemed more pronounced for the α -alumina-supported samples. After the experiments, samples were exposed to air at room temperature, analyzed by scanning transmission electron microscopy (STEM) and their metal particles sizes (D[3,2]) were determined (Table 5.1). STEM analyses revealed a gradual decrease in particle size when cobalt was substituted by nickel for all three supports. Figure 5.2 shows a more uniform distribution of the metal nanoparticles over Nb₂O₅ facilitated seemingly by the presence of nickel. The smallest particles were obtained at intermediate Co-Ni compositions, i.e., at Ni/(Ni+Co) of 0.5 at/at for TiO₂ and 0.75 at/at for Nb₂O₅ and α -Al₂O₃. Thus, metal nanoparticle dispersion on the oxidic supports was enhanced by addition of nickel, as suggested by the H₂-chemisorption measurements and in accordance with previous reports^{20,47}.

Theoretical hydrogen uptake was calculated using the corresponding STEM-derived particle sizes (Table 5.1). A comparison between theoretical H₂-uptake and experimental H₂-uptake, obtained from H₂-chemisorption measurements, shows significant discrepancies for the niobia- and titania-supported samples (Table 5.1 and Appendix D: Figure D1a and b). The differences are larger for the niobia-supported samples than for the titania-supported ones and increase with increasing nickel content in the samples. Since Nb₂O₅ and

Table 5.1 Summary of the experimental H₂-uptake determined by H₂-chemisorption measurements and STEM-derived particle diameter (D[3,2]) of the samples after the chemisorption experiments with the corresponding theoretical H₂-uptake based on the particle diameter from STEM.

Support	Ni/(Ni+Co) (at/at)	Experimental H ₂ -uptake ($\mu\text{mol}_{\text{H}_2} \cdot \text{g}_{\text{Metal}}^{-1}$)	Particle diameter D[3,2] (nm)	Theoretical H ₂ -uptake ($\mu\text{mol}_{\text{H}_2} \cdot \text{g}_{\text{Metal}}^{-1}$)
Nb ₂ O ₅	0.0	320	17	491
	0.25	441	13	658
	0.50	452	10	813
	0.75	482	9	912
	1.0	362	10	873
TiO ₂	0.0	464	15	569
	0.25	573	12	700
	0.50	647	9	908
	0.75	622	10	899
	1.0	621	10	857
α -Al ₂ O ₃	0.0	610	13	657
	0.25	731	11	799
	0.50	888	9	967
	0.75	1101	8	1115
	1.0	1056	9	949

Figure 5.2 STEM-EDX of monometallic cobalt (**a** and **b**), bimetallic cobalt-nickel (**c** and **d**, nominal Ni/(Ni+Co) = 0.50 at/at) and monometallic nickel (**e** and **f**) samples supported on niobia after reduction at 350 °C and passivation at room temperature. **a**, **c** and **e** show the dark-field STEM images and **b**, **d** and **f** the same dark-field images overlapped with the corresponding EDX maps for cobalt (shown in red) and nickel (shown in green), the scale bars represent 40 nm.

TiO₂ are both reducible oxides, the discrepancies are ascribed to the strong metal-support interaction (SMSI) effect, which means that suboxides from the support generated upon reduction treatment partially cover the metallic nanoparticles, thus decreasing the available metallic surface area^{36,48}. The niobia-supported nanoparticles were more strongly affected by this than the titania-supported ones. Moreover, the increasing discrepancies with increasing Ni content may point to stronger susceptibility to SMSI for Ni than for Co, or relate to the decrease in particle size⁴⁹. In contrast, the samples supported on α -Al₂O₃, which is a non-reducible support and hence does not display the SMSI effect, showed similar values for theoretical and experimental hydrogen-uptake (Table 5.1 and Appendix D: Figure D1c).

Characterization of metal nanoparticles supported on transition metal oxides by STEM in dark-field or bright-field is difficult due to the similar transition metal atomic number and material density, respectively, of each component (Figure 5.2 **a**, **c** and **e**). Moreover, supported bimetallic nanoparticles pose a challenge to discern the distribution of the individual elements. EDX mapping combined with STEM has therefore become a powerful tool to better study these materials⁵⁰. STEM-EDX of the bimetallic samples after reduction at 350 °C and passivation at room temperature showed that, independently of the metal composition, nickel associated with cobalt (Figures 5.2**d** and Appendix D: Figure D2a-c),

however cobalt was sometimes found without nickel, being more pronounced for the samples with more cobalt ($\text{Ni}/(\text{Ni}+\text{Co}) = 0.25$ at/at). This is better visible at higher magnification as shown in Appendix D: Figure D3a. For the nanoparticles containing both metals, a cross-section analysis of several particles (e.g. Appendix D: Figures D4 and D5) confirmed a homogeneous distribution of cobalt and nickel, implying the formation of a uniform alloy after reduction at 350 °C and passivation. Similar observations were made for the titania- and alumina-supported samples (Appendix D: Figures D6 and D7).

Further characterization by FT-IR spectroscopy with CO as a probe molecule was carried out in order to examine the electronic and structural surface properties of the metals and alloys. After reduction at 350 °C under hydrogen flow of the self-supported catalyst wafer and cooling down to 220 °C under ultra-high vacuum, CO was dosed from $1 \cdot 10^{-4}$ to 100 mbar. Figure D8 in Appendix D shows the spectra in the frequency region between 2250 and 1550 cm^{-1} for various Co-Ni compositions supported on niobia, titania and α -alumina at increasing CO pressures. Examples of the spectra of the niobia-, titania- and α -alumina-supported samples at $1 \cdot 10^{-1}$ mbar CO pressure are as well shown in Figure 5.3. For the monometallic cobalt samples ($\text{Ni}/(\text{Ni}+\text{Co}) = 0.0$ at/at), a single narrow band is observed at low pressures around 1980 cm^{-1} , increasing in intensity upon higher CO pressure, due to higher CO coverages. A second broad band around 1800 cm^{-1} appears at $P_{\text{CO}} = 1 \cdot 10^{-2}$ mbar. According to literature, the narrow band at high wavenumbers can be ascribed to linearly adsorbed CO and the broad band at lower wavenumbers to CO adsorbed in bridged mode^{51–54}. At intermediate pressures ($P_{\text{CO}} = 1$ mbar), a new band next to the linearly adsorbed CO

Figure 5.3 Deconvoluted CO-FTIR spectra of the niobia-, titania- and α -alumina-supported samples at 0.1 mbar CO pressure and at 220 °C. The corresponding $\text{Ni}/(\text{Ni}+\text{Co})$ composition is indicated for each spectrum. Spectra are plotted with a black line and curves from the deconvolution correspond to CO linearly adsorbed on cobalt (red and orange), CO linearly adsorbed on nickel (green), CO adsorbed on bridged mode (light and dark blue) and the resulting curve (dashed yellow).

band appeared around 2060 cm^{-1} , being more clear for the cobalt supported on titania sample. This new band might correspond to CO adsorbed on cobalt in close contact with the support, with a more electropositive character ($\text{Co}^{\text{d}+}$) due to the presence of oxygen at the interface, as previously reported^{51,55,56}.

For the monometallic nickel samples ($\text{Ni}/(\text{Ni}+\text{Co}) = 1.0$ at/at) on the other hand, a narrow band (~ 2020 cm^{-1}) and a broad band (~ 1850 cm^{-1}) are already observed at the lowest CO pressure. Again, the high wavenumber band can be ascribed to CO adsorbed in linear mode and the lower wavenumber band to bridged CO on nickel^{57–59}. Ni appears to favor a CO coordination in bridged mode at low CO surface coverages in line with the appearance of the low-frequency band for nickel at low pressures, in contrast to the cobalt samples. The low work function of nickel and higher valence-electron band occupation result in an interaction with CO dominated by $2\pi^*$ back-donation that favors a bridged coordination⁶⁰. An increased intensity and shift to higher wavenumbers is observed for both bands upon increasing the CO pressure, for the linear-CO band to ~ 2070 cm^{-1} and for the bridge-CO band to ~ 1920 cm^{-1} together with the appearance of a shoulder at slightly higher wavenumbers. Bands corresponding to subcarbonyl species $\text{Ni}(\text{CO})_x$ ($x = 2, 3$), precursors of volatile nickel tetracarbonyl at 2075–2090 cm^{-1} according to literature^{59,61,62}, were not observed at the highest pressure in this set of experiments ($P_{\text{CO}} = 100$ mbar). Thus, loss of nickel during the CO-FTIR measurements is not expected. In the case of the Co-Ni samples various bands emerge upon CO adsorption consisting of a combination of bands from the ones observed for the monometallic samples. Likewise, the bands increased in intensity and shifted to higher frequencies upon increasing the CO pressure.

Deconvolution of the spectra for all Co-Ni compositions supported on niobia, titania and α -alumina at 0.1 mbar CO pressure can be found in Figure 5.3. In order to distinguish between the cobalt and the nickel contributions in the spectra of the bimetallic samples the analysis focused on the linear-CO bands, since the bands corresponding to CO adsorbed in bridge mode were too broad and difficult to assign. The low-pressure spectra were used because at 1 mbar and higher CO pressures the cobalt and nickel contributions overlapped (Appendix D: Figure D8). Moreover, the low CO pressures and relative high temperature of the samples (220 °C) prevent dipole-dipole coupling between adsorbed CO molecules which can influence the CO vibration frequency⁶³. The spectra and corresponding deconvolution at CO pressures lower than 1 mbar can be found in Appendix D: Figures D9 and D10 for niobia- and α -alumina-supported samples. For the bimetallic samples it is possible to distinguish the linear-CO contributions from cobalt (red) and nickel (green). Therefore, the ratio of these areas was used to qualitatively correlate to the surface composition upon interaction with CO. Figure 5.4 shows the change in ratio of the area for cobalt to the area for nickel as a function of CO pressure for samples supported on niobia or alumina. At a CO pressure of 0.001 mbar the ratio was already different for both support materials, the surface composition for the $\alpha\text{-Al}_2\text{O}_3$ -supported samples seems to be rather independent of the overall composition, whereas for the Nb_2O_5 -supported samples their surface composition was more affected by the overall composition. Furthermore, upon increasing the CO pressure the change in area ratio behaved remarkably differently for each support, for

the Nb_2O_5 -supported samples it increased, meaning a more Co-rich surface, while for the $\alpha\text{-Al}_2\text{O}_3$ -supported ones it decreased meaning a tendency towards a Ni-rich surface. Reported heats of adsorption for CO on Co and on Ni show similar values^{64–69}, therefore, a preferred Co or Ni surface segregation upon contact with CO is not expected, indicating in our case that the metal-support interaction is affecting the surface composition of the nanoparticles.

Also changes in frequency were observed for the linear-CO bands as a consequence of Co-Ni composition on the three different supports. Figure D11 in Appendix D shows the wavenumber at maximum absorbance as a function of metal composition for the linear-CO band on cobalt and on nickel at 0.1 mbar. For the band corresponding to CO adsorbed on cobalt, substitution of cobalt by nickel led to a marked increase in the wavenumber. This increase in the C-O stretching frequency corresponds to a stronger C-O bond, due to less back-donation from cobalt in the CO 2π -antibonding orbitals. The change in wavenumber for the band corresponding to CO adsorbed on Ni was less pronounced. The observed wavenumber shifts can then point to a change in the electron density of Ni and in particular Co in the bimetallic samples, indicative of a close Co-Ni contact likely due to formation of alloyed nanoparticles^{57,70,71}.

Figure 5.4 Ratio of the IR band areas of linearly adsorbed CO on cobalt and nickel as a function of CO pressure for bimetallic nanoparticles supported on Nb_2O_5 (a) and $\alpha\text{-Al}_2\text{O}_3$ (b). Measurements were carried out at 220 °C.

5.3.3 Fischer-Tropsch synthesis

The catalysts FT performance was studied at 1 bar total pressure ($\text{H}_2/\text{CO} = 2$ v/v) and 220 °C after in-situ reduction at 350 °C for 2 h. Figure 5.5 shows a summary of the catalytic performance after 40 h-on-stream and comprehensive data can be found in Appendix D, Table D2. The metal-normalized catalytic activity of the titania- and niobia-supported catalysts proved markedly higher than the activity of the α -alumina-supported samples for all metal compositions (Figure 5.5a). Furthermore, a large increase in activity is observed for the Co-Ni catalysts supported on reducible oxides with increasing nickel content, reaching the highest activity at $\text{Ni}/(\text{Ni}+\text{Co}) = 0.75$ at/at. On the other hand, samples supported on α -alumina showed little change upon cobalt substitution by nickel, with a slightly lower

Figure 5.5 Summary of the catalytic performance after 40 h-on-stream at 1 bar ($\text{H}_2/\text{CO} = 2$ v/v) and 220 °C for samples with various cobalt to nickel ratios supported on reducible (Nb_2O_5 and TiO_2) and non-reducible ($\alpha\text{-Al}_2\text{O}_3$) oxides. **a**, Activity normalized by total metal weight loading of bi- and monometallic catalysts supported on reducible and non-reducible oxides. The corresponding selectivities for C_{5+} , $\text{C}_2\text{-C}_4$, and C_1 products are shown in **b**, **c** and **d** respectively.

activity for the nickel-rich samples ($\text{Ni}/(\text{Ni}+\text{Co}) = 0.75$ and 1.0 at/at). Turnover-frequencies (TOFs) followed a similar trend (Appendix D: Table D2), in which cobalt substitution by nickel for titania- and niobia-supported catalysts led to higher TOFs, whereas α -alumina-supported catalysts displayed lower TOFs upon addition of nickel. The selectivities of the catalysts were strongly influenced by the nature of the support and the composition of supported metals (Figure 5.5b-d). Long-chain hydrocarbons (C_{5+}) selectivities surprisingly reached values of around 80 wt.% for the intermediate Co-Ni samples supported on reducible supports, despite the low pressure applied (Figure 5.5b). In turn, C_1 and $\text{C}_2\text{-C}_4$ selectivities were lower in these samples than for the monometallic ones (Figure 5.5c and

d). In stark contrast, α -alumina-supported samples showed low C_{5+} and high C_1 and C_2 - C_4 selectivities for all metal compositions. Independently of the nanoparticles' composition selectivities did not change. Therefore, the exceptionally high C_{5+} selectivities and activities of the catalysts supported on reducible oxides emerged from a combination of nanoparticle composition and nature of the support.

In contrast to our observations, similar FT performance on reducible and non-reducible supports previously reported in the literature²⁷ might originate from the pre-treatment employed, consisting there of a pre-reduction at 400 °C, likely followed by exposure to air and reduction prior catalysis at 250 °C. These conditions might generate, besides Co-Ni segregation⁷², less suboxides from the reducible supports since the SMSI effect is sensible to reduction temperature and oxidative conditions^{36,43,73}. In turn, a decrease of the promotional catalytic effect might have resulted in a similar performance to the non-reducible-supported catalysts.

The enhanced catalytic performance of the bimetallic catalysts supported on reducible oxides can be better understood when considering the observations by CO-FTIR. First, the interaction with CO led to nanoparticles with a surface enriched in cobalt when supported on reducible oxides and not on the non-reducible oxide (Figure 5.4). High initial FT activities have been previously observed when bimetallic nanoparticles have been prepared by sequential impregnation forcing a cobalt-enriched surface, in contrast to the samples with a nickel-enriched surface or the monometallic ones²⁰. Second, we have identified a relationship between the wavenumber of maximum absorbance of linear-CO on cobalt and the corresponding TOF based on the experimental H_2 -uptake (Figure 5.6 and Appendix D: Table D3). The set of samples supported on alpha-alumina showed high TOFs as well as low wavenumber values, indicating a stronger CO adsorption to the metal surface and a weaker C–O bond. Thus, higher TOFs here are tentatively ascribed to faster CO dissociation, proposed to be the rate determining step for the alpha-alumina-supported samples. This is in agreement with the work of Filot et al.⁴, where in their model $Co/\alpha-Al_2O_3$ would fall between a regime controlled by the rate of CO dissociation and oxygen removal and addition of nickel (a less oxophilic metal) might move the rate-controlling step away from the oxygen removal regime to the one controlled by CO dissociation. That results in a carbon coverage and concomitant high methane selectivity characteristic of nickel catalysts⁷⁴. In the case of the titania- and niobia-supported samples, a reverse trend was observed, i.e. higher TOFs coincide with higher wavenumbers of adsorbed CO. We propose that CO here is weakly bonded to the metal surface, allowing a closer to optimal surface hydrogen coverage^{4,28,75}. In contrast to the alpha-alumina catalysts, CO dissociation is no longer the rate determining step for reducible supports, but more likely the hydrogenation of surface carbon. Similar to MnO on cobalt^{76–79}, NbO_x and TiO_x suboxides on the Co-Ni surface might generate active sites with altered effects on the FT mechanism and more specifically accelerate CO dissociation. Following the model of Filot et al.⁴, Co-Ni on reducible supports then diverges from the regime controlled by CO dissociation towards a regime closer to an optimal balance between CO dissociation, carbon hydrogenation and oxygen removal, similar to Ru.

Additionally, the stability of the catalysts was influenced by the support. Figure 5.7

Figure 5.6 Relationship between turn-over-frequency (TOF) and wavenumber of linear-CO on cobalt ($P_{\text{CO}} = 0.1$ mbar) for the Co- and CoNi-based catalysts supported on titania, niobia and alpha-alumina. TOFs were obtained based on the experimental H_2 -uptake derived from H_2 -chemisorption and catalytic activity at 40 h-on-stream (1 bar, $\text{H}_2/\text{CO} = 2$ v/v and 220 °C, Table S3).

shows the relative change in activity during reaction for the different metal compositions supported on niobia, titania and alpha-alumina (**a**, **b** and **c**, respectively). Catalysts containing cobalt and nickel supported on niobia or titania showed similar activity loss as the samples containing only cobalt (~20-25 %), however, the largest activity loss was observed for catalysts containing only nickel, 35 % for Nb_2O_5 and 55 % for TiO_2 . For the $\alpha\text{-Al}_2\text{O}_3$ -supported catalysts the activity loss increased with increasing nickel content relative to cobalt, with the monometallic cobalt sample being the most stable (25 % activity loss) and the monometallic nickel one the least (60 % activity loss). Activity loss in nickel-based catalysts under these conditions is often driven by a decrease of nickel specific surface area due to formation and diffusion of volatile nickel tetracarbonyl from small to large nanoparticles and leading to overall particle growth^{80,81}. Nickel carbonyl formation can be avoided by alloying nickel with another metal or by the SMSI effect with a reducible oxide as support^{44,45,82,83}. This rationalizes the stability of the Co-Ni samples supported on niobia and titania. However, for

Figure 5.7 Relative change in catalytic activity throughout time for samples supported on niobia (**a**), titania (**b**) and alpha-alumina (**c**). Reaction conditions: 1 bar ($\text{H}_2/\text{CO} = 2$ v/v), 220 °C and 40 h-on-stream. Samples were reduced in-situ under hydrogen flow at 350 °C (5 °C·min⁻¹, 2 h) prior to reaction.

the monometallic nickel samples supported on reducible oxides a reduction temperature of 350 °C prior reaction most likely is not high enough to induce a SMSI state capable of completely hampering nickel tetracarbonyl formation⁴⁵, and thus the activity loss.

STEM-EDX of the used niobia-supported Co-Ni catalysts revealed minor changes on the particle size and metal distribution compared to the freshly reduced samples (Appendix D: Figure D2d-f). In the case of the alumina-based catalyst, STEM-EDX of the sample with composition Ni/(Ni+Co) = 0.50 at/at (Appendix D: Figure D6d) showed substantial particle growth, 9 nm for the freshly reduced sample against 32 nm for the sample after FT, and areas with non-uniform cobalt and nickel distribution. The extensive particle growth most likely originated from nickel carbonyl formation and diffusion, leading subsequently to a decrease in the catalytic activity. Metal quantification by EDX and ICP analyses showed that the amount of nickel before and after reaction conditions had not changed (Appendix D: Table D4). This suggests that despite the possible formation of Ni(CO)₄, the conditions (pressure, time, etc.) were not severe enough to remove a measurable quantity of nickel from the catalyst bed at atmospheric pressure, in agreement with previous research⁸¹.

Overall, the catalytic performance results at 1 bar show that the combination of reducible oxides as support material together with bimetallic cobalt-nickel nanoparticles have the potential of highly active, selective and stable Fischer-Tropsch catalysts. Therefore, we focused on these samples and the monometallic cobalt ones (Ni/(Ni+Co) = 0.0, 0.25, 0.50 and 0.75 at/at) to evaluate their catalytic performance at higher pressures. Due to the likely formation of volatile nickel tetracarbonyl already at 1 bar for samples containing only nickel (Ni/(Ni+Co) = 1.0 at/at) and α -Al₂O₃-supported samples containing nickel, experiments at higher pressures were not carried out for these samples to avoid the risk of nickel loss from the catalysts.

The high-pressure Fischer-Tropsch catalytic performance was studied at 220 °C and 20 bar (H₂/CO = 2 v/v) for 100 h-on-stream. The catalytic activity through time is shown in Figure 5.8 for the titania- and niobia-supported catalysts (**a** and **b** respectively). Increase in the reaction pressure to 20 bar largely improved the activity of the monometallic and cobalt-rich samples. Particularly samples containing 25 % nickel (Ni/(Ni+Co) = 0.25 at/at) had an activation period during the first hours of the experiment resulting eventually in the highest metal-normalized activities and turnover-frequencies of the set of samples. Comprehensive data after 100 h-on-stream can be found in Appendix D: Table D2. Similar activation of bimetallic Co-Ni catalysts for FT has been previously observed and attributed to partial segregation of the metals during reaction²⁴. Replacement of 50 % cobalt by nickel (Ni/(Ni+Co) = 0.50 at/at) showed similar activities as the cobalt-based catalysts. However, the nickel-rich samples (Ni/(Ni+Co) = 0.75 at/at) did not show an increase in activity by increasing the reaction pressure and thus became the less active catalysts under these conditions.

Selectivity trends were similar for both support materials, the main changes were observed throughout the reaction depending on the Co-Ni composition (Figure 5.9). Cobalt-rich catalysts showed increased C₅₊ selectivities upon pressure increase. Ni/(Ni+Co) = 0.0 and 0.25 at/at samples presented the highest C₅₊ selectivities with 83 % for TiO₂ and 86 % for Nb₂O₅ (Figure 5.9a and d, respectively). C₂-C₄ selectivity increased with increasing nickel

Figure 5.8 Metal weight-normalized catalytic activity against time-on-stream for cobalt and cobalt-nickel catalysts supported on titania (a) and on niobia (b). Prior to reaction conditions, samples were reduced in-situ at 350 °C in 25 vol.% H_2 in He at 1 bar. Reaction conditions: 220 °C, 20 bar and $\text{H}_2/\text{CO} = 2$ v/v.

content (Figure 5.9b and e). During the first 20 h on stream a sharp decrease in $\text{C}_2\text{-C}_4$ selectivity was observed for all nickel-containing catalysts. At the same time, these samples also showed an initial increase in C_{5+} selectivity during the first 10 h on stream. C_1 selectivities were relatively low for all samples, but no clear trend with nickel content was found (Figure 5.9c and f). All samples showed an increase in C_1 selectivity at the beginning of the experiment, however for the bimetallic samples this increase took around 40 h-on-stream to reach stable values whereas for the monometallic samples occurred during the first 10 h-on-stream.

