**Supported cobalt nanocrystals as
model catalysts for the
Fischer-Tropsch synthesis**

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Supported cobalt nanocrystals as model catalysts for the Fischer-Tropsch synthesis

Gedragen kobaltnanokristallen als
modelkatalysatoren voor de
Fischer-Tropschsynthese

(met een samenvatting in het Nederlands)

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The background features a light gray gradient. In the top right corner, there is a dense cluster of pink brushstrokes of various lengths and orientations. A large, soft-edged pink blob is positioned in the upper middle section, containing the chapter title. In the bottom left corner, there is another smaller group of pink brushstrokes.

Chapter 1

General introduction

1.1. Catalysis

A catalyst is defined as ‘A substance that increases the rate of a reaction without modifying the overall standard Gibbs energy change in the reaction’¹ or, in other words, a catalyst speeds up a chemical reaction without changing the equilibrium of that reaction. In addition, a catalyst is in principle not consumed during the reaction. Catalysis is one of the key technologies in the chemical industry, since 95 % (by volume) or 80 % (by added value) of all chemical products are manufactured using catalysis.² Industrial catalysis can be divided into two categories: homogeneous and heterogeneous catalysis. Catalysis is classified as homogenous when the catalyst is in the same phase as the reactants and conversely, a heterogeneous catalyst is in a different phase than the reactants with the catalyst usually being a solid and the reactants being fluids (gases and/or liquids).¹ Homogeneous catalysts are mainly responsible for the production of polymers and fine chemicals; heterogeneous catalysts are involved in 80 % of the catalytic processes, for example major petrochemical and refining processes as well as ammonia synthesis.² Homogeneous catalysts are reasonably well understood at the molecular level, while heterogeneous catalysts are less defined and often feature a whole range of structures and catalytically active sites. One of the main reasons why heterogeneous catalysts have the widest applicability in industrial chemical processes is more facile handling and catalysts separation.³ Apart from enabling current chemical processes at high efficiency, catalysis is also envisaged to play a crucial role in addressing energy and climate challenges in the (near) future.

1.2. Gas-to-liquids

New fossil fuel reserves are still being discovered, especially given the current developments in shale gas and oil in the USA. When considering the restrictions on CO₂ emissions as established in the 2015 Paris Climate Change Conference agreement, the use of fossil fuels might not be limited by supply but rather by emissions. Simultaneously, the global energy demand is expected to increase until 2040 mainly because of economic growth in developing countries (Figure 1.1a).⁴ To meet this increase in demand, energy consumption from all sources is expected to grow in absolute sense, including fossil fuels. Figure 1.1b shows the projection of the demand for liquid fuels broken down per type of end-user.⁴ The demand for liquid fuels will grow in the coming two decades mainly for transportation (cars, trucks and non-road), and particularly for heavy trucks and aviation, where alternative energy carriers are as yet absent. It seems thus that liquid fuels will be needed in the coming decades, making it important to produce and apply these as efficiently as possible in order to limit CO₂ emissions.

Alternatives to traditional oil-based liquid fuels include liquified natural gas, biofuels and synthetic liquid fuels. The environmental benefit of synthetic liquid fuels strongly depends on the type of carbon-containing feedstock and overall process efficiency.⁵ For example, if associated gas from oil fields can be used as feedstock and flaring can be prevented, that offers a major reduction in overall carbon footprint. Synthetic liquid fuels can be obtained using so called X-to-liquids technology, with X being coal (CTL), natural gas (GTL) or biomass (BTL). The first step of XTL is to generate synthesis gas (an H₂/CO mixture) from the feedstock. In a second step, the synthesis gas is converted in the Fischer–

Tropsch synthesis (FT) into hydrocarbons, which are then refined in traditional installations to yield ultra-clean synthetic liquid fuels or chemicals.⁶ Currently, 0.5 million barrels per day ($\text{Mb}\cdot\text{d}^{-1}$) of synthetic liquid fuels are produced using XTL, excluding China's rapidly growing CTL production⁷ In comparison, around $100 \text{ Mb}\cdot\text{d}^{-1}$ of liquid fuel are produced from crude oil.⁸

Figure 1.1. Global energy scenarios projected until 2040. **a** Primary energy consumption forecast in tonnes of oil equivalent per year ($\text{toe}\cdot\text{yr}^{-1}$) and **b** breakdown of the projected demand for liquid fuels per consumer category in million barrels per day ($\text{Mb}\cdot\text{d}^{-1}$). Adapted from ref.⁴

FT is a polymerization reaction of CH_x -monomers that takes place on a metal surface and produces predominantly linear alkanes (Equation 1.1) and α -alkenes (Equation 1.2).⁹ The consequence of a polymerization reaction is that a statistical distribution of products of variable chain length is obtained following the Anderson-Schulz-Flory (ASF) distribution. The average chain length of the products is then determined by the chain growth probability (α , Figure 1.2). Industrial plants typically run at high α to avoid high selectivities towards undesirable methane and the long-chain wax products are subsequently cracked to maximize production in the fuel range. Apart from the main reaction, secondary reactions can take place, such as alkene readsorption or isomerization, which generally lead to deviations from the ASF distribution and to byproduct formation. Furthermore, water-gas shift (WGS, Equation 1.3) can occur as a major side reaction. WGS increases the H_2/CO ratio inside the reactor by consuming part of the CO feed together with formed H_2O in the reaction to produce H_2 and CO_2 .

Figure 1.2. Product distribution as a function of chain growth probability (α).

1.3. Fischer-Tropsch synthesis catalysts

All group 8–10 metals are active in FT, but Fe, Co, Ni and Ru have the highest activity.¹⁰ However, Ni has too high methane selectivity and forms nickel carbonyls under practical conditions and Ru is too expensive and scarce, so Fe and Co are mostly used in industry.¹¹ Of the two, Fe is cheaper and more resistant to sulfur poisoning, but Co has higher productivity at high conversion and has negligible WGS activity at low temperatures.¹² Whether Fe or Co is the most effective catalyst depends strongly on the available feedstock, because the $H_2:CO$ ratio of the synthesis gas varies with feedstock and gasification process. Synthesis gas derived from coal typically has an $H_2:CO$ molar ratio of 0.5–1 whereas synthesis gas from natural gas has a composition of $H_2:CO \sim 2$.¹³ The $H_2:CO$ stoichiometry of the FT reaction is approximately 2 (Equations 1.1 and 1.2), so GTL-synthesis gas can be used as is, while the composition of CTL-synthesis gas needs to be adjusted *in situ* by WGS, meaning that up to 50 % CO_2 -selectivity is obtained. This lowers the carbon efficiency of the process substantially. Fe has high WGS activity at typical operating temperatures and is therefore more suitable for CTL, while Co has no appreciable WGS activity and is thus preferred for GTL. Furthermore, Co is operated at low temperature (200–300 °C), while Fe can be operated at low temperature as well as high temperature (>300 °C) to produce mainly short-chain alkenes.^{14,15}

Focusing on cobalt-based FT catalysts under GTL conditions ($H_2:CO = 2$), the current high price of Co motivates efficient usage of the metal. In metal-based catalysts, where reactions take place at the metal surface, that can be achieved by nanosizing to maximize the surface-to-bulk ratio. Because metal nanoparticles (NP) are thermodynamically unstable, these NP are dispersed over a support material.¹⁶ The support essentially acts as a spacer for the NP, thereby preventing agglomeration and sintering, and provides mechanical strength at the macroscale in a reactor. Typical supports for industrial Co catalysts are metal oxides (TiO_2 , Al_2O_3 and SiO_2), which are abundant and stable and can positively influence FT performance, especially in the case of TiO_2 .^{7,17,18} In addition,

nanostructured carbon is employed in academic studies, because it has the advantages of inertness, i.e. no mixed metal-support compound formation, and facilitated imaging.^{19,20}

The performance of cobalt catalysts in FT varies with the structure of the Co NP. For example, the intrinsic activity (activity per surface site or turnover frequency, TOF) is constant for large Co NP but the TOF and C₅₊-selectivity drop sharply when the NP become smaller than 6–8 nm.^{21–23} More recently, the hcp crystal structure of Co was found to be more active than fcc.^{24–28} Nevertheless, many questions still remain, such as the effect of Co NP shape and metal-support interactions as well as the mechanism of Co-catalyzed FT at the molecular scale. Linking the structure of Co NP to their catalytic performance is highly challenging and requires fundamental research on model catalysts in which specific parameters can be precisely controlled and decoupled from others, e.g. changing NP size without changing Co loading or support interactions.

1.4. Model catalyst synthesis

Conventional catalyst synthesis techniques, such as impregnation or precipitation, have in common that a metal precursor solution is applied to a support and metal (oxide) NP are then generated on the support using heat treatments.²⁹ An alternative approach to produce model catalysts for fundamental studies is to synthesize metal particles separately using colloidal chemistry, which provides more opportunity to control their properties (size, shape or crystal structure), and anchor them to the support in a separate step.³⁰

The synthesis of metallic colloids takes place in a solvent where a metal precursor decomposes in the presence of capping agents/ligands. These ligands are typically amphiphilic molecules such as fatty acids and linear amines, or polymers such as PVP.³¹ Decomposition of the metal precursor can for example occur under the influence of temperature or chemical agents. As the precursor decomposes, initial nuclei form that grow into colloidal nanocrystals (NC).³² The ligands stabilize the NC surface and isolate the growing NC from each other, preventing unbridled sintering and growth of the NC into a bulk phase. Through selective binding, these ligands also control much of the NC properties.³⁰ Colloidal synthesis of NC has already been extensively researched, although most work focused on noble metals and the number of synthesis methods to obtain cobalt NC in the relevant size regime for catalytic models studies (1–50 nm) is rather limited.

The pre-formed colloidal NC have to be uniformly distributed over a support to prevent sintering and deactivation. The nature of the interaction between NC and support in general is still uncertain. In the case of NC and carbon nanotubes (CNT), one explanation is that NC binding proceeds via electronic interactions with the π -electrons of the graphene network, as was proposed for Pt-Co and Pt-Ni NC on CNT.³³ Furthermore, the NC are competitively bound to the support and ligands, as indicated by NC detachment from the support in the presence of excess ligand.^{33,34} Alternatively, iron oxide NC were proposed to bind through van der Waals forces, explaining why the NC bound less strong to oxidized CNT compared to pristine CNT.³⁵

Often, the ligands have to be removed prior to reaction to obtain an accessible and reactive metal surface and to be sure that the ligands do not negatively affect the reaction.^{36,37} Several options are available to remove ligands, including thermal, plasma and UV/ozone treatments.^{37–39} It is, however, questionable if and to what extent each of these

treatments affect the initially well-defined NC. Alternatively, the ligands can be replaced for other, more desirable ones through ligand exchange, as was done for example to introduce sulfur and sodium promoters for an Fe-NC-based catalyst for the Fischer-Tropsch to olefins process.⁴⁰ Overall, both the attachment of NC to the support and their activation are relatively unexplored areas of research in particular for non-noble metals, even though they are essential for proper application of colloidal NC as supported model catalysts.

Despite the potential advantages, research involving supported NC catalysts is not straightforward; certain challenges are associated with NC-based catalysts that are quite unique in the field of catalyst synthesis. If colloids are to be successfully applied as supported (model) catalysts several practical constraints on the synthesis method emerge. We identify the following points as important considerations, depending on the intended application.

- 1) The synthesis method should give high control over the NC properties.
- 2) The synthesis method should be reproducible and insensitive to subtle variations.
- 3) The synthesis method should require no elements/compounds that could act as poison or promoter and lead to unrepresentative performance.
- 4) The interparticle interactions should be limited to facilitate uniform NC distribution over the support.
- 5) The ligands should not bind the NC too strongly to facilitate competitive NC binding to the support and enable complete ligand removal using convenient treatments.
- 6) The attachment and ligand removal procedure should not affect the NC properties.
- 7) The synthesis should be scalable so that reasonable amounts of catalysts are obtained. This is more challenging for industrial application than for lab-scale model studies.
- 8) For model studies, NC properties should be adjustable by variation of only few synthesis parameters while maintaining others as constant as possible.

1.5. Cobalt nanocrystals as Fischer-Tropsch catalysts

Co-NC can be utilized in FT either unsupported in the liquid phase^{41–43}, or as supported catalysts in lab-scale FT experiments.^{23,44–54} In case of the supported catalysts, these NC were produced either via reverse-micelles or microemulsions^{23,44,47}, solvothermal synthesis^{48,49}, hot injection of $\text{Co}_2(\text{CO})_8$ ^{51–54}, or chemical reduction of a Co salt^{45,46,50}. In all of these cases, the NC were attached to oxidic supports (Al_2O_3 , SiO_2 or TiO_2) through mixing of the colloidal suspension with the support or pore filling impregnation, all at ambient temperature. The ligands were removed via high-temperature thermal treatment, except for three cases^{45,46,54} where the as-prepared NC-based catalysts were directly reduced and low intrinsic activities were obtained. The NC-based catalysts were often applied to investigate Co particle size effects. However, besides NC size, colloidal techniques could also allow control over the crystal structure, shape and composition and therefore, more diverse model studies can in principle be performed to shed light on Co structure-performance relationships in FT.⁵⁵ Simultaneously, NC-based catalyst synthesis as a whole, and in particular the application of base metal NC such as Co, should be investigated in more detail to realize this potential.

1.6. Scope of this thesis

The goal of this research is to link the structure of supported cobalt catalysts to their performance in the Fischer–Tropsch synthesis using advanced model catalysts. Supported model systems are prepared through colloidal synthesis techniques and, in addition, this work aims to investigate and expand the applicability of nanocrystal-based catalysts for fundamental studies.

Chapter 2 describes how to attach the NC to a support and how to mildly activate them in order to obtain highly active Fischer–Tropsch (FT) catalysts.

The cause for the difference in FT performance between pristine and surface-oxidized carbon nanotubes (CNT) is investigated in **Chapter 3**. Well-defined Co-NC/CNT catalysts and advanced characterization techniques (STEM–EDX mapping, *in situ* XRD) are applied to isolate these effects.

The preparation of a range of Co-NC of different sizes (3, 6, 9 and 12 nm) on TiO₂ and SiO₂ supports is reported in **Chapter 4**. Using these catalysts, the effect of particle size and support on the growth of Co-NC during activation and FT is investigated.

Chapter 5 describes the synthesis of disk-shaped Co-NC supported on SiO₂. Their FT performance is compared to that of spherical Co-NC and related to the structure of the catalysts.

Recent literature on the interaction between metal nanoparticles and supports is reviewed in **Chapter 6** with a focus on strategies to tune metal-support interactions to enhance catalytic performance.

Chapter 7 focuses on cobalt-support interactions that occur specifically on reducible supports such as TiO₂ and Nb₂O₅. A straightforward reduction–oxidation–reduction treatment is reported that doubles the accessible metallic surface area and cobalt-weight-based activity, while maintaining constant intrinsic activity.

Finally, conclusions and an outlook are provided.

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Chapter 2

Assembly and activation of supported cobalt nanocrystal catalysts for the Fischer-Tropsch synthesis

Abstract

The effect of oxidative treatments on the attachment of cobalt nanocrystals (Co-NC) to a support and subsequent ligand removal was investigated. Attachment of ϵ -cobalt NC led to extensive clustering of NC and low Fischer-Tropsch synthesis activity. Low-temperature oxidation of ϵ -cobalt NC resulted in a very uniform CoO-NC distribution and high activity whereas high-temperature oxidation to Co_3O_4 led to less uniform NC distributions and lower activity.

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2.1. Introduction

Colloidal nanocrystals (NC) can be applied to synthesize well-defined supported model catalysts.^{1,2} However, two specific challenges arise in catalyst preparation when using colloids. Firstly, the NC have to be uniformly attached to a support. This is often achieved by mixing a NC suspension with the support followed by separation and washing. Such methods lead to uniform NC distributions only if the particle-support and particle-particle interactions are optimal.³⁻⁵ Secondly, the surfaces of NC are usually covered with stabilizing ligands, which limit accessibility of the metal surface for reactants and thereby hamper catalytic activity.^{6,7} Ligands are commonly removed through oxidative treatments at high temperatures, but such severe conditions can affect for example the NC size and shape.⁸

These challenges have been investigated and largely resolved for noble-metal NC.⁹ This even led to the introduction of the first commercial NC-based catalysts containing Pd- or Pt-NC.¹⁰ In contrast, base-metal NC have been studied less for catalysis and are more challenging than noble-metal NC, because base metal NC are more susceptible to oxidation and magnetic interactions.¹¹ Furthermore, common ligands, such as oleic acid, are hard Lewis bases and bind stronger to base metals, which are hard Lewis acids compared to noble metals.¹²

As a showcase of base metal NC, this study focusses on cobalt catalysts for the Fischer-Tropsch (FT) synthesis. In FT, fuels and chemicals are produced from synthesis gas, a H₂/CO mixture that can be derived from natural gas, coal or biomass.¹³ The understanding of FT could benefit from colloidal techniques to provide more precise structure-performance relationships that are not readily obtained otherwise.^{14,15} Supported cobalt catalysts for FT have been prepared using colloidal techniques.^{4,16-24} Most were activated through high-temperature (HT) oxidation followed by reduction to arrive at high intrinsic activities.^{4,16-21} When HT-oxidative treatments were omitted, significantly lower intrinsic activities were obtained.²²⁻²⁴ The development of a milder activation procedure would reduce the impact on the Co-NC and thereby increase the potential of Co-NC for future structure-performance studies.^{2,25} In this chapter, we investigated the effect of oxidative treatments on the attachment and activation of Co-NC on carbon nanotubes (CNT) as FT catalysts.

2.2. Experimental

2.2.1. Synthesis of Co(O) nanocrystals

The synthesis of Co-NC was based on the method reported by Iablokov et al.²⁶ In this method, the introduction of elements that might ultimately affect the catalytic performance, such as phosphorus or sodium, was avoided. The synthesis was performed under N₂ atmosphere on a Schlenk line. Typically, 65 mg of oleic acid (Sigma-Aldrich, 90 %, technical grade) was transferred to a 100 mL 3-necked flask equipped with a cooler and two septa and evacuated at 120 °C for 30 min. After flushing several times with N₂, 7.5 mL of 1,2-dichlorobenzene (Sigma-Aldrich, 99 %, anhydrous) was inertly transferred to the flask and the mixture was heated to 174 °C under 750 rpm magnetic stirring. Meanwhile, 270 mg dicobalt octacarbonyl (Acros Organics, 95 %, stabilized) was dissolved

in 1.5 mL 1,2-dichlorobenzene in a glass vial inside a glovebox. Then, the cobalt precursor was rapidly injected into the flask containing the mixture at 174 °C and 750 rpm magnetic stirring. The reaction was continued for 20 minutes and quenched afterwards using a water bath. Optionally, for low-temperature (LT) oxidized nanocrystals (NC), the Co-NC were exposed to air at room temperature under 650 rpm magnetic stirring for 1 h by removing one septum in order to oxidize the NC to CoO. Subsequently, the colloidal suspension of CoO-NC was divided over two glass centrifuge tubes, both were filled up to 20 mL with 2-propanol (Sigma-Aldrich, >99 %, LC-MS Chromasolv) and centrifuged at 2200 G for 20 min. The supernatant was decanted and the precipitated colloids were redispersed in 0.5 mL n-hexane (Acros Organics, 99+ %) per tube using sonication. Again, the tubes were filled to 20 mL with 2-propanol, then centrifuged at 2200 G for 20 min and the supernatant was decanted. This washing cycle was repeated 2 times more and finally the NC were redispersed in 2 mL toluene (Acros Organics, 99+ %, extra pure) and stored in a glass vial.

2.2.2. Attachment of Co(O) nanocrystals to carbon nanotubes

The support, CNT (Baytubes c150 HP), was first sieved to a fraction of 75–150 µm. Co- and CoO-NC (10 wt% Co) were emplaced on CNT by wet impregnation at elevated temperature under nitrogen atmosphere on a Schlenk line.³ To this end, 500 mg CNT was transferred to a 100 mL 3-necked flask equipped with a cooler, septum and glass plug. 5 mL 1-octadecene (Sigma-Aldrich, 90 %, technical grade) was mixed with the colloidal suspension (in toluene) and added to the CNT under 400 rpm magnetic stirring. The suspension was degassed at 100 °C for 30 min during which the toluene evaporated, flushed several times with nitrogen and heated to 200 °C for 30 min. After cooling down to room temperature, ~20 mL acetone was added to the suspension and the supernatant was decanted. The precipitated catalyst was washed six times by first adding 2 mL n-hexane followed by 6 mL acetone and decanting of the supernatant. Finally, the catalyst was dried at 60 °C for 1 h in static air, at 120 °C for 3 h in static air and at 80 °C for 3 h under vacuum. Afterwards, the catalyst was again sieved to a fraction of 75–150 µm.

2.2.3. High-temperature oxidative treatment of CoO-NC/CNT

A batch of LT-oxidized CoO-NC on CNT was treated at high temperature in an oxidative environment. First, 100 mg of catalyst was loaded in a U-shaped quartz reactor and 37.5 mL·min⁻¹ of 20 vol% O₂ in N₂ was led through the catalyst in fixed bed mode. The catalyst was heated to 250 °C for 2 h with 2 °C·min⁻¹ and was afterwards cooled again to room temperature.

2.2.4. Characterization

A cryogenic transmission electron microscopy (cryo-TEM) sample of the suspension of metallic Co-NC under inert atmosphere was prepared using a vitrification robot (FEI Vitrobot Mark III). To prepare the sample, 3 µL of sample was applied on a 200 mesh, lacey carbon-coated Cu grid inside an environmental chamber at 20 °C with 99 % relative humidity of toluene. The grid was blotted with filter paper for 3 s and then vitrified by rapidly plunging the grid into liquid nitrogen (–196 °C). The total vitrification procedure took less than 10 s in order to minimize the contact time with air and to avoid oxidation of

the Co-NC. Cryo-TEM was performed on a TU/e CryoTitan (FEI) operating at 300 kV using low electron dose rates of $37 \text{ e}^- \cdot \text{\AA}^{-2} \cdot \text{s}^{-1}$ at the magnification used. The crystal structure of the NC was analyzed using low dose selective area electron diffraction (LDSAED).

Transmission electron microscopy (TEM) was performed using a Tecnai 12 (FEI) operating at 120 kV. A sample of a CoO-NC suspension was prepared by dropcasting the colloidal suspension in hexane on a 200 mesh, carbon-coated Cu grid. In the case of CNT supported catalysts, the powder was first suspended in 2-propanol by sonication and subsequently dropcasted on a 200 mesh holey carbon-coated Cu grid. The particle sizes were manually determined using iTEM software and at least 200 particles were analyzed to obtain a statistical analysis. The reported diameters of all Co_xO_y particles were converted to their equivalent metallic cobalt diameter and were volume/surface averaged ($D[3,2]$). Reduced and passivated samples were corrected for a 3 nm CoO layer.

High-resolution transmission electron microscopy (HR-TEM) was carried out on a Talos F200X (FEI), equipped with a high-brightness field emission gun and operated at 200 kV. Sample preparation was identical to that of TEM.

X-ray diffraction (XRD) was performed using a Bruker D2 Phaser using Co radiation (K_α , $\lambda = 1.789 \text{ \AA}$). The diffractograms were analyzed and fitted using Bruker's Eva and Topas software. The reported crystallite size was calculated using the Scherrer equation after fitting the full scan from 20 – $100^\circ 2\theta$ and analysis of the ϵ -Co [221], CoO [111] and Co_3O_4 [311] peaks.

Inductively coupled plasma-optical emission spectroscopy (ICP-OES) was measured on a SPECTRO ARCOS and samples were prepared by cobalt extraction in aqua regia.

Thermogravimetric analysis-mass spectrometry (TGA-MS) was carried out on a PerkinElmer Pyris 1 TGA. Approximately 5 mg sample was pre-dried at 50°C under N_2 and subsequently analyzed while heating to 800°C with $10^\circ\text{C} \cdot \text{min}^{-1}$ under a flow of 25 vol% H_2 in N_2 .

2.2.5. Fischer-Tropsch synthesis

The performance of the catalysts was evaluated using an Avantium Flowrence 16 parallel reactor setup. Stainless steel, plug-flow reactors were first loaded with a mixture of 15–50 mg of catalyst and 100 mg SiC diluent. Then, the catalysts were reduced *in situ* at 350°C for 8 h ($1^\circ\text{C} \cdot \text{min}^{-1}$) in 25 vol% H_2 in He at 1 bar. Subsequently, the reactors were cooled to 180°C and the pressure was increased to 20 bar under H_2 flow. Finally, synthesis gas with $\text{H}_2/\text{CO} = 2 \text{ v/v}$, 5 vol% He as internal standard and $\text{GHSV} = 2350\text{--}7850 \text{ h}^{-1}$ was introduced and the reactors were heated to 220°C with $1^\circ\text{C} \cdot \text{min}^{-1}$. The reaction products were analyzed online with an Agilent 7890A GC. The hydrocarbon products were separated on an Agilent J&W PoraBOND Q column and analyzed by a FID. The permanent gasses were separated on a ShinCarbon ST column and quantified using a TCD.

The activity was reported as CO conversion, defined as $X_{\text{CO}} = (\text{mol}_{\text{CO, in}} - \text{mol}_{\text{CO, out}}) \cdot \text{mol}_{\text{CO, in}}^{-1}$, and as cobalt time yield and turnover frequency. For the TOF calculation, the surface averaged cobalt diameter of the spent catalysts from TEM was used to determine the metallic surface area, assuming spherical particles. From the metallic surface area, the number of surface cobalt atoms was derived using a cobalt cross sectional area of 0.0662 nm^2 per atom.²⁷ Furthermore, the selectivity towards C_1 to C_4 hydrocarbons was

calculated as $S_{Cn} = \text{mol}_{Cn} \cdot n \cdot (\text{mol}_{CO, in} - \text{mol}_{CO, out})^{-1}$, where n is the carbon number (1–4) of the product. The selectivity to C_5 , was defined as $S_{C5} = 1 - S_{C1-4}$.

2.3. Results and discussion

Co-NC were synthesized using colloidal techniques. Figure 2.1 provides an overview of the different treatments applied to the Co-NC, which will be discussed step by step in the following sections. The Co-NC were imaged after synthesis using cryogenic transmission electron microscopy (cryo-TEM). The Co-NC had neither been washed nor exposed to air. The as-synthesized Co-NC were cubical and formed chains, indicating magnetic interactions between metallic Co-NC (Figure 2.2a). Electron diffraction experiments using cryo-TEM showed that the crystal structure of the freshly synthesized NC was ϵ -cobalt (Figure 2.2b, Appendix A, Table A1), which is a crystal structure of Co that is accessible via wet-chemical synthesis of Co-NC.²⁸

Figure 2.1. Schematic overview of the oxidative treatments applied to the NC. The treatments include no oxidation of Co-NC, low-temperature oxidation of Co-NC to CoO-NC and high-temperature oxidation of CoO-NC/CNT to Co₃O₄-NC/CNT.

Low-temperature (LT) oxidation of as-synthesized Co-NC was pursued by air-exposure at ambient conditions during subsequent washing steps. This reproducibly resulted in particles of 6–7 nm with a narrow particle size distribution (Figure 2.2c,d) according to transmission electron microscopy (TEM). In a typical NC synthesis, a cobalt yield of ~50 % was obtained. The final NC after the washing steps consisted of CoO, as inferred from electron diffraction (Appendix A, Figure A1, Table A1), and had become irregularly spherical, owing to their polycrystalline nature. No remaining metallic cores were detected for the CoO-NC using either TEM or electron diffraction. Consequently, the magnetic interactions were reduced and the formation of chains on the TEM grid was no longer observed (Figure 2.2c).

Both Co- and CoO-NC were attached to untreated, hydrophobic CNT through mixing at elevated temperature. This method resulted in nearly quantitative attachment of the NC to the CNT with some variation of the final metal loading due to a slightly variable NC concentration in the suspension. The supported Co-NC and CoO-NC were designated

Co1/CNT and Co2/CNT, respectively. In the case of Co1/CNT, oxidation through air-exposure was avoided by omitting the washing steps after the Co-NC synthesis. The Co-NC were exposed to air for the first time during drying after attachment to the CNT.

Figure 2.2. Overview of the Co- and CoO-NC. **a** Cryo-TEM of as-synthesized Co-NC before exposure to air with a higher magnification inset and **b** the corresponding electron diffraction pattern. **c** TEM of CoO-NC with a higher magnification inset and **d** size distribution of CoO-NC with a surface-averaged particle diameter of 6.8 nm.

The average NC sizes and distributions over CNT were investigated using TEM. Co1/CNT was non-uniform with isolated NC as well as 20–60 nm aggregates (Appendix A, Figure A2). The inhomogeneity was believed to result from magnetic interactions between NC consisting of superparamagnetic ϵ -cobalt,²⁹ which prevented the Co-NC from distributing uniformly over the CNT. Werner et al.⁴ reported similar non-uniform distributions of metallic Co-NC over silica supports and ascribed this to magnetic interactions of the Co-NC.

For Co2/CNT, the CoO-NC retained their diameter of 6–7 nm during attachment (Figure 2.3a). High-resolution transmission electron microscopy (HR-TEM) confirmed that the NC were polycrystalline and attached as rather spherical particles onto the CNT (Figure 2.3b). Yang et al.³⁰ obtained comparable polycrystalline CoO-NC through rapid oxidation at 200 °C of isolated, monocrystalline NC of hcp-Co. Furthermore, the NC were distributed uniformly over the support, indicating that the magnetic interactions were limited and that diffusion of the NC into the open porous network of the CNT was facile, which is in line with previous observations.^{3,31} Clearly, oxidation of the Co-NC to CoO under air-exposure proved crucial for their uniform distribution over CNT.

Figure 2.3. Overview of NC supported on CNT. **a** TEM and **b** HR-TEM of Co2/CNT, and **c** TEM and **d** HR-TEM of Co3/CNT.

X-ray diffraction (XRD) pointed to ϵ -Co crystallites for Co1/CNT (Table 2.1, Appendix A, Figure A3). The average crystallite size of ~ 6 nm was in the range of the NC size prior to attachment. XRD analysis of Co2/CNT indicated 2–3 nm crystalline CoO domains, which was consistent with HR-TEM (Figure 2.3b).

Table 2.1. Overview of the prepared catalysts. The metal loading was determined by ICP-OES, the particle diameter ($D[3,2]_{\text{Co-NC}}$) by TEM and the crystallite size and crystal structure by XRD.

Sample	Oxidation temp. (°C)	Cobalt loading (wt%)	$D[3,2]_{\text{Co-NC}}$ (nm) ^a	Crystallite size (nm)	Crystal structure
Co1/CNT	–	11	7–60	~ 6	ϵ -Co
Co2/CNT	25	8.8	5.7	2.9	CoO
Co3/CNT	250	8.6	5.9	4.0	Co ₃ O ₄

^a Particle size analysis using TEM of NC after attachment to CNT.

To investigate the effect of HT-oxidation, a commonly applied treatment to remove ligands, Co2/CNT was exposed to synthetic air (20 vol% O₂) at 250 °C. The obtained catalyst was labelled Co3/CNT. XRD measurements after the oxidative treatment showed that CoO was converted into Co₃O₄ (Table 2.1, Appendix A, Figure A3). The treatment did not affect the particle size and distribution as both remained largely unchanged (Figure 2.3c, Appendix A, Figure A4). However, at the local scale, HR-TEM showed that the NC now consisted of single crystalline domains although some clustering of NC and embedding into the CNT was apparent, possibly because of cobalt oxide locally catalyzing oxidation of CNT at high temperature (Figure 2.3d).

Figure 2.4. Combined TGA and MS results of Co2/CNT in 25 vol% H₂ with 10 °C·min⁻¹ heating.

The reduction of the catalysts was investigated using thermogravimetric analysis coupled with mass spectrometry (TGA-MS) in diluted H₂. For Co2/CNT, the main weight loss around 650 °C was associated with cobalt-catalyzed methanation of CNT (Figure 2.4).³² At 350 °C, CoO was reduced to Co⁰ as indicated by weight loss and water evolution. Interestingly, CH₄, CO₂ and the C₄H₇⁺ ion, a fragment ion of oleic acid, were produced as well. These signals were related to desorption and/or decomposition of oleic acid ligands simultaneously with reduction of CoO at 350 °C. Quantification of the weight loss confirmed that, besides the loss of oxygen from CoO, also ligands were removed. When assuming full reduction of CoO, ~35 % of the amount of oleic acid added in the NC synthesis was removed during reduction. For Co3/CNT, neither the C₄H₇⁺ fragment nor CH₄ was observed with TGA-MS and the observed weight loss of 3.8 % matched the theoretical weight loss of 3.1 % (Appendix A, Figure A5). The ligands had thus already been removed in the HT-oxidative treatment.

Table 2.2. Catalytic results obtained for FT at 20 bar, 220 °C, H₂/CO = 2 v/v, 80–96 h time-on-stream with TOF based on the average particle size of the spent and passivated catalysts (D[3,2]_{spent}) as determined with TEM. The GHSV was 1840 h⁻¹ (Co1/CNT), 7850 h⁻¹ (Co2/CNT) and 5970 h⁻¹ (Co3/CNT) to obtain similar CO conversion levels

Sample	CO conv. (%)	CTY ^a	TOF (10 ⁻³ s ⁻¹)	C ₁ -sel. (% _C)	C ₅₊ -sel. (% _C)	D[3,2] _{spent} (nm)
Co1/CNT	2.4	0.4	n.a.	n.a.	n.a.	15–100
Co2/CNT	18	22	116	12	78	9.0
Co3/CNT	15	17	122	9.8	82	12

^a In 10⁻⁵ mol_{CO}·g_{Co}⁻¹·s⁻¹.

Co2/CNT was highly active in FT after *in situ* reduction (Table 2.2, Appendix A, Figure A6). In fact, its cobalt time yield (CTY) was higher than that of a Co/CNT catalyst prepared by Eschemann et al.³³ via incipient wetness impregnation using a cobalt nitrate precursor solution. The high activity of our Co2/CNT implied that the surface of the cobalt particles was fully accessible to the synthesis gas reactants. Furthermore, during the first

few hours of FT, substantial activation of the Co2/CNT could indicate incomplete reduction or residual ligands desorbing from the NC surface due to the formed FT products.

The activity of Co1/CNT was close to zero. This was most likely caused by a large decrease in metallic surface area due to the clustered particles growing together under reaction conditions (Appendix A, Figure A7). Additionally, the lack of washing steps between the synthesis and attachment of the Co–NC may have increased the ligand concentration, which in turn may have led to less binding of the Co–NC to the CNT. Casavola et al.³ described a similar effect of ligands on the binding of Fe–NC.

Co3/CNT was significantly less active than Co2/CNT. The HT-oxidative treatment promoted particle growth during *in situ* reduction and FT. TEM of the spent catalysts revealed a larger particle size for Co3/CNT than for Co2/CNT (Table 2.2, Appendix A, Figure A7). An explanation for the adverse effect of HT-oxidation on the stability of the catalysts could be a different interaction of the NC with the support for Co2/CNT and Co3/CNT, as shown in Figure 2.3. Furthermore, some NC clustering was apparent for the fresh Co3/CNT, which probably led to increased particle growth during reduction and catalysis.

The C₅₊-selectivity of both Co2/CNT and Co3/CNT was comparable, although Co3/CNT was slightly more selective to C₅₊-products than Co2/CNT (Table 2.2). For Co1/CNT, no selectivity could be determined owing to its low activity.

Figure 2.5. Turnover frequencies of Co2/CNT and Co3/CNT as a function of the average cobalt particle diameter. Recalculated TOF values of NC-based catalysts for LT-oxidized Co/SiO₂ (grey open circles, ref.²²) and non-oxidized Co/TiO₂ (grey open triangles, ref.²³) are given as comparison. Details of the recalculation can be found in Appendix A. The highlighted area is the typical TOF range of conventional catalysts.

The turnover frequencies (TOF) of Co2/CNT and Co3/CNT were similar (Table 2.2), thereby proving that the higher CTY of Co2/CNT originated from a larger cobalt surface area instead of higher intrinsic activity. Because the surface of Co3/CNT was free of ligands, as shown before, the surface of the Co2/CNT must have been equally stripped to obtain a

similar TOF. When comparing the TOF with literature values for LT- or non-oxidized NC catalysts,^{22,23} it is apparent that we obtained more active catalysts, which are now at the high end of the TOF range of conventional catalysts (Figure 2.5). For the HT-oxidized Co₃/CNT, full activation and a high TOF was expected, but this is the first time, to the best of our knowledge that only LT-oxidation followed by *in situ* reduction was sufficient to fully activate a NC-based cobalt catalyst for FT.

2.4. Conclusion

In this work, we investigated how oxidative treatments of cobalt nanocrystals (NC) affect their attachment to carbon nanotubes and activation for the Fischer-Tropsch (FT) synthesis. Attachment of ϵ -cobalt NC resulted in clustering of the NC (probably due to magnetic interactions between the NC) and low activity. After low-temperature oxidation of the NC to CoO, the NC were attached uniformly. The ligands were readily removed during *in situ* reduction and high activity was obtained. In fact, it was possible to fully activate a NC-based cobalt catalyst for FT using this mild procedure. High-temperature (HT) oxidation to Co₃O₄ led to more pronounced particle growth during *in situ* reduction or FT and therefore the catalytic activity was lower. An HT-oxidative treatment was thus unnecessary and even counter-productive. These findings will facilitate the application of colloid-based catalysts to investigate structure-performance relationships in catalysis.

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Chapter 3

Cobalt nanocrystals on carbon nanotubes in the Fischer-Tropsch synthesis: impact of support oxidation

Abstract

In this chapter, we investigated the effect of oxidation of a carbon nanotube (CNT) support on the structure and catalytic performance in the Fischer-Tropsch (FT) synthesis of pre-synthesized cobalt nanocrystals (NC). CoO-NC of 6 nm were prepared using colloidal techniques and impregnated on pristine and surface-oxidized CNT (10 wt% Co). During reduction, the CoO-NC on pristine CNT were converted completely to Co while growing to 11 nm on average. In contrast, on oxidized CNT (oxCNT), only ~50 % reduction of CoO was observed and average NC growth was absent, indicating a stronger Co-support interaction on oxCNT than on CNT. In FT, the turnover frequency (TOF) after 100 h on stream was exceptionally high on pristine CNT ($150 \cdot 10^{-3} \text{ s}^{-1}$) and a factor of two lower on oxCNT ($63 \cdot 10^{-3} \text{ s}^{-1}$). In the initial stage of FT, the TOF was 35 % lower on oxCNT than on CNT, which matched well with the 32 % lower crystallinity of metallic cobalt during FT determined using *in situ* XRD. Furthermore, deactivation was observed mainly on oxCNT while NC growth, restructuring, or oxidation during FT were excluded, leaving enhanced deposition of carbonaceous species on Co-NC/oxCNT as possible causes. These results demonstrate the large impact of the support on the structure and performance of well-defined catalysts based on cobalt nanocrystals.

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3.1. Introduction

The most frequently applied supports for cobalt-based Fischer-Tropsch (FT) synthesis catalysts are oxidic compounds, such as Al_2O_3 , SiO_2 or TiO_2 , which usually interact with cobalt and influence the FT performance.¹ Carbon supports, on the other hand, present an interesting alternative, especially for fundamental studies, given their chemical inertness (limited or no cobalt-support compound formation). Various types of carbon have been applied as supports,² including activated carbon, ordered mesoporous carbon,³ and carbon nanofibers^{4,5} and carbon nanotubes.⁶ Among these, carbon nanotubes (CNT) have an open, macro- and mesoporous structure combined with a high specific surface area.⁷ Moreover, the surface of pristine CNT contains a low amount of functional groups, rendering these hydrophobic.⁸ To increase hydrophilicity, oxygen-containing functional groups can be introduced by oxidation of pristine CNT, for example using nitric and/or sulfuric acid.^{8,9} Functional groups can also act as anchoring sites for metal nanoparticles and hence, metals supported on oxidized CNT (oxCNT) typically display increased resistance towards sintering under reaction conditions.¹⁰

Several groups reported higher activity for Co/oxCNT compared to Co/CNT, while C_5+ -selectivity decreased with CNT oxidation.¹¹⁻¹³ Interestingly, Eschemann et al.⁶ showed that CNT functionalization has a major effect on the FT performance of Co/CNT catalysts, with significantly lower activity and C_5+ -selectivity for oxCNT. The different catalytic performance was tentatively ascribed to an increase in hcp Co on pristine CNT compared to oxCNT, as observed by *in situ* XRD during reduction, because often hcp Co is more active in FT than fcc Co.¹⁴⁻¹⁸ However, the exact nature of the differences between Co supported on CNT and oxCNT was not established.

More insight into the metal-support interaction after support functionalization and its effect in FT could potentially be obtained by using better defined catalysts in combination with advanced characterization techniques. Colloidal techniques offer the possibility to synthesize metal nanocrystals (NC) separately with high precision in e.g. NC size, shape or crystal structure.¹⁹ In the case of Co-NC, low-temperature oxidation to CoO facilitates their subsequent uniform attachment and ligand removal during reduction.²⁰ Because NC synthesis is decoupled from attachment to the support, the starting cobalt particles should be very similar, meaning that differences in FT must be caused by altered metal-support interactions related to functionalization of the CNT.

In this chapter, we investigated the effect of CNT surface oxidation on the structure and catalytic performance of CNT-supported cobalt nanocrystals in the Fischer-Tropsch synthesis. Catalyst were prepared via colloidal synthesis of 6 nm CoO-NC and subsequent attachment to CNT and oxCNT. CNT oxidation resulted in decreased reducibility and sintering propensity of the cobalt (oxide) phase during reduction. In FT, Co-NC on pristine CNT were highly active, while the activity on oxCNT was approximately a factor two lower. Using *in situ* XRD, the crystalline metallic Co content on oxCNT was found to be 32 % lower than on pristine CNT during 40 , making it the most probable cause for the observed 35 % lower initial TOF on oxCNT. Catalyst deactivation during FT occurred mainly on oxCNT, while particle growth, NC restructuring, or oxidation were excluded as deactivation mechanisms, leaving enhanced carbon deposition as a likely option.

3.2. Experimental

3.2.1. Oxidation of carbon nanotubes

Oxidized CNT (oxCNT) were obtained by heating 4 g CNT (Baytubes c150 HP) in 150 mL concentrated HNO_3 at 80 °C for 90 min. Afterwards, the oxCNT was washed on a vacuum filtration setup with 2.5 L deionized H_2O until the pH of the filtrate reached 5. The washed oxCNT was dried at 120 °C in static air overnight.

3.2.2. Synthesis of cobalt nanocrystals

The colloidal synthesis of cobalt nanocrystals (Co-NC) was based on a previously reported method,²¹ which was selected because the use of phosphorus-containing ligands was avoided. The synthesis was performed under N_2 atmosphere on a Schlenk line. Typically, 65 mg of oleic acid (Sigma-Aldrich, 90 %, technical grade) was transferred to a 100 mL 3-necked flask equipped with a cooler and two septa and evacuated at 100 °C for 30 min. After flushing several times with N_2 , 7.5 mL of 1,2-dichlorobenzene (Sigma-Aldrich, 99 %, anhydrous) was transferred under N_2 to the flask and the mixture was heated to 174 °C under 750 rpm magnetic stirring. Meanwhile, 270 mg dicobalt octacarbonyl (Acros Organics, 95 %, stabilized) was dissolved in 1.5 mL 1,2-dichlorobenzene inside a glovebox. When the solution in the flask reached 174 °C, the cobalt precursor was rapidly injected into the flask. The solution was left to react for 20 minutes and quenched afterwards using a water bath. The Co-NC suspension was exposed to air for one hour at room temperature under 650 rpm magnetic stirring to convert Co-NC to CoO-NC. Subsequently, the colloidal CoO dispersion was transferred to glass centrifuge tubes, filled up to 20 mL with 2-propanol (Sigma-Aldrich, >99 %, LC-MS Chromasolv) and centrifuged at 2200 G for 20 minutes. The supernatant was decanted and the precipitated CoO-NC were re-dispersed in n-hexane (Acros Organics, 99+ %) using sonication. This washing cycle with 2-propanol was repeated 3 times more and finally the NC were re-dispersed in 2 mL toluene (Acros Organics, 99+ %, extra pure) and stored in a glass vial.

3.2.3. Attachment of cobalt oxide nanocrystals on CNT and oxCNT

The supports were sieved to a grain size of 75–150 μm prior to being used. Attachment of 10 wt% of CoO-NC on CNT and oxCNT was performed by pore-filling impregnation with the colloidal dispersion. For this, the (ox)CNT were dried at 80 °C under vacuum for 1 h. After cooling to room temperature, $2.5 \text{ mL} \cdot \text{g}_{\text{support}}^{-1}$ of colloidal dispersion in toluene, equivalent to the pore volume of (ox)CNT, was injected to the support under magnetic stirring. The toluene evaporated upon contact with the vacuum, immediately emptying the syringe. After mixing, the sample was dried at 60 °C for 1 h in static air, 120 °C for 3 h in static air and 80 °C for 3 h under vacuum.

3.2.4. Characterization

CNT and oxCNT were titrated using a Radiometer Analytical TitrLab TIM880 automatic titration setup. Between 25–30 mg of sample was suspended in 30 mL 0.1 M KCl by sonication, flushed for 10 min with N_2 to remove CO_2 and subsequently titrated with 0.01 M

NaOH in 0.1 M KCl under N₂ atmosphere. The data was analyzed as described by Eschemann et al.⁶, i.e. a second-degree equation ($y = ax^2 + bx + c$) was fitted to the first derivative of the pH curve and the inflection point was calculated using $x_{\text{inflection}} = -b/2a$.

N₂-physisorption was measured on a Micromeritics Tristar 3000. The samples were pre-dried under N₂ flow at 120 °C for 80 h for CNT and 150 °C for 20 h for oxCNT. Both samples were analyzed over $P/P_0 = 0-0.995$ at -196 °C. The surface area was determined using the BET method and the mesopore volume by single point analysis of the desorption isotherm at $P/P_0 = 0.995$.