When compared to cobalt-nickel supported on non-reducible oxides from literature, the activity of the niobia- and titania-supported catalysts proved superior at similar reaction conditions, while maintaining similar C_{5+} selectivities (Appendix D: Figure D12 and Table D5). Hence, the promotional effect of reducible oxides on Co-Ni nanoparticles was maintained at high pressures.

STEM-EDX of the used Co-Ni catalysts supported on niobia showed a quite uniform composition in the metal nanoparticles, some particle growth and some areas of the support depleted of nanoparticles (Appendix D: Figure D2g-i). For the Co-rich sample, nanoparticles containing only cobalt, that were observed after reduction and after low-pressure catalysis (Appendix D: Figure D3), were no longer observed; all nanoparticles contained both cobalt and nickel. Similar changes were observed in the titania-supported $\text{Ni}/(\text{Ni}+\text{Co}) = 0.50$ at/at catalyst (Appendix D: Figure D7). Furthermore, some nanoparticles in the sample with highest initial nickel content ($\text{Ni}/(\text{Ni}+\text{Co}) = 0.75$ at/at) supported on niobia showed a surface enriched with cobalt, confirmed by a cross section of the Co-Ni distribution (Appendix D: Figure D13). The rearrangement of the metals might originate from a structure change during the high-pressure conditions^{84,85}, a faster oxidation of cobalt when exposed to air after the experiment accompanied by the Kirkendall effect^{72,86,87} or nickel interparticle transport related to the high CO partial pressure^{88,89}. Quantification of the EDX maps for various sam-

ples revealed even a loss in nickel relative to the cobalt content confirmed by ICP (Appendix D: Table D4). Despite the loss of nickel, Co-Ni catalysts compared to the monometallic cobalt showed similar C_{5+} selectivities and higher Fischer-Tropsch activities for the samples Ni/(Ni+Co) = 0.25 at/at supported on titania and Ni/(Ni+Co) = 0.25 and 0.50 at/at supported on niobia.

The set of samples was additionally studied at higher temperatures, namely 240 and 260 °C, and 20 bar, since reducible supports have shown potential for operating at high temperatures without sacrificing C_{5+} selectivity⁹⁰. Figures D14 and D15 in Appendix D show a summary of the catalytic performance after 100 h-on-stream, 20 bar and 220-260 °C (the exact values can be found in Appendix D: Table D2). A temperature increase magnified the

Figure 5.9 Selectivities against time-on-stream for catalysts supported on TiO_2 (a, b and c) and Nb_2O_5 (d, e, f). Selectivities are divided in C_{5+} (a and d), C_2-C_4 (b and e) and C_1 (c and f). Prior to reaction, samples were reduced in-situ at 350 °C (1 °C·min⁻¹, 8 h) in 25 vol.% H_2 in He at 1 bar. Reaction conditions: 220 °C, 20 bar and $H_2/CO = 2$ v/v.

activity trends already observed at 220 °C, in the order $0.25 > 0.50 > 0.0 > 0.75$ at/at for the niobia-supported samples and $0.25 > 0.0 > 0.50 > 0.75$ at/at for the titania-supported samples. More surprisingly, selectivity trends drastically changed with the increase in reaction temperature. For both titania- and niobia-supported samples the increase in temperature resulted in a notorious increase in C_1 and C_2-C_4 products at the expense of C_{5+} ones (Appendix D: Figures D14 and D15 b, c and d). This behavior attenuated upon increasing the nickel content, thus the monometallic cobalt catalysts showed the largest increase in C_1 and C_2-C_4 selectivities whereas the nickel-rich catalyst (Ni/(Ni+Co) = 0.75 at/at) had an almost unchanged selectivity upon increasing the reaction temperature. The selectivity trends observed at 220 °C had practically inverted at 260 °C.

Apparent activation energies were derived from the catalytic activities at temperatures of 220–260 °C and plotted as a function of Ni/(Ni+Co) for both supports (Figure 5.9). At high nickel content (Ni/(Ni+Co) = 0.75 at/at) the activation energy had increased compared to the monometallic cobalt catalysts on both supports. A substitution of 50 % of the cobalt by nickel displayed similar activation energy as for the cobalt-only catalysts. Finally, substitution of cobalt by 25 % nickel decreased the activation energy, indicating that up to a certain nickel concentration, it functioned as a promoter, which was also reflected by increased turnover frequencies.

Figure 5.9 Apparent activation energies for catalysts with different cobalt to nickel ratios supported on titania (blue squares) and niobia (red circles). Apparent activation energies were obtained from the slopes of the Arrhenius equation in the linear form (Figure S18), reaction conditions: 20 bar, H₂/CO = 2 v/v, after 100 h-on-stream and temperatures of 220, 240 and 260 °C.

4.4 Conclusions

Bimetallic Co-Ni nanoparticles supported on reducible (TiO₂ and Nb₂O₅) and non-reducible (α -Al₂O₃) oxides were synthesized and characterized, and their catalytic performance in the Fischer Tropsch (FT) synthesis was evaluated. Samples were prepared by co-impregnation of aqueous solutions with varying cobalt to nickel atomic ratio. After calcination, samples were characterized by TPR where a shift towards lower temperatures in the reduction profiles of the bimetallic samples was observed, in comparison to the monometallic samples, indicative of a close interaction between the cobalt and nickel oxides. TEM of the reduced samples revealed that gradual substitution of cobalt by nickel led to a decrease in nanoparticle size on all support materials. However, comparison of the theoretical and experimental H₂-uptakes (derived from TEM and H₂-chemisorption, respectively) showed a discrepancy for the samples supported on reducible oxides, which was ascribed to the SMSI effect. Whereas the samples supported on the non-reducible support did not show this difference. STEM-EDX analysis of the reduced and passivated catalysts demonstrated

that while nickel was always found together with cobalt, cobalt could be found without nickel. Nanoparticles containing both metals showed a uniform Co-Ni distribution. Moreover, CO-FTIR results suggested that for the reducible supports, the metal nanoparticles likely underwent a cobalt-enrichment at their surface upon increasing the CO pressure, while the nanoparticles supported on alumina did not. This indicated that the surface composition of the nanoparticles was affected by the metal-support interaction.

The low-pressure catalytic performance showed substantially higher activities, C_{5+} selectivities and stabilities for the bimetallic nanoparticles supported on reducible oxides. In contrast, the alumina-based catalysts showed low activities and C_{5+} selectivities independently of the Co-Ni composition and, moreover, a continuous loss of activity. The marked difference in catalytic performance was tentatively coined to a shift of the rate determining step, as derived from the trend between TOF and CO-FTIR. For Co-Ni supported on reducible oxides, a weaker adsorption of CO was inferred, which improves H adsorption and the catalytic activity. The catalytic performances of the samples supported on reducible supports were also studied at 20 bar and various temperatures. At 220 °C, the cobalt-rich samples benefited from the increase in pressure resulting in high activity and C_{5+} selectivities. However, higher reaction temperatures inverted the selectivity trend. Yet, a comparison to non-reducible-supported catalysts from the literature showed the promotional effect of reducible oxides on bimetallic nanoparticles. 25 % substitution of cobalt by nickel led to lower apparent activation energy values, implying that nickel acted as promotor in these samples. In summary, we showed that the combination of cobalt and nickel supported on reducible oxides allowed for increased FT performance. Reducible oxides used as support material strongly modify the reactivity of bimetallic nanoparticles thus opening up avenues to arrive at more efficient catalysts.

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6 Stable Niobia-Supported Nickel Catalysts for the Hydrogenation of Carbon Monoxide to Hydrocarbons

Stability of metal nanoparticles under reaction conditions is crucial in many catalytic processes. Nickel-based catalysts often encounter severe particle growth in the presence of carbon monoxide due to the formation and migration of nickel carbonyl. In this research, we showed that the reduction temperature of nickel oxide supported on niobia (Nb_2O_5) influenced the stability of the resulting nickel catalyst during subsequent carbon monoxide hydrogenation. Low reduction temperatures resulted in high initial nickel-normalized activity towards long-chain hydrocarbons (C_{5+}), but fast deactivation throughout the experiment. High reduction temperatures led to a shift in product distribution towards shorter hydrocarbons and a decreased initial nickel-normalized activity, while during the first hours of the experiment an increase in turnover frequency and nickel-normalized activity was observed, resulting eventually in a stable catalytic performance. Electron microscopy analysis revealed extensive particle growth after catalysis when the catalyst had been reduced at low temperatures and no significant changes in particle size when reduced at high temperatures. By use of in-situ FT-IR spectroscopy, nickel subcarbonyl species which are precursors of volatile nickel tetracarbonyl were detected on $\text{Ni/Nb}_2\text{O}_5$ after low temperature reduction and exposure to CO, but not after high temperature reduction. Hence, particle growth is explained by the formation and diffusion of nickel carbonyl and subsequent Ostwald ripening, that leads to larger nickel particles with concomitant decrease in nickel-normalized activity. The stability of the catalyst reduced at high temperature was linked to the formation of niobium suboxides and their partial coverage of the nickel particles limiting the formation of nickel carbonyl and slowing down particle growth.

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6.1 Introduction

Metal nanoparticles are commonly used to catalyze many chemical processes¹. Since catalytic reactions occur at the metal surface, the high surface-area-to-volume-ratio of a nanoparticle provides an effective number of active sites per weight of metal in the overall catalyst. One of the biggest challenges for any catalytic system is to maintain this maximum amount of active sites throughout the lifespan of a solid catalyst². Particularly in the case of metal nanoparticles, their growth is a prevailing phenomenon in which the efficient utilization of the metal in a catalyst is compromised, usually leading to a detriment in catalytic performance^{3–5}. In order to stabilize the nanoparticles and prevent their growth, these are typically dispersed over a support material. The nature of the support is crucial in delivering this stability and offers an opportunity to develop improved solid catalysts.

Reducible oxides used as support material display characteristic interactions with metal nanoparticles. During reductive conditions, one effect that arises is coverage of the nanoparticles by in-situ generated suboxides from the support^{6,7}, the so called Strong Metal-Support Interaction (SMSI)^{8,9}. This effect can modify the available metal surface area, the electronic state of the metal and the particle shape^{10–12}. An interesting example is the substantial change in reactivity of nickel during carbon monoxide hydrogenation: nickel supported on non-reducible oxides (e.g. Al_2O_3 , SiO_2) selectively hydrogenates carbon monoxide to methane, whereas when supported on reducible oxides like TiO_2 or Nb_2O_5 the product distribution shifts towards heavier hydrocarbons^{13–17}. Furthermore, previous reports have suggested that reducible supports can also deliver unique stability to nickel-based catalysts^{13,18}.

The interest to achieve stable nickel-based systems in the presence of carbon monoxide arises from the extensive utilization of nickel catalysts in reactions involving carbon monoxide as reactant, intermediate or product^{19–23} and the poor stability of nickel in the presence of carbon monoxide at low temperatures^{24,25}. Deactivation of nickel-based catalysts during carbon monoxide hydrogenation proceeds most often through particle growth by the formation and diffusion of volatile nickel carbonyl^{25–27}. This phenomenon is a classic example of Ostwald ripening, where species containing metal atoms, in this case nickel carbonyl, diffuse from smaller towards larger nanoparticles leading to metal sintering^{28,29}. In order to prevent this, the reaction is typically operated at high temperatures and low CO pressures, since these conditions disfavor the formation of nickel carbonyl^{24,26,30}. However, such conditions compromise the product selectivity mainly towards methane and therefore hamper the application of nickel catalysts for the synthesis of more commercially attractive products, such as long-chain hydrocarbons (C_{5+}) or olefins^{31,32}. Alternative strategies to inhibit the formation of nickel carbonyl in these catalysts have been explored in literature, for instance, by alloying nickel with copper^{33,34} or by depositing nickel on titania, a reducible support¹³.

Here, we studied the effect of SMSI in nickel supported on niobia for the hydrogenation of carbon monoxide. For this, different reduction temperatures (250 - 450 °C) on $\text{NiO/Nb}_2\text{O}_5$ were used prior to H_2 -chemisorption, in order to determine the extent of SMSI, and prior to CO hydrogenation. H_2 -uptake suppression was observed when increasing

the reduction temperature which is characteristic of the SMSI effect. Simultaneously, an increase in reduction temperature led to a decrease in nickel-based catalytic activity, however stable catalytic performance was gained in return with high selectivity for long-chain hydrocarbons. Ni/Nb₂O₅ showed higher turnover frequency and C₅₊ selectivity compared to nickel supported on a non-reducible support (α -Al₂O₃). The overall results obtained pointed out to an inhibition of nickel carbonyl formation by SMSI in Ni/Nb₂O₅, leading to a stable supported nickel catalyst for CO hydrogenation.

6.2 Experimental

Synthesis. Niobium oxide (Nb₂O₅) was used as support and obtained by crystallization of niobium oxide hydrate (Nb₂O₅·*n*H₂O, HY-340, AD/4465), which was provided by Companhia Brasileira de Metalurgia e Mineração – CBMM. The crystallization was carried out in stagnant air at 600 °C during 4 h with a ramp of 5 °C·min⁻¹. The obtained Nb₂O₅ had a pseudo-hexagonal TT-phase, a specific surface area of 9 m²·g⁻¹ and a specific mesopore volume of 0.05 cm³·g⁻¹.

A nickel supported on niobia catalyst was prepared using the incipient wetness impregnation method. Prior to impregnation the support (75 – 150 μ m grains) was dried under vacuum at 80 °C for 1 h, thereafter the impregnation was performed at room temperature with a 4.2 M aqueous solution of Ni(NO₃)₂·6H₂O (Acros, 99 %) for a 6 wt.% Ni. In the next step, the catalyst was dried for 1 h at 60 °C in a fixed bed reactor under N₂ flow and subsequently in the same reactor and gas flow calcined for 2 h at 350 °C (3 °C·min⁻¹). Nickel supported on α -alumina (BASF) was prepared in the same way. Metal loadings were defined as the mass of metallic Ni per gram of reduced catalyst.

Characterization. Temperature programmed reduction (TPR) analyses were performed using a Micromeritics Autochem 2990 instrument, where 100 mg sample was dried at 120 °C for 1 h in Ar flow followed by reduction from room temperature up to 700 or 1000 °C (5 °C·min⁻¹) in a 5 vol% H₂/Ar flow. Powder X-ray diffractograms were measured using a Bruker-AXS D2 Phaser X-ray diffractometer, Co-K α radiation (λ = 1.789 Å).

Bright field transmission electron microscopy (TEM) and Scanning transmission electron microscopy (STEM-EDX) images were acquired with a Philips Tecnai-20 FEG (200 kV) microscope equipped with an energy dispersive X-ray (EDX) and high-angle annular dark-field (HAADF) detector. The reduced and subsequently passivated samples for the microscopy analysis were prepared by suspending the catalysts in 2-propanol (>99.9 %, Sigma-Aldrich) using sonication and dropcasting the suspension on a carbon-coated Cu grid (200 mesh). The nickel particle size was determined using the iTEM software by analyzing at least 500 particles. Particle surface average diameters or Sauter mean (D[3,2]) were then calculated and corrected for a 2 nm NiO shell³⁵.

H₂-chemisorption was measured on a Micromeritics ASAP 2020C using ~100 mg of sample. Prior to the measurement, the calcined catalyst was reduced in H₂ flow at different temperatures during 2 h (5 °C·min⁻¹). The sample was then evacuated, cooled to 150 °C and

H₂-chemisorption was measured at that temperature.

Inductively coupled plasma-optical emission spectroscopy (ICP-OES) was performed on a SPECTRO ARCOS in order to establish the nickel content before and after catalysis; samples were extracted using aqua regia.

Fourier-transform Infrared (FT-IR) spectroscopy measurements were carried out in a Specac “High Temperature High Pressure” transmission FT-IR cell. A self-supported catalyst wafer was prepared by applying on a sample a force of 4000 kg for 20 s, yielding a wafer of 16 mm diameter, and < 1 mm thickness. Catalyst wafers were reduced in-situ, each at different temperatures of 250, 350 and 450 °C (N₂/H₂ = 2 v/v; both Linde, 5.0). Subsequently, a sample was cooled down to 230 °C flushed with 5.0 purity N₂ for 10 min, after which flowing CO (Linde, 5.0) was added with a ratio N₂/CO = 2 v/v at 1 bar total pressure. Due to low photon-transmittance of the Nb₂O₅-supported Ni catalyst, 256 spectra were averaged to improve signal-to-noise. Spectra were recorded with a resolution of 4 cm⁻¹.

Catalytic performance. Catalytic performance was carried out in a quartz glass plug-flow reactor, loaded with 15-20 mg catalyst (38–150 μm) diluted with ~200 mg SiC. Catalysts were reduced in situ at 250, 350 or 450 °C (5 °C·min⁻¹, 2 h) in an Ar/H₂ = 2.0 v/v flow (GHSV = 190000 h⁻¹). After reduction, CO hydrogenation was performed at 230 °C, 1 bar, H₂/CO = 2.0 v/v, GHSV = 28000 h⁻¹ and CO conversion < 5%. Reaction was carried out for 90 h. Finally, the CO flow was stopped and the H₂ flow and temperature were kept for one hour in order to remove remaining hydrocarbons for further analysis of the catalyst. C1-C18 products were analyzed by online gas chromatography (Varian 430 GC, CP sil-5 column). the corresponding hydrocarbon product.

6.3 Results and discussion

6.3.1 Reduction temperature

A nickel supported on niobia catalyst was synthesized by incipient wetness impregnation method. After subsequent drying and calcination, the nickel content was determined by ICP-OES, being 5.6±0.1 wt.%. Nickel supported on α-alumina was also synthesized as comparative system, with a nickel content of 5.5±0.1 wt.% as determined by ICP-OES. Temperature programmed reduction was carried out on the support (Nb₂O₅), the calcined NiO/Nb₂O₅ and NiO/α-Al₂O₃ samples. The corresponding reduction profiles for the niobia-based samples are shown in figure 6.1. Nb₂O₅ showed a gradual consumption of hydrogen starting at 600 °C and a maximum consumption rate at 940 °C. The hydrogen consumption was assigned to the reduction of the Nb₂O₅ surface to NbO₂, along with the change in color of the sample to deep indigo, characteristic of Nb⁴⁺ ions^{36,37}. The reduction profile for the NiO/Nb₂O₅ sample showed a small hydrogen consumption signal at 200 °C which might be attributed to the reduction of Ni³⁺. The main hydrogen consumption between 230 and 430 °C was attributed to the reduction of NiO to metallic Ni^{38,39}. Hydrogen consumption continued above 700 °C related to reduction of Nb₂O₅, catalyzed by the metallic nickel³⁷. The consumption peak at 780 °C might correspond to the initial reduction of the support

surface (Nb_2O_5 to NbO_2) and further consumption above 810 °C to the reduction of bulk Nb_2O_5 and possibly subsequent reduction of NbO_2 to Nb_2O_3 . Nickel oxide supported on $\alpha\text{-Al}_2\text{O}_3$ showed a similar reduction profile to the niobia-based sample (Appendix E: Figure E1), with a small hydrogen consumption signal at 220 °C ascribed to Ni^{3+} reduction and a main signal between 250 and 450 °C for NiO reduction to Ni. For both Nb_2O_5 - and $\alpha\text{-Al}_2\text{O}_3$ -supported samples, the total hydrogen consumption below 450 °C corresponded to the complete reduction of all nickel oxide to metallic nickel.

Figure 6.1 H_2 temperature programmed reduction profile of the Nb_2O_5 support (red dashed line) and of the calcined $\text{NiO}/\text{Nb}_2\text{O}_5$ sample (black line).

Based on the $\text{NiO}/\text{Nb}_2\text{O}_5$ TPR profile, four different reduction temperatures, namely 250, 350 and 450 °C, were chosen to study their effect on CO hydrogenation. The degree of reduction for the low temperatures (250 and 350 °C) was calculated by measuring TPR of $\text{NiO}/\text{Nb}_2\text{O}_5$ with an additional dwell step of 2 h at 250 or at 350 °C. The isothermal step at 250 °C resulted in two main distinctive signals in hydrogen uptake for the reduction of nickel oxide (Appendix E: Figure E2a). The first one was observed by reaching 250 °C with a sharp increase in hydrogen uptake which gradually decreased back to the baseline throughout the 2 h at 250 °C. Based on the hydrogen uptake the degree of reduction at this temperature was 58 %. The second main hydrogen uptake signal was observed after the isothermal

Table 6.1 H_2 -uptake for $\text{Ni}/\text{Nb}_2\text{O}_5$ at different reduction temperatures measured by chemisorption.

Support	Reduction temperature (°C)	H ₂ -chemisorption		TEM	
		Experimental H ₂ -uptake	Particle size	Particle size D[3,2]	Theoretical H ₂ -uptake
		($\mu\text{mol}_{\text{H}_2} \cdot \text{g}_{\text{Ni}}^{-1}$)	(nm)	(nm)	($\mu\text{mol}_{\text{H}_2} \cdot \text{g}_{\text{Ni}}^{-1}$)
Nb_2O_5	250	936	10	12	716
	350	626	15	12	740
	450	16	539	11	785
$\alpha\text{-Al}_2\text{O}_3$	350	1328	6	9	955
	450	1078	8	12	716

step with a maximum at 360 °C ($t = 200$ min), this indicates that temperatures higher than 250 °C are necessary to completely reduce the nickel oxide to metallic nickel. The hydrogen uptake observed at 360 °C might relate to the observed shoulder at the same temperature in Figure 6.1, which might correspond to the reduction of nickel oxide species with a stronger interaction with the support. The TPR profile with an isotherm step at 350 °C (Appendix E: Figure E2b) showed a main hydrogen uptake signal which corresponded to a degree of reduction of 96 %, indicating that most of the nickel oxide is reduced to metallic nickel at 350 °C.

Table 6.1 shows the hydrogen uptake determined by H_2 -chemisorption for Ni/Nb₂O₅ and Ni/ α -Al₂O₃ after reduction at different temperatures. An increase of the reduction temperature resulted in a decrease in hydrogen uptake for Ni/Nb₂O₅, resulting in an apparent increase in the derived particle size. This suppression of hydrogen chemisorption by reducible oxidic supports, the so called strong metal-support interaction (SMSI) effect, is a well-documented phenomenon attributed to coverage of the metal nanoparticles by suboxides from the support upon reductive conditions^{6,8}. The degree of coverage by the suboxides

Figure 6.2 TEM images of the Ni/Nb₂O₅ catalyst after reduction at different temperatures and passivation (denoted as reduced) and after catalysis (denoted as spent). The corresponding histograms show the particle size distribution for the ‘reduced’ (black bars) and ‘spent’ (red bars) with their corresponding surface-average particle sizes.

is a temperature-dependent phenomenon, in which higher reduction temperatures enhance the mobility of these species and coverage of the nanoparticles⁴⁰. Powder X-ray diffraction (Appendix E: Figure E3) neither showed the formation of new crystalline species (e.g. nickel niobates) nor provided indications of SMSI after reduction of Ni/Nb₂O₅. Reduction at 250 °C showed a substantial hydrogen uptake even though nickel oxide was not completely reduced at 250 °C as shown by the TPR results, indicating that most of the particles' surface consisted of metallic nickel. The Ni/ α -Al₂O₃ sample showed also a decreased in the hydrogen uptake upon increasing the reduction temperature, however this decrease was not as severe as the one observed for Ni/Nb₂O₅.

After the chemisorption measurement and exposure to air at room temperature, the samples were analyzed by TEM (Figure 6.2 and Appendix E: Figure E4). TEM images showed for all Ni/Nb₂O₅ samples a uniform distribution of nickel nanoparticles over the niobia. Furthermore, a similar nickel particle size (~ 12 nm) was determined based on TEM as shown in Table 6.1, indicating no significant effect of the reduction temperature on the nickel particle size and confirming that the suppressed hydrogen chemisorption results related to the SMSI effect. In the case of the Ni/ α -Al₂O₃ sample, TEM images (Appendix E: Figure E4) revealed a slight increase in particle size upon increasing the reduction temperature, in line with the results obtained from hydrogen chemisorption. The discrepancy observed here between the experimental and theoretical H₂-uptake can be explained by the more significant impact of larger particles when determining the D[3,2] value, a surface-based diameter. Since a considerable amount of very small nanoparticles would not be detected by TEM.

6.3.2 CO hydrogenation

The catalytic performance of the Ni/Nb₂O₅ and Ni/ α -Al₂O₃ catalysts was evaluated by varying the reduction temperature similar to the H₂-chemisorption experiments and a summary of the results is shown in Table 6.2. Nickel-normalized catalytic activity (Nickel Time Yield, NTY) plotted against time-on-stream (TOS) up to 90 h is shown in figure 6.3. The

Table 6.2 Summary of the catalytic performance for the Ni/Nb₂O₅ and Ni/ α -Al₂O₃ catalysts. Reaction conditions: 230 °C, 1 bar, H₂/CO = 2.0 v/v, GHSV = 28 000 h⁻¹ and CO conversion < 5%.

Support	Reduction temperature (°C)	Nickel-Time-Yield (10 ⁻⁵ mol _{CO} g _{Ni} ⁻¹ s ⁻¹)		TOF ^a (10 ⁻³ s ⁻¹)		TOF _{app} ^b (10 ⁻³ s ⁻¹)	Selectivity ^c (wt.%)			α ^d	Olefin/ Parffin ^e
		TOS = 0 h	TOS = 90 h	TOS = 0 h	TOS = 90 h		C ₁	C ₂₋₄	C ₅₊		
Nb ₂ O ₅	250	7.9	2.2	46	39	42	18	33	49	0.65	0.9
	350	7.1	3.9	45	42	59	15	30	55	0.70	1.0
	450	1.6	2.7	11	20	605	22	45	33	0.58	1.6
α -Al ₂ O ₃	350	2.0	0.6	11	10	8	54	35	11	0.46	0.8
	450	1.7	0.5	12	8	8	55	35	10	0.45	0.9

a. Based on TEM particle size distribution in fresh (for TOS = 0 h) and spent (for TOS = 90 h) catalyst.

b. Based on H₂-chemisorption of fresh catalyst.

c. Selectivity is reported at TOS = 90 h and up to C₁₈.

d. Values were determined for C₁-C₁₁ concentration values.

e. Molar ratios determined for C₄-C₇.

Figure 6.3 Nickel-Time-Yield (NTY) plotted against time-on-stream for Ni/Nb₂O₅ reduced at different temperatures prior to reaction. *In-situ* reduction: 1 bar, Ar/H₂ = 2 v/v, GHSV = 190 000 h⁻¹, T = 250 °C (pink ■), 350 °C (blue ●, grey ▼) or 450 °C (green ◆, black ▲). Reaction conditions: 1 bar, H₂/CO = 2 v/v, GHSV = 28 000 h⁻¹, T = 230 °C, CO conversion: 1-4 %.

initial NTY (TOS = 0) showed consistency with the H₂-chemisorption results, i.e. reduction at low temperatures for the niobia-supported sample displayed high H₂-uptake along with markedly high initial NTY whereas an increase of the reduction temperature led to a suppression of the H₂-uptake and a decrease in the initial NTY. However, the decrease in initial NTY is not proportional to the decrease in H₂-uptake for unknown reasons. The stability throughout time significantly varied for each reduction temperature. Reduction at 250 °C led to severe deactivation, down to 70 % loss in NTY at TOS = 90 h. A less pronounced deactivation was observed when the reduction temperature was increased to 350 °C with only 40 % loss in NTY, however the catalyst did not reach steady state during the experiment due to continuous deactivation. In stark contrast, reduction at 450 °C showed a catalytic performance, with a low initial NTY which increased during the first 30 h of the reaction followed by a stable conversion until the end of the experiment. This might indicate a partial recover of the available metallic surface area during reaction conditions, which has been associated in literature to re-oxidation of the suboxides (e.g. NbO_x) by water produced during reaction, hence modifying the SMSI effect⁴¹.

Contrary to the Ni/Nb₂O₅ sample, the reduction temperature had a minor effect on the catalytic performance of the Ni/α-Al₂O₃ as shown in figure 6.3. Reduction at 350 °C led to a small increase in NTY than when reduced at 450 °C at the beginning of the experiment, this difference originated from their different initial particle size as revealed by their same initial turnover frequencies (TOF). Their prevalent decrease in NTY during the experiment resulted in almost similar NTY values at TOS = 90 h. The niobia-supported sample showed

independently of the reduction temperature higher NTY values than the alumina-supported sample at the end of the experiment. The nickel content was determined after catalysis by ICP-OES showing no metal loss during the experiment for all samples.

The promotional effect of niobia was maintained in all cases as shown by the TOFs compared to Ni/ α -Al₂O₃, determined either by particle size distribution from TEM or H₂-chemisorption (Table 6.2). Initial TOFs based on TEM particle size distributions showed the highest values for Ni/Nb₂O₅ reduced at low temperatures (250 and 350 °C) and decreased when increasing the reduction temperature to 450 °C. The inverse trend was observed for the apparent initial TOFs based on chemisorption results (TOF_{app}, Table 6.2); an increase in reduction temperature led to a substantial increase in TOF_{app} due to the hydrogen chemisorption suppression by SMSI (*vide supra*). However, the nickel surface under reaction conditions is expected to change and therefore these TOFs are indicated as ‘apparent’. Interestingly, Ni/Nb₂O₅ reduced at 250 °C shows consistent values for both initial TOFs indicating that coverage of the nickel nanoparticles by suboxides from the support has not taken place at this temperature. Consequently, the resulting high TOF might originate from the interphase of the nickel nanoparticles and the support. For Ni/ α -Al₂O₃, the apparent TOFs and TOFs based on TEM have the same values and SMSI does not play a role in this catalyst system.

The change in reduction temperature additionally influenced the selectivity of the niobia-supported catalyst, as shown with the Anderson–Schulz–Flory (ASF) product distribution plot in figure 6.4 and in table 6.2. For all reduction temperatures, niobia-supported catalysts showed higher selectivity towards long-chain hydrocarbons when compared to the

Figure 6.4 Anderson–Schulz–Flory-plot (ASF-plot) at TOS = 90 h for Ni/Nb₂O₅ after different reduction temperatures and for the Ni/ α -Al₂O₃ reference catalyst. W_n = weight fraction of olefins plus paraffins of given carbon number n in total hydrocarbon products.

alumina-supported catalyst. At TOS = 90h, the catalyst reduced at 350 °C had the highest α value, with the highest selectivity to C_{5+} products, followed by the reduction temperature at 250 °C. Reduction at 450 °C led to a shift in product distribution to shorter hydrocarbons and therefore a smaller α value. Suppressed olefin to paraffin ratio was observed for the catalyst reduced at 250 or 350 °C, which has been attributed in the case of cobalt-based catalysts to re-adsorption of olefins to the metal surface to further increase chain-growth^{42,43}. However, reduction at 450 °C did not show this behavior, instead a slight increase in the olefin selectivity was observed, as shown in table 6.2. Re-adsorption of olefins could be hindered on the metal surface, shifting the selectivity to shorter hydrocarbons. On the other hand, Ni/ α -Al₂O₃ showed the lowest α value, a high selectivity for methane and to a lesser extent for C₂ to C₁₀ products for both reduction temperatures. The formation of C₂₊ products in this case might be due to some small nickel metal nanoparticles (< 3 nm) found in this catalyst (Appendix E: Figure E4), which agrees with previous research reports⁴⁴.

6.3.3 SMSI and nickel carbonyl formation

The Ni/Nb₂O₅ samples after catalysis were analyzed by TEM and the results are shown in figure 6.2. Significant changes for the nickel nanoparticles were observed for the spent catalyst reduced at 250 °C: broadened particle size distribution and increased average particle size (12 nm to 27 nm) were observed. Likewise, large particles were observed for the spent catalyst after reduction at 350 °C leading to a particle mean size of 18 nm. The observed nickel particle growth agreed with the stability of the catalyst during reaction; where reduction at 250 °C led to the severest deactivation and the most pronounced particle growth, increase of the reduction temperature to 350 °C attenuated the particle growth and diminished the deactivation rate. The resulting particle sizes and catalytic activity at TOS = 90 h led to similar TOFs for both reduction temperatures when compared to initial TOFs (Table 6.2). This is an indication that the decrease in NTY was mainly due to particle growth. The slight decrease in TOF might relate to carbon deposition over the nickel surface. In a similar way, TEM of the spent Ni/ α -Al₂O₃ catalysts revealed a substantial increase in nickel particle size (Appendix E: Figure E5), indicating that the decrease in NTY originated mainly from particle growth. Particle growth for nickel-based catalysts under these reaction conditions most likely occurs via Ostwald ripening by the formation of Ni(CO)₄^{25–27}. In contrast, the nickel particles remained well distributed over the support for the Ni/Nb₂O₅ sample reduced at 450 °C. No significant change in particle size was observed after catalysis, with a final mean particle size of 12 nm. Therefore, the increase in CO conversion during the first hours of the experiment means that sites more active became available and thus the TOF almost doubled (Table 6.2). These results suggest that SMSI inhibited the formation of Ni(CO)₄ on a Nb₂O₅ support leading to a more stable catalyst. Ni(CO)₄ formation rate has been reported to depend on the nickel surface morphology with particularly low coordinated Ni atoms readily reacting to form carbonyls^{45,46}, thus NbO_x species might be responsible for blocking or modifying the electron density of these sites.

Fourier-Transform Infrared (FT-IR) spectroscopy was used to study the differences for the sample reduced at 250, 350 and 450 °C in their tendencies to form nickel carbonyl.

Figure 6.5 FT-IR spectra under CO atmosphere of Ni/Nb₂O₅ after reduction at 250, 350 or 450 °C.

In-situ reduction of the wafer was carried out at these three different temperatures. Thereafter FT-IR spectra were recorded at 230 °C under atmospheric pressure of CO/N₂ = 2 v/v flow (Figure 6.5). Interestingly, a pronounced sharp band at 2080 cm⁻¹ can be observed when the sample was reduced at 250 °C. This band is ascribed to subcarbonyl Ni(CO)_x (x = 2, 3) species, precursors of Ni(CO)₄, in accordance with literature^{46–48}. These species were also detected for the catalyst reduced at 350 °C and in both cases the band disappeared after flushing with N₂. In contrast, reduction at 450 °C did not give rise to this subcarbonyl Ni(CO)_x band. These results show that there is a reduction temperature dependency in nickel carbonyl formation. Lower reduction temperatures thus most likely led to rapid deactivation during CO hydrogenation due to Ni particle growth via the formation and diffusion of Ni(CO)₄ originated from the detected Ni(CO)_x species. High reduction temperature showed stable catalytic activity (Figure 6.3), suggesting that the SMSI effect suppressed the formation of Ni(CO)_x species and hence Ni(CO)₄, avoiding the diffusion of nickel over the support.

Furthermore, the FT-IR spectra plotted in Figure 6.5 show that the degree of CO activation in the adsorbed state is affected by the reduction temperature. That is, a reduction at 250 °C shows a large contribution of Ni(CO)_x at 2090 cm⁻¹ corresponding to the strongest carbon-oxygen bond based on the relatively high wavenumber of this band. A band at 1580 cm⁻¹ is also observed which is attributed to carboxylate-type species, these may have originated from the oxidation of CO by the remaining NiO in this sample as shown by the TPR results. For a slightly higher reduction temperature (350 °C) besides the band at 2090 cm⁻¹, a broad peak at around 1960 cm⁻¹ is observed, which is ascribed to C=O adsorbed in a 2-fold bridge position^{49,50}. At the highest reduction temperature (i.e., 450 °C) a small peak at ~ 1266 cm⁻¹ appears, which can be ascribed to the weakest CO bond⁵¹, or lowest wavenumber observed in this set of experiments.

Two effects of the SMSI can explain the inhibition of nickel carbonyl formation. On one hand, NbO_x suboxides might physically block the more reactive low-coordinated Ni atoms on the surface of the nanoparticles, preventing the formation of subcarbonyl Ni(CO)_x

species. A similar effect has been shown in literature by addition of alkali metals or sulfur to nickel-based catalysts^{52,53}. On the other hand, the suboxides partially covering the nickel nanoparticle's surface are capable of transferring electrons to the nickel^{54–56}. In this case, Nb^{4+} or Nb^{3+} in the NbO_x suboxides might transfer electron density to the metallic nickel, resulting in electron-rich Ni^δ atoms at the surface. Upon CO chemisorption at the nickel surface, Ni^δ increases the back-donation to the CO $2\pi^*$ antibonding orbital weakening the C-O bond, as suggested by FT-IR, and thus avoiding the formation of $\text{Ni}(\text{CO})_x$ species. Furthermore, an electron-rich metallic surface could hinder the re-adsorption of electron-rich molecules, explaining the increased olefin to paraffin ratios when the catalyst was reduced at high temperatures.

6.4 Conclusions

The effect of different reduction temperatures was studied for nickel nanoparticles supported on niobia. An increase of the reduction temperature led to H_2 -chemisorption suppression, a typical phenomenon caused by reducible oxidic supports in which suboxides from the support cover partially the metal nanoparticles. The initial nickel-based catalytic activity was in line with the chemisorption results where high H_2 -uptake corresponded to high initial CO conversion. However, low reduction temperatures turned into a fast deactivation due to nickel particle growth as shown by TEM, whereas a high reduction temperature led to stable catalytic performance and no significant particle growth. Interestingly, reduction of the niobia-supported catalyst at high temperature brought about an activation period during the first hours under reaction conditions followed by stable nickel-based activity. FT-IR measurements of CO adsorbed on $\text{Ni}/\text{Nb}_2\text{O}_5$ showed that nickel subcarbonyls readily formed after low but not after high reduction temperature. This could explain the particle growth involving the formation and diffusion of nickel tetracarbonyl, which formed from the detected nickel subcarbonyls. The inhibition of nickel tetracarbonyl formation after high temperature reduction is associated to the presence of suboxide species over the nickel surface, by either physically blocking exposed low-coordination nickel atoms, or by enhancing the electron density on the nickel surface and facilitating C-O bond rupture instead of nickel tetracarbonyl formation. The reduction treatment had a strong influence in the product distribution, where the highest selectivity towards C_{5+} was obtained after reduction at 350 °C, while a further increase of the reduction temperature shifted the product distribution towards lighter products. Finally, the promotional effect of reducible oxides, such as niobia, in CO hydrogenation was clearly shown since independently of the reduction temperature nickel supported on niobia showed higher nickel-based activity, TOF and C_{5+} selectivity compared to nickel supported on α -alumina, a non-reducible support. We have shown that niobia used as support material offers the possibility to make stable nickel-based catalysts for CO hydrogenation with tunable product spectrum.

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7

Niobium-based Solid Acids in Combination with a Methanol Synthesis Catalyst for the Direct Production of Dimethyl Ether from Synthesis Gas

The production of dimethyl ether as compared to methanol from synthesis gas allows for increased conversions in a single pass. A challenge in this process is the combination of methanol synthesis and dehydration functionalities in a single catalyst without mutual negative interference of their performances. Here, we studied the use of hydrated niobium pentoxide ($\text{Nb}_2\text{O}_5 \cdot n\text{H}_2\text{O}$) and niobium phosphate (NbOPO_4) in combination with a copper-based methanol synthesis catalyst in the direct synthesis of DME while gamma-alumina ($\gamma\text{-Al}_2\text{O}_3$) was used as a reference material. The three solid acids combined with the copper-based catalyst proved active and selective in the production of DME, however all of them showed some degree of deactivation throughout the reaction. Characterization of the used catalysts pointed out that while the $\gamma\text{-Al}_2\text{O}_3$ -based mixture deactivated most likely due to coke deposition on the alumina and structural changes in the methanol synthesis catalysts, the $\text{Nb}_2\text{O}_5 \cdot n\text{H}_2\text{O}$ and NbOPO_4 -based catalysts lost activity probably as a result of copper migration from the methanol synthesis catalyst to the acid component. In view of the high volume-based activity of the Nb-based solid acids it is concluded that these are promising components for the direct catalytic conversion of synthesis gas to DME.

Hernández Mejía, C., Verbart, D. M. A. & de Jong, K. P. Niobium-based solid acids in combination with a methanol synthesis catalyst for the direct production of dimethyl ether from synthesis gas. *Catal. Today*, accepted.

7.1 Introduction

Synthesis gas, a mixture of hydrogen and carbon monoxide, is a versatile feedstock for the production of various chemicals and fuels. The conversion of synthesis gas to a desired product relies substantially on the catalyst employed. Whereas a primary hydrogenation function, typically a late-transition metal, can selectively produce chemicals such as alcohols, olefins or paraffins, addition of a second catalyst can be employed to couple reactions and expand the diversity of products^{1,2}. Ideally, both functionalities in a catalyst mixture should result solely in a positive synergetic performance, which is feasible by selecting the appropriate chemical properties and an optimal degree of intimacy³⁻⁶. However, achieving the ideal composition without negative interferences remains a challenge in these multi-functional catalytic systems.

Dimethyl ether (DME) is commonly utilized in the aerosol industry as propellant and in the chemical industry as methylating agent, and it has shown potential in the production of bulk chemicals such as olefins, aromatics and acetic acid⁷⁻¹⁰. Moreover, DME has attracted interest during the last decades as a clean fuel owing to its similar physicochemical properties to LPG and low particulate emissions¹¹⁻¹⁵. DME can be directly produced by coupling the synthesis of methanol from synthesis gas with the dehydration of methanol to DME. Haldor Topsøe initially recognized the industrial advantages of combining both reactions in a single process, showing that the direct production of DME from synthesis gas could improve energy efficiencies and reduce capital costs^{13,14,16}. Figure 7.1 shows the rele-

Figure 7.1 Thermodynamic equilibrium for stoichiometric quantities of reactants for the individual reactions involved in the synthesis of DME. Calculations were performed using the HSC software from Outotec, v 7.14 in the temperature range from 250 – 350 °C, considering all species in the gas phase and 40 bar total pressure. Conversion refers to that of CO (eq. 1, 3 and 5), CO₂ (eq. 4) or methanol (eq. 2).

vant reaction equations for the synthesis of DME and their corresponding thermodynamic equilibria. While methanol formation from synthesis gas is an equilibrium-limited reaction (Figure 7.1, eq. 1), in-situ conversion of methanol towards DME shifts this equilibrium towards higher conversions in a single pass, a benefit of combining both reactions (Figure 7.1, eq. 2 and 5). The additional water formed during the dehydration can bring about the water-gas-shift reaction, in which H_2O and CO react to form CO_2 and H_2 (Figure 7.1, eq. 3). This can be beneficial when using hydrogen-deficient synthesis gas but also the presence of CO_2 can enhance the synthesis of methanol¹⁷ (Figure 7.1, eq. 4). However, an excess of water can further boost the water-gas-shift reaction at the expense of methanol synthesis decreasing the DME yield of the catalyst¹⁸. Water can also lead to detrimental effects on the catalysts' structure, such as sintering or poisoning of active sites, resulting in an accelerated deactivation^{18,19}. The direct synthesis of DME from synthesis gas is therefore a clear example of the advantages and challenges in bifunctional catalysis^{20,21}.

Currently, the most efficient methanol synthesis catalysts are copper-based and hence widely used in industry²². Methanol synthesis is an exothermic reaction and it is accompanied with a volumetric contraction, the preferred reaction conditions are therefore low temperatures and high pressures according to Le Chatelier's principle (Figure 7.1, eq. 1). Thus, methanol synthesis catalysts are typically operated at pressures between 30 – 50 bar and temperatures in the range of 220 – 300 °C, such conditions result in methanol selectivity greater than 99 % and reduced formation of by-products^{23,24}. Furthermore, it is well known that methanol can be synthesized from CO_2 -enriched synthesis gas (Figure 7.1, eq. 4),

Figure 7.2 Equilibrium composition of species involved in the direct synthesis of DME as a function of temperature at 40 bar. The thermodynamic calculation was carried out considering all species in the gas phase, a synthesis gas composition of $\text{H}_2:\text{CO} = 2 \text{ v/v}$ and DME, methanol, water and CO_2 as possible species. The HSC software from Outotec (v 7.14) was used to perform the calculation.

making it a target for research on CO₂ utilization^{25,26}. Methanol dehydration to form DME (Figure 7.1, eq. 2) is also an exothermic process and can be performed at relatively low temperatures (150 – 300 °C). Thus, the similarity of the process conditions makes it possible to operate methanol synthesis and DME production in a single reactor. The synergy generated by introducing the methanol dehydration reaction leads to a significant increase in CO conversion per pass (Figure 7.1, eq 5), this in marked contrast to the two-step process in which methanol is produced separately, stored and further converted to DME. The resulting equilibrium composition as a function of temperature for the direct DME synthesis is shown in figure 7.2, when considering the presence of CO, H₂, methanol, DME, CO₂ and H₂O at 40 bar total pressure. It is possible to observe that DME is favored as the main product at temperatures below 300 °C, and the other molecules can be recycled to produce more DME.