Transmission electron microscopy (TEM) was performed on an FEI Tecnai 12 operating at 120 kV. Scanning transmission electron microscopy with energy-dispersive X-ray spectroscopy (STEM-EDX) was performed in high-angle annular dark-field (HAADF) mode on a Talos F200X (Thermo Fisher Scientific). The microscope was equipped with a high-brightness field emission gun (X-FEG) and a Super-X G2 EDX detector and was operated at 200 kV. Samples of colloidal dispersions in hexane were prepared by drop casting on a carbon coated Cu grid. In the case of supported catalysts, the powder was first suspended in 2-propanol by sonication and subsequently drop casted on a holey carbon coated Cu grid. The particle sizes were manually determined using iTEM software and at least 200 particles were analyzed to allow a statistical analysis. All reported particle sizes were recalculated to equivalent metallic Co size by correcting for the lattice expansion of a 3 nm CoO passivation layer (Co-NC and reduced/spent catalysts). All particle sizes are reported as volume/surface mean diameter ($D[3,2]$).

Inductively coupled plasma-optical emission spectroscopy (ICP-OES) was measured on a SPECTRO ARCOS and samples were prepared by cobalt extraction in aqua regia.

Temperature programmed reduction (TPR) was measured using a Micromeritics AutoChem 2920. 25 mg of sample was reduced by heating to 800 °C with 5 °C·min⁻¹ in a flow of 5 vol% H₂ in Ar.

X-ray diffraction (XRD) was performed on a Bruker D2 Phaser using Co radiation ($K\alpha_1$ 1.789 Å). The diffractograms were analyzed and fitted using Bruker's Eva and Topas software. After fitting the full scan from 20-100 ° 2 θ , the crystallite size was calculated using the Scherrer equation to analyze the CoO [111] peak.

In situ XRD patterns were measured on a Bruker D8 Discover with a Mo ($K\alpha_1$ 0.709 Å) source in Debye-Scherrer transmission (capillary) geometry. The X-ray beam was focused on a quartz capillary with 1000 µm OD and a wall thickness of 10 µm using a Göbel-mirror. The setup was equipped with an energy dispersive LynxEye XE Position Sensitive Detector (PSD). Details on the complete setup can be found in recent publications.^{22,23} The patterns were measured between 9 and 39 ° 2 θ with an increment of 0.07 ° and time per step of 15.3 s. Multiple scans were accumulated to improve the signal-to-noise ratio only if the patterns were identical. Rietveld Quantitative Phase Analysis (Rietveld QPA) was performed on the measured diffractograms using Bruker TOPAS (v5) software. Details of the Rietveld refinement procedure are given in Appendix B. Typically, 3.5 mg sample in the sieve fraction 75-150 µm was loaded in the capillary and fixed with quartz wool at either end, resulting in a catalyst bed length of ~20 mm. The capillary was placed in the setup and the catalysts were reduced *in situ* at 350 °C for 8 h (1 °C·min⁻¹) in a 1.2 mL·min⁻¹ flow of 25

vol% H₂ in He at 1 bar. After reduction, the temperature was lowered to 180 °C with 3 °C·min⁻¹ and at this temperature, a 3.0 mL·min⁻¹ flow of synthesis gas H₂/CO = 2 (v/v) was introduced. After 10 min stabilization, the back-pressure regulator was set to 10.6 bar. Only after the pressure was reached and stable, the temperature was increased to 220 °C with 1 °C·min⁻¹, which was defined as TOS = 0 h. *In situ* XRD patterns were recorded both during reduction and FT.

3.2.5. Fischer-Tropsch synthesis

The performance of the catalysts was evaluated using an Avantium Flowrence 16 parallel reactor setup. Stainless steel plug-flow reactors (2.6 mm ID) were loaded with a mixture of 15–25 mg of catalyst (75–150 μm) and 100 mg SiC diluent (212–425 μm). The catalysts were reduced *in situ* at 350 °C for 8 h (1 °C·min⁻¹) in 25 vol% H₂ in He flow at 1 bar. Subsequently, the reactors were cooled to 180 °C and the pressure was increased to 20 bar under H₂ flow. Synthesis gas with H₂/CO = 2 (v/v), 5 vol% He as internal standard and GHSV = 5950–8900 h⁻¹ was introduced and the reactors were heated to 220 °C with 1 °C·min⁻¹. The reaction products were analyzed online with an Agilent 7890A GC. The hydrocarbon products were separated on an Agilent J&W PoraBOND Q column and analyzed by an FID. The permanent gasses were separated on a ShinCarbon ST column and quantified using a TCD. Catalytic activity was reported as CO conversion (X_{CO}), cobalt-time yield (CTY) and turnover frequency (TOF). The selectivity (in %_C) to C₁–C₄ hydrocarbons was determined as $S_{C1-C4} = 100 \cdot F_{Cn} \cdot n \cdot (F_{CO,in} \cdot X_{CO})^{-1}$ with n being the carbon number of the products and F the flow of the hydrocarbon or CO. The selectivity to C₅₊ hydrocarbons was calculated as $S_{C5+} = 100 \%_C - S_{C1-4}$.

3.3. Results and discussion

3.3.1. Oxidation of carbon nanotubes

Pristine CNT were oxidized using nitric acid to introduce O-containing functional groups and defects in the CNT surface. An increase in acidic groups was found (Table 3.1) with values similar to what has been obtained previously in our group using gas phase oxidation (~0.5 mmol·g⁻¹ acidic groups).⁶ In addition, the structure of CNT and oxCNT was investigated using N₂-physisorption (Table 3.1, isotherms in Appendix B, Figure B1). The specific surface area increased by 50 m²·g⁻¹ as a result of the functionalization, probably due to surface roughening and the creation of defects. The pore volume, determined at p/p₀ = 0.995, was somewhat lower for oxCNT. Overall, these results were well in line with previous reports.^{6,13}

Table 3.1. Structural properties of the pristine and functionalized CNT. The number of acidic groups was determined by titration and the structural properties of the CNT by N₂-physisorption.

Support material	Acidic groups (mmol·g ⁻¹)	BET (m ² ·g ⁻¹)	Pore volume (mL·g ⁻¹)
CNT	0.02	198	1.5
oxCNT	0.72	248	1.3

3.3.2. Synthesis of cobalt oxide nanocrystals

Metallic Co-NC were synthesized, exposed to air to allow oxidation to CoO and analyzed using TEM (Figure 3.1a,b). The NC were rather spherical and the surface-volume averaged size ($D[3,2]$) of the NC was consistently between 6–7 nm with a standard deviation below 1 nm.

Figure 3.1. TEM results of as-synthesized CoO-NC and the CNT- and oxCNT supported samples after NC attachment and drying. **a** TEM image of CoO-NC with a Co-equivalent surface-volume averaged size ($D[3,2]_{Co}$) of 6.5 ± 0.9 nm and **b** the corresponding particle size distribution with lognormal distribution. TEM images of CoO-NC deposited on **c** CNT and on **d** oxCNT.

3.3.3. Catalyst preparation

Model catalysts were prepared by attaching CoO-NC to CNT and oxCNT through impregnation with a colloidal suspension. The cobalt loading of the catalysts was ~10 wt%, as determined by ICP-OES (Table 3.2), and the catalysts were imaged by TEM (Figure 3.1c-d). The CoO-NC were uniformly distributed over oxCNT and appeared somewhat more clustered on CNT. In both cases, the NC were predominantly located on the external surface of the CNT. Analysis of the surface-volume averaged particle sizes (Table 3.2) revealed that the CoO-NC sizes of 6–7 nm was unchanged after attachment.

The crystal structure of the NC was investigated with XRD (Figure 3.2a, Table 3.2). The 6–7 nm NC consisted of multiple CoO crystallite domains of 2.2 nm on average, which was caused by the low-temperature oxidation treatment directly after their synthesis, as shown before.²⁰

Table 3.2. Properties of the as-prepared samples.

Sample	Metal loading (wt %) ^a	D[3,2] _{Co} (nm) ^b	Average crystallite size (nm) ^c
CoO–NC/CNT	9.7	5.9 ± 1.0	2.2 (CoO)
CoO–NC/oxCNT	9.6	6.7 ± 1.3	2.2 (CoO)

^a Metal loading determined with ICP–OES.

^b Particle size analysis from TEM of NC after attachment to (ox)CNT.

^c Average crystallite size derived from XRD.

Figure 3.2. Analysis of the crystal structure and reduction behavior of the catalysts. **a** *Ex situ* XRD patterns of CNT and the as-prepared samples. **b** TPR of the CoO–NC/CNT and CoO–NC/oxCNT in 5 % H₂ in Ar with a heating ramp of 5 °C·min⁻¹.

3.3.4. Reduction

Reduction of the pristine samples was investigated using TPR (Figure 3.2b). The CoO–NC were reduced in a single step to Co⁰ (single sharp peak), in contrast to a two-step reduction of Co₃O₄/CNT that is often reported (Co₃O₄ to CoO and CoO to Co⁰).^{6,13} Reduction of CoO occurred at 75 °C higher temperature with support functionalization. Furthermore, the broad feature around 350 °C for CoO–NC/oxCNT could be related to reduction of oxygen-containing functional groups, defective carbon or cobalt species associated to those, as this contribution was absent in the CNT-supported sample. Finally, the high-intensity peak

around 600 °C for CoO-NC/oxCNT was assigned to cobalt-catalyzed methanation of the support, which did not occur for CoO-NC/CNT in the investigated temperature range. The degree of reduction (DOR) of CoO was determined from the integral of the peak(s) at 350 °C (CoO-NC/CNT) and 350 and 425 °C (CoO-NC/oxCNT). On CNT, the DOR was 99 %, while it was only 46 % on oxCNT. Overall, the different reduction behavior implied stronger interaction of the NC with oxCNT than with pristine CNT.

The catalysts after reduction and passivation were investigated using TEM and STEM-HAADF combined with EDX (Figure 3.3). The NC on CNT grew to 11 nm on average, while those on oxCNT grew only marginally to 8 nm. Thus, functionalization of CNT invoked higher stability of the particles during reduction, probably through more uniform distribution of the NC and/or stronger anchoring of the cobalt particles to the support.^{13,24} On oxCNT, ~3 nm particles were observed after reduction and passivation, which were absent in the as-prepared state (Appendix B, Figure B2). This meant that re-dispersion of Co had taken place most likely during reduction and/or passivation. The observation of small particles could be linked to the lower DOR derived from TPR (Figure 3.2b), as cobalt oxide particles below 4 nm are more difficult to reduce.^{25–27} Furthermore, HR-TEM revealed that the cobalt particles were not covered by carbon and that attachment of the NC to the support appeared similar for both catalysts after reduction and passivation (Appendix B, Figure B3).

Figure 3.3. Electron microscopy of the catalysts after reduction and passivation. TEM results of **a** Co-NC/CNT and **b** Co-NC/oxCNT are shown together with STEM-HAADF results including cobalt EDX maps of **c** Co-NC/CNT and **d** Co-NC/oxCNT. The cobalt signal is shown in orange.

3.3.5. Fischer–Tropsch synthesis

The cobalt–weight–based activity (cobalt–time yield, CTY) of the catalysts was evaluated over 100 h on stream (Figure 3.4). After the initial 20 h on stream, the activity of Co–NC on CNT was substantially higher than on oxCNT. Co–NC/CNT was remarkably active, since CTY values of $26 \cdot 10^{-5} \text{ mol}_{\text{CO}} \cdot \text{g}_{\text{Co}}^{-1} \cdot \text{s}^{-1}$ at the prevailing reaction conditions are rarely reported in literature for nonpromoted cobalt catalysts at the prevailing conditions. Furthermore, the activity profile of Co–NC/CNT was quite stable after the initial period of 20 h on stream, while the Co–NC/oxCNT deactivated more rapidly.

During the initial 20 h on stream, both catalysts first activated rapidly before deactivation took over. Activation could be caused by loss of residual ligands under FT conditions through extraction by the formed reaction products. When omitting this strong activation, extrapolation to 0 h gave approximately the same activity for both catalysts and the difference in activity on both supports only set in later. The same was evident from the evolution of C_{5+} –selectivity of the NC–based catalysts with time–on–stream (Appendix B, Figure B4), i.e. initially similar selectivity that later diverged to 82 % on CNT and 78 % on oxCNT, qualitatively in line with previous literature.⁶ These results suggest that differences in catalytic performance take several hours to develop under FT conditions.

Figure 3.4. Cobalt–time yield of Co–NC/CNT and Co–NC/oxCNT during 100 h on stream at 20 bar, 220 °C, $\text{H}_2/\text{CO} = 2$, GHSV = 5950–8900 h^{-1} and CO conversion levels between 15 and 40 %.

The catalytic results obtained after ~90 h on stream are summarized in Table 3.3. The cobalt–weight–based activity is reported both as initial and final CTY. Furthermore, surface–volume averaged cobalt particle sizes in the spent and passivated state after >100 h on stream were determined by TEM (Table 3.3, Appendix B, Figure B5). Very few particles larger than 20 nm were observed and omitted in the particle size analysis.

The cobalt particle size distributions of used catalysts were compared to those of the catalysts in the pristine and reduced state to show the evolution of particle size (Figure 3.5a). On pristine CNT, growth of the initially 6 nm NC had occurred during reduction and the average size after FT was 10 nm. In contrast, the average NC size on oxCNT remained constant at ~7 nm during reduction and FT and the particle size distribution was close to its original form (Appendix B, Figure B2). Overall, oxidation of

CNT prevented average growth of the Co-NC during reduction/FT, probably because of a stronger interaction between Co and oxCNT.

Table 3.3. Fischer-Tropsch synthesis results obtained at 20 bar, 220 °C, 2 H₂/CO (v/v), GHSV = 5950–8900 h⁻¹. The data was averaged between 80–96 h on stream unless stated otherwise.

Sample	X _{Co} (%)	CTY _{initial} a,b	CTY _{final} a	TOF _{initial} (10 ⁻³ s ⁻¹) b,c	TOF _{final} (10 ⁻³ s ⁻¹) d	S _{Cl} (%C)	S _{C5+} (%C)	D[3,2] Co, spent (nm) ^e
Co-NC/CNT	25	29	26	190	150	11	82	9.6 ± 2.9
Co-NC/oxCNT	23	26	15	120	63	12	78	7.2 ± 1.6

^a In (10⁻⁵ mol_{Co}·g_{Co}⁻¹·s⁻¹).

^b Reported at maximum CTY between 0–10 h on stream.

^c Based on the metallic surface area calculated from the average Co particle size of the reduced and passivated catalyst.

^d Based on the metallic surface area calculated from the average Co particle size of the spent and passivated catalyst.

^e Determined by TEM; very few large particles (>20 nm) were excluded, if present.

The average particle sizes were used to calculate the cobalt-specific metallic surface areas. From these areas, cobalt-surface-based activities (turnover frequencies, TOF) after 100 h on stream were derived using the final CTY and particle size of the spent catalyst (Table 3.3). Comparison of the final TOF showed that Co-NC on CNT (150·10⁻³ s⁻¹) were significantly more active than on oxCNT (63·10⁻³ s⁻¹). In fact, Co-NC/CNT was exceptionally active, considering that TOF values between 10·10⁻³ s⁻¹ and 100·10⁻³ s⁻¹ are typically obtained.²⁰

The TOF was calculated as well for the initial stage of the reaction using the initial (maximal) CTY and particle size of the catalysts after reduction. The TOF decreased from the initial to the final stage of the reaction by 19 % for Co-NC/CNT and by 47 % for Co-NC/oxCNT. Hence, deactivation was predominantly caused by declining intrinsic activity over the course of the reaction and not by particle growth.

As a potential explanation for differences in catalytic performance, we investigated the crystal structure of cobalt in the NC-based catalysts during reduction and under FT conditions using *in situ* XRD at 10 bar, 220 °C and an H₂/CO ratio of 2 v/v (Figure 3.5b, refined patterns in Appendix B, Figure B6). The data was analyzed using Rietveld refinement. To improve the refinement results, it was necessary to include preferred orientations of hcp Co crystallites. Rather than having anisotropic crystallites (for which no evidence was observed in TEM), we propose that this was caused by an intergrown Co⁰ structure. XRD analysis of metallic cobalt can be complicated by stacking faults and the extent to which these are present depends strongly on the catalyst synthesis and treatments.^{14,28} Our refinement using only hcp and fcc Co phases did not account for an intergrowth structure, but did accommodate much of its features by increasing the intensity of the hcp Co (0002) peak, therefore possibly overestimating the fraction of hcp Co.

Figure 3.5. Evolution of Co particle size and Co crystal structure under FT conditions. **a** Average particle sizes ($D[3,2]_{Co}$) determined by TEM of the catalysts in the as-prepared, reduced and passivated, and spent and passivated state. The error bars indicate the standard deviation. **b** Background-subtracted and normalized diffraction patterns of Co-NC on CNT and oxCNT during FT as obtained with *in situ* XRD and subsequent Rietveld refinement. The diffractograms were obtained between 32 and 42 h on stream at 10 bar, 220 °C and $H_2/CO = 2 v/v$ by accumulating five scans of 2 h. No change in the diffraction patterns was apparent over the course of the reaction. Reference patterns of the bare supports were measured at ambient conditions. Contributions from the background and amorphous phases were determined using Rietveld refinement (Appendix B, Figure B7), subtracted from the experimental patterns, and the residual patterns were normalized to the maximum intensity of the CNT (002) peak at 12 ° 2θ. Bars represent reference patterns of hcp Co (PDF 04-001-3273) and fcc Co (PDF 04-001-2681).

The width of the peaks between 18 and 25 ° 2θ was the main difference between the diffraction patterns of Co-NC on CNT and oxCNT and is related to Co^0 crystallite size (Figure 3.5b). Especially for Co-NC/CNT, satisfying refinement results were not obtained using a combination of an hcp and fcc phase (Appendix B, Figure B6), probably due to a highly intergrown Co^0 structure. The pattern of the Co^0 phase on CNT did bear a strong resemblance to spherical 10 nm Co^0 crystallites reported by Sławiński et al.²⁸ with a hcp-fcc stacking probability of 0.5, i.e. random stacking. In our case, an average crystallite size of 9.9 nm was also found for the fcc phase, whereas the hcp Co crystallites were only 4.0 nm.

This small size of hcp Co was most likely an artefact caused by inefficient modeling of the intergrowth structure. Therefore, the Co⁰ crystallites were estimated to be approximately 10 nm in line with literature²⁸ and TEM results, assuming monocrystalline Co-NC. In comparison, the pattern of Co-NC/oxCNT could be modelled better and the average sizes of hcp and fcc Co domains were only 2.9 and 3.9 nm, respectively. As this is smaller than the average particle size from TEM, it meant that polycrystalline Co-NC were formed on oxCNT upon reduction. Furthermore, neither appreciable differences in hcp/fcc ratio nor significant amounts of crystalline CoO were detected.

More crystalline Co⁰ appeared present on CNT than on oxCNT, as evidenced by the higher integral between 18–25 ° 2 θ . Rietveld refinement indicated a crystalline phase composition of Co-NC/CNT of 8.8 wt% Co⁰ and 91.2 wt% CNT, close to the value from ICP (9.7 wt% Co, Table 3.2). In the case of Co-NC/oxCNT, the crystalline Co⁰ phase was only 6.1 wt% with 93.9 wt% oxCNT, while its nominal cobalt content from ICP was 9.6 wt%. Oxidation of CNT thus resulted in less crystalline cobalt in the active catalyst, which is qualitatively in line with observations by Chernyak et al.²⁹. It is unsure whether the remaining amorphous cobalt was present in ionic or metallic form. Nevertheless, the 32 % lower crystallinity of metallic Co for Co-NC/oxCNT matched very well with its 36 % lower initial TOF suggesting that differences in crystalline Co⁰ caused the difference in initial TOF.

The diffraction patterns did not change from the final stage of reduction to 40 h on stream under FT conditions (Appendix B, Figure B7). Hence, restructuring or growth during FT was unlikely, meaning that deactivation occurring on oxCNT (Figure 3.4) had a different origin than changing crystal structure and size. Yu et al.²⁴ observed a similar strong deactivation of Co on oxidized CNF. However, they ascribed the deactivation to oxidation of Co⁰ during FT, which our *in situ* XRD results did not reveal. In our case, a possible explanation for the deactivation could be enhanced deposition of carbonaceous species³⁰ under the influence of defects/oxygen groups on CNT or amorphous cobalt, as has been observed before on oxidized CNT,²⁹ but this would require further research. Overall, precise synthesis of Co-NC of a particular size combined with uniform attachment to both supports resulted in very similar as-prepared catalysts, varying only in the CNT surface composition. These proved to be excellent model systems to investigate the effect of CNT functionalization on FT in detail.

3.4. Conclusion

We investigated the impact of surface oxidation of carbon nanotube (CNT) supports on the structure and performance of cobalt nanocrystals (Co-NC) in the Fischer-Tropsch (FT) synthesis. Well-defined 6 nm colloidal CoO-NC were synthesized and attached to CNT or oxidized CNT (oxCNT) with a loading of 10 wt% Co. After reduction and passivation, NC growth and complete reduction of the NC were observed on CNT, while growth was absent on oxCNT and only ~50 % CoO reduction was obtained. The turnover frequency (TOF) of the Co-NC after 100 h of FT was exceptionally high on CNT with $150 \cdot 10^{-3} \text{ s}^{-1}$ against $63 \cdot 10^{-3} \text{ s}^{-1}$ oxCNT. Using *in situ* XRD, 32 % less crystalline metallic cobalt was found on oxidized CNT under FT conditions, probably causing the 35 % lower initial TOF compared to Co-NC/CNT. Furthermore, the Co-NC on oxCNT deactivated more, which could not be

explained by particle growth, NC restructuring, or oxidation during FT, leaving enhanced deposition of carbonaceous species as a probable cause. This study illustrates the potential of nanocrystal-based model catalyst synthesis for the investigation of structure–performance relationships.

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Chapter 4

Preparation of cobalt nanocrystals supported on metal oxides to study particle growth in Fischer-Tropsch catalysts

Abstract

Colloidal synthesis of nanocrystals (NC) followed by their attachment to a support and activation is a promising route to prepare model catalysts for research on structure-performance relationships. Here, we investigated the suitability of this method to prepare well-defined Co/TiO₂ and Co/SiO₂ catalysts for the Fischer-Tropsch (FT) synthesis with high control over the cobalt particle size. To this end, Co-NC of 3, 6, 9 and 12 nm with narrow size distributions were synthesized and attached uniformly on either TiO₂ or SiO₂ supports with comparable morphology and Co loadings of 2–10 wt%. After activation in H₂, the FT activity of the TiO₂-supported 6 and 12 nm Co-NC was similar to that of a Co/TiO₂ catalyst prepared by impregnation, showing that full activation was achieved and relevant catalysts had been obtained, however, 3 nm Co-NC on TiO₂ were less active than anticipated. Analysis after FT revealed that all Co-NC on TiO₂ as well as 3 nm Co-NC on SiO₂ had grown to ~13 nm while the 6 and 9 nm Co-NC on SiO₂ had remained stable. It was found that the 3 nm Co-NC on TiO₂ already grew to 10 nm during activation in H₂. Furthermore, substantial amounts of Co (up to 60 %) migrated from the Co-NC to the support during activation on TiO₂ against only 15 % on SiO₂. We showed that the stronger interaction between cobalt and TiO₂ leads to enhanced catalyst restructuring as compared to SiO₂. These findings demonstrate the potential of the NC-based method to produce relevant model catalysts to investigate phenomena that could not be studied using conventionally synthesized catalysts.

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4.1. Introduction

Colloidal synthesis of cobalt nanocrystals (NC) offers the possibility to develop new model catalysts that can potentially aid in linking the structure of cobalt catalysts to their performance in the Fischer–Tropsch (FT) synthesis reaction.^{1–3} However, base metal NC are challenging to utilize in supported catalysts. First, homogeneous attachment of base metal NC on a support can be hindered by magnetic interactions between the NC.⁴ Second, removal of the stabilizing ligand shell can be incomplete, blocking active sites and lowering catalytic activity, or harsh treatments are applied that may compromise the well-defined nature of the catalyst.^{5,6} We demonstrated uniform attachment and successful ligand removal for Co–NC supported on carbon nanotubes by applying a mild, low-temperature oxidation to the NC in suspension prior to attachment.⁷ The cobalt-catalyzed FT reaction is reported to be structure sensitive, related to both cobalt particle size^{8,9} and cobalt crystal structure^{10–12}. So far, most research involving Co–NC for FT concentrated either on slurry-phase FT, in which the unsupported Co–NC remain in suspension^{13–15}, or on Co–NC supported on irreducible oxides (mainly SiO₂ or Al₂O₃)^{16–23}. However, reducible oxides such as TiO₂ are also interesting supports for cobalt-based FT catalysts, for both industry²⁴ and academia²⁵.

TiO₂-supported cobalt catalysts can be considered more complex than Co/SiO₂ or Co/Al₂O₃, since TiO₂ can be partially reduced under reaction conditions, leading to special interphase phenomena known as strong metal–support interactions (SMSI).^{26,27} The effects of these metal–TiO₂ interactions remain poorly understood, in part because synthesis procedures for well-defined catalysts are lacking, especially for <10 nm Co particles. Monodisperse particles on TiO₂ can be synthesized with conventional methods, but the control over the average particle size is limited.^{28,29} Furthermore, there are only few reports of NC-based Co/TiO₂ catalysts and these either contained boron impurities owing to the synthesis method^{30,31} or the Co–NC were 10 nm or larger^{18,32}. Therefore, it would be highly desirable to expand the applicability of Co–NC to TiO₂ as support.

In this chapter, we report the synthesis and catalytic performance of well-defined catalysts containing 3–12 nm Co–NC on TiO₂ and SiO₂ and demonstrate their use as model systems by studying particle growth under FT conditions. The Co–NC were synthesized by a hot-injection method. After low-temperature oxidation, the CoO–NC were homogeneously attached to either TiO₂ or SiO₂. Their catalytic performance was comparable to that of Co/TiO₂ prepared by impregnation, except for 3 nm Co–NC on TiO₂, whose activity was substantially lower. The TiO₂-supported Co particles and 3 nm Co–NC on SiO₂ sintered during reduction and/or FT, indicating that both the support and initial NC size affected the stability of Co–NC under reaction conditions. We show that the followed NC-based methodology enabled the synthesis of size-controlled Co/TiO₂ and Co/SiO₂ with relevant catalytic performance. Their potential as model systems is underlined by investigating NC particle growth, revealing phenomena that are not observed with conventionally prepared catalysts.

4.2. Experimental

4.2.1. Synthesis of CoO nanocrystals

Cobalt nanocrystals of different sizes were synthesized by a hot injection method based on literature³³ and our previous work⁷. A schematic summary of the NC synthesis procedure is shown in Appendix C, Figure C1. The benefit of this method is that the required chemicals contain no elements such as phosphorus or boron that might affect the catalyst and its final catalytic performance. The syntheses were performed on a Schlenk line in N₂ atmosphere. In a typical synthesis, 65 mg oleic acid (Sigma-Aldrich, 90 %, technical grade) was degassed under vacuum at 100 °C for 30 min in a 3-necked 100 mL flask with a cooler and two septa. After flushing and switching to N₂, 7.5 mL 1,2-dichlorobenzene was added under inert atmosphere and the solution was heated to temperatures between 165–182 °C related to the desired NC size. Simultaneously, inside a glovebox, 270 mg dicobalt octacarbonyl (Acros Organics, 95 %, stabilized) was dissolved in 1.5 mL 1,2-dichlorobenzene. This cobalt precursor was then rapidly injected (needle: Ø0.9 x 70 mm) into the heated solution under 750 rpm magnetic stirring and decomposed instantly. The reaction was quenched after 20 min using a water bath. Once at ambient temperature, the N₂ supply was switched off and one septum was removed to allow low-temperature oxidation by air-exposure under 650 rpm stirring. After 1 h, the mixture was divided over two glass centrifuge tubes and filled to 20 mL with 2-propanol (Sigma-Aldrich, >99 %, LC-MS Chromasolv) and centrifuged at 2200 G for 30 min. The supernatant was decanted and the residue re-dispersed in 0.5 mL n-hexane (Acros Organics, 99+ %) per tube by sonication. The tubes were filled to 20 mL with 2-propanol and centrifuged at 2200 G for 40 min. This washing cycle was repeated twice and after the last step, the residue was re-dispersed and combined in a total of 2 mL n-hexane.

4.2.2. Attachment of CoO nanocrystals to a support

The Co-NC were attached to a support according to the method developed by Casavola et al.³⁴. A schematic summary of the NC attachment procedure is shown in Appendix C, Figure C1. The supports were TiO₂ (Evonik, Aeroxide P25) or SiO₂ (Evonik, Aerosil OX 50), both sieved to a fraction of 75–150 µm. To regulate the final cobalt loading, between 0.4–2.5 g of support was suspended in a mixture of the colloidal suspension and 5–31 mL 1-octadecene (Sigma-Aldrich, 90 %, technical grade) inside a 100 mL 3-necked flask. A cooler, glass plug and septum were connected to the flask, the magnetic stirring was set to 400 rpm and the suspension was degassed under vacuum at 100 °C for 15 min, during which the n-hexane from the colloidal suspension evaporated. The setup was then flushed, switched to N₂ and heated to 200 °C. The heating was stopped after 30 min at 200 °C and the solution cooled to ambient temperature in approximately 30 min. The suspension was divided over two glass centrifuge tubes, centrifuged at 1500 G for 5 min and the supernatant was decanted. The residue was re-suspended in 2 mL n-hexane, sonicated for 1 min, diluted with 6 mL acetone, centrifuged at 1500 G for 5 min and the supernatant was again decanted. This washing cycle was repeated five times, followed by re-suspending the residue in 20 mL acetone, sonicating for 1 min, centrifuging at 1500 G for 5 min and decanting the supernatant. Afterwards, the samples were dried at 60 °C for 1 h in static air, followed by

120 °C for 3 h in static air and 80 °C for 3 h under vacuum. Finally, the samples were sieved to a grain size of 75–150 µm.

4.2.3. Incipient wetness impregnation

A comparison Co/TiO₂ sample was prepared by incipient wetness impregnation following the procedure by Eschemann et al.²⁸. First, 2 g TiO₂ (Evonik, Aeroxide P25) was sieved to 75–150 µm and then dried at 80 °C for 1 h under vacuum. The vacuum was released and impregnated directly afterwards with a pore-filling amount of precursor solution consisting of Co(NO₃)₂·6H₂O (Acros Organics, 99+ %) in Mili-Q water. The solution was added dropwise under magnetic and manual stirring. After the addition, the powder was dried and heat treated in a U-shaped, glass reactor in fluidized bed mode (1 L·min⁻¹ upward flow of N₂). Drying took place at 80 °C for 2 h and was followed directly by a thermal treatment at 250 °C for 2 h, both with 2 °C·min⁻¹. The sample was finally sieved again to a grain size of 75–150 µm.

4.2.4. Plasma cleaning

Optionally, pristine Co-NC samples were plasma cleaned to remove the ligands prior to reduction and FT. Typically, 100 mg of sample was treated for 8 h in a home-made container inserted into a Fischione Model 1020 Plasma Cleaner. The plasma was generated using a 25 % O₂ in Ar flow and a 13.56 MHz oscillating electromagnetic field.

4.2.5. Characterization

Transmission electron microscopy (TEM) was performed either on a Tecnai 12 (FEI), operated at 120 kV, or on a Tecnai 20 (FEI), operated at 200 kV. TEM samples of Co-NC suspensions were prepared by sonicating and dropcasting a diluted sample directly on a carbon-coated TEM grid. To prepare a sample of supported Co-NC, the solid was first suspended in 2-propanol by sonication and then dropcasted on a TEM grid. In the case of samples after catalysis, the samples were washed three times using toluene and 30 min sonication and once using n-hexane to remove the hydrocarbon reaction products before dropcasting on a TEM grid. The sizes of >200 particles were determined manually using ImageJ software. All particle sizes are reported as the Sauter mean diameter (volume/surface mean, D[3,2]) of the equivalent metallic cobalt particles, meaning that (partial) cobalt oxide particles were corrected based on the densities of the oxide and the metal.

Scanning transmission electron microscopy combined with energy-dispersive X-ray spectroscopy (STEM-EDX) was performed in high-angle annular dark-field (HAADF) mode on a Talos F200X (FEI), equipped with a high-brightness field emission gun (X-FEG) and a Super-X G2 EDX detector and operated at 200 kV. Particle size analysis was similar to that of TEM, with the exception that <200 particles were analyzed for some samples, depending on the particle size and cobalt loading.

HAADF-STEM-EDX of the same positions of 12 nm Co-NC on TiO₂ before and after reduction was performed using a SiN TEM chip (TEMWindow SN100-A50Q33). After imaging the pristine sample, the SiN TEM chip was transferred to a glass U-shaped reactor and the sample on the chip was reduced *ex situ* inside in 25 % H₂ in Ar flow at 350 °C

for 8 h with $1\text{ }^{\circ}\text{C}\cdot\text{min}^{-1}$ and cooled down afterwards under the same atmosphere. Subsequently, the chip was transferred back to the microscope and analyzed again. During the transfer, the sample was exposed to air at ambient conditions.

N_2 -physisorption of the bare supports was measured at $-196\text{ }^{\circ}\text{C}$ on a Tristar 3000 (Micromeritics). The samples were dried in He at $300\text{ }^{\circ}\text{C}$ for 14–20 h prior to the analysis.

Inductively coupled plasma-optical emission spectroscopy (ICP-OES) was carried out on a SPECTRO ARCOS and the sample was digested in aqua regia to extract the cobalt.

Temperature programmed reduction (TPR) profiles were measured on an Autochem 2920 (Micromeritics). Approximately 100 mg of sample was reduced in 5 % H_2 in Ar flow from $50\text{ }^{\circ}\text{C}$ to $800\text{ }^{\circ}\text{C}$ with $5\text{ }^{\circ}\text{C}\cdot\text{min}^{-1}$.

X-ray diffraction (XRD) was performed on a Bruker D2 Phaser, equipped with a Co radiation source ($\lambda = 1.789\text{ \AA}$). The sample was measured between $20\text{--}100\text{ }^{\circ} 2\theta$ with an increment of 0.05 ° .

4.2.6. Fischer-Tropsch synthesis

The catalytic performance in the Fischer-Tropsch synthesis was investigated using an Avantium Flowrence 16 parallel reactor setup. Stainless steel plug flow reactors of 2.0 or 2.6 mm ID were loaded with 25–110 mg catalyst (75–150 μm) diluted with 100 mg SiC (200–425 μm). Prior to reaction, the catalysts were reduced *in situ* at 1 bar in 25 % H_2 in He flow at either $350\text{ }^{\circ}\text{C}$ (TiO_2 -samples) or $500\text{ }^{\circ}\text{C}$ (SiO_2 -samples) for 8 h with $1\text{ }^{\circ}\text{C}\cdot\text{min}^{-1}$. Afterwards, the reactors were cooled to $180\text{ }^{\circ}\text{C}$ and pressurized to 20 bar. At these conditions, the atmosphere was switched to synthesis gas with 2 H_2/CO (v/v) and 5 % He as internal standard. Subsequently, the reactors were heated to $220\text{ }^{\circ}\text{C}$ with $1\text{ }^{\circ}\text{C}\cdot\text{min}^{-1}$ and product analysis was started after 1 h. The reaction products were analyzed online using an Agilent 7890A GC equipped with two channels. The first channel contained an Agilent J&W PoraBOND Q column connected to an FID to detect the hydrocarbon products and the second one consisted of an ShinCarbon-ST column connected to a TCD to analyze the permanent gasses.

The catalytic activity was reported as CO conversion (X_{CO}), cobalt time yield (CTY) and turnover frequency (TOF). The TOF was based on the activity and the Sauter mean diameter ($D[3,2]$) of the spent Co-NC after correction for a 3 nm CoO passivation layer, assuming a cross-sectional area of 0.0662 nm^2 per cobalt atom.³⁵ The selectivity (%) to C_1 – C_4 products was defined as $S_{\text{C}_1\text{--C}_4} = 100 \cdot F_{\text{C}_n} \cdot n \cdot (F_{\text{CO, in}} \cdot X_{\text{CO}})^{-1}$ with n being the product's carbon number and F being the flow of the corresponding hydrocarbon or CO. The selectivity to C_{5+} was defined as $S_{\text{C}_{5+}} = 100 - S_{\text{C}_1\text{--C}_4}$.

4.3. Results and discussion

4.3.1. Cobalt nanocrystal synthesis

Well-defined cobalt nanocrystals were synthesized with distinct sizes between 3–12 nm and a polydispersity of 11–18 % (Figure 4.1, additional particle size distributions in Appendix C, Figure C2). The Co-NC were designated as CoX, with X denoting the average diameter of the NC. The size of the Co-NC size was regulated by varying the temperature of

the hot injection synthesis, which is in line with literature.^{33,36} The Co-NC size correlated with the synthesis temperature in the range of 170–183 °C and became less reproducible at lower temperature (Figure 4.1d). After the synthesis, low-temperature oxidation by air-exposure at ambient conditions was applied to facilitate attachment and activation of the Co-NC.⁷ Of the synthesized Co-NC in Figure 4.1d, those of 3, 6, 9 and 12 nm were attached to TiO₂ or SiO₂, thus omitting the Co-NC of 4 and 8 nm.

Figure 4.1. Overview of the as-synthesized Co-NC. TEM images of **a** Co₃, **b** Co₆ and **c** Co₁₂ and **d** the resulting Co-NC size as a function of the hot-injection temperature. **e** Histograms and lognormal distributions of selected sizes of Co-NC.

4.3.2. Catalyst preparation

The Co-NC were attached to titania and to silica with comparable specific surface areas ($\sim 50 \text{ m}^2 \cdot \text{g}^{-1}$) but different mesopore volumes (0.3 and $0.1 \text{ mL} \cdot \text{g}^{-1}$, respectively) as determined by N₂-physisorption (Appendix C, Figure C3, Table C1). The cobalt loading was

adjusted to obtain similar cobalt metal surface areas per unit weight of catalyst in the pristine samples with the aim to avoid major differences in catalyst-weight-based activities during FT (Table 4.1). Furthermore, the Co-NC on the supports were analyzed with TEM (Figure 4.2). The Co-NC distribution was uniform over both supports, similar to previous results with a carbon support.^{7,34} In addition, a reference Co/TiO₂ sample was prepared by conventional techniques, in this case incipient wetness impregnation of a cobalt nitrate solution (designated as IWI-Co/TiO₂, details in Table 4.1 and TEM results in Appendix C, Figure C4). Its average particle size was most comparable to Co6/TiO₂, but the particle size distribution was substantially broader.

Figure 4.2. Overview of the Co-NC attached to a support. The TiO₂-supported samples are in the left column and the SiO₂-supported ones in the right column. **a** Co3/TiO₂, **b** Co3/SiO₂, **c** Co6/TiO₂, **d** Co6/SiO₂, **e** Co12/TiO₂ and **f** Co9/SiO₂. The insets are at double the magnification of the original image.

Table 4.1. Characteristics of the supported Co-NC and IWI-Co samples. The Sauter mean diameter ($\pm$ standard deviation) of the Co-NC was analyzed by TEM before attachment and recalculated to the corresponding CoO particle sizes. The Co loading was determined by ICP-OES. Based on these two results, a Co specific surface area of the pristine catalysts was calculated.

Sample	$D[3,2]_{\text{Co-NC}}$ (nm)	Co loading (wt%)	Initial Co surface area ($\text{m}_{\text{Co}}^2 \cdot \text{g}_{\text{Cat}}^{-1}$)
Co3/TiO ₂	2.9 ± 0.4	2.4	5.7
Co6/TiO ₂	6.0 ± 0.8	4.6	5.5
Co12/TiO ₂	12 ± 1.5	8.7	5.4
IWI-Co/TiO ₂	7.3 ± 2.5	6.7	6.2
Co3/SiO ₂	2.8 ± 0.5	3.6	6.8
Co6/SiO ₂	5.6 ± 0.6	6.8	9.2
Co9/SiO ₂	8.6 ± 1.1	9.6	7.7

The sizes of the Co-NC remained unchanged during the attachment treatment as concluded from TEM (Figure 4.2). The Co-NC of 3 and 6 nm consisted completely of CoO⁷ while for the 9 and 12 nm Co-NC only an outer layer of CoO was formed and a metallic core with higher contrast was observed. This CoO shell had a thickness of 4.5 nm in the case of Co12/TiO₂, which exceeds the CoO passivation layer of 3 nm that is typically observed upon exposure of metallic cobalt particles to air at ambient conditions.³⁷ The increased oxidation of the Co-NCs could have occurred during drying at 120 °C, as this is close to the temperature range where Kirkendall effects have been observed.³⁸ The Kirkendall effect occurs upon oxidation of metals at elevated temperatures and leads to the formation of hollow metal oxide particles.^{6,39}

The reducibility of the Co-NC on TiO₂ samples was investigated by temperature-programmed reduction (TPR, Figure 4.3a). Two reduction peaks were observed between 250–450 °C for all samples next to a negative peak at higher temperatures, which is attributed to the desorption/decomposition of remaining ligands.⁷ As expected, the reduction temperature shifts to lower values with increasing particle size, because small oxide particles often display lower reducibility.^{40–42} Furthermore, the total H₂-uptake related to the first two peaks increased with the particle size following the increase in cobalt content. Interestingly, when comparing the total H₂-uptake of the Co-NC/TiO₂ samples normalized to the amount of Co, the H₂-uptake of Co12/TiO₂ was only 89–92 % of that of the 3 and 6 nm NC (deconvolutions in Appendix C, Figure C5). This indicated that ~10 % of the cobalt in Co12/TiO₂ was still present in the core of the NC as metallic cobalt, which was in line with the earlier TEM observation of a metallic core and a CoO passivation layer (Figure 4.2).

Figure 4.3. Reduction and catalytic activity of the TiO₂-supported samples. **a** Reduction profiles obtained by TPR normalized to the mass of sample and **b** catalytic activity (CTY) for FT as a function of time-on-stream performed at 20 bar, 220 °C, 2 H₂/CO (v/v), GHSV = 1950–5900 h⁻¹ and X_{CO} = 5–60 %

4.3.3. Fischer-Tropsch synthesis

The cobalt-weight-based activity (cobalt time yield, CTY) of the TiO₂-supported samples was evaluated over 100 h on stream (Figure 4.3b, Table 4.2). Co6/TiO₂ was the most active after 100 h followed by Co12/TiO₂, which was initially more active but deactivated faster. Co3/TiO₂ was a factor 5 less active per unit weight of cobalt over the entire time range studied. Interestingly, the 6 and 12 nm Co-NC catalysts were similar or even higher in CTY than the IWI-Co/TiO₂ catalyst, indicating that these Co-NC were adequately activated and that relevant catalytic results were obtained with these NC-based model systems. Furthermore, the selectivity towards C₅₊ products was around 85 % for all TiO₂-supported samples, except for Co3/TiO₂ whose C₅₊-selectivity was only 57 % (Table 4.2).

The catalytic activity of the Co/SiO₂ samples was investigated over 100 h on stream at CO conversion levels between 15–30 % (Appendix C, Figure C6, Table 4.2). The cobalt-weight-based activities of Co6/SiO₂ and Co9/SiO₂ were the highest of all investigated catalysts. The 3 nm Co-NC displayed again the lowest activity of the series, yet Co3/SiO₂ was a factor 6 more active per unit weight of cobalt than Co3/TiO₂. The C₅₊-selectivities of the SiO₂-supported catalysts varied between 76 and 79 % and were overall lower than that

of most TiO₂-supported catalysts (~85 %). This observation corresponds well with earlier findings of TiO₂ promoting the C₅₊-selectivity of cobalt catalysts in FT.⁴³

The deactivation and observed differences in activity could be caused by several mechanisms, such as carbon deposition⁴⁴, metal-support compound formation⁴⁵ or net particle growth⁴⁵. To investigate the occurrence of particle growth in more detail, the spent catalysts were analyzed with TEM (Table 4.2, Fig 4, Appendix C, Figure C7). All Co-NC supported on TiO₂, as well as the IWI-Co/TiO₂, had grown to ~13 nm on average, which was in line with recently reported particle sizes of a Co-Re/TiO₂ catalyst after various periods on stream.⁴⁵ On SiO₂, the initially 3 nm Co-NC had also sintered to 13 nm, while the 6 and 9 nm Co-NC were stable.

Using the particle sizes of the spent catalysts and the activities at 90–100 h on stream, the surface-specific activities (turnover frequencies, TOF) were calculated (Table 4.2). The TOF of all TiO₂-supported catalysts except Co3/TiO₂ was around 65·10⁻³ s⁻¹, in line with previous reports.^{46–48} The identical TOF of 6 and 12 nm Co-NC on TiO₂ and the IWI-Co/TiO₂ catalyst showed that the active cobalt sites were not affected by the presence of residual ligands or other factors specific to the NC-based synthesis method. The apparent TOF of Co3/TiO₂, based on the particle size of the catalyst and the end-of-run activity, was only 12·10⁻³ s⁻¹ (Table 4.2). This was remarkable, because the Co particles in Co3/TiO₂ had grown outside of the size regime where particle size effects typically cause low activities (<6–8 nm).^{8,9,16} Therefore, a TOF similar to the others (65·10⁻³ s⁻¹) should have been obtained. Instead, the low apparent TOF was ascribed to loss of cobalt from the metal particles to the TiO₂ resulting in less metallic surface area available for catalysis. Judging from the decrease in TOF, up to 80 % of the cobalt was lost in this manner.

Table 4.2. Catalytic performance at 20 bar, 220 °C and 2 H₂/CO (v/v). The reported data was obtained after 90–100 h on stream. The TOF was based on the end-of-run activity and Co particle size (D[3,2]) of the spent samples. The Sauter mean diameter (± standard deviation) of the Co-NC was analyzed in the spent and passivated state and corrected for the lattice expansion due to the 3 nm CoO passivation layer.