Methanol dehydration can be catalyzed by Brønsted as well as Lewis acid sites and the most studied solid acids for this reaction are γ -Al₂O₃ and zeolites^{20,21,27,28}. Too strong acid sites and high temperatures can favor the further dehydration of DME to olefins and hydrocarbons²⁹, compromising the selectivity of the catalyst. This is the case for most zeolites, which contain strong acid sites favoring DME dehydration at the required temperatures for methanol synthesis³⁰. Even though various strategies exist to tune the zeolites' acidity^{31,32}, their microporous structure can restrain the diffusion of methanol, DME and hydrocarbons leading to further polymerization reactions and coke formation, inactivating and blocking the active sites³³. γ -Al₂O₃ on the other hand, possesses milder acid sites, mainly of the Lewis type, making it more selective for DME and used for industrial catalysts^{13,34,35}. Nonetheless, competitive adsorption of water as well as crystal phase transformation aided by steam make γ -Al₂O₃ sensitive to the formed water during dehydration and thus diminishes its catalytic activity^{34,36,37}.

Hydrated niobium pentoxide (Nb₂O₅•*n*H₂O) and niobium phosphate (NbOPO₄) are interesting solid acids, possessing both Brønsted and Lewis acid sites, which have shown exceptional catalytic performance for various acid-catalyzed reactions^{38–40}. Contrary to many solid acids, these materials are capable of maintaining high catalytic activity and stability when water is involved. This resistance to water poisoning has been reported to originate from Lewis acid sites, in this case coordinatively unsaturated Nb⁵⁺ cations in NbO₄ tetrahedral arrangements, capable of forming active NbO₄-H₂O adducts that preserve an effective positive charge^{41–43}. Thus, niobium-based materials have raised the research interest as stable solid acids for hydration and dehydration reactions. Several studies have reported the application of niobium-based and niobium-modified materials for the dehydration of methanol to form DME^{44–46} and for the direct synthesis of DME from synthesis gas^{47,48}. These studies have shown the potential of niobium-based materials as active and selective catalysts for the synthesis of DME, however little attention has been paid to their stability.

In this research we studied the catalytic performance of Nb₂O₅•*n*H₂O and NbOPO₄ acting as solid acids in concert with a Cu-based catalyst in the direct synthesis of DME from synthesis gas. Particularly, this research focused on the stability of such materials under industrially relevant conditions (40 bar total pressure and 260 or 280 °C). For this end, we worked with physical mixtures composed of a commercial methanol synthesis catalyst and

a solid acid, $\text{Nb}_2\text{O}_5 \cdot n\text{H}_2\text{O}$, NbOPO_4 or $\gamma\text{-Al}_2\text{O}_3$, which was used as reference material. The mixtures of the niobium-based solid acids showed comparable activity and DME selectivity than the gamma-alumina one, while all catalysts showed deactivation throughout the reaction. Characterization of the used materials indicated that migration of copper from the methanol synthesis catalyst to the niobium-based materials contributed to the loss in methanol and DME production, whereas in the case of the gamma-alumina mixtures, coke deposition on the alumina and structural alteration of the copper-based catalyst were the main causes of deactivation.

7.2 Experimental

Materials. Hydrated niobium pentoxide ($\text{Nb}_2\text{O}_5 \cdot n\text{H}_2\text{O}$, HY-340) and niobium phosphate (NbOPO_4) were provided by Companhia Brasileira de Metalurgia e Mineração – CBMM. The gamma-alumina ($\gamma\text{-Al}_2\text{O}_3$) was obtained from BASF as extrudates (Al-3992E1/8”), which were grinded and sieved after thermal treatment. Thermal treatment of the solid acids was performed in stagnant air at different temperatures in all cases for 4 h with a ramp of $5\text{ }^\circ\text{C}\cdot\text{min}^{-1}$. Thereafter, the materials were sieved in a $38 - 75\text{ }\mu\text{m}$ fraction. The methanol synthesis catalyst employed was obtained from Alfa Aesar (I06Z036), with a reported composition of 10.1% Al_2O_3 , 63.5% CuO , 24.7% ZnO and 1.3% MgO . The catalyst pellets were grinded and sieved in a $75 - 150\text{ }\mu\text{m}$ fraction.

The bulk density of the sieved solid acids and methanol synthesis catalyst was determined by using a $200\text{ }\mu\text{L}$ spoon. The corresponding mass was measured by weighting the volume of material obtained with the spoon. This was repeated for five times and the average of weights was used to calculate the density (Table 7.1).

The physical mixtures for the direct synthesis of DME were prepared by weighting the desired amount of methanol synthesis catalyst and solid acid, mixed with $\sim 200\text{ mg}$ of SiC ($212 - 425\text{ }\mu\text{m}$) and loaded in the reactor. For the experiment in stacked-bed configuration, an amount of solid acid fixed to have the same amount of acid sites per reactor ($6 \cdot 10^{-3}\text{ mmol}_{\text{NH}_3}$ at $260\text{ }^\circ\text{C}$ and $3 \cdot 10^{-3}\text{ mmol}_{\text{NH}_3}$ at $280\text{ }^\circ\text{C}$ from ammonia TPD) was mixed with $\sim 60\text{ mg}$ SiC ($212 - 425\text{ }\mu\text{m}$) and placed downstream of the methanol synthesis catalyst with $\sim 40\text{ mg}$ of SiC ($212 - 425\text{ }\mu\text{m}$) separating both catalysts beds. Around 20 mg of copper-based methanol synthesis catalyst were used for the experiments at $260\text{ }^\circ\text{C}$ and around 10 mg for the experiments at $280\text{ }^\circ\text{C}$, diluted with $\sim 60\text{ mg}$ of SiC ($212 - 425\text{ }\mu\text{m}$).

Characterization. Powder X-ray diffractograms of passivated samples were measured using a Bruker-AXS D2 Phaser X-ray diffractometer, Co-K α radiation ($\lambda = 1.7903\text{ \AA}$) with a 1.0 mm fixed slit. Reduced Cu-based methanol synthesis catalyst (25 vol% H_2/N_2 flow, 2 h at $250\text{ }^\circ\text{C}$, heating rate of $5\text{ }^\circ\text{C}\cdot\text{min}^{-1}$) was placed in an air-tight sample holder and diffraction patterns were recorded on a Bruker D8 advance, equipped with a variable slit and Co-K α radiation ($\lambda = 1.7903\text{ \AA}$). Patterns were compared with the PDF-4+-database. Cu crystallite size was calculated using the Scherrer equation ($k = 0.94$) to the (111) diffraction line at $2\theta = 50.7^\circ$, with the Fityk 1.3.1 software⁴⁹.

A micromeritics TriStar 3000 apparatus was used to perform N_2 -physisorption at $-196\text{ }^\circ\text{C}$. Prior to analysis the samples were dried at $200\text{ }^\circ\text{C}$ for 16 h in N_2 flow. Specific surface area was calculated using the BET theory for $p/p_0 = 0.06 - 0.25$. The pore size distribution was determined using the BJH theory applied to the adsorption branch. The specific mesopore volume was calculated using single point at $p/p_0 = 0.98$.

Thermogravimetric measurements were performed using a Perkin Elmer TGA8000, hyphenated with a Hiden HPR-20 mass spectrometer. The experiments took place under an oxidizing flow composed of 20 vol.% O_2 /Ar. First, the temperature of the sample was held at $30\text{ }^\circ\text{C}$ for 5 min. and thereafter heated to $800\text{ }^\circ\text{C}$ at $10\text{ }^\circ\text{C}\cdot\text{min}^{-1}$. The mass spectrometer was used to monitor carbon dioxide ($m/z = 44$) and water ($m/z = 18$) throughout the experiment.

Ammonia temperature programmed desorption (NH_3 -TPD) analyses were performed using a Micromeritics AutoChem 2990 instrument equipped with a TCD detector. Typically, 100 mg of sample were dried in a He flow at the corresponding calcination temperature for each sample. The samples were then cooled to $100\text{ }^\circ\text{C}$ in a He flow, followed by pulses of 10 vol% NH_3 /He until saturation was reached. The temperature ($100\text{ }^\circ\text{C}$) and He flow were maintained for 1 h. Thereafter, the sample was heated under He flow to $400\text{ }^\circ\text{C}$ ($Nb_2O_5\cdot nH_2O$ and $NbOPO_4$) or $600\text{ }^\circ\text{C}$ ($\gamma\text{-Al}_2O_3$) at a rate of $10\text{ }^\circ\text{C}\cdot\text{min}^{-1}$, the desorption of ammonia was monitored by the TCD detector. NH_3 -TPD profiles can be found in Appendix F: Figure F1.

FTIR spectroscopy of adsorbed pyridine was carried out using a Bruker Vertex 70v spectrometer. Each sample was pressed into a self-supporting wafer (diameter 13 mm) and placed in an environmental transmittance IR cell. Samples were first pre-treated under dynamic vacuum ($\sim 10^{-6}$ mbar) at their corresponding calcination temperature (300 , 400 or $500\text{ }^\circ\text{C}$, $10\text{ }^\circ\text{C}\cdot\text{min}^{-1}$), thereafter the sample was cooled down to room temperature and exposed to an excess of pyridine. Then, dynamic vacuum ($\sim 10^{-6}$ mbar) was applied to the sample and heated to $150\text{ }^\circ\text{C}$ for 1 h. Spectra were recorded in the $4000 - 1000\text{ cm}^{-1}$ range. The quantitative determination of Lewis and Brønsted acid sites was made using the bands at 1448 and 1540 cm^{-1} following the procedure reported in ref 50.

Scanning transmission electron microscopy (STEM) images were acquired with a FEI Talos F200X microscope operated at 200 kV equipped with 4 energy dispersive X-ray (EDX) detectors, a high-angle annular dark-field (HAADF) and a bright field detector. Samples were prepared by dipping the Au sample grid into the used catalyst.

Catalytic performance. The catalytic performance was evaluated using an Avantium Flowrence 16 parallel, continuous flow, fixed bed reactor system. The catalysts were reduced in-situ at atmospheric pressure in a 25 vol% H_2 /He flow, for 2 h at $250\text{ }^\circ\text{C}$ (heating rate of $5\text{ }^\circ\text{C}\cdot\text{min}^{-1}$), this in order to activate the methanol synthesis catalyst by reducing the copper oxide to metallic copper. Thereafter, the gas stream was switched to $H_2/CO = 2.0\text{ v/v}$, with different GHSV depending on the catalyst. Reactors were pressurized to 40 bar and subsequently heated to reaction temperature 260 or $280\text{ }^\circ\text{C}$ ($1\text{ }^\circ\text{C}\cdot\text{min}^{-1}$). Products were analyzed using an on-line three-channel gas chromatograph (GC, Agilent 7890B). Hydrogen, carbon monoxide, helium, nitrogen and carbon dioxide were separated on a MolSieve 5A column (2.4 m, 1/8 inch inner diameter) and quantified using a thermal conductivity detector. Meth-

anol, dimethyl ether and C₁-C₄ hydrocarbons were separated using a GS-GasPro column (GS-Gaspro 30 m x 0.32 mm ID) and a HP-Innowax column (6 m, 0.32 mm ID) and analyzed by flame ionization detectors. The integrated peak areas were used to determine the gas phase composition, with He as the internal standard. Selectivities reported here were based on carbon atoms (%C) within hydrocarbon formed and excluding CO₂. All experiments showed a selectivity of ~ 26 % for CO₂, which is in the range of the thermodynamic equilibrium. Gas-Hourly-Space-Velocities (GHSV) were defined as total gas flow divided by the total catalyst volume.

7.3 Results and discussion

7.3.1 Structural, textural and acidic properties of the solid acids

Nb₂O₅·*n*H₂O and NbOPO₄ are known to have various crystal structures and metastable polymorphs depending on the thermal treatment to which they have been exposed^{51,52}. In general, crystallization in these materials occurs around 500 °C for Nb₂O₅·*n*H₂O and 800 °C for NbOPO₄, when treated below these temperatures both remain amorphous^{40,53,54}. Powder X-ray diffraction (XRD) patterns in figure 7.3a and b show that effectively after calcination at 200 or 400 °C for Nb₂O₅·*n*H₂O and 200, 400 or 600 °C for NbOPO₄, both materials did not show sharp diffraction signals but broad scattered diffraction patterns characteristic of a largely amorphous structure. Higher calcination temperatures induced crystallization. An increase of the temperature treatment is also accompanied by a loss in specific surface area as previously reported for niobium pentoxide^{54,55}. This was the same case for niobium phosphate as shown by the results obtained from N₂-physisorption for samples calcined at different temperatures (Figure 7.3c). Previous reports have shown that the decrease of surface area occurs together with a decrease of the concentration and strength of acid sites^{42,53,56}.

Figure 7.3 a, b and d XRD patterns of the materials after calcination at different temperatures indicated on each diffractogram. Diffractograms of Nb₂O₅·*n*H₂O (a), NbOPO₄ (b) and γ-Al₂O₃ (d). c, Change in specific surface area (green diamonds) and specific pore volume (red circles) for NbOPO₄ as a function of calcination temperature. Data obtained from N₂-physisorption.

Table 7.1 Summary of the properties of the solid acids.

Solid acid	Bulk density (g·mL ⁻¹)	Specific Surface Area ^a (m ² ·g ⁻¹)	NH ₃ -uptake ^b		Acid sites surface concentration (mmol _{NH3} ·m ⁻²)	Lewis/Brønsted acid sites ratio ^c	
			(mmol _{NH3} ·g ⁻¹)	(mmol _{NH3} ·mL ⁻¹)		Pre-treated at 300 °C	Pre-treated at 400 °C
Nb ₂ O ₅ · <i>n</i> H ₂ O	0.78	92	0.31	0.24	0.0034	0.9	1.4
NbOPO ₄	0.90	238	0.60	0.54	0.0025	0.5	0.7
γ-Al ₂ O ₃	0.53	190	0.62	0.33	0.0033	-	-

a. Determined by N₂-physisorption.b. Determined by NH₃-TPD after pretreatment at 400 °C for Nb₂O₅·*n*H₂O and NbOPO₄ and at 600 °C for γ-Al₂O₃.

c. Determined by FT-IR with pyridine as probe molecule.

Therefore, in order to maintain the acidic properties of both materials and considering the optimal reaction temperature for the direct synthesis of DME (250 - 300 °C), a calcination temperature of 400 °C (4 h, 5 °C·min⁻¹) was selected as pre-treatment for both materials. γ-Al₂O₃ was calcined at 600 °C to ensure the gamma phase (Figure 7.3d). Table 7.1 summarizes the characterization results for Nb₂O₅·*n*H₂O, NbOPO₄ and γ-Al₂O₃ obtained from N₂-physisorption, NH₃-temperature programmed desorption (NH₃-TPD) and FT-IR with pyridine as probe molecule.

The interaction of pyridine with the surface of the solid acids was used to assess the nature of such acid sites. The FT-IR spectra region between 1700–1400 cm⁻¹ shows the vibrations of pyridine interacting with a solid acid^{57–60} and employed to determine the ratio of Lewis and Brønsted acid sites (Table 7.1). The corresponding spectra are shown in figure F2 Appendix F, in which IR bands can be observed at ~1446 and 1606 cm⁻¹ corresponding to pyridine coordinated to Lewis acid sites (highlighted in green), whereas IR bands corresponding to pyridinium ion on Brønsted acid sites are observed at ~1639 and 1540 cm⁻¹ (highlighted in red). Additionally, a common IR band for both sites is observed at 1489 cm⁻¹ (highlighted in yellow). Nb₂O₅·*n*H₂O and NbOPO₄ show bands corresponding to both Lewis and Brønsted acid sites, however NbOPO₄ compared to Nb₂O₅·*n*H₂O shows more intense bands at ~1639 and 1540 cm⁻¹ (more pyridinium ion on Brønsted acid sites) and a lower ratio of Lewis to Brønsted acid sites. The γ-Al₂O₃ sample displayed only bands at ~1446 and 1606 cm⁻¹ and not at ~1639 and 1540 cm⁻¹, an indication that mainly Lewis acid sites are present on the surface of the alumina and no strong Brønsted acid sites to form pyridinium ions. Spectra for Nb₂O₅·*n*H₂O and NbOPO₄ pretreated at 300 °C are also included in figure F2 Appendix F. For both materials it can be observed that an increment of the pre-treatment temperature from 300 to 400 °C increased the relative intensity of the band at ~1446 cm⁻¹ and decreased the one at ~1540 cm⁻¹, therefore the Lewis to Brønsted acid sites ratio increased which is consistent with previous reports^{53,55,61}. In summary, the two niobium-based solid acids presented both Lewis and Brønsted acid sites, NbOPO₄ with more Brønsted acid sites compared to Nb₂O₅·*n*H₂O, and γ-Al₂O₃ showed mainly Lewis acid sites. Both types of acids can catalyze de dehydration of methanol, however differences in their catalytic performance can be expected due to their distinct mechanisms for DME formation^{62–64}.

Table 7.2 Summary of the reactor composition and catalytic performance results for the physical mixtures, Reaction conditions: 40 bar, $H_2/CO = 2$ v/v, GHSV (physical mixtures) = 1050 h⁻¹, GHSV (methanol synthesis catalyst) = 15000 h⁻¹, 260 or 280 °C and TOS = 120 h.

Reactor composition						Catalytic performance ^a					
Reaction temperature (°C)	Solid acid	Mass of Methanol Synthesis Catalyst (g)	Mass of Solid Acid (g)	Total Volume (mL)	Total Amount acid sites ^b (mmol _{NH3})	DME Productivity (g _{DME} ·h ⁻¹ ·mL ⁻¹)	CO Conversion (%)	DME Yield (%)	DME Selectivity (%)	MeOH Selectivity (%)	C ₁ -C ₄ Hydrocarbon selectivity (%)
Physical Mixtures											
260	Nb ₂ O ₅ · <i>n</i> H ₂ O	0.021	0.152	0.21	0.0047	0.26	62	55	89	8	3
	NbOPO ₄	0.020	0.178	0.23	0.0107	0.26	53	51	96	3	1
	γ-Al ₂ O ₃	0.021	0.108	0.21	0.0067	0.21	44	41	94	5	1
280	Nb ₂ O ₅ · <i>n</i> H ₂ O	0.020	0.161	0.22	0.0050	0.37	75	69	92	3	5
	NbOPO ₄	0.020	0.181	0.23	0.0109	0.37	73	69	94	3	2
	γ-Al ₂ O ₃	0.020	0.105	0.21	0.0065	0.34	69	65	94	4	2
Methanol synthesis catalyst											
260	-	0.020	-	0.015	-	-	16	0.0	0.0	99.1	0.9
280	-	0.020	-	0.015	-	-	25	0.0	0.0	98.6	1.4

a. Selectivities and yield are reported excluding CO₂

b. Determined by NH₃-TPD

7.3.2 Catalytic performance

The catalytic performance of the three solid acids was evaluated by preparing physical mixtures with a copper-based methanol synthesis catalyst. These physical mixtures were made by mechanically mixing the 20 mg of copper-based methanol synthesis catalyst (sieve fraction 75 – 150 μm) and ~ 0.2 mL of the solid acid (sieve fraction 38 – 75 μm), 1:13 v/v Cu-based catalyst to solid acid. Therefore, each reactor contained similar volumes of catalyst and hence similar Gas-Hourly-Space-Velocities (GHSV). The exact compositions and the corresponding results of the catalytic performance for all physical mixtures can be found in Table 7.2.

DME synthesis was carried out with an H_2 to CO ratio of 2, at 40 bar and for 120 h. The performance was evaluated at 260 or 280 $^\circ\text{C}$, since it has been reported⁶⁵ that water poisoning on $\gamma\text{-Al}_2\text{O}_3$ was avoided by raising the reaction temperature above 270 $^\circ\text{C}$. A reaction temperature of 280 $^\circ\text{C}$ might then diminish the detrimental effects of water on the solid acids. The physical mixtures in all cases triple the CO conversion for both temperatures compared to the Cu-based catalyst only (Table 7.2). This increase in conversion by the addition of the solid acid to the copper-based catalyst originates by two effects: first, the conversion of methanol to form DME shifts the equilibrium to higher CO conversions and second, water formed from the DME synthesis enables the water-gas-shift reaction, producing CO_2 (observed as one of the products) which accelerates methanol production (Figure 7.1).

Addition of any of the solid acids to the methanol synthesis catalyst effectively changed the selectivity from almost exclusively methanol to mainly DME. Particularly NbOPO_4 and $\gamma\text{-Al}_2\text{O}_3$ showed the highest DME selectivities, the rest of the products consisted of methanol and a small fraction of $\text{C}_1\text{-C}_4$ hydrocarbons, mainly CH_4 and C_2H_6 and in a lesser amount C_2H_4 , C_3H_6 , C_3H_8 , C_4H_8 and C_4H_{10} . The reported selectivities exclude CO_2 since in an in-

Figure 7.4 Normalized DME yield as a function of time-on-stream at 260 $^\circ\text{C}$ (a) or 280 $^\circ\text{C}$ (b) for the physical mixtures composed of 20 mg of copper-based methanol synthesis catalyst and ~ 0.2 mL of solid acid. Reaction conditions: 40 bar, $\text{H}_2/\text{CO} = 2$ v/v and initial CO conversion between 61 and 71 % at 260 $^\circ\text{C}$ and between 79 and 82 % at 280 $^\circ\text{C}$.

dustrial process it can be recycled with the unconverted synthesis gas to form more DME. On the other hand, the formation of hydrocarbons constitutes a loss of available carbon to further form methanol or DME and thus undesired in this process.

An increase of the reaction temperature from 260 to 280 °C increased the activity in all cases but also in the case of $\text{Nb}_2\text{O}_5 \cdot n\text{H}_2\text{O}$ improved the DME selectivity while decreasing the methanol selectivity. An increase in methanol dehydration activity to DME in this temperature range has been previously observed for $\text{Nb}_2\text{O}_5 \cdot n\text{H}_2\text{O}$ ⁴⁴, which is also observed in this study. Volume-based DME productivity was higher for the physical mixtures containing niobium-based acids compared to the $\gamma\text{-Al}_2\text{O}_3$ -based mixtures, due to the high density of the niobium materials. Furthermore, the mixtures with $\text{Nb}_2\text{O}_5 \cdot n\text{H}_2\text{O}$ and NbOPO_4 also showed a higher yield towards DME.

The relative change in DME yield through time is shown in figure 7.4 for the different physical mixtures. NbOPO_4 and $\gamma\text{-Al}_2\text{O}_3$ showed similar trends in relative DME yield, losing ~ 30 % at 260 °C and ~ 15 % at 280 °C, while $\text{Nb}_2\text{O}_5 \cdot n\text{H}_2\text{O}$ lost ~ 15 % at 260 °C and ~ 10 % at 280 °C.

As previously mentioned, formation of hydrocarbons constitutes undesired products for this reaction. The change in hydrocarbons selectivity through time is shown in figure 7.5 for the different physical mixtures and the methanol synthesis catalyst, in all cases a slight increase in the selectivity to hydrocarbons was observed during the experiment. At a reaction temperature of 260 °C, the mixtures containing NbOPO_4 and $\gamma\text{-Al}_2\text{O}_3$ had similar selectivities as the methanol synthesis catalyst throughout the experiment (Figure 7.5a), an indication that these products might have mainly originated from the copper-based catalyst. The $\text{Nb}_2\text{O}_5 \cdot n\text{H}_2\text{O}$ -based mixture however showed an increased hydrocarbon selectivity compared to the other catalysts, particularly at the first hours of the experiment.