Sample	GHSV (h ⁻¹)	X _{CO} (%)	CTY ^a	TOF (10 ⁻³ s ⁻¹)	S _{Cl} (% _C)	S _{C2-C4} (% _C)	S _{C5+} (% _C)	D[3,2] _{spent} (nm)
Co3/TiO ₂	1950	4.6	1.4	12	21	21	57	15 ± 5.1
Co6/TiO ₂	3100	23	11	66	9.2	8.1	83	11 ± 3.3
Co12/TiO ₂	6900	24	8.6	68	8.2	5.9	86	13 ± 4.0
IWI-Co/TiO ₂	7550	18	8.4	68	8.7	7.0	84	14 ± 5.9
Co3/SiO ₂	1500	25	8.5	67	13	12	76	13 ± 5.5
Co6/SiO ₂	5500	16	21	82	14	11	76	6.7 ± 1.4
Co9/SiO ₂	10750	21	19	106	13	9	79	9.6 ± 2.1

^a in 10⁻⁵ mol_{CO}·g_{Co}⁻¹·s⁻¹

The TOF of the SiO₂-supported catalysts increased with initial particle size (Table 4.2). In the case of the initially 3 nm Co-NC on SiO₂, the TOF was 67·10⁻³ s⁻¹, which was similar to most Co/TiO₂ catalysts and already somewhat higher than previously reported for Co/SiO₂ catalysts.⁴⁹ However, the intrinsic activities of 6 and 9 nm Co-NC on SiO₂ were

exceptionally high in comparison to literature. A possible explanation for the different TOF of Co-NC and conventional catalysts could be that the Co-NC approach led to cobalt particles with a higher fraction of hcp Co, which is more active in FT than fcc Co^{10-12,50}. Alternatively, the Co-NC could have less interaction with the support, because the Co-NC were formed prior to attachment to the support. For example, when comparing the TEM results of spent Co/SiO₂, the grown particles of Co₃/SiO₂ were mainly confined between primary SiO₂ particles where the contact area with the support was maximal (Appendix C, Figure C7). The Co-NC in Co₆/SiO₂ and Co₉/SiO₂, on the other hand, were still distributed uniformly over the support and as such, a higher fraction of the cobalt surface area would be accessible to reactants.

Overall, the employed NC-based approach to catalyst synthesis yielded well-defined model systems with reasonable control over the initial NC size and relevant catalytic performance. It is therefore anticipated that these model catalysts are suitable to investigate structure-performance relationships and already some interesting phenomena were observed here, especially on the growth of NC of specific sizes under reaction conditions. These observations will be investigated and discussed in more detail in the next section.

4.3.4. Sintering of cobalt nanocrystals

To investigate the growth of Co-NC, the particle sizes were analyzed using TEM after reduction as well as after catalysis (Figure 4.4). 3 nm Co-NC on TiO₂ sintered to particles of 10 nm already during reduction and the particles grew further to 15 nm during FT. The 3 nm Co-NC on SiO₂ ultimately grew to the same extent, but in this case the particles predominantly sintered during FT. The reduction barely affected the particle size of Co₃/SiO₂ even though the reduction was performed at 500 °C.

EDX maps of the reduced and passivated TiO₂-supported catalysts and Co₃/SiO₂ were quantified to investigate the location of Co on the supports (Table 4.3, see Appendix C, Figure C8 for results and experimental details). Compared to ICP (Table 4.1), the total cobalt loading from EDX was 30-50 % higher on TiO₂ and 50 % lower on SiO₂. Therefore, relative differences for one and the same sample were considered more representative than the absolute values.

For the reduced and passivated Co/TiO₂ samples, ~2.5 wt% of Co was found dispersed in the support and not in particles, regardless of NC size and loading. In the case of Co₃/TiO₂, this amounted to approximately 60 % of the total cobalt content from EDX and might be partially responsible for its low CTY. Furthermore, the Co signal in the EDX maps occasionally followed the contours of TiO₂ particles with increased intensity at the surface (Appendix C, Figure C8). This means that a higher Co concentration existed at the surface than in the bulk of the TiO₂ particles. In contrast, only 16 % of the Co was found on the silica support for Co₃/SiO₂ and the remaining 84 % was still present in Co particles. Consequently, no contours of the support were observed in the Co signal from EDX at locations without any particles (Appendix C, Figure C8). These EDX results show that, during reduction, cobalt migrated to the support more with TiO₂ than with SiO₂, as illustrated in Figure 4.4c,d. These cobalt species on the support were not detected in XRD (Appendix C, Figure C9), probably because of their low concentration and/or low

crystallinity. Additionally, the amount of cobalt on the support was assumed to remain constant during FT, because the Co/TiO₂ catalysts did not activate during FT, which would be expected if the cobalt species on the support were reduced under reaction conditions (Figure 4.3b).

Figure 4.4. Average cobalt particle sizes of the samples in the pristine, reduced and spent state. **a,b** Average Co-NC sizes from TEM analysis of the TiO₂- and SiO₂-supported samples, respectively. The error bars give the standard deviation of the average particle size. Schematic illustration of the sintering behavior of the different sizes on **c** TiO₂ and on **d** SiO₂ after different treatments. In these illustrations, Co²⁺ or Co³⁺ is depicted in yellow and Co⁰ in blue. Migration of Co to TiO₂ during reduction was observed by EDX.

Table 4.3. Quantification of the cobalt present in the support and in particles after reduction of Co/TiO₂ and Co3/SiO₂. The total Co loading and the fractions of Co in particles and Co in the support were derived from HAADF-STEM-EDX (Appendix C, Figure C8).

Sample	Co _{total} (wt%)	Co _{particles} (wt%)	Co _{support} (wt%)	Co _{particles} / Co _{total}	Co _{support} / Co _{total}
Co3/TiO ₂	3.3	1.3	2.0	0.38	0.62
Co6/TiO ₂	6.8	4.1	2.7	0.61	0.39
Co12/TiO ₂	11	9.2	2.2	0.81	0.19
Co3/SiO ₂	2.4	2.0	0.4	0.84	0.16

Small particles have a higher thermodynamic potential⁵¹ and are therefore more prone to sintering.^{52,53} Interestingly, in these earlier studies, growth took place via monomers that were created upon exposure to CO under reaction conditions. For example, in the case of Co/Al₂O₃, cobalt subcarbonyls were proposed as monomers that migrate over the support and give rise to particle growth via Ostwald ripening.⁵⁴⁻⁵⁶ However, in our Co₃/TiO₂ sample, a large part of the growth took place already during reduction, so sintering was not induced by CO. When combining these results with the tendency of 60 % of the cobalt in the NC to 'leach' to the surface of the TiO₂, we propose that different mobile species, possibly cobalt titanates⁵⁷, spread out over the support and cause a few particles to grow large. This hypothesis is in line with thermodynamic calculations (Appendix C, Figure C10), which showed that it is thermodynamically possible to form small amounts of cobalt titanates under reduction conditions, and agrees with previous observations.⁵⁸⁻⁶⁰ Notably, Cats et al.⁵⁸ observed a thin layer of Co species surrounding TiO₂ particles, albeit in spent and not in reduced catalysts.

On SiO₂, the formation of cobalt silicates during reduction is thermodynamically limited (Appendix C, Figure C10) and the growth of 3 nm Co-NC occurred mainly during FT. The sintering might therefore be ascribed to CO-induced Ostwald ripening as observed before by Kistamurthy et al.⁶¹ or particle migration and coalescence. Furthermore, 8 h plasma cleaning of the pristine samples to remove ligands reduced the particle growth for Co₃/SiO₂, but not for the Co/TiO₂ (Appendix C, Figure C11). This further confirmed that the mechanism responsible for particle growth is different on both supports even though the final particle size is similar.

6 nm Co-NC on TiO₂ did not grow during reduction (Figure 4.4). The driving force for sintering during reduction was thus less than for Co₃/TiO₂ because of the larger particle size. However, the NC on TiO₂ did grow to 11 nm during FT. Growth of the 6 nm Co-NC was not observed on SiO₂ even after catalysis, showing that the Co-NC are less stable on TiO₂ compared to SiO₂. Interestingly, Co₆/TiO₂ had sintered less than IWI-Co/TiO₂ after FT, with final particles sizes of 11 and 14 nm, respectively (Appendix C, Figure C12). Because the average particle sizes of both samples were initially comparable while the polydispersity of IWI-Co/TiO₂ was higher, this shows the impact of the width of the particle size distribution on the stability of the cobalt nanoparticles.⁶²⁻⁶⁴ It nicely illustrates the advantage of the NC-based approach over the traditional synthesis techniques to arrive at more stable catalysts.

On average, 12 nm Co-NC on TiO₂ did not grow but the particle size distribution did become broader already after reduction (Figure 4.4). Both smaller and larger particles were thus formed, which implied Ostwald ripening or re-dispersion of cobalt, possibly via cobalt-ion migration, under reducing conditions. No evidence of Co-NC growth or re-dispersion was apparent on Co₉/SiO₂ indicating that Co mobility was more extensive with the TiO₂ support or the somewhat larger Co-NC sizes. Extending the reduction to 16 h instead of 8 h did not change the particle size distribution further (Appendix C, Figure C13). This observation is qualitatively in line with the results of Xaba et al.⁶⁵ on titania P25, although their Co particles were substantially larger (~50 nm).

The size evolution of individual Co-NC in Co12/TiO₂ was followed before and after reduction and passivation to investigate the re-dispersion in more detail (Figure 4.5). No particles were found that had moved from their original position, indicating low mobility of the Co-NC as a whole and making migration and coalescence unlikely as a pathway for particle growth during reduction. Furthermore, approximately 5 % of the particles broke up into multiple smaller particles (Figure 4.5c,d highlighted area, Appendix C, Figure C14). This re-dispersion caused an increase in the fraction of 5–8 nm particles, resulting in broadening of the particle size distribution.

Figure 4.5. The size evolution of individual Co-NC in Co12/TiO₂ during reduction. **a,c** HAADF-STEM images of pristine Co12/TiO₂ and **b,d** HAADF-STEM images of the same locations after reduction at 350 °C for 8 h. The highlighted area contains two particles that disintegrated during reduction and formed multiple smaller particles.

Two reasons can be proposed for the disintegration of the NC. First, it might be favorable for certain particles to maximize their contact area with the support, since the interaction between metals and reducible supports such as TiO₂ can lead to dynamic systems under reducing conditions.³⁸ Second, the core-shell structure in pristine Co12/TiO₂ could be an intermediate stage of the Kirkendall effect.⁶ Sasdavian et al.³⁹ investigated this effect for Co-NC of different sizes on SiO₂ and reported similar core-shell particles in the case of incomplete oxidation of 29 nm particles. Completely oxidized, hollow cobalt oxide particles of 29 nm disintegrated into multiple smaller particles upon reduction, whereas smaller hollow particles returned to their original size of 11 nm. Based on these results, our 12 nm Co-NC, being similar in size to their 11 nm particles, are not expected to disintegrate upon reduction.

4.4. Conclusion

Here, we investigated the preparation of well-defined TiO_2 - and SiO_2 -supported catalyst via colloidal synthesis of Co-NC and evaluated their catalytic performance in the Fischer-Tropsch synthesis. 3–12 nm Co-NC were synthesized by a hot-injection method, oxidized at low temperature to restrict magnetic interactions and subsequently attached to TiO_2 or SiO_2 . The catalytic activity of most TiO_2 -supported samples was in line with that of a Co/ TiO_2 sample prepared by impregnation of cobalt nitrate, proving that relevant catalytic data was obtained with these model catalysts. The cobalt-weight based activity of 3 nm Co-NC on TiO_2 was five-fold lower than expected and this was partially ascribed to loss of cobalt to the support. Furthermore, the TiO_2 -supported Co particles and 3 nm Co-NC on SiO_2 sintered, while 6 and 9 nm Co-NC on SiO_2 were stable during reduction and FT. We showed that the interaction between Co(O) and TiO_2 was responsible for the decreased stability of the Co-NC. This study illustrates the promise of synthesizing model catalysts using colloidal techniques, as the high precision in particle size enabled the investigation of effects that have not have been revealed earlier with conventional synthesis techniques.

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Chapter 5

Disk-shaped cobalt nanocrystals as Fischer-Tropsch synthesis catalysts under industrially relevant conditions

Abstract

Colloidal synthesis of metal nanocrystals (NC) offers control over size, crystal structure and shape of nanoparticles, making it a promising method to synthesize model catalysts for the investigation of structure–performance relationships. In the cobalt-catalyzed Fischer-Tropsch (FT) synthesis, the influence of Co-NC shape in FT has hardly been studied under industrially relevant reaction conditions. Here, we investigated the synthesis of disk-shaped Co-NC, their attachment to a support and FT performance. From the NC synthesis, either spheres only or a mixture of disk-shaped and spherical Co-NC was obtained. The disks had an average diameter of 15 nm, a thickness of 4 nm and consisted of hcp Co exposing (0001) on the base planes. The spheres were 11 nm on average and consisted of ϵ -Co. After mild oxidation, the CoO-NC were attached to SiO₂ with numerically 66 % of the NC being disk-shaped according to electron tomography. After reduction, the catalyst with spherical plus disk-shaped Co-NC had 50 % lower intrinsic activity for FT synthesis (20 bar, 220 °C, H₂/CO = 2 v/v) than the catalyst with spherical NC only, while C₅–selectivity was similar. Surprisingly, TEM analysis showed that the Co-NC morphology was unchanged after catalysis. Using XPS it was established that nitrogen-containing ligands were largely removed and *in situ* XRD revealed that both catalysts consisted of 65 % hcp Co and 21 or 32 % fcc Co during FT. Furthermore, 3–5 nm polycrystalline domains were observed, suggesting that during catalysis hcp (0001) was exposed on the base planes of the disks. Through exclusion of several phenomena, we conclude that the high fraction of (0001) facets in disk-shaped Co-NC decrease FT activity and, although very challenging to pursue, that metal nanoparticle shape effects can be studied at industrially relevant conditions.

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5.1. Introduction

Controlled synthesis of supported metal nanoparticles is one of the main challenges in designing heterogeneous catalysts for major industrial processes as well as fundamental research.^{1–3} Traditional catalyst synthesis methods have in common that nanoparticle formation takes place on the support.⁴ Recent advances in catalyst synthesis include the use of colloidal techniques to synthesize nanocrystals (NC) in solution followed by attachment to a support.^{4,5} By separating the NC synthesis from attachment to the support, the properties of the NC can be manipulated with greater precision, leading for example to NC of particular sizes, crystal structures and shapes.⁶ Among these properties, nanoparticle shape is arguably the hardest to tune using conventional techniques, so here colloidal methods could offer a clear advantage over existing catalyst synthesis techniques, provided that challenges regarding NC attachment to the support and ligand removal are solved.⁷

Anisotropic NC are often metastable compared to spherical NC, which are usually the equilibrium shape in particular in the case of metals.^{8,9} By using ligands that bind preferentially to specific surface facets, it is possible to inhibit growth in certain directions and to drive the process towards a kinetically controlled product.^{10,11} Distinct crystal facets are exposed at the surface of these particles, which may lead to distinct catalytic performance. Additionally, different shapes also imply different relative amounts of corner, edge and terrace sites, the reactivity of which can vary depending on the type of reaction.¹² The effect of NC shape on catalytic performance has already been investigated mainly for noble metal^{13–15} or for metal oxide NC,¹⁶ yet few accounts of shape variation for supported base metal NC catalysts exist.

The shape of NC plays an important role if the catalyzed reaction is structure sensitive. One pronounced example of such a reaction is the Fischer–Tropsch (FT) synthesis.¹² In FT, a mixture of H₂ and CO called synthesis gas is converted into hydrocarbon fuels and chemicals over a catalyst, typically based on Fe or Co.¹⁷ The cobalt–catalyzed FT reaction is sensitive to various structural aspects of the Co particles.¹⁸ For example, a size dependency of the catalytic performance of cobalt is generally reported, with the surface-specific activity and C₅₊-selectivity decreasing sharply below a particle size of 6–8 nm.^{19–21} Additionally, several studies indicated that the crystal structure of Co is relevant, with hcp being more active than fcc,^{22–26} although this topic remains controversial.²⁷ Given the potential influence of the crystal structure, the shape of Co particles might be important as well, as shape partially governs the surface structure of nanoparticles.

For the potential effect of the NC shape on catalytic FT performance we should resort mainly to theoretical and surface science studies, as little experimental data is available on complex model catalysts under high-pressure conditions. Theoretical studies predict that the B5 surface ensemble is essential for CO-dissociation, which is considered an important step for activity and selectivity. The occurrence of coordinatively unsaturated sites, including B5 sites, varies with particle size^{28,29} and crystal structure²⁹ and offers one explanation for the observed structure sensitivity. Furthermore, a computational comparison of the FT activity of various Co crystal planes indicated that higher index planes of hcp Co are orders of magnitude more active than the close packed (0001).²⁵ Surface science experiments on single crystal planes of hcp Co showed that relatively more CH₄ is

produced on hcp (0001) than on higher index planes, leading to a lower selectivity towards C_{5+} -products.^{30,31} However, a recent experimental study indicated that hcp (0001) displayed intermediate activity and C_{5+} -selectivity, with both increasing in the order hcp $\{11\bar{2}0\} > \{0001\} > \{10\bar{1}1\}$.³² All of these aspects of surface composition could in principle be affected by the shape of the Co-NC, although it is also possible that surface defects,³³ hydrocarbon coverage³⁴ or CO-induced surface reconstruction^{35–41} might in practice annihilate the effects of Co-NC shape.

Surface science cannot always be directly translated to more complex catalysts and high-pressure systems.⁵ To bridge the gap between surface science and supported catalysts under industrially relevant reaction conditions, 3D model catalysts containing anisotropic Co particles are required. Examples of anisotropic cobalt nanoparticles in FT include unsupported particles, such as $CoMnO_x$ nanoprisms,⁴² Co nanocubes,⁴³ bimetallic nanorods⁴⁴ and Co_3O_4 nanorods,⁴⁵ plates or cubes³². Furthermore, hcp nanorods supported either on $SiO_2-Al_2O_3$ ⁴⁶ or on Ni or Cu foams⁴⁷ have also been employed. Clearly, synthetic approaches are still required to produce anisotropic model systems that closely resemble conventional supported cobalt catalyst, with stable Co-NC shapes yet without additives, such as a second metal, that might influence the FT performance.

In this chapter, we report our efforts to advance the synthesis, characterization and testing of shape-controlled Co-NC dispersed on a support as relevant model catalysts for the Fischer–Tropsch synthesis. We consistently obtained a mixture of disk-shaped and spherical Co-NC. The disks were 15 nm in diameter with a thickness of 4 nm and consisted of hcp Co with (0001) terminating the base planes, while the spherical particles consisted of ϵ -Co. After low-temperature oxidation of the Co-NC, the CoO-NC were attached to SiO_2 ($50\text{ m}^2\cdot\text{g}^{-1}$). Numerically 66 % of the NC were disks, leading to a higher occurrence of hcp (0001) on the cobalt surface compared to purely spherical Co-NC. The FT activity of the disks/spheres mixture was half that of spheres only, while the C_{5+} -selectivity was identical. Remarkably, the shape endured the FT conditions, as 62 % of the NC after catalysis were disks of the original dimensions. Nitrogen-containing ligands were largely removed, and both catalysts featured the same crystalline composition, leaving the possibility for enhanced hcp (0001) exposure in disks. Based on these experiments, it was concluded that the disk shape of Co-NC had a strong influence on the FT performance, most probably caused by the introduction of a high number inactive low-index Co planes.

5.2. Experimental

5.2.1. Synthesis of disk-shaped nanocrystals

A mixture of disk-shaped and spherical Co-NC was synthesized based on an adapted procedure originally developed by Puentes et al.^{10,48} The ligands, 50 mg oleic acid (90 % technical grade, Sigma–Aldrich) and 600 mg octadecylamine (>99.0 % (GC), Sigma–Aldrich), were transferred to a three-necked 100 mL flask with two septa and a reflux condenser connected to a Schlenk line. The mixture was heated to 80 °C under vacuum using a heating mantle while magnetically stirring at 600 rpm. After 30 min, the setup was flushed three times with N_2 before switching to N_2 for the remainder of the synthesis. Then,

7.5 mL 1,2-dichlorobenzene (99 % Anhydrous, Sigma-Aldrich) was added to the mixture without air-exposure, a thermocouple was inserted and the mixture was heated to reflux temperature (188 °C). Meanwhile, 270 mg dicobalt octacarbonyl (95 %, stabilized with hexane, Acros Organics) was transferred to a vial in an N₂-glovebox and the vial was left open inside the glovebox for 40 min to age. After ageing, the Co₂(CO)₈ was dissolved in 1.5 mL 1,2-dichlorobenzene and the vial was closed using a cap with a septum and removed from the glovebox. Once the liquid was at reflux temperature, the cobalt precursor was rapidly injected into the center of the flask using a syringe with a Ø 1.2 x 40 mm needle under 600 rpm stirring. The synthesis was quenched after 5 min using a water bath. The water bath was removed after ~3 min when the temperature of the reaction mixture was below 30 °C. Simultaneously, the stirring was stopped and the stirring plate placed 5 cm below the flask to magnetically separate the reaction product. The top 7 mL contained the highest concentration of disk-shaped Co-NC and was transferred to a glass centrifuge tube after 5 min and exposed to air from this point on. Consequently, the NC were oxidized to CoO to facilitate their uniform distribution over a support at a later stage.⁷ The centrifuge tube was filled to 20 mL with 2-propanol (≥99.5 % (GC), Merck) and centrifuged at 2500 G for 10 min. The purple/brown supernatant was decanted and the residue redispersed in 0.5 mL n-hexane (99 %, Acros Organics) using sonication. Another precipitation-redispersion cycle was performed by filling the tube to 20 mL with 2-propanol, centrifuging at 2500 G for 40 min, decanting the supernatant and finally redispersing the residue in 10 mL n-hexane using sonication.

5.2.2. Attachment of disk-shaped nanocrystals

The disk-shaped CoO-NC were attached to SiO₂ (Aerosil OX 50, Evonik) within 4 h after synthesis. To obtain enough material with sufficient metal loading, two NC synthesis batches were attached consecutively to the same batch of support. A glass round bottom vessel with an overhead mechanical stirrer was placed in a sonication bath. 300 mg SiO₂ and 20 mL n-hexane were added and the top of the vessel was loosely covered with aluminum foil. Stirring and sonication were applied to suspend the SiO₂ for 20 min and then the first CoO-NC batch in 10 mL n-hexane was added dropwise in 15 min under continued stirring and sonication. The mixture was left for 45 min after the addition and then the n-hexane was slowly evaporated in 15 min by applying a flow of N₂ through the vessel, all under sonication and stirring. This entire procedure was repeated a second time by suspending the dried uniformly grey powder again in 20 mL n-hexane and adding the second batch of CoO-NC. Afterwards, the dried powder was suspended in 10 mL n-hexane and transferred to a glass centrifuge tube. The solid was precipitated by centrifuging at 2500 G for 1 min and the supernatant was decanted. The residue was 5 times resuspended in 5 mL n-hexane and precipitated by centrifuging at 2500 G for 1 min and finally dried at ambient temperature under vacuum for 16 h. The dry powder was pressed and sieved to a grain size of 75–150 µm (100 mg was obtained).

5.2.3. Synthesis of spherical nanocrystals

Exclusively spherical Co-NC were synthesized according to a comparable hot-injection method, however, only oleic acid was used as ligand according to a procedure described

before⁴⁹. The synthesis was performed in N₂ atmosphere using a Schlenk line. 65 mg oleic acid was degassed under vacuum at 100 °C for 30 min under 650 rpm magnetic stirring in a 3-necked 100 mL flask with a condenser and two septa. The flask was flushed with N₂ and the synthesis was continued under N₂. Then, 7.5 mL 1,2-dichlorobenzene was added under N₂ atmosphere and the solution was heated to 165 °C. Meanwhile, 270 mg dicobalt octacarbonyl was dissolved in 1.5 mL 1,2-dichlorobenzene and sealed under N₂ atmosphere inside a glovebox. This cobalt precursor was then rapidly injected (needle: Ø0.9 x 70 mm) into the pre-heated solution at 750 rpm stirring and reacted vigorously. After 20 min, the reaction was quenched and cooled to ambient temperature using a water bath. One septum was then removed to oxidize the Co-NC to CoO-NC by air-exposure at low temperature for 1 h (650 rpm stirring). The suspension was divided after over two glass centrifuge tubes, which were filled further to 20 mL with 2-propanol and centrifuged at 2200 G for 30 min to precipitate the NC. The supernatant was decanted, the precipitate redispersed in 0.5 mL n-hexane by sonication and the tubes were filled again to 20 mL with 2-propanol and centrifuged at 2200 G for 40 min. This precipitation-redispersion cycle was repeated two more times and afterwards, the residue was redispersed and combined in 2 mL n-hexane in total.

5.2.4. Attachment of spherical nanocrystals

The spherical CoO-NC were attached on the same type of low surface area SiO₂ as the disk-shaped CoO-NC, according to a method described before.⁴⁹ The SiO₂ had already been pressed and sieved to a fraction of 75–150 µm. The support (500 mg) was transferred to a 100 mL 3-necked flask and a mixture of the Co-NC in n-hexane and 6.5 mL 1-octadecene (90 %, technical grade, Sigma-Aldrich) was added under 400 rpm magnetic stirring. The flask was then equipped with a condenser, glass plug and septum and connected to a Schlenk line. The suspension was degassed under vacuum at 100 °C for 15 min and as a result, the n-hexane in the suspension evaporated. Then, the flask was flushed with N₂ and the attachment was continued under N₂. The suspension was heated to 200 °C for 30 min, after which the heating mantle was removed, causing the solution to cool to room temperature within 30 min. The sample was washed by first centrifuging at 1500 G for 5 min and decanting the supernatant. Subsequently, the precipitate was resuspended in 2 mL n-hexane through sonication, 6 mL acetone was added and the sample was isolated by centrifuging at 1500 G for 5 min and decanting the supernatant. This precipitation-resuspension cycle was repeated five times, followed by a last cycle in which the n-hexane/acetone mixture was replaced by 20 mL acetone. Finally, the sample was dried in three consecutive steps, i.e. 60 °C for 1 h in static air, 120 °C for 3 h in static air and 80 °C for 3 h under vacuum, and pressed and sieved to a grain size of 75–150 µm.

5.2.5. Characterization

Transmission electron microscopy (TEM) was performed on a Tecnai 20 (FEI) operated at 200 kV. Samples of colloidal suspension were prepared by drop casting a diluted sample directly on a carbon-coated TEM grid. In the case of SiO₂-supported CoO-NC, the powder was first suspended in 2-propanol by sonication and subsequently drop casted on a carbon-coated TEM grid. The TEM images of supported CoO-NC were manually analyzed using

ImageJ. In the case of the colloidal suspensions, the images of CoO-NC were automatically classified as either disks or spheres and manually reviewed before analysis. All reported NC sizes are number averaged and recalculated to the equivalent Co⁰ size to compensate for lattice expansion due to a 3 nm thick CoO passivation layer. Because of the limited height of the disks, these NC were assumed to oxidize completely to CoO. The metallic surface area was calculated using the surface area weighted mean diameter, again after correcting for the 3 nm CoO passivation layer. A cross-sectional area of 0.0662 nm² per cobalt atom was assumed in order to calculate the metallic surface area.⁵⁰

Vitrification of freshly synthesized colloidal suspensions for cryogenic transmission electron microscopy (cryo-TEM) was performed using a Vitrobot Mark IV (FEI) vitrification robot. The Co-NC were vitrified in the original reaction suspension within 30 min from magnetically separating the synthesis product. For the vitrification, 3 μ L of Co-NC suspension was applied to a 200 mesh, lacey carbon-coated Cu grid at 25°C in a chamber saturated with toluene vapor. Subsequently, the grid was blotted for 3 s with filter paper and plunge-frozen in liquid N₂ (-196 °C). The samples were kept in liquid N₂ for several hours and loaded into the Titan Krios (FEI) equipped with a field emission gun operating at 300 kV and energy filter. Images were recorded using a 2k $\times$ 2k Gatan charge coupled device (CCD) camera. High-resolution transmission electron microscopy (HR-TEM) was performed in areas where no solvent appeared present. Low dose selective area diffraction (SAED) was used for structure analysis and the diffraction patterns were processed according to the method described by Leijten et al.⁵¹

Electron tomography was carried out using an FEI Talos F200X operated at 200 kV in bright field TEM mode. The CoO-NC/SiO₂ sample was suspended in ethanol by ultrasonication. A few droplets of the suspension were deposited onto a Quantifoil R2/1 carbon film supported parallel-bar Cu grid which already contained Au nanoparticles of 5 nm in diameter. TEM images were recorded with a Ceta camera (4096 $\times$ 4096 pixels) over a tilt range of -66 ° to +76 ° with tilt increments of 2 ° at a nominal magnification of 74,000 times. The tilt series was aligned using IMOD software⁵² using the Au nanoparticles as fiducial markers. The aligned tilt series were binned by 4 and reconstructed using the back-projection algorithm. The resulting reconstructed volumes had a final voxel size of (0.572 nm)³. Segmentation of disk-shaped CoO-NC, spherical CoO-NC and the SiO₂ support in the reconstructed volumes was performed in FIJI.⁵³ Adequate threshold values were applied to median-filtered reconstructed volumes. Disk-shaped NC, spherical NC and the SiO₂ support were defined in 3D by manually delimiting their boundary. Volume rendering of the segmented volumes was carried out in FIJI.

Inductively coupled plasma-optical emission spectroscopy (ICP-OES) was performed on a SPECTRO ARCOS after digestion of the sample in aqua regia.

X-ray photoelectron spectroscopy (XPS) was measured on a Kratos Axis Ultra DLD with an X-ray source operating at 225 W and 15 keV, and equipped with an Al anode (EK α = 1486.6 eV). The samples were fixed using Ag-tape at ambient conditions and loaded in the setup. High-resolution spectra of Co2p, Si2p, O1s and C1s were measured at 40 eV pass energy, while N1s and the survey scan were recorded at 160 eV pass energy. Kratos Axis sensitivity factors were used for quantification. XPS measurements were

performed on three distinct locations on all samples and the results were averaged. In case of the N1s scan, multiple measurements of the same location were accumulated to improve the signal-to-noise ratio. The binding energies were calibrated by setting the C–C/C–H bond peak to 284.8 eV.

In situ X-ray diffraction (XRD) was performed on a Bruker D8 Discover with a Mo ($K_{\alpha 1}$ 0.709 Å) source in Debye–Scherrer transmission (capillary) geometry. The X-ray beam was focused on a quartz capillary with 1000 µm OD and a wall thickness of 10 µm using a Göbel-mirror. The setup was equipped with an energy dispersive LynxEye XE Position Sensitive Detector (PSD). Details on the complete setup can be found in recent publications.^{54,55} The patterns were measured between 5 and 39 ° 2θ with an increment of 0.07 ° and time per step of 20.5 s. Multiple scans were accumulated to improve the signal-to-noise ratio only if the patterns were identical. Rietveld Quantitative Phase Analysis (Rietveld QPA) was performed on the measured diffractograms using Bruker TOPAS v5 software. Details of the Rietveld refinement procedure are given in Appendix D.

Co–S/SiO₂ was diluted with 2 mass equivalents SiO₂ (Aerosil OX 50) to obtain a similar overall cobalt loading as Co–D/SiO₂. Typically, 7 mg sample in the sieve fraction 75–150 µm was loaded in the capillary and fixed with quartz wool at either end, resulting in a catalyst bed length of ~20 mm. The capillary was placed in the setup and the catalysts were reduced *in situ* at 350 °C for 8 h (1 °C·min^{−1}) in a 1.2 mL·min^{−1} flow of 25 vol% H₂ in He at 1 bar. After reduction, the temperature was lowered to 180 °C with 3 °C·min^{−1} and at this temperature, a 3.0 mL·min^{−1} flow of synthesis gas H₂/CO = 2 (v/v) was introduced. After 10 min stabilization, the back-pressure regulator was set to 10.6 bar. Only after the set pressure was reached and stable, the temperature was increased to 220 °C with 1 °C·min^{−1}, which was defined as TOS = 0 h. *In situ* XRD patterns were recorded both during reduction and FT.

5.2.6. Fischer-Tropsch synthesis

The Fischer–Tropsch synthesis performance of the catalysts was investigated using a Flowrence (Avantium) 16 parallel reactor setup. 80 mg Co–D/SiO₂ and 12 mg Co–S/SiO₂ were first diluted with 100 mg SiC (212–425 µm) and then loaded into stainless steel plug-flow reactors of 2.6 and 2.0 mm (ID), respectively. The samples were dried for 2 h in an He flow and reduced *in situ* in a 25 vol% H₂ in He flow at 350 °C for 8 h after a heating ramp of 1 °C·min^{−1}. After reduction, the temperature was lowered to 180 °C with 3 °C·min^{−1} and the reactors were pressurized to 20 bar in an H₂ flow. Then, the synthesis gas feed was introduced with H₂/CO = 2 v/v and 5 vol% He as internal standard and after 1 h stabilization, the reactors were heated to 220 °C with 1 °C·min^{−1}, which was defined as the starting point for FT. After the run, the catalysts were treated in H₂ at 200 °C for 10 h to remove carbonaceous products from the catalyst surface and cooled down further under He.

The reaction products were analyzed online using an Agilent 7890A GC with two separate channels. In the first channel, the hydrocarbon products were analyzed using an Agilent J&W PoraBOND Q column in combination with an FID. In the second channel, the permanent gasses were separated on a ShinCarbon–ST column and analyzed using a TCD. The catalytic activity was given as CO conversion (X_{CO}) cobalt-time yield (CTY) and

turnover frequency (TOF). The TOF was based on the CTY and the average metallic surface area of the spent catalyst, as determined by TEM. The selectivity (in %) to C₁-C₄ hydrocarbons was determined as $S_{C1-C4} = 100 \cdot F_{Cn} \cdot n \cdot (F_{CO,in} \cdot X_{CO})^{-1}$ with n representing the product's carbon number and F the flow of the hydrocarbon or CO. The selectivity to C₅+ hydrocarbons was calculated as $S_{C5+} = 100 \% - S_{C1-4}$.

5.3. Results and discussion

5.3.1. Cobalt nanocrystal synthesis

Cobalt nanocrystals (NC) were synthesized by a hot-injection synthesis using oleic acid and octadecylamine as ligands with the aim to synthesize disk-shaped NC and the results were analyzed by TEM (Figure 5.1). Both disk- and spherical-shaped CoO-NC were obtained from a single synthesis with the ratio between the two varying strongly with the reaction conditions, which made separation necessary, in line with literature.¹⁰ Enrichment of the disk-shaped over spherical NC was realized by a magnetic field, using the difference in the magnetic properties between the different NC. In our case, the large magnetic moment of the spheres resulted in faster precipitation from the solution compared to the disks under the weak magnetic field of the stirring plate (Appendix D, Figure D1). This led to enhanced concentrations of disks in the top layer of the reaction mixture (Figure 5.1a-e). After magnetic separation, the work-up procedure also affected the disk-to-sphere ratio, as the disk yield decreased with more precipitation-redispersion cycles (Figure 5.1a-c). This indicates that spheres were preferentially precipitated during centrifugation or alternatively, that the fraction of disks already varied in the original reaction mixture of different batches.

The elongated, rod-like particles (mainly visible in Figure 5.1a) were identified as stacks of disk-shaped particles orientated side to side. From these particles, the average dimensions of the disks were determined (Appendix D, Figure D2). The average diameter of the disks was 15.5 ± 3.5 nm and the thickness 4.2 ± 0.6 nm, leading to an aspect ratio (height/diameter) of 0.27. As a comparison, all-spherical CoO-NC of 8.3 ± 1.1 nm were synthesized using only oleic acid as ligand, as described before⁴⁹ (Figure 5.1f).

A batch containing disk-shaped NC after three precipitation-redispersion cycles was analyzed in more detail (Figure 5.1c). The NC in the TEM image were semi-automatically divided into two groups (Figure 5.1e) based on their contrast, which is a measure for their thickness, in relation to their size and morphology. The large, low-contrast NC were (truncated) hexagonally-shaped and the smaller, high-contrast NC were spherical. To examine the 3D shape of these NC, the stage was tilted 50 ° inside the TEM (Figures 1d and A3). Analysis of 100 NC from both groups (Appendix D, Figure D4) revealed that the size of the particles was 15.4 nm at 0 ° and 11.9 nm at 50 ° in the case of the low-contrast particles, proving that these NC were indeed smaller in the z direction as expected for disk-shaped NC. When considering an aspect ratio of 0.27, the 2D projection length at 50 ° should be 13.1 nm (Appendix D, Figure D5), which matches the experimental value quite well. On the other hand, the smaller, high-contrast particles were 10.7 nm at 0 ° and 10.6 nm at 50 °, showing that their diameter was the same in all directions and that these NC were indeed

spherical. Because the shapes of the CoO–NC could be accurately distinguished, the numerical disk yield could be determined and was 53 % for the batch after three precipitation–redispersion cycles.

Figure 5.1. TEM images of several batches of mixed spheres/disks CoO–NC after different washing procedures followed by dispersion and drying on the carbon foil **a–e**. The washing procedures consisted of **a** one precipitation–redispersion cycle, **b** two precipitation–redispersion cycles and **c–e** three precipitation–redispersion cycles. **c–e** Images of the same location with **d** showing the sample after tilting by 50 ° and **e** with an overlay highlighting the particles that were identified as disks (red) and spheres (aqua). **f** Spherical CoO–NC synthesized using only oleic acid as ligand.

Disk-shaped Co–NC are a metastable phase,^{8,56} making the synthesis results highly susceptible to small variations in the procedure. Therefore, optimizing the reaction conditions was essential to obtain a high fraction of anisotropic particles. Important synthesis parameters included the speed of magnetic stirring and the speed of precursor injection, as faster stirring or slower injection through a thinner needle led to enhanced formation of 10–30 nm spherical NC and a lower yield of disk-shaped NC. Furthermore,

higher disk yields were obtained with batches of $\text{Co}_2(\text{CO})_8$ that had been aged 40 min in the glovebox prior to use in synthesis. These phenomena have not been reported before for this synthesis method and illustrate the delicate nature of this approach.

The crystal structure of the as-synthesized Co-NC before oxidation was analyzed using a combined cryo- and high-resolution-TEM approach (Figure 5.2). A Co-NC suspension was vitrified shortly after NC synthesis and transported and loaded in liquid N_2 to avoid oxidation of the Co-NC. The vitrification protected the sample from oxidation and HR-TEM was possible because there was little to no solvent present in the TEM sample. Electron diffraction of the area in Figure 5.2a resulted in the diffraction pattern in the inset of Figure 5.2a and was radially averaged to give Figure 5.2b. The main peak at $d = 2.06 \text{ \AA}$ could not be unambiguously assigned to one crystal structure, as this lattice spacing is present in all three metallic cobalt phases (Appendix D, Figure D6). The diffraction peak at $d = 2.19 \text{ \AA}$, however, only matched hcp cobalt. Furthermore, the peaks at d -values of 1.26 and 2.19 $\text{\AA}$ could be ascribed to $\{11\bar{2}0\}$ and $\{10\bar{1}0\}$ of hcp cobalt, respectively, which were more intense than expected. Considering that $\{11\bar{2}0\}$ and $\{10\bar{1}0\}$ have periodicity in the x,y direction and not in the z direction, this proved that the hcp cobalt was present in anisotropic, disk-shaped NC and that the short z axis is along the $[0001]$ direction, in line with literature.¹⁰ Based on the intensity ratios of the hcp Co phase, it is likely that the peak at $d = 2.06 \text{ \AA}$ has another dominant contribution either from fcc or ϵ -cobalt.

Figure 5.2. High-resolution TEM under cryogenic conditions of as-synthesized disk-shaped and spherical Co-NC with little to no solvent present. **a** Overview of several clustered Co-NC with the selected area electron diffraction pattern in the inset. **b** Intensity profile obtained by radially averaging and baseline correcting the SAED pattern. **c** Several Co-NC at higher magnification. The framed area contained a 15 nm, low contrast NC that was classified as a disk; the inset gives the Fourier transform of the framed area.

Further information on the crystal structure of the NC before oxidation was obtained by investigating an individual NC in more detail with HR-TEM on the same cryogenic sample. The Co-NC in the framed area in Figure 5.2c was identified as a disk-shaped NC because of its low contrast and diameter of 15 nm. Lattice fringes of this particle were imaged and the Fourier transform revealed hexagonal symmetry of the crystal lattice, indicative of hcp cobalt. The determined lattice spacings were 2.28 and 1.29 $\text{\AA}$, which were

again matched to $\{11\bar{2}0\}$ and $\{10\bar{1}0\}$ of hcp Co. Additionally, the other prominent particle of 11 nm with higher contrast was identified as a spherical NC and did not show hexagonal symmetry. Its lattice spacings matched ϵ -cobalt best (Appendix D, Figure D7), indicating that the other crystal structure observed by electron diffraction was most likely ϵ -cobalt, which is consistent with literature.¹⁰ It should be emphasized that this concerned the crystal structure of the Co-NC before oxidation and that it is uncertain what crystal structure would evolve after low-temperature oxidation, *in situ* reduction and catalysis.

Figure 5.3. TEM images of pristine samples of CoO-NC attached to SiO₂. **a** An area of Co-D/SiO₂ with a uniform distribution of CoO-NC and **b** the same location with an overlay highlighting the NC that were identified as disks (red) and spheres (aqua). **c** An area of Co-D/SiO₂ where the CoO-NC were clustered. **d** Co-S/SiO₂ with a uniform CoO-NC distribution.

5.3.2. Cobalt nanocrystal attachment

The CoO-NC after two precipitation–redispersion cycles were attached to low surface area SiO₂ (50 m²·g⁻¹) using a method that avoids the use of high temperatures to affect the NC shape as little as possible. This particular type of SiO₂ was selected, because it had yielded very stable Co-NC based catalysts under FT conditions before.⁴⁹ The sample containing mainly disk-shaped NC was designated as Co-D/SiO₂. Two washing steps after NC synthesis were the optimal compromise between uniform attachment of the CoO-NC with lower ligand concentration on one hand (Appendix D, Figure D8) and progressively lower NC yields on the other. Based on ICP–OES, a cobalt loading of 1.4 wt% was obtained using this attachment method. The Co-D/SiO₂ sample was analyzed by TEM (Figure 5.3a–c). The NC were largely uniformly distributed over the support, although some areas with clustered disk-shaped and spherical NC were encountered as well (Figure 5.3c). Despite

this occasional clustering of NC, NC were largely well dispersed on the support, making the catalyst useful for further investigations.

Figure 5.4. Electron tomography results of the pristine Co-D/SiO₂ sample, consisting of a mixture of disk-shaped and spherical CoO-NC attached to SiO₂. **a** TEM image of Co-D/SiO₂ at 0° tilt angle. The small (~5 nm), high-contrast particles are gold fiducial markers on the TEM grid. **b** The same TEM image with an overlay highlighting the NC that were identified as disks (red) and spheres (aqua). This location was reconstructed and the framed area was segmented. **c** Volume-rendered 3D reconstruction of the framed area in (b), shown at two different angles obtained by rotation along the z axis (dashed line). The z axis also indicates the direction of the projection in the original TEM image **a,b**. The SiO₂ support is depicted in grey, disk-shaped CoO-NC in red and spherical CoO-NC in aqua. An animation showing a 360° rotation of this segmented sample together with the tilt series and the full reconstruction file can be found online as supporting movies of the original article.

It was challenging to distinguish the disk-shaped NC from the SiO₂ support because of the low contrast of the CoO-NC associated with their limited thickness when orientated perpendicular to the electron beam. However, based on a combination of contrast, size and morphology, it was possible to identify the CoO-NC and discriminate between disks and spheres (Figure 5.3a,b). After analysis of 203 NC, 66 % of the NC were classified as disks and 34 % as spheres. In addition, a reference catalyst containing exclusively spherical CoO-NC was prepared by attaching the 8.3 nm CoO-NC to the same type of low surface area SiO₂ (Figure 5.3d). This catalyst was designated as Co-S/SiO₂. The obtained cobalt loading was 9.6 wt% based on ICP-OES. Furthermore, the CoO-NC were uniformly distributed over the support and no areas containing clustered NC were observed. This catalyst was described in more detail in an earlier publication.⁴⁹

Electron tomography of Co-D/SiO₂ was performed to investigate the morphology of the NC on the support in more detail (Figure 5.4). The disks could be clearly distinguished from the spheres using the tilt series, because only the projected aspect ratio of the disks varied with the tilting angle. The accuracy of the method applied before to classify the NC as disks or spheres based on size, morphology and contrast was confirmed by tomography and the obtained results for this limited sample size (only 26 NC in field of view) matched the earlier observation of ~65 % of the NC present as disks. Furthermore, a 3D representation of a selected part of the sample was obtained through reconstruction and segmentation of the tilt series (Figure 5.4c). From this representation, the morphology of NC can be clearly inferred as well as their interaction with the support. It showed that the disk-shaped NC typically attached to SiO₂ with one base plane.

5.3.3. Fischer-Tropsch synthesis

The FT performance of the catalysts was evaluated over 100 h on stream at similar CO conversion levels (Figure 5.5, Table 5.1). The cobalt-weight-based activity (cobalt-time yield, CTY) against TOS is shown in Figure 5.5b. Co-S/SiO₂ was twice as active per unit weight of cobalt as Co-D/SiO₂. Because of the different particle sizes and shapes, the activity was compared as cobalt-surface-based activity (turnover frequency, TOF). The metallic surface area necessary for the TOF was calculated from the NC sizes in the spent catalyst, which will be discussed later (Table 5.1). The TOF of Co-D/SiO₂ was 49·10⁻³ s⁻¹ and the TOF of Co-S/SiO₂ was 86·10⁻³ s⁻¹, the former value being in line with other work on Co/SiO₂ using conventional catalyst preparation techniques such as impregnation.⁵⁷ However, the TOF of Co-S/SiO₂ was remarkably high, possibly pointing to a higher fraction of more active hcp Co²²⁻²⁶ resulting from the NC-based synthesis compared to conventional synthesis methods.

Table 5.1. Fischer-Tropsch synthesis results for Co-D/SiO₂ and Co-S/SiO₂ reported at similar CO conversions and averaged between 90-100 h on stream at 20 bar, 220 °C and H₂/CO = 2 v/v.