Figure 7.5 Hydrocarbon selectivity, comprising C_1 to C_4 products, as a function of time-on-stream at 260 °C (a) or 280 °C (b) for the physical mixtures composed of 20 mg of copper-based methanol synthesis catalyst and ~ 0.2 mL of solid acid and of only the methanol synthesis catalyst (grey diamonds). Reaction conditions: 40 bar, $\text{H}_2/\text{CO} = 2$ v/v.

An increase of the reaction temperature to 280 °C increased also the selectivity to hydrocarbons for all catalysts (Figure 7.5b), although in different proportion for each of them. The methanol synthesis catalysts showed a constant selectivity after 20 h on stream resulting in 1.4 %_C hydrocarbons at the end of the experiment, 0.5 % more than at a reaction temperature of 260 °C. The hydrocarbon selectivities for the physical mixtures containing NbOPO₄ and γ -Al₂O₃ were around 2 %_C at the end of the experiment, however their increase throughout the experiment was markedly different. While the NbOPO₄-based catalyst showed a less pronounced increase in hydrocarbon selectivity after 20 h on stream, the γ -Al₂O₃-based catalyst showed a continuous increase throughout the experiment. The Nb₂O₅•*n*H₂O-based mixture showed also at 280 °C the highest hydrocarbon selectivity. Hydrocarbon formation at 280 °C seemed to originate for all physical mixtures not only from the methanol synthesis catalysts but also from the addition of the solid acid.

The catalytic performance of the materials was further evaluated in a stacked-bed configuration, with the solid acid downstream of the methanol synthesis catalyst, this to further understand the synergy between the methanol synthesis catalyst and the solid acids. Table 7.3 summarize the results for this experiment, the amount of solid acid was adjusted to have same amount of acid sites per reactor. Contrary to the physical mixtures, the CO conversion in this case was limited by the methanol synthesis catalyst and thus no major differences in conversion were observed within reactors. CO₂ was not detected as a product since the copper-based catalyst was not exposed to the water formed from the dehydration of methanol and then the water-gas-shift reaction did not take place. Throughout the experiment, reactors with stacked-bed showed a decrease in activity similar to only the methanol synthesis catalyst at both reaction temperatures (Appendix F: Figure F3a and b), implying that the activity loss originated mainly from the methanol synthesis catalyst and not the solid acids at these reaction conditions. The product distribution changed by addition of the solid acid downstream of the methanol synthesis catalyst, by forming DME at the expense of methanol. At both reaction temperatures, γ -Al₂O₃ showed the highest selectivity for DME, followed by NbOPO₄ and finally Nb₂O₅•*n*H₂O. The differences in DME selectivity might be explained by the dissimilar densities and acid sites concentrations of each solid acid. Increasing the amount of Nb₂O₅•*n*H₂O, the solid acid with the lowest concentration of acid sites per volume, indeed resulted in an increase in the DME selectivity (Table 7.3, second line).

In contrast to the physical mixtures, the hydrocarbon selectivities of the reactors with solid acid and of only the methanol synthesis catalyst were similar throughout the experiment and increased to similar values by increasing reaction temperature (Appendix F Figure F3c and d). The close contact of the methanol synthesis and dehydration functionalities in the physical mixtures, contrary to the stacked-bed configuration, could be then linked to the additional formation of hydrocarbons.

7.3.3 Characterization of the used catalysts

In order to further understand the reason behind deactivation in the physical mixtures, the used catalysts were separated by sieving them into the Cu-based methanol synthe-

Table 7.3 Summary of the reactor composition and catalytic performance results in stacked-bed configuration, with the solid acid downstream of the methanol synthesis catalyst. Results of only the methanol synthesis catalysts are shown for comparison. Reaction conditions: 40 bar, $H_2/CO = 2$ v/v, 260 or 280 °C and TOS = 120 h.

Reactor composition						Catalytic performance ^a				
Reaction temperature (°C)	Solid acid	Mass of Methanol Synthesis Catalyst (g)	Mass of Solid Acid (downstream) (g)	Total Volume (mL)	Total Amount acid sites ^b (mmol _{NH3})	GHSV (h ⁻¹)	CO Conversion (%)	DME Selectivity (%)	MeOH Selectivity (%)	C ₁ -C ₄ Hydrocarbon selectivity (%)
260	Nb ₂ O ₅ ·nH ₂ O	0.015	0.020	0.037	0.0063	6000	9	41	58	1
		0.016	0.030	0.049	0.0093	4500	8	65	34	1
	NbOPO ₄	0.016	0.010	0.023	0.0062	9600	8	52	47	1
	γ-Al ₂ O ₃	0.015	0.010	0.029	0.0061	7700	9	81	19	1
280	-	0.015	-	0.011	-	20100	9	0	99	1
	Nb ₂ O ₅ ·nH ₂ O	0.010	0.011	0.022	0.0034	10000	8	59	39	2
	NbOPO ₄	0.010	0.005	0.014	0.0030	16000	7	63	35	2
	γ-Al ₂ O ₃	0.011	0.006	0.019	0.0037	12000	7	84	14	2
	-	0.010	-	0.008	-	28000	7	0	98	2

a. Determined by NH₃-TPD

sis catalyst and the solid acid components. XRD patterns of the used solid acids (Appendix F: Figure F4) did not show significant changes in comparison to the diffractograms of the materials before reaction. The niobium-based materials maintained an amorphous structure while the alumina remained in the gamma phase. Thus, a change in the crystal phase of the solid acid did not occur during the reaction despite the high water partial pressures and the deactivation of the catalysts is not explained by this³⁷. XRD characterization of their used Cu-based methanol synthesis catalyst showed growth of the Cu crystallite size in all cases (Appendix F: Figure F5 and Table F1), particularly after the reaction at 280 °C. The actual crystallite size of the used catalysts might be slightly larger since these samples were passivated in air and part of the exposed copper most likely has been oxidized. Solely the Cu-based catalyst without solid acid after reaction showed a Cu crystallite size of 7.1 nm at 260 °C and of 7.6 nm at 280 °C compared to the reduced catalyst (6.6 nm). The Cu-based catalyst in the physical mixtures with the different solid acids displayed a larger crystallite growth compared to the catalyst without solid acid. However, the crystallite size variations within them could not be correlated to their deactivation trends.

Thus, only copper growth cannot explain the differences observed in loss of activity for the different physical mixtures. Besides metal growth, other structural changes aided by the presence of water could have taken place in the catalyst. Phenomena in the methanol synthesis catalyst such as re-crystallization of the ZnO or oxidation of the copper surface are relevant in the deactivation of the catalyst^{66,67}. Here it was not possible to clearly observe

Figure 7.6 a, Thermogravimetric analysis plotted in weight percentage as a function of temperature, for the solid acids after reaction at 260 °C (solid lines) or 280 °C (dashed lines). The weight is normalized to the weight at $T = 200$ °C, temperature in which CO₂ ($m/z = 44$) started to be detected by mass spectrometry as shown in plot 'b' for samples after reaction at 260 °C and plot 'c' at 280 °C.

Figure 7.7 STEM-EDX characterization results for the used mixtures of copper-based catalyst with $\text{Nb}_2\text{O}_5 \cdot n\text{H}_2\text{O}$ (a-d) or $\gamma\text{-Al}_2\text{O}_3$ (e-h). a, Dark-field image for the $\text{Nb}_2\text{O}_5 \cdot n\text{H}_2\text{O}$ -based mixture. b, Overlap of the EDX-maps for Nb (blue) and Cu (red). The corresponding niobium and copper maps are shown in c and d respectively. e, Dark-field image for the $\gamma\text{-Al}_2\text{O}_3$ -based mixture. f, overlap of the EDX-maps for Al (light blue) and Cu (red). The corresponding aluminum and copper maps are shown in g and h respectively.

such fine changes for all catalysts, only the Cu-based catalyst in the mixture with $\gamma\text{-Al}_2\text{O}_3$ after 280 °C reaction temperature (Appendix F: Figure F5j) showed a sharp diffraction peak at $2\theta = 40.7^\circ$. This diffraction can correspond to the ZnO (002) reflection (PDF 00-003-0752), characteristic of ZnO nanowires^{68,69}. Deterioration of the methanol synthesis catalyst during the reaction can then hamper the CO conversion and further DME formation.

The used solid acids were also characterized by thermogravimetric analysis in an oxidative atmosphere and monitored by MS in order to determine if deactivation might relate to coke deposition (Figure 7.6). At temperatures below 200 °C the weight loss corresponded to the elimination of adsorbed water. Above 200 °C the weight loss was accompanied by the detection of CO_2 ($m/z = 44$, Figure 7.6b and c), which most likely corresponded to burning of deposited coke. The change in weight was therefore normalized to the weight at 200 °C and weight loss was more pronounced for $\gamma\text{-Al}_2\text{O}_3$ (~ 4 %_w), followed by NbOPO_4 (~ 2 %_w) and $\text{Nb}_2\text{O}_5 \cdot n\text{H}_2\text{O}$ (~ 1 %_w). No marked difference in mass loss was observed when the catalysts had a reaction temperature at either 260 or 280 °C. Coke formation in solid acids can originate from accumulation and side reactions of methoxy groups⁷⁰ (intermediate species for methanol dehydration) and even though weak acid sites typically show less tendency of coke formation³⁰, still constitutes a relevant source of deactivation^{71,72}.

Scanning transmission electron microscopy with energy dispersive X-ray spectra mapping (STEM-EDX) was used to characterize the used mixtures and the used solid acids after reaction at 260 °C. Figure 7.7 shows the dark-field images and EDX elemental maps for the mixtures composed of the Cu-based catalyst and $\text{Nb}_2\text{O}_5 \cdot n\text{H}_2\text{O}$ (left) or $\gamma\text{-Al}_2\text{O}_3$ (right). The

EDX maps show the signal for Nb in dark blue, for Al in light blue and for Cu in red, Zn in all cases was found together with Cu so its EDX maps are not presented here for simplicity. In the case of $\text{Nb}_2\text{O}_5 \cdot n\text{H}_2\text{O}$ it is possible to observe that Nb and Cu in some areas are very close together and even showing some overlap. On the left side of the EDX maps it seems that Cu is dispersed on the niobium oxide and on the right side the big copper particle seems to be covered with some niobium oxide. For $\gamma\text{-Al}_2\text{O}_3$, the areas corresponding to Al and Cu are also close together but they seem to be more localized, it is possible to observe an overlap in the particle on the right side of the Cu with Al because the methanol synthesis catalyst also contains alumina, however the big particles with Al which correspond to $\gamma\text{-Al}_2\text{O}_3$ do not show an overlap with the Cu signal. It has been previously shown that migration of ions in bifunctional systems occurs, leading to a deterioration of the catalytic performance with time⁴. The overlap in Cu and Nb signal might be an indication that metals from the methanol synthesis catalyst might have migrated to the $\text{Nb}_2\text{O}_5 \cdot n\text{H}_2\text{O}$ during the reaction, compromising the performance of both the methanol synthesis catalyst and the solid acid. Moreover, this close contact of the copper and acid functionality might have had a relationship with the increased hydrocarbon selectivity of the physical mixtures via methoxy migration and decomposition^{73,74}.

EDX maps of only the used solid acids (Appendix F: Figure F6) showed a uniform overlap of Cu and Nb for NbOPO_4 and $\text{Nb}_2\text{O}_5 \cdot n\text{H}_2\text{O}$, an indication that the copper might be homogeneously distributed over the surface of these solid acids after reaction. The Cu-K α signal of the corresponding spectra was more intense for NbOPO_4 than for $\text{Nb}_2\text{O}_5 \cdot n\text{H}_2\text{O}$ or $\gamma\text{-Al}_2\text{O}_3$. Furthermore, the niobium-based materials had a green grayish color after reaction, an indication of a copper compound on their surface, whereas the alumina remained white. Migration of copper to the surface of the niobium-based materials could have been aided by the presence of Brønsted acid sites, which alumina did not show, via an ion exchange aided transport.

7.4 Conclusions

In this study we investigated the catalytic performance of hydrated niobium pentoxide and niobium phosphate as solid acids combined with a copper-based methanol synthesis catalyst for the direct synthesis of DME from synthesis gas. Gamma-alumina, a commonly used solid acid for this reaction, was investigated as a reference material. The solid acids were physically mixed with the copper-based methanol synthesis catalyst and their catalytic performance was evaluated at 40 bar, $\text{H}_2/\text{CO} = 2$ v/v and two different reaction temperatures (260 or 280 °C) for 120 h on stream. The mixing of the methanol synthesis catalyst and the solid acid led to increased CO conversions, compared to the methanol synthesis catalyst without solid acid or arranged in stacked-bed configuration with the solid acid downstream of the methanol synthesis catalyst. All physical mixtures showed excellent activity and DME selectivity. Particularly, niobium phosphate performed as good as gamma-alumina, with improved DME productivity per unit volume due to its high density and acid site concentration. However, the close contact between both functionalities in all mixtures also led to a

slight increase in C_1 - C_4 hydrocarbon selectivities. Furthermore, the stabilities of all mixtures differed depending on the nature of the solid acid, indicative of different deactivation mechanisms. The used catalysts were characterized in order to understand the main cause of deactivation. XRD results showed that the solid acids maintained their initial crystal structures after the reaction, therefore a major structural rearrangement in the solid acids was not the cause of deactivation under the reaction conditions used here. Cu crystallite size of the methanol synthesis catalyst grew during reaction conditions, but their growth was similar within the different mixtures so deactivation could not be solely explained by the loss of copper surface area. However, other structural changes in the Cu-based catalyst could not be completely excluded, one of the Cu-based catalysts in a mixture with γ - Al_2O_3 after reaction showed an extra diffraction peak corresponding to ZnO nanostructure, an indication that the methanol catalyst could be susceptible to structural changes during DME synthesis. Thermogravimetric analysis of the used solid acids showed that γ - Al_2O_3 accumulated more coke compared to the niobium-based materials, which might partially explain the loss in DME production particularly for γ - Al_2O_3 . EDX analysis of STEM images of the used catalysts revealed that the niobium-based solid acids and not the alumina one ended up with some copper on their surface after reaction. This might be an indication of ion migration from the copper-based methanol synthesis catalyst to the surface of the solid acids, and most likely compromising the performance of both the methanol synthesis catalyst and the acid sites. $Nb_2O_5 \cdot nH_2O$ and $NbOPO_4$ showed Lewis and Brønsted acid sites, while γ - Al_2O_3 showed only Lewis acid sites, this might explain the susceptibility of Cu migration in the case of the niobium-based materials. To summarize, the catalytic performance and characterization results point out that deactivation of the physical mixtures originated mainly from structural changes in the methanol synthesis catalysts. In the case of $Nb_2O_5 \cdot nH_2O$ and $NbOPO_4$, the deactivation might relate mainly to the migration of copper from the methanol synthesis catalyst to the Brønsted acid sites of these materials, while in the case of γ - Al_2O_3 deactivation might have generated from crystallite reconstruction of the ZnO in the methanol synthesis catalyst and coke deposition on the acid sites.

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8

Summary, Conclusions and Outlook

Summary and conclusions

Liquid fuels play a crucial role in the fulfilment of the current global energy demand, especially for the transportation sector. This large demand has promoted the efficient production of fuels and feedstock diversification. In this regard, synthesis gas has become an attractive alternative source for the production of chemicals and fuels. Within the key catalytic processes for this transformation are the Fischer-Tropsch synthesis (FT) and methanol synthesis reactions. The catalysts that enable these processes need to be active, selective and stable and therefore are subjects of research and continuous innovation.

Cobalt-catalyzed FT produces mainly long-chain hydrocarbons (C_{5+}), which can be further upgraded to liquid fuels such as gasoline and diesel. The selectivity to C_{5+} hydrocarbons of cobalt FT catalysts is enhanced when reducible metal oxides (e.g. Nb_2O_5 , TiO_2) are used as promoters and/or support material. These oxides display strong metal-support interaction (SMSI) with transition metals, which occurs during partial reduction of the support and consequent suboxides formation. These suboxides can migrate over the surface of the supported metal. Partial surface coverage with these suboxides is known to promote the intrinsic catalytic activity and selectivity towards C_{5+} products of the metal. Methanol synthesis in industry is currently performed by copper-based catalysts, co-promoted with ZnO. The catalysts are highly selective for methanol, although the conversion levels are thermodynamically restricted. Combination however with a solid acid can enhance the synthesis gas conversion levels to other chemical such as DME and olefins, the formation of which is thermodynamically more favored than that of methanol.

Transition metal oxides can promote the activity and/or selectivity as components of catalysts for synthesis gas conversion. Although less known, niobium oxide, or niobia, can effectively promote the activity and C_{5+} selectivity of cobalt-based FT catalysts. Throughout most of the research in this thesis, niobia was used as support material, for cobalt in chapters 3 and 4, for cobalt-nickel in chapter 5 and for nickel in chapter 6. Different synthetic strategies were explored in order to understand and expand the performance of niobium-supported metal catalysts. Furthermore, In chapter 7, Hydrated niobium pentoxide and niobium phosphate were studied in combination with a methanol synthesis catalyst for the direct synthesis of DME, particularly focusing on the stability of such systems. These solid acids are capable of maintaining high catalytic activity and stability when water is involved which is an attractive feature for dehydration reactions. Hereafter, highlights of the results of each chapter are summarized.

The literature analysis on metal-support interactions and tuning strategies presented in **chapter 2** demonstrated that supports are more than an inert structural matrix and that their chemical properties can be applied to enhance catalytic performance. The various strategies recently reported in literature were systematically arranged and discussed. Moreover, we provided a quantitative analysis of the scale of performance enhancement achieved in C1 chemistry, showing that effective tuning of the metal-support interactions can improve catalytic activity by one order of magnitude. It was also observed that metal nanoparticles smaller than four nanometers are more susceptible to metal-support interaction

effects. We provided a perspective of recent available synthetic tools to effectively control metal-support interactions and the design of catalysts for enhanced performance.

The first experimental chapter, **chapter 3**, introduced some of the necessary properties of niobia to serve as support material for cobalt-based FT catalysts. A comprehensive study was reported based on crystal phase, porosity and cobalt loading for an effective catalytic performance. Niobia crystallization above 400 °C prior to cobalt deposition proved necessary to obtain an active catalyst. The precursor, niobium oxide hydrate, was too reactive and led to non-reducible cobalt-niobium oxide species. The high temperature crystallization treatment, however, caused a collapse of the porous structure of the precursor and loss of specific surface area, limiting the cobalt loading. To circumvent this, a carbon templating method was used to restrict the structural collapse during crystallization. The resulting crystalline niobia maintained an important fraction of the 2–5 nm mesopores from the niobium oxide hydrate. The porous structure allowed higher cobalt loadings leading to an increased catalyst-weight-normalized catalytic activity.

A reduction-oxidation-reduction (ROR) pre-treatment in **chapter 4** was applied to cobalt supported on reducible supports (niobia and titania) to tune the coverage of cobalt nanoparticles by SMSI-species. This resulted in a twofold increase in accessible cobalt metal surface area and a proportional enhancement of the cobalt-based FT catalytic activity. In contrast, a decrease in cobalt surface area and activity was observed when ROR was applied to a cobalt supported on alpha-alumina (a non-reducible oxide) catalyst. The increased activity for niobia and titania was attributed to more accessible cobalt metal surface sites as revealed by the constant turnover frequency in FT, while maintaining the full promotional effect of the SMSI-species. Coincidentally, hollow cobalt oxide nanoparticles were observed after oxidation as part of ROR for the samples that subsequently showed the highest activities. Formation of these hollow oxide nanoparticles was proposed to be instrumental in tuning the coverage by SMSI-species.

In **chapter 5**, we showed that the combination of cobalt-nickel bimetallic nanoparticles and reducible metal oxides as support (e.g. niobia and titania) allowed for increased FT performance. Addition of nickel to cobalt increased the dispersion of the metal nanoparticles and aided the reduction of the mixed metal oxides. Low-pressure FT performance results showed substantially higher activities, C_{5+} selectivities and stabilities for the bimetallic nanoparticles supported on reducible oxides. On the other hand, alumina-supported catalysts showed low activities and C_{5+} selectivities than Co independent of the Co-Ni composition and, moreover, a continuous loss of activity. The marked contrast in catalytic performance was tentatively coined to a shift of the rate determining step, as derived from the trend between TOF and CO-FTIR. A weaker CO adsorption was inferred for Co-Ni supported on reducible oxides, which in turn was proposed to improve hydrogen adsorption and the catalytic activity.

Nickel supported on niobia for CO hydrogenation was studied in **chapter 6** with focus on different reduction temperatures. We showed that niobia used as support material offers the possibility to obtain stable nickel-based catalysts for CO hydrogenation with tunable product spectrum. Low reduction temperatures provided high initial activities but

fast deactivation due to nickel particle growth, whereas a high reduction temperature led to lower but stable activity and no significant particle growth. FTIR measurements of CO adsorbed on Ni/Nb₂O₅ showed that nickel subcarbonyls readily formed after low but not after high reduction temperature. We inferred that the particle growth involved the formation and diffusion of nickel carbonyls that bring about Ostwald Ripening. Moreover, the reduction treatment had a strong influence in the product distribution. The highest selectivity towards C₅₊ (55 wt.%) was obtained after reduction at 350 °C, while a further increase of the reduction temperature shifted the product distribution towards lighter products.

In **chapter 7**, hydrated niobium pentoxide and niobium phosphate were used in combination with a methanol synthesis catalyst for production of DME from synthesis gas. All physical mixtures showed excellent activity and DME selectivity. Particularly, niobium phosphate performed as good as gamma-alumina (used as reference material), with improved DME productivity per unit volume due to its high density and acid site concentration. Furthermore, the stabilities of all mixtures differed depending on the nature of the solid acid, indicative of different deactivation mechanisms. STEM-EDX analysis of the used catalysts revealed that the niobium-based solid acids and not the alumina one ended up with some copper on their surface after reaction. This might be an indication of ion migration from the copper-based methanol synthesis catalyst to the surface of the solid acids, and most likely compromising the performance of both the methanol synthesis catalyst and the acid sites.

Outlook

As usual in scientific research, solving some of the research questions in this thesis led to new ones. From chapter 3 we learned that mesopores from the precursor for crystalline niobia can be partially maintained. These mesopores appear as small cavities (2-5 nm) over the niobia and seem to be characteristic of niobium oxides. The formation mechanism of these mesopores remains however unclear. The cavities might be used to restrain small nanoparticles, for example to avoid particle mobility and metal sintering. The size of such cavities is not optimal for FT or methanol synthesis catalysts, however other reactions particularly involving nanoparticles of precious metals might benefit.

The SMSI effect is a phenomenon that was extensively discussed throughout the thesis, although we could only present indirect evidence of its structure and impact. It is indeed still a scientific challenge to directly detect the suboxide coverage of metal nanoparticles during SMSI, particularly for base metals. Nowadays, coverage by suboxides has been possible to observed by high-resolution TEM for noble metals and at extreme conditions (e.g. pure hydrogen and reduction temperatures higher than 500 °C). More sensitive detectors, 'transparent' cells capable to withstand higher gas pressures and a better understanding of the effects of the electron beam on gas systems at high pressure are needed in order to study SMSI of a working catalyst. Similarly, Near-Ambient Pressure XPS (NAP-XPS) is another attractive characterization technique that might be able to help us to study the SMSI effect. The phenomenon has been observed by XPS but mainly for model systems. Moreover, NAP-

XPS has the same challenges as with microscopy techniques. We explored the use of NAP-XPS at the synchrotron facility BESSY II, however the results showed that the relatively low gas pressures of the cell did not lead to reduction of the supported cobalt oxide. The mobility of the suboxides, their crystallinity and their Lewis acidity are some of the unknown characteristics that remain to be solved. Knowing this could help us to understand why for instance titania used as support for cobalt or cobalt-nickel nanoparticles presents a higher TOF than niobia as support. As well it can increase our understanding of the promotional effect of reducible supports on chain-growth and C_{5+} selectivity.

In chapter 4, one of the important observations was the formation of hollow cobalt oxide nanoparticles by the Kirkendall effect for the most active samples. This was proposed to be instrumental in tuning the surface composition of the metallic cobalt nanoparticles and hence the increased activity. An in-depth study of this mechanism can be of great interest to further understand the possible re-distribution of the suboxides. This will require extremely sensible characterization techniques, capable of operating at the various reductive and oxidative conditions. Moreover, from previous research it is known that cobalt supported on niobia shows high surface specific activity when promoted with a noble metal (Pt), and now the question arises whether or not this CoPt system also would benefit from the ROR pre-treatment.

For the bimetallic cobalt-nickel system from chapter 5 the very high activities and particularly high C_{5+} selectivities at already 1 bar were remarkable. A future research challenge would be to maintain those active sites at higher pressures. First, a kinetic study of these catalysts can improve our understanding of the nanoparticle's composition and support interaction. Second, we could explore synthetic strategies to maximize the promotional effect of the reducible supports and bimetallic nanoparticles. The ROR pre-treatment might improve the distribution of suboxides and perhaps their effectiveness. However, Co-Ni dealloying might take place upon oxidation, most likely resulting in a core-shell arrangement since cobalt will undergo oxidation before nickel. This might be beneficial for the active sites, since it was observed a similar phenomenon of surface enrichment with cobalt upon CO adsorption for the most active samples. Beside this, we also observed an increase in dispersion of the metal nanoparticles over the support when nickel was added to cobalt, this however makes it difficult to disentangle the effects from particle size and nanoparticle composition. Colloidal synthesis of bimetallic nanoparticles is a tool that can help us understand these systems better. Although difficult to execute, the nanoparticles' properties can be better controlled by use of a colloidal synthesis than with standard synthesis methods. In this way we could explore different particle sizes and the distribution of the metals within a nanoparticle.

An additional challenge would be to avoid the formation of nickel tetracarbonyl at higher CO pressures for CoNi catalysts using for example a higher reduction temperature, as learned from chapter 6. The metal-support interaction was not fully optimized for these systems and the ROR pre-treatment might improve the performance after a high initial reduction temperature. The ample techniques to tune the metal-support interaction in the literature, as shown in chapter 2, might serve as inspiration to tackle these challenges.

The use of hydrated niobium oxide and niobium phosphate in chapter 7 showed promising results in the application of these materials for DME synthesis. Ion migration from the copper-based methanol synthesis catalyst to these materials was observed, leading most likely to a loss in activity and increased hydrocarbon selectivity. This might be avoided by quenching the Brønsted acid sites, which are typically linked to the ion migration phenomenon. There are several niobium-base acidic materials, with various structures, types of acid sites and strengths, which can allow an optimal design as stable DME synthesis catalysts. However, the mechanism of ion migration during reaction conditions, and similar deactivation mechanisms, remains poorly understood. The recent interest in use of bifunctional systems for synthesis gas conversion has attracted attention into studying the stability of such systems. Characterization techniques that can be used at elevated pressure will be important to increase our knowledge of these catalysts.

Overall, the aim of this thesis was to reflect the potential and versatility of niobium-based catalysts in synthesis gas conversion, to understand the underlying mechanisms for improved catalytic performance and expand the available synthetic tools for catalyst design.

Nederlandse samenvatting

Vloeibare brandstoffen spelen een cruciale rol in de huidige globale vraag naar energie, met name in de transportsector. Deze enorme vraag naar energie heeft efficiënte productie van brandstoffen en diversificatie van grondstoffen gestimuleerd. Wat betreft diversificatie van grondstoffen is synthesesegas, verkregen uit grondstoffen zoals aardgas en biomassa, een interessant alternatief voor de productie van chemicaliën en brandstoffen. De belangrijke katalytische processen voor deze transformatie zijn de Fischer-Tropschsynthese (FT) en methanolsynthese. De katalysatoren die deze processen mogelijk maken dienen actief, selectief en stabiel te zijn en zijn daarom het onderwerp van onderzoek en innovatie.

Door kobalt gekatalyseerde FT produceert hoofdzakelijk koolwaterstoffen met lange ketens van koolstofatomen (C_{5+}), die verder verwerkt kunnen worden tot vloeibare brandstoffen zoals benzine en diesel. De selectiviteit voor C_{5+} koolwaterstoffen van FT katalysatoren gebaseerd op kobalt wordt verhoogd wanneer reduceerbare metaaloxiden (e.g. Nb_2O_5 , TiO_2) gebruikt worden als promotor en/of dragermateriaal. Deze oxiden vertonen sterke metaal-dragerinteracties (SMSI) met transitie-metalen, welke plaatsvinden gedurende gedeeltelijke reductie van de drager en de daaropvolgende formatie van suboxiden. Deze suboxiden kunnen zich over de oppervlakte van het metaaldeeltjes verplaatsen. Het is bekend dat gedeeltelijke bedekking van het metaaloppervlak met deze suboxiden de intrinsieke katalytische activiteit en selectiviteit naar C_{5+} producten van het metaal bevorderen. Methanolsynthese wordt momenteel uitgevoerd in de industrie door koper-gebaseerde katalysatoren, gepromoteerd door ZnO. De katalysatoren zijn zeer selectief voor methanol, ondanks dat de conversieniveaus beperkt zijn door het thermodynamisch evenwicht van synthesesegas en methanol. Combinatie met een vast zuur daarentegen kan de conversieniveaus van het synthesesegas via methanol tot andere chemicaliën, zoals DME en olefinen, verhogen. De formatie van deze andere chemicaliën is thermodynamisch gunstiger dan die van methanol.

Wanneer transitie-metaaloxiden als component aan de katalysator voor synthesesegasconversie worden toegevoegd, kunnen deze de katalytische activiteit en/of selectiviteit verhogen. Hoewel minder bekend, kan niobiumoxide, ook wel niobia genoemd, de activiteit en C_{5+} -selectiviteit van kobalt-gebaseerde FT katalysatoren efficiënt verhogen. Gedurende het overgrote deel van het onderzoek in dit proefschrift werd niobia gebruikt als dragermateriaal. Niobia werd als dragermateriaal gebruikt voor kobalt in hoofdstuk 3 en 4, voor kobalt-nikkel in hoofdstuk 5 en voor nikkel in hoofdstuk 6. Verschillende synthesesstrategieën zijn onderzocht om de prestatie van niobium-gedragen metaalkatalysatoren te begrijpen en te verbeteren. Verder zijn in hoofdstuk 7 gehydrateerde niobiumpentoxide en niobiumfosfaat bestudeerd in combinatie met een methanolsynthesekatalysator voor de directe synthese van DME, met als focus de stabiliteit van zulke systemen. Wanneer er water bij betrokken is, zijn deze vaste zuren in staat om hoge katalytische activiteit en stabiliteit te behouden, wat een interessante eigenschap is voor dehydratiereacties. Hierna worden de hoogtepunten van de resultaten van ieder hoofdstuk omschreven.

De literatuurstudie van metaal-dragerinteracties en strategieën om die te beïnvloeden die in **hoofdstuk 2** gepresenteerd wordt, toont aan dat dragers meer dan een structu-

rele matrix zijn en dat de chemische eigenschappen gebruikt kunnen worden om de katalytische prestaties te verbeteren. De verschillende strategieën die recentelijk gerapporteerd zijn in de literatuur zijn systematisch geordend en bediscussieerd. Bovendien presenteren wij een kwantitatieve analyse van de schaal van prestatie-verbetering behaald in C1-chemie, waarbij wordt aangetoond dat efficiënte regulering van de metaal-dragerinteracties de katalytische activiteit met een orde van grootte kan verbeteren. Ook werd geobserveerd, dat metalen nanodeeltjes kleiner dan 4 nanometer gevoeliger zijn dan grotere deeltjes voor de effecten van metaal-dragerinteracties. Wij bieden een perspectief op de huidige beschikbare synthetische gereedschappen om metaal-dragerinteracties efficiënt te controleren en katalysatoren te ontwerpen met verbeterde prestaties.

In **hoofdstuk 3**, het eerste experimentele hoofdstuk, worden enkele van de eigenschappen van niobia gepresenteerd die noodzakelijk zijn om als dragermateriaal voor kobalt-gebaseerde FT katalysatoren te kunnen fungeren. Een uitgebreide studie wordt beschreven die gebaseerd was op kristalfase, porositeit en de gebruikte hoeveelheid kobalt (kobaltbelading) voor efficiënte katalytische prestaties. Kristallisatie van niobia boven 400 °C, voor afzetting van kobalt, bleek nodig te zijn om een actieve katalysator te verkrijgen. De uitgangsstof, niobiumoxidehydraat, was te reactief en leidde tot niet-reduceerbare varianten van kobaltniobiumoxide. De kristallisatiebehandeling bij hoge temperatuur, daarentegen, leidde tot een afname van de porositeit van de uitgangsstof en een verlies van het specifiek oppervlak, waardoor de kobaltbelading gelimiteerd werd. Om dit te omzeilen werd een ‘templating’ methode met koolstof gebruikt om de structurele degradatie gedurende kristallisatie te beperken. Het resulterende kristallijne niobia behield een belangrijke fractie van de 2-5 nm mesoporiën van het niobiumoxidehydraat. De poreuze structuur liet een hogere kobaltbelading toe, wat leidde tot een toename van de op katalysatorgewicht genormaliseerde katalytische activiteit.

Een reductie-oxidatie-reductie (ROR) voorbehandeling werd toegepast in **hoofdstuk 4** op kobalt op reduceerbare dragers (niobia en titania) om de bedekking van kobalt-nanodeeltjes door SMSI-verbindingen te reguleren. Dit resulteerde in een toename van het beschikbare kobalt metaaloppervlak en een proportionele verbetering van de kobalt-gebaseerde katalytische FT activiteit met een factor twee. In tegenstelling, een afname in kobaltoppervlak en activiteit werd waargenomen toen ROR toegepast werd op een kobalt-katalysator gedragen op een alfa-alumina (een niet-reduceerbaar oxide). De toegenomen activiteit voor niobia en titania werd toegeschreven aan de toename van beschikbare kobalt metaaloppervlakteplekken met identieke structuur, met een de constante oppervlak-gebaseerde omzettingsfrequentie in FT die erop wijzen dat de effecten van de SMSI-verbindingen werden behouden. Tegelijkertijd werden holle kobaltoxidenanodeeltjes waargenomen na oxidatie als onderdeel van de ROR behandeling in de monsters die de hoogste activiteit vertoonden. Formatie van deze holle oxidenanodeeltjes werd als belangrijk verondersteld in de regulering van de bedekking door SMSI-verbinding.

In **hoofdstuk 5** wordt getoond dat de combinatie van kobalt-nikkel nanodeeltjes en reduceerbare metaaloxiden als drager (e.g. niobia en titania) verbeterde FT prestaties leveren. De toevoeging van nikkel aan kobalt verhoogde de verdeling van de metalen nano-

deeltjes over de drager en bevorderde de reductie van de metaaloxiden. De resultaten van FT reactie onder lage druk toonden substantieel hogere activiteit, C_{5+} selectiviteit en stabiliteit voor de CoNi-nanodeeltjes op reduceerbare oxiden. Anderzijds toonden alumina-gedragen bimetallische katalysatoren lagere activiteit en C_{5+} selectiviteit dan Co, onafhankelijk van de kobalt-nikkel samenstelling. De nikkel-houdende katalysatoren op alumina vertoonden bovendien een voortdurende afname in activiteit. Het contrast in katalytische prestaties wordt voorlopig toegeschreven aan een verandering in de snelheidsbepalende stap, zoals afgeleid uit de trend tussen TOF en CO-FTIR. Een lagere CO-adsorptie werd gevonden voor Co-Ni gedragen op reduceerbare oxiden, wat vervolgens werd voorgesteld als reden voor de verbetering van waterstofadsorptie en de katalytische activiteit.

Nikkel op niobia voor CO-hydrogenatie wordt beschreven in **hoofdstuk 6** met focus op verschillende reductietemperaturen. We tonen aan dat niobia, wanneer gebruikt als dragermateriaal, de mogelijkheid biedt om stabiele nikkel-gebaseerde katalysatoren te verkrijgen voor CO-hydrogenatie met een variabel productspectrum. Lage reductietemperaturen zorgden voor hoge initiële activiteiten maar snelle deactivering door de groei van nikkeldeeltjes, terwijl een hoge reductietemperatuur leidde tot lagere maar stabielere activiteit en geen significante groei van deeltjes. FTIR metingen van CO geadsorbeerd op Ni/Nb₂O₅ toonden dat nikkel-subcarbonylen vormden na lage reductietemperaturen, maar niet na hoge reductietemperaturen. Wij leidden hieruit af dat bij de groei van deeltjes de formatie en diffusie van nikkelcarbonylen via zogenaamde Ostwald Ripening betrokken waren. Bovendien had de reductiebehandeling een sterke invloed op de productdistributie. De hoogste selectiviteit naar C_{5+} (55 wt. %) werd behaald na reductie op 350 °C, terwijl een verdere toename van de reductietemperatuur de productdistributie verschoof naar lichtere producten.

In **hoofdstuk 7** werden gehydrateerde niobiumpentoxide en niobiumfosfaat gebruikt in combinatie met een methanolsynthesekatalysator voor de productie van DME uit synthesesgas. Alle fysische mengsels vertoonden excellente activiteit en DME-selectiviteit. Met name niobiumfosfaat presteerde even goed als gamma-alumina (gebruikt als referentiemateriaal), met verhoogde DME-productiviteit per eenheid volume door de hoge dichtheid en concentratie van zure plaatsen. Verder verschilde de stabiliteit van alle fysische mengsels, afhankelijk van het type vast zuur, wat wijst op verschillende deactivatiemechanismen. STEM-EDX analyse van de gebruikte katalysatoren toonde aan dat de niobium-gebaseerde vaste zuren, en niet degenen gebaseerd op alumina, eindigden met wat koper op het oppervlak na de reactie. Dit kan een indicatie zijn van migratie van koperionen van de methanolsynthesekatalysatoren naar het oppervlak van de vaste zuren, wat hoogstwaarschijnlijk leidt tot een vermindering van de prestaties van zowel de methanolsynthesekatalysator als ook van de zure katalysator.

Appendix A

Supporting Information Chapter 2

Control of Metal-Support Interactions in Heterogeneous Catalysts to Enhance Activity and Selectivity

Table A1 Overview of analyzed MSI modification strategies and their effect on catalytic performance in C1 chemistry. References can be found in the main text Chapter 2.

Tuning category	Main MSI effect	Tuned catalyst	Reference catalyst	Metal particle size tuned catalyst (nm)	Reaction temperature (°C)	Activity descriptor	Activity tuned catalyst	Activity reference catalyst	Selectivity descriptor	Selectivity tuned catalyst	Selectivity reference catalyst	Productivity enhancement factor	Ref.
Support, composition	Interfacial perimeter	Au/TiO ₂	Au/Al ₂ O ₃	2.9	CO oxidation/20	Rate/mol _{CO} mol _{wt} ⁻¹ s ⁻¹	0.7	0.2	-	-	-	4.3	50
Support, composition	Charge transfer	Rh/TiO ₂ light	Rh/TiO ₂ dark	2.5	Stream reforming CH ₄ /260	H ₂ production rate/μmol g ⁻¹ min ⁻¹	120	40	-	-	-	3	54
Support, morphology	Charge transfer	Pt/TiO ₂ Spheres	Pt/TiO ₂ concave cubes	3.0	MeOH oxidation/60	TOF/s ⁻¹	48.6	15.3	S _{HOOCCH₃} /%	67	56.8	3.7	67
Support, morphology	Morphology	7-8 nm Pd/θ-Al ₂ O ₃	7-8 nm Pd/γ-Al ₂ O ₃	7.5	CH ₄ oxidation/300	TOF/s ⁻¹	0.6	0.1	-	-	-	10.5	62
Support, morphology	Morphology	Strain Pattern 7	Strain Pattern 3	5.2	CO oxidation/827 ^a	TOF/10 ⁻⁴ s ⁻¹	53.0	20.0	-	-	-	2.7	35
Support, morphology	Interfacial perimeter	Au/TB-ZnO	Au/NR-ZnO	4.0	CO oxidation/20	Rate/10 ² mol _{CO} g _{cat} ⁻¹ h ⁻¹	293.0	1.9	-	-	-	153.4	71
Support, morphology	Interfacial perimeter	Au/CeO ₂ cube	Au/CeO ₂ octahedra	3.0	CO oxidation/240	TOF/s ⁻¹	0.69	0.17	-	-	-	4.1	70
Support, morphology	SMSI	Co-Ru/Ti-L	Co-Ru/Ti-H	9.1	Fischer-Tropsch/220	CTY/10 ³ mol _{CO} g _{Co} ⁻¹ h ⁻¹	134.1	56.6	SC ₅ /%	73.9	56.8	3.1	65
Support, morphology	SMSI	Co-Ru/Ti-R	Co-Ru/Ti-A	6.0	Fischer-Tropsch/220	CTY/10 ³ mol _{CO} g _{Co} ⁻¹ h ⁻¹	113.5	53.2	SC ₅ /%	79.1	62	2.7	63

Support, morphology	SMSI	Ru/TiO ₂ -3	Ru/TiO ₂ -1	1.6	CO methanation/190	TOF/10 ⁻³ s ⁻¹	4.4	0.7	S _{CO} /%	88	58	10.3	66
Support, morphology	Charge transfer	Pt/h-BNNS	Pt/h-BN	5.0	CO oxidation/47	X _{CO} /%	70.0	30.0	-	-	-	2.3	72
Support, morphology	Interfacial perimeter	Ni@SiXNS-EtOH	Ni@SiXNS-H ₂ O	10.3	CO ₂ hydrogenation/300	Rate/mmol g _{Ni} ⁻¹ h ⁻¹	50.3	68.6	S _{CH₄} /%	89.8	53.4	1.2	73
Support, morphology	Chemical composition	1% Pt/Nb ₂ CTx-MXene	1.5% Pt/Al ₂ O ₃	2.6	WGS/300	Rate/10 ⁻² mol _{H₂} mol _{Pt} ⁻¹ s ⁻¹	1.6	1.4	-	-	-	1.1	75
Support, doping	Charge transfer	Cu/ZnO:Al	Cu/ZnO	10.0	MeOH synthesis/230	TOF/μmol MeOH μmol Cu _{surf} ⁻¹ s ⁻¹	0.018	0.016	-	-	-	1.1	92
Support, doping	Charge transfer	Pt/4%FeZnO	Pt/ZnO	2.4	CO oxidation/126	TOF/s ⁻¹	5.4	0.6	-	-	-	9.0	88
Support, doping	Charge transfer	Cu/NG-10	Cu/rGO	7.5	MeOH oxidation/120	TOF/h ⁻¹	16.9	6.3	S _{BMC} /%	97.6	92.3	2.8	79
Support, doping	Interfacial perimeter	Ni/La10	Ni/Al	7.5	Dry reforming CH ₄ /600	X _{CH₄} /%	40.0	17.0	-	-	-	2.4	86
Support, doping	Interfacial perimeter	Ir/Ce _{0.9} Pr _{0.1} O ₂	Ir/CeO ₂	4.5	Dry reforming CH ₄ /600	Rate/mol _{CH₄-CO₂} mol _{Ir} ⁻¹ h ⁻¹	2818.0	849.0	-	-	-	3.3	89
Support, doping	Interfacial perimeter	Ni/1.0Fe	Ni/0Fe	9.0	Dry reforming CH ₄ /750	STY/mol _{CO} kg _{Ni} ⁻¹ s ⁻¹	67.0	57.0	-	-	-	1.2	84
Support, doping	Interfacial perimeter	Au5YCeCP	Au/CeO ₂	2.4	WGS/230	X _{CO} /%	97.0	83.0	-	-	-	1.2	90

Support, doping	Chemical composition	2/Mg@Al ₂ O ₃ (A-THF)	2/Al ₂ O ₃ (A-THF)	1.3	Dry reforming CH ₄ /650	Rate/molCH ₄ mol ⁻¹ s ⁻¹	0.4	0.0	-	-	14.0	85
Support, surface modification	Morphology	CSN_1b	CS_1a	2.6	MeOH synthesis/260	TOF/10 ⁻³ s ⁻¹	0.9	0.7	-	-	1.3	102
Support, surface modification	Morphology	Co/CNT-EtOH	Co/CNT-GPO-EtOH	7.0	Fischer-Tropsch/220	TOF/10 ⁻³ s ⁻¹	73.0	31.0	90	S _{CS} /%	2.6	95
Support, surface modification	Interfacial perimeter	Pr/C-In ₂ O ₃	Pt/P-In ₂ O ₃	3.0	CO ₂ reduction/25	Rate/μmol _{CO2} h ⁻¹	154.5	30.8	81.9	S _{CO} /%	4.7	103
Support, surface modification	SMSI	CoRu/TiO ₂ @AO	CoRu/YO ₂ @AO	13.3	Fischer-Tropsch/220	CTY/mol _{CO} g _{Co} ⁻¹ h ⁻¹	0.2	0.1	41	S _{CS} /%	9.6	104
Support, surface modification	Morphology	Co/CNT90	Co/CN-T120A	2.7	Fischer-Tropsch/210	TOF/10 ⁻³ s ⁻¹	1.94	1.00	32	S _{CS} /%	2.3	93
Metal nanoparticle, size	Morphology	3% Ru/Al ₂ O ₃	1% Ru/Al ₂ O ₃	1.3	CO ₂ hydrogenation/?	TOF/s ⁻¹	0.3	0.3	0.36	S _{CO} /%	1.2	108
Metal nanoparticle, size	Interfacial perimeter	Ru(NC)/CeO ₂	Cu(NP)/CeO ₂	1.2	CO ₂ hydrogenation/190	TOF/10 ⁻³ s ⁻¹	7.4	0.5	100	S _{CH₄} /%	14.0	107
Metal nanoparticle, composition	Chemical composition	PtNi/SBA-15	Ni/SBA-15	1.0	rWGS/400	TOF/mol _{CO2} mol _{metal} ⁻¹ min ⁻¹	5.4	8.5	98.3	S _{CO} /%	0.8	115
Metal nanoparticle, composition	Chemical composition	Au ₁₀ Cu ₉₀ /SiO ₂	Au ₁₀ Cu ₉₀ /Al ₂ O ₃	14.0	CO oxidation/150	X _{CO} /%	98.0	11.0	-	-	8.9	113
Metal nanoparticle, composition	Morphology	NiSi-OAmc	NiSi-OAc	4.6	Dry reforming CH ₄ /700	TOF _{CH₄} /s ⁻¹	2.8	2.2	-	-	1.3	119