Sample	GHSV (h ⁻¹)	X _{CO} (%)	CTY ^a	TOF _{app} (10 ⁻³ s ⁻¹) ^b	S _{C1} (% _C)	S _{C2-C4} (% _C)	S _{C5+} (% _C)	α	Co SA _{spent} (m ² ·g _{Co} ⁻¹)
Co-D/SiO ₂	1560	8.9	6.9	49	16	8.6	75	0.78	56
Co-S/SiO ₂	39900	8.1	15	86	13	9	78	0.76	71

^a in 10⁻⁵ mol_{CO}·g_{Co}⁻¹·s⁻¹

^b based on the CTY and the metallic Co surface area of the spent catalyst as derived by TEM.

The selectivities towards C₅₊- as well as C₁- and C₂-C₄-products were similar (Table 5.1) and overall ~5 % lower than on conventionally prepared Co/SiO₂ catalysts.⁵⁷ Consequently, the ASF distributions and derived chain growth probabilities (α) were comparable as well. Plots of the C₅₊-selectivity as a function of TOS and ASF distributions are included as Appendix D, Figure D9. The effect of crystal structure on selectivity is still under debate, as some reports indicated no difference between hcp and fcc Co,^{22,27} while others observed higher C₅₊-selectivity on hcp Co.^{24,58} However, in our case with anticipated enhanced (0001) for Co-D/SiO₂, major differences in selectivity would be unexpected considering that the inactive surfaces, e.g. (0001), contribute only marginally to the overall product

spectrum. Thus, changing the NC shape from spheres to disks did not influence the selectivity of the catalyst. Overall, the main difference in performance was the factor 2 lower intrinsic activity of the disk-containing Co-D/SiO₂ sample, which could have several reasons. First, the activity could be lower as a result of the shape and thus the exposed facets, which would match the theoretical and experimental finding that hcp (0001) is less active than higher-index hcp or fcc facets.^{25,32} Second, residual ligands could still be present in the case of Co-D/SiO₂ and block part of the cobalt surface. Third, the surface area of Co-D/SiO₂ could be lower than expected if the degree of reduction is low or if there is substantial NC growth, for example in the areas where clustering of NC was observed (Figure 5.3c). These potential explanations were investigated in more detail and are described below.

Figure 5.5. Fischer-Tropsch synthesis results of Co-D/SiO₂ and Co-S/SiO₂ at 20 bar, 220 °C and H₂/CO = 2 v/v. **a** CO conversion and **b** cobalt-time yield as a function of time-on-stream.

5.3.4. Characterization of spent catalysts

The structure of the spent catalysts was analyzed after FT and subsequent passivation using TEM (Figure 5.6). The sizes and shapes of 160 cobalt nanocrystals in Co-D/SiO₂ were quantified (Figure 5.6a,b), showing numerically 62 % disk-shaped NC with $d = 14.5 \text{ nm}$ and 38 % spherical NC with $d = 10.2 \text{ nm}$. The aspect ratio of the disks could not be reliably determined for this sample and was assumed to have remained unchanged. These results

were very similar to those of the pristine catalyst and the disk shape was thus remarkably stable under FT conditions. Furthermore, a more clustered part of the catalyst was also observed where some particle growth had occurred (Figure 5.6c). This area probably originated from an area of clustered CoO–NC in the pristine catalyst. The size of the NC in Co–S/SiO₂ was unchanged as well with spherical particles of 8.7 nm on average (Figure 5.6d). The stability of the Co–NC in terms of both size and shape under reaction conditions meant that catalytic performance might be related to the disk shape.

Figure 5.6. TEM images of Co/SiO₂ samples after >100 h of Fischer–Tropsch synthesis and passivation. **a** An area of Co–D/SiO₂ with a uniform distribution of NC and **b** the same location with an overlay highlighting the NC that were identified as disks (red) and spheres (aqua). **c** An area of Co–D/SiO₂ where the NC were clustered. **d** Co–S/SiO₂ with a homogeneous NC distribution.

Two types of ligands were used to synthesize disk-shaped Co–NC (oleic acid and octadecylamine) while spherical Co–NC were synthesized using only oleic acid. For oleic acid, efficient ligand removal has been shown,⁷ but could be different for linear amines. We assessed the influence of the octadecylamine ligand in FT by investigating the amount of surface nitrogen species using XPS on the catalysts as-prepared and after 100 h FT followed by passivation. Low concentrations of N were detected on both as-prepared catalysts and on bare SiO₂ (Figure 5.7a, complete survey scans in Appendix D, Figure D10). The N-to-Co atom ratio was 4 times higher on Co–D/SiO₂ (0.07) than on Co–S/SiO₂ (0.02). After FT and passivation, Co–D/SiO₂ was partially covered in carbon and only an indication of N was observed. Spent Co–S/SiO₂ was too covered in carbon to yield useful data on Co and N contents. The N/Co atom ratio of spent Co–D/SiO₂ seemed similar to that of as-prepared Co–S/SiO₂, so excess N-species in Co–D/SiO₂ from the NC synthesis procedure were

removed during reduction/FT. Harmel et al.⁴⁶ quantified that the content of the ligand hexadecylamine decreased from 8 wt% to 3 wt% during reduction under H₂ at 270 °C, which is substantially lower than the reduction temperature of 350 °C applied here. Therefore, it seemed that our reduction procedure was sufficient to activate the catalyst and minimize the effect of remaining N-species.

To get more insight into the structure of the catalysts under FT conditions, *in situ* XRD was performed on both catalysts at 10 bar, 220 °C and an H₂/CO ratio of 2 v/v (Figure 5.7b, A11). To obtain satisfying Rietveld refinement results, it was necessary to allow preferred orientations of hcp Co crystallites, similar to what has been reported before.⁵⁵ We ascribe this to polymorphism of Co in the Co-NC/SiO₂ samples, since XRD analysis of metallic cobalt is complicated by the propensity of cobalt to include stacking faults.^{22,59} Our analysis method did not quantify this intergrowth structure, but accommodated much of it in the hcp contribution by increasing the intensity of the (0002) peak. The fraction of hcp Co could therefore be overestimated. However, both samples were refined using the same method and given the similarity of the results for both samples, it appears that polymorphism, if present, took place to the same extent in both samples.

The crystalline cobalt phase in both catalysts consisted of approximately 65 % hcp Co. The fcc Co and CoO compositions were 21 % fcc Co and 12 % CoO for Co-D/SiO₂ and 32 % fcc Co and 3 % CoO for Co-S/SiO₂. These values are in line with results obtained by Andreev et al.⁶⁰ using NMR on Co/SiC at elevated temperatures under static Ar atmosphere and in reasonable agreement with Cats et al.⁵⁴ who used *operando* XRD on Co/TiO₂ under FT conditions. In general, however, direct comparison of these results to literature is cumbersome, since the obtained Co phase strongly depends on particle size, metal precursor, support and activation procedure.^{61,62} Furthermore, the average crystallite sizes of metallic cobalt was 3–5 nm, significantly smaller than the particle dimensions obtained by TEM. This probably indicated that the Co-NC were polycrystalline, which could be related to the occurrence of stacking faults.

The degree of reduction of the crystalline phase was high with 88 % for Co-D/SiO₂ and 97 % for Co-S/SiO₂ and therefore excluded as a reason for substantial activity differences. Once in the reduced state, the XRD profiles remained unchanged for the duration of the experiment. The crystallites thus remained stable without sintering or restructuring during reduction and the first 18 h FT, in line with the TEM analyses. This also indicated that a significant loss of surface area in Co-D/SiO₂ due to sintering of NC was unlikely. Furthermore, the hcp Co content in Co-D/SiO₂ was similar to that in Co-S/SiO₂, but nevertheless substantial in both samples. Finally, the average crystallite dimensions of 3–5 nm prevented any conclusions on potential preferred orientations and surface termination in disk-shaped NC with a diameter of 16 nm and 4 nm thickness. Overall, activity differences due to enhanced hcp Co content was excluded, but preferred crystallite orientations within the polycrystalline disk-shaped NC and with that enhanced hcp (0001) terminations were still possible.

Figure 5.7. Nitrogen species on the catalysts before and after 100 h FT followed by passivation, and cobalt crystal structure during FT. **a** N1s XPS signal around 400 eV of the catalysts in the pristine and spent state and a bare SiO₂ reference. The data was offset with 1500 CPS increment at 380 eV binding energy, except for Co-S/SiO₂ spent (offset -8000 CPS). **b** cobalt phase composition during Fischer–Tropsch synthesis as determined using *in situ* XRD and Rietveld refinement. The average crystallite sizes per metallic Co phase are indicated next to the corresponding columns. The amount of CoO was too low to reliably determine a crystallite size. The diffractograms were obtained over the first 18 h on stream at 10 bar, 220 °C and H₂/CO = 2 v/v by accumulating six scans of 3 h. No change in the diffraction patterns was observed over the course of the reaction.

Combining the obtained data on the ligands and NC size, shape and crystal structure of the catalysts under reaction conditions, the cobalt specific surface area and the fraction of the surface terminated by hcp (0001) were calculated (Figure 5.8). This served as an estimation of the structural difference between the Co-NC disk-containing catalyst and the catalyst containing exclusively spherical NC. To do so, we assumed that the base planes of the disks were terminated by hcp (0001) and that the disks were attached to SiO₂ with one base plane (Figure 5.4), thereby rendering that plane inaccessible for reactants. This is a conservative estimate, as the curvature of the SiO₂ might in practice make these base planes partially accessible, which would increase the relative occurrence of hcp (0001). Furthermore, the dimensions of the as-synthesized NC were used in surface area calculations, i.e. disks with $d = 15.5 \text{ nm}$ and $h = 4.2 \text{ nm}$ and spheres with $d = 10.7 \text{ nm}$.

Figure 5.8. Calculated accessible Co specific surface area (open bars) of Co-D/SiO₂ and Co-S/SiO₂ under FT conditions. The hcp (0001) surface area is indicated and broken down for the disk-shaped (red) and spherical (aqua) Co-NC.

Besides the surface of the disks, also the surface of the spheres has to be considered. According to Wulff reconstructions of spherical hcp cobalt particles by Liu et al.²⁵, 18 % of the surface of a spherical hcp cobalt particle is terminated by (0001). Therefore, the maximal hcp (0001) occurrence in Co-S/SiO₂ was 18 %. Compared to an estimated hcp(0001) occurrence of 39 % in Co-D/SiO₂, this means that 21 % of the metallic cobalt surface area of Co-S/SiO₂ is in a higher index and probably more active form than for the disk-containing Co-D/SiO₂. This holds when all NC consist of hcp Co, while a difference in hcp (0001) exposure of 33 % would be obtained if only disks were hcp Co. Considering the uncertainty and error margin in this analysis, we conclude that the difference in hcp (0001) exposure could be of the right magnitude to account for much of the observed activity difference.

This is, to the best of our knowledge, the first time that a supported model catalyst has been synthesized to investigate the effect of Co-NC shape in FT without complications of a secondary metal or interference of ligands and it illustrates the potential of colloidal techniques for model catalyst synthesis. Furthermore, based on these results, we tentatively propose that the extended low-index surface facets of the disks are the main contributor to the lower TOF.

5.4. Conclusions

We investigated the synthesis of disk-shaped cobalt nanocrystals (Co-NC), their attachment to a support and the subsequent effect of their anisotropy on the Fischer-Tropsch synthesis. Disk-shaped hcp Co-NC were synthesized mixed with spherical ϵ Co-NC. After oxidation to CoO, these NC were attached to low surface area silica. Electron microscopy analysis revealed that numerically 66 % of the attached CoO-NC were disks and 34 % were spheres. After *in situ* reduction of the CoO-NC to Co, the Fischer-Tropsch activity of disk-containing catalyst was only half that of a catalyst containing only spherical NC. Interestingly, the catalysts were stable and the size and shape of the NC were

retained, even for the disk-shaped Co-NC. XPS showed that most of the amine ligands were removed during activation/FT and *in situ* XRD revealed that the crystal structure of both catalysts was similar, with NC with 3–5 nm polycrystalline domains and approximately 65 % hcp Co and 21 to 32 % fcc Co. Based on these experiments, we tentatively propose that changing the Co-NC shape from spheres to disks reduced FT activity because of hcp (0001) facets prevailing. This work clearly demonstrates the potential of colloidal methods to synthesize new, well-defined model catalysts to investigate structure–performance relationships in catalysis even under high-pressure conditions.

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Chapter 6

Control of metal-support interactions in heterogeneous catalysts to enhance activity and selectivity

Abstract

Metal nanoparticles stabilized on a support material catalyze 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 rationalization of the field is lacking due to the great diversity in catalysts, reactions and MSI modification strategies. In this review chapter, we cover and categorize 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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6.1 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 immobilize 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 optimize 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 chapter 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.

6.2 Metal-support interactions

Impact on catalysis originates from interactions between metal nanoparticles and their supporting matrix (Figure 6.1Error! Reference source not found.a). 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.

Figure 6.1. 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.

Charge transfer. The interface between a metal NP and the support can give rise to a rearrangement of electrons within both materials.⁵ 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 localized 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 synchronized reactions.^{15,16} Furthermore, it has been shown that upon charge transfer, atoms at the perimeter favor the accumulation of excess charges.¹⁷ 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 stabilize 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, $-\text{OCH}_3$, 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 distances.²⁵

Nanoparticle 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 favorable or unfavorable 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 shapes.²⁹ 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 minimization of its total surface free energy. Contact with the support can lower the surface energy of certain NP's planes, favoring 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 NP.³⁵ Additionally, the effect of lattice mismatching is more pronounced for smaller metal nanoparticles, as observed for gold nanoparticles smaller than 3 nm supported on titania.³⁶

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 performance. 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 recognized 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 systems.⁴⁰

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 interface.⁴¹ 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 minimization 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 performance.⁴⁹

6.2.1 Modification of metal–support interactions

The 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 6.1b). Through this distinction, we aim to emphasize the similarities within one strategy, when applied to different families of catalysts, supports and reactions. In section 3 we start by discussing reports targeting modification mainly of the support, divided into strategies involving support composition,

morphology, doping and surface modifications. In section 4, strategies that focus on nanoparticle modifications are discussed, particularly changes in NP's size and composition. In section 5, we cover the approaches to tune MSI on as-prepared catalysts by use of treatments. The identified treatments include thermal, reducing agent, reduction-oxidation cycles, overlayer deposition and adsorbate-mediated treatments.

6.3 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.

6.3.1 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 Al₂O₃ compared to TiO₂. 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 TiO₂, given that carbonates bind stronger to Al₂O₃ than to TiO₂ 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 TiO₂ 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 % O₂), or dilution with inert SiC. For example, it has been reported that the mechanism of CO oxidation changes with reaction temperature.⁵²

The activity for benzyl alcohol oxidation followed the opposite trend as for CO oxidation with the intrinsic activity decreasing in the order

Au/Al₂O₃ > Au/SiO₂ > Au/TiO₂ > Au/ZnO (Figure 6.2a).⁵³ 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 6.2b).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 NPs.⁵⁵ 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 effect.⁵⁶

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 fibers 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 reaction.⁶⁰ 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 synthesize 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 perovskites.⁶¹

6.3.2 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 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 -Al₂O₃.⁶² 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 CeO₂.³⁵ 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 2·10⁻³ and 5·10⁻³ 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 TiO₂-supported Ru-promoted cobalt catalysts for the Fischer-Tropsch synthesis⁶³ and rhodium catalysts for steam reforming of propane⁶⁴, suboxide coverage was more extensive on TiO₂ 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 TiO₂-anatase support was shown to also influence the extent of SMSI and activity on Ru-Co/TiO₂ catalysts for the Fischer-Tropsch synthesis⁶⁵ and Ru/TiO₂ 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/TiO₂ for methanol oxidation⁶⁷, Co/CeO₂ and Ru/CeO₂ for ammonia synthesis^{68,69} and Au/CeO₂ (Figure 6.2c) 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 synthesizing nanostructured support particles of controlled shapes. The reason for the modified catalytic performance varied, however, from facilitated reactant/intermediate binding and charge transfer (Pt/TiO₂), enhanced support reduction (Co and Ru on CeO₂) to the occurrence of more vacancies (Au on CeO₂ 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-Au_{Zn} 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.

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 O₂ adsorption and increased CO oxidation activity from 30 to 70 % conversion at 47 °C. Similarly, the selectivity towards CH₄ of Ni NPs on planar siloxenes in CO₂ 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 support.⁷³ 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 Pt.⁷⁴ 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 Nb₂CT_x (where T accounts for various elements/groups) has been used as support for platinum nanoparticles and applied for the water–gas shift reaction.⁷⁵ The two-dimensionality of this carbide material aided in the formation of a Pt–Nb surface alloy by H₂ 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 H₂O activation. These exposed niobium atoms in contact with the Pt–Nb surface alloy showed strong affinities for H₂O 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/Al₂O₃ reference catalyst. The same research group has employed this material, platinum supported on niobium carbide (Pt/Nb₂CT_x), as well as platinum supported on titanium carbide (Pt/Ti₃C₂T_x) as catalysts for dehydrogenation of light alkanes.⁷⁶ In this case, Pt–Ti (Pt₃Ti) or Pt–Nb (Pt₃Nb) 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 photocatalysis is limited. This can be rationalized 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 TiO₂ 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 TiO₂, making photocatalytic water splitting more efficient.

Figure 6.2. 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).

6.3.3 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 stabilities.⁷⁹ 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 optimizing 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 support.⁸¹ These materials have a higher standard electrochemical potential than gold and are therefore termed noble carbons.⁸² This means that even gold is electron deficient, when supported on C_2N , resulting in active materials for ammonia synthesis via electrocatalytic reduction of nitrogen.⁸³ 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 methane.⁸⁴ During the reduction process, Ni catalyzed 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 methane.⁸⁵ 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+} ions.⁸⁶ 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 observed.⁸⁷ This resulted in 3 to 5 times higher Pt mass specific activity in electrocatalytic oxygen reduction than obtained with only one dopant (Figure 6.3a). 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 oxidation.⁸⁸ 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 stabilize the metal oxide by changing their reducibility. Trivalent dopants (Al^{3+} , Ga^{3+}) increased the conductivity of the support and activity in reverse water-gas shift and methanol synthesis, whereas divalent Mg^{2+} lowered the activity.

6.3.4 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 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 recognized for example by two groups working on surface functionalization 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-oxidized 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 functionalized support and noble metal nanoparticles substantially altered catalytic performance (Figure 6.3b).

Metal oxides can also be functionalized 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 catalysts.¹⁰²

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 metal.¹⁰³ 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.¹⁰⁴ utilized 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 catalysts. 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 6.3c). 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.

Figure 6.3. 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), oxidized (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-normalized 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).

6.4 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.

6.4.1 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 topic.¹⁰⁵ Focusing 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 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/CeO₂ catalyst (Figure 6.4a). 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 Ce³⁺ seems the limit for CeO₂ 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 6.7b). 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/CeO₂ in CO₂ hydrogenation varying between single atoms, 1 nm clusters and 4 nm NP. With increasing NP size, the electronic MSI interaction decreased which facilitated CO₂ activation and increased reactivity (Figure 6.4b). At the same time, H-spillover increased with NP size, hindering H₂O 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 CH₄ 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 CO₂ hydrogenation on γ -Al₂O₃. CO formation via reverse WGS was favored for Ru clusters while the selectivity shifted to CH₄ for larger NPs. One possible explanation for the different observations could be the nature of the supports that were employed (CeO₂ and γ -Al₂O₃), because the support was involved in the reaction in both cases. Notably, in Ru/ γ -Al₂O₃, the interface oxygen (Ru–O–Al) was shown via isotope labelling to exchange oxygen atoms with CO₂ during the reaction.

6.4.2 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 TiO₂(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 TiO₂. This has been experimentally observed for Au–Rh nanoparticles supported on titania nanorods¹¹⁰ (Figure 6.4c) and employed for tetralin hydrogenation in the presence of H₂S¹¹¹. The Au/Rh/TiO₂ stacking configuration had a detrimental effect on the initial hydrogenation activity. Eventually, Au/Rh/TiO₂ was more stable due to the stabilizing effect of gold against H₂S poisoning of Rh. Likewise, a

segregation of iridium from Au-Ir nanoparticles towards TiO₂ has been experimentally observed, resulting in higher resistance towards sintering than Au/TiO₂ during thermal treatments.¹¹²

For Au-Cu on Al₂O₃ and SiO₂ the NPs de-alloyed under oxidizing conditions on both supports to form Au NPs and a CuO_x phase. However, on Al₂O₃, CuO_x formed separate patches on the support, which prevented the creation of active Au-CuO_x interfacial sites present on SiO₂.¹¹³ Consequently, Au-CuO/SiO₂ approached 100 % CO conversion while Au-CuO/Al₂O₃ 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 TiO₂-induced metal segregation upon reduction using H₂, 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/TiO₂ 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 (Pt₃Ni) intermetallic compound thus favoring the formation of active Pt-Ni bonds rather than Ni-Ni. This in turn increased the selectivity of CO₂ reduction to CO instead of CH₄, 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/CeO₂ and non-supported Rh-Pd nanoparticles showed segregation of palladium to the surface. However, at conditions close to ethanol steam reforming the metals in the non-supported nanoparticles re-arranged back to a uniform distribution, whereas the CeO₂-supported ones maintained the Pd-rich surface. Because the Rh-CeO₂ interaction was stronger, the core-shell structure was maintained. Furthermore, the CeO₂-supported nanoparticles presented higher oxidation states, especially at the outermost layers due to H₂O activation at the CeO₂ surface. The high H₂ 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 TiO₂ 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 TiO₂. The ligands were decomposed using an N₂ treatment to form a carbon shell, which protected Au NPs from sintering. The higher overall CO oxidation activity of the N₂-treated sample was ascribed to smaller NP size. Gao et al.¹¹⁹ co-impregnated a nickel precursor and ligands on SiO₂ 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 CH₄ conversion, while the surface-specific activity remained unchanged ($\sim 2.5 \text{ s}^{-1}$).

Figure 6.4. 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 CO₂ methanation (ref.¹⁰⁷). **c** HAADF images and model reconstruction showing Rh segregation to the TiO₂ support for a reduced AuRh/TiO₂ sample and the energy scheme for two binding configurations of AuRh clusters to TiO₂ derived from DFT. Calculations point to Rh segregation to the support as the most favorable configuration (ref.¹¹⁰).

6.5 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.

6.5.1 Thermal treatment

Tang et al. investigated MSI for various group 11 metals on TiO₂ and for Au supported on various reducible oxidic supports.¹²⁰ 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 oxidizing 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–nanorods.¹²² Wang et al.¹²³ even avoided the necessity for reducing or oxidizing 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 effects.¹²⁴ 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 °C (Figure 6.5a).¹²⁵ The metal–support interface was maximized 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. Another example of the influence of temperature on support reduction was reported for Pd/TiO₂ in formaldehyde oxidation.¹²⁶ 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 Ni_7Si_3 phase was observed. The most active catalyst was obtained at 1000 °C with silicon-enriched phases $\text{Ni}_{31}\text{Si}_{12}$ and Ni_2Si . Additionally, coverage of metal nanoparticles by support suboxides generated at elevated temperature can steer hydrogenation selectivity, as summarized before¹²⁸.

6.5.2 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 agent. The SMSI state, characterized by suppressed CO chemisorption, negatively charged Pt NPs, and oxygen vacancies formation, was beneficial for toluene oxidation activity, which decreased in the order NaBH₄ > formaldehyde > H₂. Furthermore, the MSI effect was stronger on anatase than on rutile or P25, again highlighting the importance of the support morphology as discussed in section 3.2.