Treatment, thermal	Charge transfer	Au/TiO ₂ O400	Au/TiO ₂ CO400	2.6	CO oxidation/80	TOF/s ⁻¹	3.4	1.8	-	-	1.9	52
Treatment, thermal	SMSI	Ni@TiO ₂ (450)	Ni@TiO ₂ (600)	12.5	WGS/350	TOF/s ⁻¹	3.8	1.9	S _{GS} /%	95.1	2.1	125
Treatment, thermal	SMSI	RR2Ti 500 °C red.	RR2Ti 400 °C ox.	5.0	CO oxidation/80	X _{CO} /%	90.0	5.0	-	-	18.0	120
Treatment, thermal	SMSI	Au/LDO-400	Au/LDO-700	2.4	CO oxidation/190	X _{CO} /%	86.0	65.0	-	-	1.3	123
Treatment, thermal	SMSI	Ni/Nb ₂ O ₅ 450 °C red.	Ni/Nb ₂ O ₅ 250 °C red.	27.0	Fischer-Tropsch/230	NTY/10 ⁵ mol _{CO} g _{Ni} ⁻¹ s ⁻¹	2.7	2.2	S _{GS} /%	33.0	0.8	124
Treatment, thermal	SMSI	Pt/HAP-O	Pt/TiO ₂ -H500	2.0	CO oxidation/400	Rate/mol _{CO} g _{Ni} ⁻¹ h ⁻¹	570.0	630.0	-	-	0.9	122
Treatment, reducing agent	Interfacial perimeter	Pt/CeO ₂ -Al ₂ O ₃ -CO	Pt/CeO ₂ -Al ₂ O ₃ -C ₆ H ₆	1.0	CO oxidation/150	X _{CO} /%	63.0	8.0	-	-	7.9	131
Treatment, reduction-oxidation cycles	Charge transfer	Au/TiO ₂ O400	Au/TiO ₂ CO400	2.5	CO oxidation/80	TOF/s ⁻¹	3.7	0.3	-	-	12.3	51
Treatment, reduction-oxidation cycles	SMSI	RO200R-TiO ₂	R-TiO ₂	10.0	Fischer-Tropsch/220	CTV/10 ⁵ mol _{CO} g _{Co} ⁻¹ s ⁻¹	15.7	6.7	S _{GS} /%	88.0	2.5	133
Treatment, overlayer deposition	Morphology	Co/TiO ₂ @mSiO ₂ 450 °C red.	Co/TiO ₂ 450 °C red.	11.8	Fischer-Tropsch/220	CTV/10 ² mol _{CO} g _{Co} ⁻¹ h ⁻¹	1.2	1.0	S _{GS} /%	80.6	1.3	135
Treatment, overlayer deposition	Morphology	Au/TiO ₂ 500	Au/TiO ₂ 500#	3.8	CO oxidation/25	TOF/s ⁻¹	1.0	0.3	-	-	3.8	134

Treatment, overlay deposition	Interfacial perimeter	Cu/Zr _{0.5} /SiO ₂	Cu/SiO ₂	3.0	MeOH synthesis/250	Rate/mmol-MeOH _{formed} g ⁻¹ h ⁻¹	3.9	0.7	-	-	5.6	138
Treatment, overlay deposition	Interfacial perimeter	Cu/SiO ₂ /DPA calc.	Cu/SiO ₂ /IM calc.	6.8	MeOH decomposition/240	Rate/MPa ₄₂ h ⁻¹	1.2	0.1	S ₁₁₂ /%	84.2	12.8	143
Treatment, overlay deposition	SMSI	TiO ₂ /Rh/SiO ₂	Rh/SiO ₂	2.7	CO hydrogenation/250	TOF/10 ⁻³ s ⁻¹	14.0	3.4	S _{C24K} /%	18.4	9.8	140
Treatment, overlay deposition	SMSI	0.35 ML TiO ₂ -Ox/Pt(111)	0.0 ML TiO ₂ -Ox/Pt(111)		CO oxidation/200	TOF/s ⁻¹	0.8	0.2	-	-	3.4	136
Treatment, overlay deposition	SMSI	Pt/SiO ₂ @TiO ₂	Pt/SiO ₂	2.4	CO oxidation/155	X _{CO} /%	40.0	3.0	-	-	13.3	139
Treatment, overlay deposition	SMSI	0.8% Au/TiO ₂ -wSMSI	0.9 % Au/TiO ₂	2.0	CO oxidation/25	TOF/mol _{CO} mol ⁻¹ s ⁻¹ g _{Au} ⁻¹	0.7	0.3	-	-	2.6	142
Treatment, adsorbate-mediated	SMSI	Cu/CeO ₂ -SMSI-400	Cu/CeO ₂	29.5	WGS/300	X _{CO} /%	86.0	47.0	-	-	1.8	146
Treatment, adsorbate-mediated	SMSI	Rh/TiO ₂ /20CO ₂ /2H ₂	Rh/TiO ₂ Red.	2.0	CO ₂ Hydrogenation/200	Rate/mmol h ⁻¹ g _{Re} ⁻¹	25.0	51.0	S _{CO} /%	92.0	14.0	145

a. Theoretical study. No experimental catalytic results.

Appendix B

Supporting Information Chapter 3

Crystalline Niobia with Tailored Porosity as Support for Cobalt Catalysts for the Fischer-Tropsch Synthesis

Figure B1 Bright field TEM images for niobium oxide hydrate calcined at 120 °C (a) and calcined at 600 °C (b). Reproduced from den Otter, J. H. Niobia-supported Cobalt Catalysts for Fischer-Tropsch Synthesis. (Utrecht University, 2016).

Figure B2 Thermogravimetric analysis (TGA) for the carbon deposited on niobia in air flow.

Table B1 Catalytic results for the Fischer–Tropsch reaction at 20 bar, 220 °C and $H_2/CO = 2$, GHSV = 4500 h⁻¹, TOS = 100h.

Support	Cobalt loading (wt.%)	Catalytic Activity			Selectivity (wt.%)			Olefin/Parffin	
		CO conversion (%)	Weight-Time-Yield (10 ⁻⁶ mol _{CO} g _{Cat.} ⁻¹ s ⁻¹)	Cobalt-Time-Yield (10 ⁻⁵ mol _{CO} g _{Co} ⁻¹ s ⁻¹)	C ₁	C ₂₋₄	C ₅₊	C ₃ H ₆ / C ₃ H ₈	C ₄ H ₈ / C ₄ H ₁₀
Crystalline Nb ₂ O ₅ (calc. 600 °C)	6	19	2.7	4.5	12	8	80	1.5	0.91
	6	18	2.8	4.2	12	8	80	1.4	0.94
Nb ₂ O ₅ -MC	10	25	4.0	3.7	11	8	81	1.8	1.0

Appendix C

Supporting Information Chapter 4

Activity Enhancement of Cobalt Catalysts by Tuning Metal-Support Interactions

Table C1 Cobalt loading of Co/TiO₂, Co/Nb₂O₅ and Co/ α -Al₂O₃, as determined by inductively coupled plasma-optical emission spectroscopy (ICP-OES).

Sample	Cobalt loading (wt.%)
Co/TiO ₂	6.8
Co/Nb ₂ O ₅	5.7
Co/Al ₂ O ₃	6.0

Figure C1 Additional electron microscopy images of the TiO₂-supported samples upon reduction-oxidation-reduction treatments. STEM-HAADF combined with EDX mapping of Co/TiO₂ at various stages of the ROR treatment. Co is depicted in yellow. **a, b, c, d**, Samples after reduction at 350 °C and passivation (R-TiO₂); **e, f, g, h**, samples after reduction at 350 °C and oxidation at 200 °C (RO200-TiO₂); **i, j, k, l**, samples after reduction at 350 °C, oxidation at 200 °C and reduction at 220 °C (RO200R-TiO₂) and passivation.

Figure C2 Additional electron microscopy images of the Nb_2O_5 -supported samples upon reduction-oxidation-reduction treatments. STEM-HAADF combined with EDX mapping of $\text{Co}/\text{Nb}_2\text{O}_5$ at various stages of the ROR treatment. Co is depicted in yellow. **a, b, c, d**, Samples after reduction at 350 °C and passivation ($\text{R-Nb}_2\text{O}_5$); **e, f, g, h**, samples after reduction at 350 °C and oxidation at 200 °C ($\text{RO200-Nb}_2\text{O}_5$); **i, j, k, l**, samples after reduction at 350 °C, oxidation at 200 °C and reduction at 220 °C ($\text{RO200R-Nb}_2\text{O}_5$) and passivation.

Figure C3 Additional electron microscopy images of the Al_2O_3 -supported samples upon reduction-oxidation-reduction treatments. **a, d, g, h, i**, STEM-HAADF and **b, c, e, f**, bright-field TEM of $\text{Co}/\text{Al}_2\text{O}_3$ at various stages of the ROR treatment. **a, b, c**, Samples after reduction at 350 °C and passivation ($\text{R-Al}_2\text{O}_3$); **d, e, f**, samples after reduction at 350 °C and oxidation at 200 °C ($\text{RO200-Al}_2\text{O}_3$); **g, h, i**, samples after reduction at 350 °C, oxidation at 200 °C and reduction at 220 °C ($\text{RO200R-Al}_2\text{O}_3$) and passivation.

Figure C4 TPR profiles used to determine the degree of reduction of cobalt. The baseline is shown for the peaks that were integrated as cobalt that had not been reduced and thus lowered the degree of reduction. The degree of reduction was determined after reduction at 350 °C (R-samples), after reduction at 350 °C, oxidation at 200 °C and reduction at 220 °C (RO200R-samples) and after reduction at 350 °C, oxidation at 400 °C and reduction at 220 °C (RO400R-Nb₂O₅).

Table C2 The degree of cobalt reduction (DOR) at various stages of the ROR treatment, as measured by TPR. The degree of reduction was determined after reduction at 350 °C (R-samples), after reduction at 350 °C, oxidation at 200 °C and reduction at 220 °C (RO200R-samples) and after reduction at 350 °C, oxidation at 400 °C and reduction at 220 °C (RO400R-Nb₂O₅).

Sample	DOR (%)		
	R	RO200R	RO400R
Co/TiO ₂	97	86	n.d.
Co/Nb ₂ O ₅	98	93	84
Co/Al ₂ O ₃	98	95	n.d.

Figure C5 Particle growth at higher oxidation temperature. Histogram of particle sizes of RO200R-TiO₂ and RO400R-TiO₂. The samples were reduced under hydrogen flow at 220 °C and then exposed to air at room temperature. Afterwards, the samples were analyzed by STEM-EDX mapping.

Figure C6 Cobalt-weight-based activity over time-on-stream. Cobalt-weight-based catalytic activity of Co/TiO₂ (a), Co/Nb₂O₅ (b) and Co/Al₂O₃ (c) after various reduction-oxidation-reduction treatments plotted against time-on-stream. Reaction conditions: 20 bar, 220 °C, H₂/CO = 2 V/V, GHSV = 1000-13000 h⁻¹ and CO conversion = 15-34 % (TiO₂), 17-25 % (Nb₂O₅), 8-12 % (Al₂O₃).

Table C3 Summary of the catalytic performance. Reaction conditions: 20 bar, 220 °C and $H_2/CO = 2$ V/V. The reported data was averaged over three data points between 90-100 h on stream.

Sample	GHSV	CO conv.	Cobalt-Time-Yield	TOF	Selectivity (%)		
	(h ⁻¹)	(%)	(10 ⁻³ mol _{CO} ·g _{Co} ⁻¹ ·s ⁻¹)	(s ⁻¹)	C ₁	C ₂₋₄	C ₅₊
TiO ₂							
R-TiO ₂	5560	20.6	6.7	0.10	8.5	7.5	84.0
RO100R-TiO ₂	8290	18.2	9.8	0.11	7.0	5.0	88.0
RO200R-TiO ₂	13540	19.3	15.7	0.10	7.5	4.5	88.0
RO300R-TiO ₂	13540	15.1	10.5	0.074	8.8	5.4	85.8
RO400R-TiO ₂	5640	34.0	10.8	0.11	6.8	4.7	88.5
Nb ₂ O ₅							
R-Nb ₂ O ₅	3266	17.0	4.7	0.087	8.6	6.1	85.3
RO100R-Nb ₂ O ₅	3024	19.6	5.6	0.051	7.8	3.9	88.3
RO200R-Nb ₂ O ₅	3874	24.6	8.9	0.068	6.7	4.2	89.1
RO300R-Nb ₂ O ₅	3070	25.5	6.2	0.058	8.5	3.6	87.9
RO400R-Nb ₂ O ₅	2954	19.3	5.5	0.077	11.4	4.6	85.0
Al ₂ O ₃							
R-Al ₂ O ₃	1249	12.5	3.3	0.025	10.9	14.2	85.8
RO50R-Al ₂ O ₃	940	9.62	2.0	0.031	5.8	4.4	89.8
RO200R-Al ₂ O ₃	952	8.98	2.8	0.035	6.2	4.1	89.7
RO400R-Al ₂ O ₃	956	8.17	1.7	0.029	7.6	6.0	86.4

Figure C7 Literature overview of cobalt-weight-based activities as a function of H_2 -uptake. Values obtained from literature were divided into two plots: **a** shows cobalt-based catalysts supported on reducible oxides (TiO_2 and Nb_2O_5) and **b** shows cobalt-based catalysts supported on irreducible oxides ($\alpha\text{-Al}_2\text{O}_3$, $\gamma\text{-Al}_2\text{O}_3$ and SiO_2). Open symbols refer to non-promoted, pristine cobalt catalysts and solid symbols to cobalt catalysts with enhanced activity either via noble metal/Mn promotion or via an ROR treatment (this work). H_2 -uptake values were calculated based on the reported particle sizes from either H_2 -chemisorption (refs. 7,13), TEM or XRD. Activity values were recalculated to match the units reported here. FT was performed at 20 bar and $\text{H}_2/\text{CO} = 2$ V/V in all cases, except ref. 9 where $\text{H}_2/\text{CO} = 1$ V/V. When the catalytic performance was reported at a temperature different than 220 °C, the activity was recalculated to that at 220 °C using the Arrhenius equation with an apparent activation energy of 100 $\text{kJ} \cdot \text{mol}^{-1}$.

Table C4 Lewis acidity of various metal oxides. Data obtained from ref 14.

Formal oxidation state of the cation (Nm)	Formula of the corre- sponding metal oxide	Lewis acid character ($N_M - 2\delta_M$) ^a
5+	Nb ₂ O ₅	3.895
4+	TiO ₂	3.046
	NbO ₂	2.877
3+	Ti ₂ O ₃	1.930
	Nb ₂ O ₃	1.883
	Al ₂ O ₃	2.274

a. δ_M corresponds to the Sanderson's partial charge of the cation.

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Appendix D

Supporting Information Chapter 5

Cobalt-Nickel Nanoparticles Supported on Reducible Oxides as Fischer-Tropsch Catalysts

Table D1 Co and Ni weight loadings for the different samples supported on niobia, titania and alpha-alumina and the corresponding H₂-uptake derived from the temperature programmed reduction (TPR) analyses. The last column shows the molar ratio of hydrogen consumed by the total metal content.

Support	Ni/(Ni+Co) (at/at)	Metal loading (wt.)		H ₂ -uptake ($\mu\text{mol}_{\text{H}_2} \cdot \text{g}_{\text{Metal}}^{-1}$)	H ₂ -uptake/Metal loading (mol/mol)
		Co	Ni		
Nb ₂ O ₅	0.0	6.1	0.0	1423	1.4
	0.25	4.5	1.6	1231	1.2
	0.50	3.0	2.9	1236	1.2
	0.75	1.5	4.4	997	1.0
	1.0	0.0	6.5	1101	1.0
TiO ₂	0.0	7.8	0.0	1821	1.4
	0.25	5.4	1.9	1477	1.2
	0.50	4.0	4.0	1798	1.3
	0.75	2.0	5.8	1430	1.1
	1.0	0.0	7.8	1291	1.0
α -Al ₂ O ₃	0.0	8.0	0.0	1867	1.4
	0.25	4.7	1.6	1420	1.3
	0.50	3.3	3.2	1420	1.3
	0.75	1.6	4.7	1376	1.3
	1.0	0.0	6.0	979	1.0

Figure D1 Theoretical and experimental H₂-uptake for all the different metal compositions supported on niobia (a), titania (b) and alpha-alumina (c). Experimental hydrogen uptake was measured by hydrogen-chemisorption. After the chemisorption measurements, samples were analysed by TEM to obtain the average particle size and these values were used to derive the corresponding theoretical hydrogen uptake. Values can be found in Table 5.1 in the main text.

Ni/(Ni+Co) = 0.25 Ni/(Ni+Co) = 0.50 Ni/(Ni+Co) = 0.75

Figure D2 STEM-EDX of niobia-supported samples after reduction at 350 °C and passivation at room temperature (a, b and c), after 40 h on stream at 1 bar total pressure ($H_2/CO = 2$ v/v), 220 °C (d, e and f) and after 100 h on stream at 20 bar total pressure ($H_2/CO = 2$ v/v), 220 °C (g, h and i). Nominal Ni/(Ni+Co) = 0.25 at/at (a, d and g), 0.50 at/at (b, e and h) and 0.75 at/at (c, f and i). The main images correspond to an overlap of Dark-field STEM with the EDX mapping for cobalt (shown in red) and nickel (shown in green), the scale bars correspond to 40 nm.

Figure D3 STEM-EDX of the niobia supported sample ($\text{Ni}/(\text{Ni}+\text{Co}) = 0.25$ at/at): **a**, after reduction at 350 °C and passivation at room temperature. **b**, after FT catalytic performance at 1 bar, 220 °C and 40 h-on-stream. **c**, after FT catalytic performance at 20 bar, 220 °C and 100 h-on-stream. Signal corresponding to cobalt is shown in red, to nickel in green and to niobium in blue. Scale bars are equivalent to 20 nm.

Figure D4 STEM-EDX and atomic Co-Ni distribution of the niobia-supported sample with composition $\text{Ni}/(\text{Ni}+\text{Co}) = 0.25$ at/at, after reduction at 350 °C and passivation at room temperature. Cobalt is shown in red and nickel in green. Co-Ni distribution cross-section analysis of the indicated nanoparticles is shown on the right side.

Figure D5 STEM-EDX and atomic Co-Ni distribution of the niobia-supported sample with composition $\text{Ni}/(\text{Ni}+\text{Co}) = 0.75$ at/at, after reduction at 350°C and passivation at room temperature. Cobalt is shown in red and nickel in green. Co-Ni distribution cross-section analysis of the indicated nanoparticles is shown on the right side.

Figure D6 STEM-EDX of the α -alumina-supported sample ($\text{Ni}/(\text{Ni}+\text{Co}) = 0.50$ at/at) after reduction at 350 °C and passivation at room temperature (**a, b** and **c**) and after FT catalytic performance at 1 bar, 220 °C and 40 h-on-stream (**d, e** and **f**). EDX signal for cobalt is shown in red and for nickel in green. **a** and **d** show an overlap of the dark-field image and EDX mapping of cobalt and nickel. **b** and **e** show the corresponding cobalt EDX map and **c** and **f** show the corresponding nickel EDX map. Scale bars correspond to 50 nm.

Figure D7 STEM-EDX of the titania-supported sample ($\text{Ni}/(\text{Ni}+\text{Co}) = 0.50$ at/at) after reduction at 350 °C and passivation at room temperature (**a, b** and **c**) and after FT catalytic performance at 20 bar, 220 °C and 100 h-on-stream (**d, e** and **f**). EDX signal for cobalt is shown in red and for nickel in green. **a** and **d** show an overlap of the dark-field image and EDX mapping of cobalt and nickel. **b** and **e** show the corresponding cobalt EDX map and **c** and **f** show the corresponding nickel EDX map. Scale bars correspond to 30 nm.

Figure D8 Fourier transform infrared spectra of CO as probe molecule (CO-FTIR) of the in-situ reduced samples supported on niobia, titania and alpha-alumina at different CO pressures and at 220 °C. For each sample's set of spectra, the Ni/(Ni+Co) composition is indicated on the top right.

Figure D9 Deconvoluted CO-FTIR spectra of the niobia-supported samples at CO pressures from $1 \cdot 10^{-3}$ to $1 \cdot 10^{-1}$ mbar and at 220°C . Ni/(Ni+Co) composition is indicated above the spectra. Spectra are plotted with a black line. Deconvoluted curves correspond to linearly CO adsorbed on cobalt (red), linearly CO adsorbed on nickel (green), CO adsorbed on bridged mode (light and dark blue) and the resulting curve (dashed yellow). Areas of linearly adsorbed CO on cobalt and nickel for the bimetallic samples were normalized by the areas of the linearly adsorbed CO of the corresponding monometallic sample.

Figure D10 Deconvoluted CO-FTIR spectra of the α -alumina-supported samples at CO pressures from $1 \cdot 10^{-3}$ to $1 \cdot 10^{-1}$ mbar and at 220°C . Ni/(Ni+Co) composition is indicated on top. Spectra are plotted with a black line. Deconvoluted curves correspond to linearly CO adsorbed on cobalt (red and orange), linearly CO adsorbed on nickel (green), CO adsorbed on bridged mode (light and dark blue) and the resulting curve (dashed yellow). Areas of linearly adsorbed CO on cobalt and nickel for the bimetallic samples were normalized by the areas of the linearly adsorbed CO of the corresponding monometallic sample.

Figure D11 Wavenumber values of maximum absorbance of linear-CO on cobalt and on nickel for the different Co-Ni compositions on titania, niobia or alpha-alumina at $P_{\text{CO}} = 0.1$ mbar.

Table D2 Comprehensive data of the catalytic performance for the samples with various cobalt to nickel ratios supported on reducible (Nb₂O₅ and TiO₂) and non-reducible (α -Al₂O₃) oxides. The values are reported at 40 h-on-stream for the 1 bar experiments and at 100 h-on-stream for the 20 bar experiments and in all cases the synthesis gas composition corresponded to H₂/CO = 2 v/v. Prior reaction conditions, samples were in-situ reduced under hydrogen flow at 350 °C.

Pressure (bar)	Temp. (°C)	Support	Ni/(Ni+Co) (at/at)	Activity (10 ⁻⁵ mol _{CO} /g _{Metal} ⁻¹ ·s ⁻¹)	CO conversion (%)	TOF (10 ² s ⁻¹)		Selectivity (wt.%)		
						A	B	C ₁	C ₂₄	C ₅
1	220	Nb ₂ O ₅	0.0	2.4	1.4	3.7	2.4	51	28	21
			0.25	4.7	2.6	5.3	3.6	69	16	15
			0.50	6.0	2.9	6.7	3.7	77	13	10
			0.75	6.7	3.7	7.0	3.7	76	15	9
			1.0	3.4	2.4	4.7	2.0	61	26	13
		TiO ₂	0.0	3.6	1.2	4.0	3.2	55	32	28
			0.25	4.9	2.9	4.3	3.5	71	14	15
			0.50	5.8	3.4	5.1	3.6	76	13	12
			0.75	7.4	4.4	6.0	4.2	76	15	9
			1.0	2.1	1.4	1.7	1.2	54	31	15
		α -Al ₂ O ₃	0.0	1.0	0.8	0.8	0.8	26	33	41
			0.25	1.1	0.7	0.8	0.7	31	30	39
			0.50	1.3	1.0	0.7	0.7	26	31	43
			0.75	1.0	0.6	0.5	0.4	31	31	39
			1.0	0.5	0.5	0.2	0.3	23	36	40
20	220	Nb ₂ O ₅	0.0	6.2	17	9.8	6.4	86	6	8
			0.25	10.0	20	11.4	7.7	83	7	11
			0.50	7.5	16	8.4	4.7	74	11	15
			0.75	5.3	12	6.5	3.4	71	15	13
		TiO ₂	0.0	10.5	28	18.3	14.9	82	6	12
			0.25	12.3	27	13.6	11.1	83	7	10
			0.50	9.0	21	8.7	6.2	75	13	12
			0.75	4.3	15	5.9	4.1	68	18	13
		Nb ₂ O ₅	0.0	17.3	16	35.8	23.3	74	11	16
			0.25	21.3	20	32.7	21.9	72	11	17
			0.50	19.4	18	29.3	16.3	72	12	16
			0.75	14.3	12	18.2	9.6	74	13	13
	240	TiO ₂	0.0	18.8	20	25.3	20.6	69	11	20
			0.25	25.5	26	27.9	22.8	76	10	14
			0.50	19.5	23	19.3	13.8	74	12	14
			0.75	12.8	17	15.5	10.7	72	15	14
		Nb ₂ O ₅	0.0	42.8	19	87.4	56.9	67	14	19
			0.25	58.2	26	84.3	56.6	68	14	19
			0.50	53.4	22	76.4	42.5	69	15	17
			0.75	40.6	22	48.5	25.6	70	15	15
		TiO ₂	0.0	51.7	22	71.3	58.0	68	13	19
			0.25	56.5	32	75.9	62.1	68	13	18
			0.50	48.3	21	48.6	34.6	70	14	16
			0.75	28.1	13	29.7	20.5	73	12	15

A. Derived from H₂-chemisorption

B. Derived from TEM

Table D3 Values for figure 5.6 in the main text comprasing the wavenumber of maximum absorbance of linear-CO on cobalt ($P_{\text{CO}} = 0.1$ mbar) and turn-over-frequency (TOF, based on the experimental H_2 -uptake) for the different Co-Ni compositions on niobia, titania and alpha-alumina.

Support	Ni/(Ni+Co) (at/at)	Wavenumber (cm^{-1})	TOF (10^2 s^{-1})
Nb_2O_5	0.0	1984	3.7
	0.25	2002	5.3
	0.50	2009	6.7
	0.75	2012	7.0
TiO_2	0.0	2002	4.0
	0.25	2004	4.3
	0.50	2014	5.1
	0.75	2021	6.0
$\alpha\text{-Al}_2\text{O}_3$	0.0	1995	0.8
	0.25	1997	0.8
	0.50	2007	0.7
	0.75	2017	0.5

Table D4 Metal composition expressed as Ni/(Ni+Co) at/at quantified by ICP and/or EDX. The Ni/(Ni+Co) was derived from the Co/Ni ratio for samples after reduction at 350 °C, FT catalytic performance at 220 °C and 1 bar (40 h-on stream) or 20 bar (100 h-on-stream).

Support	Ni/(Ni+Co) (at/at)						
	Nominal	ICP			EDX		
		After re- duction	After 1 bar FT	After 20 bar FT	After re- duction	After 1 bar FT	After 20 bar FT
Nb_2O_5	0.25	0.26	0.25	0.20	0.24	0.26	0.21
	0.50	0.50	0.50	0.37	0.50	0.49	0.41
	0.75	-	-	-	0.74	0.78	0.58
TiO_2	0.25	-	-	-	0.31	-	0.21
	0.50	0.51	0.51	0.35	-	-	-
$\alpha\text{-Al}_2\text{O}_3$	0.50	0.50	0.48	-	0.52	0.50	-
	0.75	0.75	0.76	-	-	-	-

Figure D12 Literature overview of metal-weight-based activities at 220 °C as a function of cobalt-nickel composition for different supports. FT was performed at high pressure (10 - 20 bar) and $\text{H}_2/\text{CO} = 2$ v/v in all cases. Values from Table D5.

Table D5 Literature overview comparing the FT catalytic performance of cobalt-nickel supported on different supports. FT was performed in fix-bed configuration, at high pressures and $H_2/CO = 2$ v/v in all cases. Activity values were recalculated to match the units reported here; when the catalytic performance was reported at a temperature different than 220 °C, the activity was recalculated to that at 220 °C using an apparent activation energy of 100 kJ·mol⁻¹.

Support	Temperature (°C)	Pressure (bar)	TOS (h)	Ni/(Ni+Co) (at/at)	Activity (10 ⁻⁵ mol _{CO} ·g _{Metal} ⁻¹ ·s ⁻¹)	C ₅ selectivity (wt.%)	Activity at 220 °C (10 ⁻⁵ mol _{CO} ·g _{Metal} ⁻¹ ·s ⁻¹)	Ref.
Nb ₂ O ₅	220	20	100	0.0	6.2	86	6.2	This work
				0.25	10.0	83	10.0	
				0.50	7.5	74	7.5	
				0.75	5.3	71	5.3	
TiO ₂	220	20	100	0.0	10.5	82	10.5	This work
				0.25	12.3	83	12.3	
				0.50	9.0	75	9.0	
				0.75	4.3	68	4.3	
α-Al ₂ O ₃	220	20	100	0.0	3.3	86	3.3	1
α-Al ₂ O ₃	210	20	100	0.0	4.1	85	6.8	2
				0.14	3.8	85	6.3	
				0.20	3.4	85	5.6	
θ-Al ₂ O ₃	230	10	8	0	5.1	76	3.1	3
				0.05	5.4	77	3.3	
				0.25	4.3	67	2.6	
				0.50	3.5	59	2.1	
Al ₂ O ₃	240	10	12	0.50	2.5	83	0.96	4
SiO ₂ -Al ₂ O ₃	230	20	-	0.50	6.1	81	3.76	5
				0.33	5	87	3.08	
				0.25	5.1	89	3.14	
				0.17	5.1	88	3.14	
SiO ₂	250	10	-	0.25	1.1	45	0.27	6
				0.50	3.1	35	0.76	
La ₂ O ₃	220	10	15	0.20	0.57	-	0.57	7

Figure D13 STEM-EDX and atomic Co-Ni distribution of the used niobia-supported catalyst with composition Ni/(Ni+Co) = 0.75 at/at, after high-pressure FT (220 °C, 20 bar, TOS = 100 h and $H_2/CO = 2$ v/v). Cobalt is shown in red, nickel in green and niobium in blue.

Figure D14 Catalytic activities (**A**), C_{5+} , C_2-C_4 and C_1 selectivities (**B**, **C** and **D** respectively) for the niobia-supported catalysts at 220, 240 and 260 °C, 20 bar ($\text{H}_2/\text{CO} = 2$ v/v) and after 100 h-on stream. Prior to reaction conditions, samples were reduced in-situ at 350 °C in 25 vol.% H_2 in He at 1 bar.

Figure D15 Catalytic activities (**A**), C_{5+} , C_2-C_4 and C_1 selectivities (**B**, **C** and **D** respectively) for the titania-supported catalysts at 220, 240 and 260 °C, 20 bar ($\text{H}_2/\text{CO} = 2$ v/v) and after 100 h-on stream. Prior to reaction conditions, samples were reduced in-situ at 350 °C in 25 vol.% H_2 in He at 1 bar.

Figure D16 Arrhenius plots for the niobia- and titania-supported catalysts (**A** and **B** respectively). Apperrent activation energies (E_a) were obtained from the slopes of the Arrhenius equation in the linear form: $\ln(-\ln(1-\text{Activity})) = \ln A - E_a(RT)^{-1}$, in which Activity corresponds to the metal-normalized catalytic activity (Table D1), A to the pre-exponential factor, R to the gas constant ($8.3145 \text{ J}\cdot\text{K}^{-1}\cdot\text{mol}^{-1}$) and T to the reaction temperature (K). Reaction conditions: 20 bar, $\text{H}_2/\text{CO} = 2 \text{ v/v}$, after 100 h on stream and 220, 240 and 260 °C.

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Appendix E

Supporting Information Chapter 6

Stable Niobia-Supported Nickel Catalysts for the Hydrogenation of Carbon Monoxide to Hydrocarbons

Figure E1 H₂-TPR profile of the calcined NiO/α-Al₂O₃ sample. Heating ramp of 5 °C·min⁻¹ with a 5 vol% H₂/Ar flow.

Figure E2 TPR experiments for the calcined nickel oxide supported on niobia with a 2 h dwell at 250 °C (a) or 350 °C (b). Heating ramp of 5 °C·min⁻¹ with a 5 vol% H₂/Ar flow.

Figure E3 Powder X-ray diffractograms for nickel supported on niobia after reduction at 450 °C and passivation at room temperature (a), the pristine support (b) and a comparison in the 2θ range from 45° to 55° (c). The diffraction peak observed at $2\theta = 52.6^\circ$ for the $\text{Ni/Nb}_2\text{O}_5$ sample was attributed to metallic nickel (hexagonal crystal phase, ID: PDF-04-002-8298 or cubic crystal phase, ID: PDF-04-010-6148).

Figure E4 TEM images of nickel-supported on α -alumina after reduction at 350 °C (**a** and **b**) or 450 °C (**c** and **d**) followed by hydrogen chemisorption measurements and exposure to air. In the case of the bright-field images (**a** and **b**) the dark colored supported particles correspond to nickel nanoparticles and for the dark-field images (**c** and **d**) the light colored supported particles correspond to nickel nanoparticles.

Figure E5 Bright-field TEM images of the spent nickel-supported on α -alumina catalyst after reduction at 350 °C with a D[3,2] value of 28 nm (a) or 450 °C with a D[3,2] value of 36 nm (b). Reaction conditions: 230 °C, 1 bar, $H_2/CO = 2.0$ v/v, GHSV = 28 000 h^{-1} and 90 h TOS. The dark colored supported particles correspond to nickel nanoparticles.

Appendix F

Supporting Information Chapter 7

Niobium-based Solid Acids in Combination with a Methanol Synthesis Catalyst for the Direct Production of Dimethyl Ether from Synthesis Gas

Figure F1 Ammonia Temperature Programmed Desorption (NH₃-TPD) results for Nb₂O₅·nH₂O and NbOPO₄ (a) and γ-Al₂O₃ (b), reaching the temperature to which the materials were previously dried, 400 °C for the niobium based materials and 600 °C for γ-Al₂O₃.

Figure F2 FTIR with pyridine as probe molecule of the solid acids (indicated on the right part of the plot) after different calcination temperatures. IR bands highlighted in red at 1639 and 1540 cm⁻¹ correspond to pyridinium ion on Brønsted acid sites, IR bands highlighted in green at 1446 and 1606 cm⁻¹ correspond to pyridine coordinated to Lewis acid sites and the IR band highlighted in yellow at 1489 cm⁻¹ corresponds to a common band for both acid sites.

Figure F3 A CO conversion as a function of time at 260 °C (a) or 280 °C (b) and the respective hydrocarbon selectivities (c and d) for the catalysts in stacked-bed configuration, with the solid acid downstream of the methanol synthesis catalyst. Around 15 mg of copper-based methanol synthesis catalyst were used for the experiments at 260 °C and around 10 mg for the experiments at 280 °C, the performance of only the methanol synthesis catalyst is also shown (grey diamonds). The amount of solid acid used was fixed to have the same amount of acid sites per reactor, $6 \cdot 10^{-3} \text{ mmol}_{\text{NH}_3}$ at 260 °C and $3 \cdot 10^{-3} \text{ mmol}_{\text{NH}_3}$ at 280 °C. Reaction conditions: 40 bar, $\text{H}_2/\text{CO} = 2 \text{ v/v}$.

Figure F4 Powder XRD diffractograms of solid acids: hydrated niobium pentoxide on the left, niobium phosphate on the center and gamma-alumina on the right. **a**, **d** and **g** solid acids before reaction. Used solid acids after reaction (40 bar, $H_2/CO = 2$ v/v, TOS = 120h) at 260 °C (**b**, **e** and **h**) and at 280 °C (**c**, **f** and **i**). In all cases, hydrated niobium pentoxide and niobium phosphate maintained an amorphous diffraction pattern and alumina a gamma phase (JPCS data 10-0425).

Figure F5 Powder XRD diffractograms of the copper-based methanol synthesis catalyst after reduction at 250 °C (**a** and **b**). Passivated catalyst after reaction (40 bar, $H_2/CO = 2$ v/v, TOS = 120h) at 260 °C (**b**-**e**) or 280 °C (**g**-**j**). Diffractograms '**b**' and '**g**' correspond to the used copper-based catalyst without solid acid, diffractograms '**c**' and '**h**' correspond to the used copper-based catalyst from the physical mixture with $Nb_2O_5 \cdot nH_2O$, '**d**' and '**i**' from the physical mixture with $NbOPO_4$ and '**e**' and '**j**' from the physical mixture with $\gamma-Al_2O_3$.

Table F1 Summary of the copper crystallite size obtained from powder XRD (Figure F7) of the Cu-based catalyst after reduction (25 % vo H_2/N_2 flow, 2 h at 250 °C) and after reaction (40 bar, 260 or 280 °C, $\text{H}_2/\text{CO} = 2$, TOS = 120h) used in the physical mixture or in itself.

Sample	Reaction Temperature (°C)	Corresponding Diffractogram from Figure F7	Solid Acid in the physical mixture	Cu crystallite size ^b (nm)	Increase relative to the reduced catalyst (%)
Reduced Cu-based catalyst ^a	-	a, f	-	6.6	-
Cu-based catalyst after reaction	260	b	-	7.1	7
Cu-based catalyst in physical mixture after reaction		c	Nb ₂ O ₅ ·nH ₂ O	7.6	13
		d	NbOPO ₄	7.7	14
		e	γ-Al ₂ O ₃	7.9	16
Cu-based catalyst after reaction	280	g	-	7.6	14
Cu-based catalyst in physical mixture after reaction		h	Nb ₂ O ₅ ·nH ₂ O	8.9	27
		i	NbOPO ₄	8.3	20
		j	γ-Al ₂ O ₃	8.7	24

a. 'Reduced Cu-based catalyst' was reduced and placed in an air-tight sample holder to record the diffraction pattern, the other samples were exposed to air after reaction, sieved and characterized.

b. Obtained from the copper (111) diffraction line.

Figure F6 STEM-EDX mapping results of the used (40 bar, $\text{H}_2/\text{CO} = 2 \text{ v/v}$, GHSV = 1050 h^{-1} , 260 °C and TOS = 120 h) solid acids: $\text{Nb}_2\text{O}_5 \cdot n\text{H}_2\text{O}$ (left column), NbOPO_4 (center column) and $\gamma\text{-Al}_2\text{O}_3$ (right column). Dark-field images are shown for each material with the corresponding EDX-mapping of Nb (dark blue), Al (light blue), Cu (red) and the spectra in the energy region of Cu-K α , the Au-L α signal originates from the grid supporting the sample.

List of publications and presentations

Publications in this thesis

- Chapter 2: van Deelen, T. W., Hernández Mejía, C. & de Jong, K. P. Control of metal-support interactions in heterogeneous catalysts to enhance activity and selectivity. *Nat. Catal.* **2**, 955–970 (2019).
- Chapter 3: Hernández Mejía, C., den Otter, J. H., Weber, J. L. & de Jong, K. P. Crystalline niobia with tailored porosity as support for cobalt catalysts for the Fischer–Tropsch synthesis. *Appl. Catal. A Gen.* **548**, 143–149 (2017).
- Chapter 4: Hernández Mejía, C., van Deelen, T. W. & de Jong, K. P. Activity enhancement of cobalt catalysts by tuning metal-support interactions. *Nat. Commun.* **9**, 4459 (2018).
- Chapter 5: Hernández Mejía, C., van der Hoeven, J. E. S., de Jongh, P. E. & de Jong, K. P. Cobalt-nickel nanoparticles supported on reducible oxides as Fischer-Tropsch catalysts. *ACS Catal.* **10**, 7343–7354 (2020).
- Chapter 6: Hernández Mejía, C., Vogt, C., Weckhuysen, B. M. & De Jong, K. P. Stable niobia-supported nickel catalysts for the hydrogenation of carbon monoxide to hydrocarbons. *Catal. Today* **343**, 56–62 (2020).
- Chapter 7: Hernández Mejía, C., Verbart, D. M. A. & de Jong, K. P. Niobium-based solid acids in combination with a methanol synthesis catalyst for the direct production of dimethyl ether from synthesis gas. *Catal. Today*, *accepted*.

Other publications

- Weber, J.L., Hernández Mejía, C., de Jong, K.P & de Jongh, P.E. Fuels and Chemicals from Synthesis Gas via Bifunctional Catalysis – Chances and Challenges. Review article in preparation.
- Straß-Eifert, A., van der Wal, L. I., Hernández Mejía, C., Weber, J.L., Yoshida, H., Zečević, J., de Jong, K. P. & Güttel, R. Bifunctional core-shell catalysts for Fischer-Tropsch synthesis: Descriptors affecting the product distribution. In preparation.

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Oral presentations

International Conferences

“Co-Ni Supported on Reducible Oxides as Highly Active and Selective Fischer-Tropsch Catalysts”

12th Natural Gas Conversion Symposium

San Antonio, U.S.

June 2nd – 6th, 2019

“Impact of Reduction-Oxidation-Reduction Treatments on Supported Cobalt Catalysts”

18th Nordic Symposium on Catalysis

Copenhagen, Denmark

August 26th – 28th, 2018

“Activity Enhancement by Reduction-Oxidation-Reduction Treatments of Supported Cobalt Catalysts for the Fischer-Tropsch Synthesis”

13th European Congress on Catalysis

Florence, Italy

August 27th – 31st, 2017

“Activity Enhancement in Cobalt Fischer–Tropsch Catalysts by Reduction-Oxidation-Reduction Treatments”

25th North American Catalysis Society Meeting

Denver, U.S.

June 4th – 9th, 2017

National Conferences and Lectures

“Support Effects on the Catalytic Behaviour of Cobalt-Nickel Alloy Catalysts for the Fischer-Tropsch Synthesis”

The Netherlands’ Catalysis and Chemistry Conference XX

Noordwijkerhout, The Netherlands

March 4th – 6th, 2019

“Activity Enhancement of Cobalt Catalysts by Tuning Metal-Support Interactions”

Debye Lunch Lecture

Utrecht, The Netherlands

November 14th, 2018

“Activity Enhancement in Niobia-Supported Cobalt Fischer–Tropsch Catalysts by Reduction-Oxidation-Reduction treatments”

The Netherlands’ Catalysis and Chemistry Conference XVIII

Noordwijkerhout, The Netherlands

March 6th – 8th, 2017

“Porosity Enhancement of Niobia-Supported Cobalt Catalysts for Fischer–Tropsch Synthesis

Chemistry as Innovating Science (CHAINS) conference”

Veldhoven, The Netherlands

December 6th - 8th, 2016

Poster presentation

“Reduction–Oxidation–Reduction Treatment for Niobia Supported Cobalt Catalysts”

The Netherlands’ Catalysis and Chemistry Conference XVII

Noordwijkerhout, The Netherlands

March 7th – 9th, 2016

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Niobia refers to the oxide of the element niobium (Nb). Niobium's name comes from Niobe, daughter of king Tantalus in the Greek mythology. The elements niobium and tantalum were originally thought to be identical due to their similar chemical properties, hence the names. The story of Niobe revolves around the killing of her daughters and sons at the hands of Apollo and Artemis in response to Niobe's arrogance. Because of her many daughters and sons, she believed she was better than Leto, mother of Apollo and Artemis. The story has little to do with the element niobium or its compounds, however it can be a good reminder of humility, particularly in science where no man is an island.

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Curriculum vitae

Carlos Hernández Mejía was born the 4th of July 1989 in Tijuana, Mexico. He studied chemistry at Universidad Nacional Autónoma de México (UNAM) in Mexico City. There he developed his interest for inorganic chemistry (particularly for transition metals), vastly from the enthusiasm and teachings of Prof. Dr. Laura Gasque Silva. During his studies he had the opportunity of doing an exchange at the University of Amsterdam, where he initially discovered the field of heterogeneous catalysis while doing a research internship under the supervision of Dr. Santiago Gómez Quero and Prof. Dr. Gadi Rothenberg.

After completing his bachelor's degree thesis on multiferroic ceramics supervised by Prof. Dr. Elizabeth Chavira Martinez and Dr. Ivonne Rosales Chavez at UNAM's Materials Institute, he moved back to the Netherlands in 2013 to follow a master's program at the University of Amsterdam. He carried out the master's research project at the group of Prof. Dr. Gadi Rothenberg supervised by Dr. Shiju Raveendran, the project focused on the upgrade of biomass-derived feedstocks to fine chemicals by use of heterogeneous catalysts, in particular studying Ru/TiO₂ for hydrogenation reactions. Then he did an internship at Albemarle in Amsterdam under the supervision of Dr. Jaap Bergwerff, to study the synthesis of transition metal sulfide nanoparticles.

In 2015, Carlos started a PhD research project supervised by Prof. Dr. Krijn de Jong at the Inorganic Chemistry and Catalysis group from Utrecht University and with financial support from Companhia Brasileira de Metalurgia e Mineração (CBMM). The research focused on the synthesis and understanding of niobia-supported metal catalysts for their application in the conversion of synthesis gas to chemicals, mainly on the Fischer-Tropsch synthesis. The results of this research are described in this thesis, published in renowned scientific journals and presented at several national and international conferences.