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 section 3.3).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 6.5c) 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).

6.5.3 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. 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 Pt 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 O_2) and H_2O_2 decomposition rate. By covering the small NPs and having a Pd^{2+} containing surface on the larger NPs, the H_2O_2 decomposition was almost completely suppressed, resulting in hydrogen selectivities towards H_2O_2 of 95 %.

Figure 6.5. 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 PtO_x on ceria 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), Co/Nb_2O_5 (red diamonds) and Co/Al_2O_3 (violet triangles). Singly reduced samples are indicated by open symbols (ref.¹³³).

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 treatment.⁴⁸ 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 6.5d-e). 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 oxidize 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.

6.5.4 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 stabilize the NPs via immobilization, as was the case for a carbon¹³⁴ and SiO₂¹³⁵ 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 state.¹³⁶ 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 SiO₂ over Pt/Al₂O₃ and observed the formation of Brønsted acid Si-O-Al sites. The SiO₂ overlayer decreased activity in cinnamaldehyde hydrogenation, possibly via site blockage by SiO₂, 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-ZrO₂ in a Cu/SiO₂ catalyst.¹³⁸ These interface sites enhanced the intrinsic activity for ethyl acetate formation from ethanol and for methanol synthesis from CO₂ by one order of magnitude. Furthermore, Moon et al.¹³⁹ applied an overlayer of various reducible oxides to a Pt/SiO₂ catalyst and investigated its effect on CO oxidation. The activity followed the order TiO₂>CeO₂>Pt/SiO₂>Ta₂O₅≈Nb₂O₅ and the increased activity was mainly ascribed to the formation of interfacial perimeter sites between Pt and the TiO₂ or CeO₂ overlayer. In addition, the overlayer made the catalyst more resistant towards sintering of Pt NP at elevated temperature.

Yang et al.¹⁴⁰ prepared Rh/SiO₂ catalysts covered with TiO₂ or Al₂O₃ and applied these for CO hydrogenation. The Al₂O₃ overlayer decreased the activity through site blockage. The TiO₂ overlayer, on the other hand, increased the intrinsic activity and selectivity towards C₅ alkanes and alkenes, while the selectivity towards higher alcohols remained unchanged. Its catalytic performance was similar to that of Rh NPs on TiO₂-coated SiO₂, 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 rationalized considering that overlayer deposition can be used to create artificial support suboxide coverage on NPs, thereby mimicking an SMSI state.¹⁴¹

Treatment of Au/TiO₂ with TiCl₃ at room temperature resulted in the formation of a TiO_x overlayer on Au, similar to SMSI.¹⁴² The TiO_x overlayer increased the activity of the catalyst for CO oxidation (0.68 vs. 0.26 mol_{CO}·mol_{Au}⁻¹·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 adsorption.

Copper phyllosilicates have been employed as precursor for the formation of silica-supported metal nanoparticles upon reduction in H₂, leading to high Cu loadings (~40–50 wt.%) with uniform distribution and particle size. The role of the generated Cu–SiO₂ interface in these materials has been exploited, for example, in the decomposition of methanol to hydrogen and dimethoxymethane in the liquid phase,¹⁴³ 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 optimized by use of a mesoporous silica layer coating the copper phyllosilicate prior H₂ activation (Figure 6.6a).¹⁴⁴ In ester hydrogenation, the bare Cu/SiO₂ obtained from copper phyllosilicate gave a TOF of 6.4·10⁻³ s⁻¹ and a selectivity to ethylene glycol of 23 %, whereas the performance of Cu/SiO₂ with a mesoporous silica layer increased with a TOF of 11.4·10⁻³ s⁻¹ and a selectivity to ethylene glycol of 96 %. The Cu–O–SiO_x interface was shown to stabilize the transition state of the ester (in this case dimethyl oxalate) and to activate H₂ in a heterolytic way forming Cu–H^{δ-} and SiO–H^{δ+}, as previously discussed for H₂ activation with nanosized non-reducible supports.

6.5.5 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/TiO₂ catalysts for CO₂ hydrogenation and found that a treatment in 20 % CO₂, 2 % H₂, 78 % He atmosphere at 250 °C caused the formation of HCO_x adsorbates on the Rh NPs. In the untreated 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 6.6b). 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.

Figure 6.6. 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/TiO₂ after a treatment in H₂ at 550 °C which induced a TiO_x bilayer (SMSI overlayer) and after treatment in 20CO₂:2H₂ at 250 °C which induced an amorphous TiO_x overlayer (A-SMSI overlayer). Production rates of CH₄ (red) and CO (grey) are shown on the chart for Rh supported on alumina or titania after H₂ or 20CO₂:2H₂ treatments (ref.¹⁴⁵).

6.6 Discussion

We analyzed 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.

Figure 6.7a 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 catalyst.¹⁰⁷

For the enhancement of selectivity, the largest increases were reported for treatments to modify MSI in catalysts for CO₂ hydrogenation (78–85 %), where preferential blockage/sintering of small Rh or Ru NPs or single atoms leads to a strong shift in selectivity from CH₄ towards CO.^{145,147} However, these strong increases in selectivity were accompanied by decreased activity, leading to productivity enhancement factor between 3 and 6. Besides these two examples, 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 analyzed.

The enhancement of productivity can be correlated with metal particle size of the catalyst after MSI tuning (Figure 6.7b, 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 rationalized 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.

Figure 6.7. Enhancement of catalytic performance in C_1 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.

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 functionalization for charge transfer to occur on a noticeable scale.¹⁰¹ 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 limited.¹⁴⁸ 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 table.¹⁴⁹ 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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Chapter 7

Activity enhancement of cobalt catalysts by tuning metal-support interactions

Abstract

Interactions between metal nanoparticles and support materials can strongly influence the performance of catalysts. In particular, reducible oxidic supports can form suboxides 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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7.1. 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, 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 sites.¹⁴ 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 metal²⁶⁻²⁹. 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 chapter, 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 $\text{Co/Nb}_2\text{O}_5$ 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.

7.2. Experimental

7.2.1. 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, TiO₂ (P25, Evonik, SA_{BET} : 50 m²·g⁻¹, PV: 0.30 cm³·g⁻¹), Nb₂O₅ (pseudo-hexagonal TT-phase, CBMM, SA_{BET} : 9 m²·g⁻¹, PV: 0.06 cm³·g⁻¹) and α -Al₂O₃ (BASF, SA_{BET} : 7 m²·g⁻¹, PV: 0.02 cm³·g⁻¹), were sieved to a grain size of 75–150 μ m. Nb₂O₅ was obtained from amorphous niobium oxide hydrate (HY-340, AD/4465, CBMM) by calcination in a muffle oven at 600 °C for 4 h.

For a typical impregnation, 2 g of support was pre-dried at 80 °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/TiO₂, 2 g of sample was dried and heat treated in fluidized bed mode in a U-shaped glass reactor following a previously reported procedure.³⁰ The sample was first dried at 80 °C for 2 h and heat treated directly afterwards at 250 °C for 2 h. Both steps were performed in 1 L·min⁻¹ N₂ upward flow with a heating ramp of 2 °C·min⁻¹. Co/Nb₂O₅ and Co/ α -Al₂O₃ catalysts were dried for 12 h at 60 °C overnight in stagnant air and subsequently calcined in a fixed bed reactor under N₂ flow (1 L·min⁻¹) at 350 °C for 2 h with a heating ramp of 3 °C·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 μ m.

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 °C for 2 h (2 °C·min⁻¹) in 120 mL·min⁻¹ of 25 vol.% H₂ in N₂ and subsequently cooled to 100 °C. At this point, the reactor was flushed with N₂ and cooled down further to 30 °C. The oxidation step followed directly after the reduction and was performed in 95 mL·min⁻¹ of 5 vol.% O₂ in N₂ at various temperatures up to 400 °C for 2 h with a 2 °C·min⁻¹ heating ramp.

7.2.2. 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 %, Sigma-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 volume/surface mean 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 ($1\text{ }^{\circ}\text{C}\cdot\text{min}^{-1}$) 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 nm^2 , an H/Co stoichiometry of 1 and spherical cobalt particles.³¹

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 $5\text{ }^{\circ}\text{C}\cdot\text{min}^{-1}$ 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.

7.2.3. 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 ($1\text{ }^{\circ}\text{C}\cdot\text{min}^{-1}$) 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 ($3\text{ }^{\circ}\text{C}\cdot\text{min}^{-1}$) 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 $1\text{ }^{\circ}\text{C}\cdot\text{min}^{-1}$. 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 7.1), CTY according to (Equation 7.2) and TOF according to (Equation 7.3). In these equations, X_{CO} is the CO conversion, $F_{\text{CO},\text{in}}$ is the flow of CO into the reactor and $F_{\text{CO},\text{out}}$ 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 nm^2 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 7.4) and the selectivity towards the heavier fraction ($n \geq 5$) as in (Equation 7.5) 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.

$X_{CO} = (F_{CO,in} - F_{CO,out}) \cdot F_{CO,in}^{-1}$	(Equation 7.1)
$CTY = F_{CO,in} \cdot X_{CO} \cdot V_m^{-1} \cdot m_{Co}^{-1}$	(Equation 7.2)
$TOF = CTY \cdot N_A \cdot d_{Co} \cdot SA_{Co}^{-1}$	(Equation 7.3)
$S_{Cl-C4} = F_{Cn} \cdot n \cdot (F_{CO,in} \cdot X_{CO})^{-1}$	(Equation 7.4)
$S_{C5+} = 1 - S_{Cl-C4}$	(Equation 7.5)

7.3. Results and discussion

7.3.1. 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 Appendix E, Table E1. 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 microscopy-energy-dispersive X-ray spectroscopy (STEM-EDX, Figure 7.1a-c). The cobalt particles were rather uniformly distributed over TiO₂ and Nb₂O₅ while the spatial distribution was more heterogeneous on α-Al₂O₃.

Table 7.1. 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] ± standard deviation (nm) ^a	Theoretical H ₂ -uptake (μmol _{H₂} ·g _{Co} ⁻¹) ^a	Experimental H ₂ -uptake (μmol _{H₂} ·g _{Co} ⁻¹) ^b
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

H₂-chemisorption and STEM-EDX results for the R-samples are given in Table 7.1. 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 H_2 -chemisorption measurement. It is important to note that the total amount of suboxide species is probably low, because no overlayers 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 study.³² 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.

Figure 7.1. Electron microscopy images of the samples upon reduction-oxidation-reduction treatments. STEM-EDX mapping of Co/TiO_2 , $\text{Co}/\text{Nb}_2\text{O}_5$ and $\text{Co}/\alpha\text{-Al}_2\text{O}_3$ 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 E, Figures E1-3.

7.3.2. 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 7.2a. 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.

Figure 7.2. 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.

The RO-samples were characterized by STEM-EDX mapping. Samples oxidized at low temperatures appeared unchanged (Figure 7.2b,c). However, at oxidation temperatures of 200 °C, hollow cobalt oxide particles were observed (Figure 7.1d-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.

7.3.3. Reduction-oxidation-reduction

The samples after an ROR cycle were characterized by H_2 -chemisorption (Figure 7.3a). 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- TiO_2 to $783 \mu\text{mol}_{\text{H}_2} \cdot \text{g}_{\text{Co}}^{-1}$ for RO200R- TiO_2 . Similarly, for Nb_2O_5 it increased from $265 \mu\text{mol}_{\text{H}_2} \cdot \text{g}_{\text{Co}}^{-1}$ for R- Nb_2O_5 to $657 \mu\text{mol}_{\text{H}_2} \cdot \text{g}_{\text{Co}}^{-1}$ for RO200R- Nb_2O_5 . 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- Nb_2O_5 (Appendix E, Figure E4 and Appendix E, Table E2). 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 7.1g-i). The spatial distribution of the particles over the supports was not markedly different from that in the R-samples (Figure 7.1a-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 7.3b-d, Table 7.1). 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 7.3e). 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 7.1f), 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 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.

Figure 7.3. 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.

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 E, Figure E5). This reduced the metallic surface area and counteracted the positive effect of the ROR treatment on the SMSI.

Figure 7.4. 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.

Further indications for the optimization of SMSI effects through ROR were found when the second reduction was performed at a higher temperature (Figure 7.4). The H₂-uptake decreased for the RO200R-TiO₂ and RO200R-Nb₂O₅ samples with increasing reduction temperature. At 350 °C, the H₂-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 H₂-uptakes of the R-samples at reduction temperatures of 220 and 350 °C were comparable. The substantial increase in H₂-uptake for the RO200R-samples was thus not merely caused by reduction at lower temperature. In contrast, the H₂-uptake of the Co/α-Al₂O₃ catalysts increased slightly at higher reduction temperatures.

7.3.4. Fischer-Tropsch synthesis

The catalytic activity of Co/TiO₂ and Co/Nb₂O₅ in FT after ROR followed the same trend as H₂-chemisorption, i.e. increased activity with the optimum at 200 °C (Figure 7.5a).

Notably, the activity doubled on TiO_2 and Nb_2O_5 as a result of the RO200R treatment and the enhancement was stable over at least 100 h time-on-stream (Appendix E, Figure E6). As expected, the activity of $\text{Co}/\alpha\text{-Al}_2\text{O}_3$ was not enhanced, indicating that the positive effect of the ROR treatment was specific for catalysts supported on reducible oxides. The C_{5+} -selectivity for all catalysts was 85–89 % and did not change significantly as a result of the ROR treatments (Appendix E, Table E3).

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 E, Figure E7). 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.

Figure 7.5. 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 hydrogen 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.

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 7.5b), indicating that the surface-specific activity or turnover frequency (TOF, based on activity and H_2 -chemisorption data; see SI for details) 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 $\text{Co/Nb}_2\text{O}_5$ 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 7.5b for $\text{Co/Nb}_2\text{O}_5$. Reduction at 250 °C gave only a moderate increase in H_2 -chemisorption and a corresponding increase in activity, while reduction at 220 °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 strength.⁴⁶ 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 E, Table E4). The values reported for the supports used in our work do predict higher TOF for TiO_2 and Nb_2O_5 compared to Al_2O_3 , but the comparison between TiO_2 and Nb_2O_5 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. Ti^{3+} , Nb^{4+} or Nb^{3+}) 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.

7.4. Conclusion

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 (TiO_2 and Nb_2O_5) and irreducible ($\alpha\text{-Al}_2\text{O}_3$) oxides followed by controlled oxidation led to hollow cobalt oxide particles via the Kirkendall effect. A second reduction resulted in a twofold increase in H_2 -uptake for the TiO_2 - and Nb_2O_5 -supported samples and a decrease for the $\alpha\text{-Al}_2\text{O}_3$ -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 TiO_2 and Nb_2O_5 and decreased slightly on $\alpha\text{-Al}_2\text{O}_3$. 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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Chapter 8a

Summary and concluding remarks

Summary

Heterogeneous catalysis is an essential technology for the production of fuels and chemicals. The demand for fossil fuels, and in particular liquid fuels for transportation, is expected to grow in the next two decades while limitations on CO₂ emissions are likely to become a major constraint for the production. Gas-to-liquids technology has the potential to reduce the overall CO₂ footprint of liquid fuels and to produce ultra clean fuels as an additional benefit.

The Fischer-Tropsch (FT) synthesis, i.e. the catalytic conversion of CO and H₂ to long-chain hydrocarbons, is an important component of the gas-to-liquids process. Nanosized cobalt particles on a support material are often used to catalyze FT and the structure of the nanoparticles can strongly affect their catalytic performance. For example, Co nanoparticle size and crystal structure effects have already been reported.

Further studies of cobalt structure performance relationships in FT could be facilitated with well-defined model catalysts based on cobalt nanocrystals (Co-NC), prepared using colloidal techniques. This provides, in principle, control over the size, shape, and composition of the Co-NC. However, subsequent attachment of the Co-NC to a support and activation are equally important for catalytic applications, but these are relatively unexplored research fields for non-noble metals. The aim of the research described in this thesis is to study the preparation and application of Co-NC-based model catalyst in FT to establish cobalt structure-performance relationships.

In **Chapter 2**, we investigated the effect of oxidative treatments of Co-NC on their attachment to carbon nanotubes (CNT) and activation for the Fischer-Tropsch synthesis. Attachment of ϵ -cobalt NC resulted in clustering of the NC and low activity. After low-temperature oxidation of the NC to CoO, the NC were attached uniformly to the CNT. The ligands were readily removed during *in situ* reduction and high activity was obtained. In fact, it was possible to fully activate a NC-based cobalt catalyst for FT using this mild procedure. High-temperature oxidation to Co₃O₄ led to more pronounced particle growth during *in situ* reduction or FT and therefore the catalytic activity was lower. A severe oxidative treatment was thus unnecessary and even counter-productive. Overall, mild, low-temperature oxidation was thus the preferred treatment for assembly and activation of the Co-NC-based catalysts.

In **Chapter 3**, we investigated the impact of CNT support oxidation on the structure and performance of cobalt-based catalysts in FT. Well-defined model catalysts on CNT and oxidized CNT (oxCNT) with 10 wt% Co loading were synthesized through attachment of colloidal 6 nm CoO-NC. The CoO-NC on pristine CNT were reduced completely to Co-NC and grew to 11 nm during reduction. In contrast, on oxCNT, only ~50 % CoO reduction was observed and the NC remained 7 nm, indicating a stronger metal-support interaction on oxCNT. Co-NC/CNT were exceptionally active in FT with a turnover frequency (TOF) of $150 \cdot 10^{-3} \text{ s}^{-1}$ and relatively stable. In comparison, the TOF on oxCNT was only $63 \cdot 10^{-3} \text{ s}^{-1}$ and the catalyst deactivated more extensively. Using *in situ* XRD, oxidation of CNT was found to result in 32 % less crystalline, metallic cobalt, which coincided with a 35 % lower initial TOF. The stronger deactivation with Co-NC on oxidized CNT could not be explained by

particle growth, NC restructuring, or Co oxidation during FT, leaving increased deposition of carbonaceous species as a possible cause.

In **Chapter 4**, we investigated the preparation of Co-NC supported on TiO₂ and SiO₂ and evaluated their catalytic performance in FT. 3–12 nm Co-NC were synthesized by a hot-injection method, oxidized at low temperature to restrict magnetic interactions and subsequently attached to TiO₂ or SiO₂. The catalytic activity of most TiO₂-supported samples was in line with that of a Co/TiO₂ sample prepared by impregnation of cobalt nitrate, proving that relevant catalytic data was obtained with these model catalysts. The cobalt-weight based activity of 3 nm Co-NC on TiO₂ was five-fold lower than expected and this was partially ascribed to loss of cobalt to the support. Furthermore, the TiO₂-supported Co particles and 3 nm Co-NC on SiO₂ sintered during reduction and FT, while 6 and 9 nm Co-NC on SiO₂ were stable. We proposed that the interaction between Co(O) and TiO₂ was responsible for the decreased stability of the Co-NC.

In **Chapter 5**, we investigated the synthesis of disk-shaped Co-NC, their deposition on a support and the effect of their anisotropy on FT. Disk-shaped hcp Co-NC were synthesized simultaneously with spherical ϵ Co-NC. After oxidation to CoO, these NC were deposited on low surface area silica. Electron microscopy analysis revealed that numerically 66 % of the deposited CoO-NC were disks and 34 % were spheres. After *in situ* reduction of the CoO-NC to Co, the Fischer-Tropsch activity of the disk-containing catalyst was only half that of a catalyst containing only spherical NC. Interestingly, the catalysts were stable and the size and shape of the NC were retained even for the disk-shaped Co-NC. XPS showed that most of the amine ligands were removed during activation/FT and *in situ* XRD revealed that the crystal structure of both catalysts during FT was similar, with NC with 3–5 nm polycrystalline domains and approximately 65 % hcp Co and 21–32 % fcc Co. Based on these experiments, we tentatively propose that changing the Co-NC shape from spheres to disks reduced FT activity because of enhanced occurrence of hcp (0001) facets.

In **Chapter 6**, we reviewed recent literature on tuning of metal-support interaction (MSI), focussing on strategies to enhance catalytic performance. This topic has received much attention in recent years, however, a systematic rationalization of the field is lacking due to the great diversity in catalysts, reactions and MSI modification strategies. In this review, we covered and categorized the recent progress in MSI tuning strategies to enhance catalytic performance for various reactions. Furthermore, we quantified recently reported productivity enhancements in C₁ chemistry resulting from MSI control. Our analysis showed that up to 15-fold productivity enhancement has been achieved and that MSI has large impact for metal nanoparticles smaller than 4 nm.

In **Chapter 7**, we investigated reduction-oxidation-reduction (ROR) treatments as a tool to tune MSI in supported cobalt catalysts to improve their FT performance. 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 MSI rather than re-dispersion of the cobalt phase. The

modified MSI doubled the catalytic FT activity of Co on TiO_2 and Nb_2O_5 while it decreased slightly for Co on $\alpha\text{-Al}_2\text{O}_3$. This increase in activity was caused by more accessible cobalt surface sites as revealed by the constant TOF, 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 FT catalysts.

Concluding remarks

The first aim was to develop a method to prepare supported model cobalt catalysts relevant for the Fischer-Tropsch synthesis. Oxidation of as-synthesized Co-NC at room temperature was identified as preferred treatment for uniform distribution of Co-NC on a support and their efficient activation, while minimizing the impact on NC properties. In chapters 2 to 5 we showed the versatility of this approach, as it was applied to prepare Co-NC on CNT (untreated and oxidized) and on the oxidic supports TiO_2 and SiO_2 . The main drawback of this approach for model catalyst synthesis is the inevitable loss of control over the crystal structure of the metal due to oxidation. We anticipate that this strategy of on purpose oxidizing as-synthesized NC at low temperature to circumvent magnetic interactions and consequent clustering of NC might prove useful for uniformly attaching other ferromagnetic metal NC to supports as well.

At present, these NC-based catalysts are suitable mainly for model studies and not for industrial application, because of their typically delicate and expensive synthesis procedure. Very few NC-based catalysts are therefore commercially available. However, relevance for industry comes from the insights that can potentially be gained from the model studies that can now be performed. Several examples of such studies are presented in this thesis, in which the synthesized NC-based catalysts are employed to establish structure-performance relationships.

First, functional groups and defects on CNT strengthened the metal-support interaction and made the catalysts more resistant to sintering, but also reduced catalytic intrinsic activity and selectivity through lowering of the amount crystalline Co and increasing the rate of deactivation. Notably, the activity of the Co-NC on pristine CNT was exceptionally high with a TOF of $150 \cdot 10^{-3} \text{ s}^{-1}$. Nevertheless, open questions still remain, such as the type of oxygen-containing functionalities on CNT, the location of the amorphous Co and the cause for the observed deactivation on oxCNT. If the understanding of these metal-support interactions progresses, it can hopefully be extrapolated to design optimal interfaces on industrially more relevant supports.

Second, the resistance of Co-NC to particle growth was higher on SiO_2 than on TiO_2 . Growth strongly depended on NC size with 3 nm being less stable than 6 nm and all initial sizes growing to approximately 12 nm on TiO_2 . The implication of these observations is that cobalt particles smaller than 12 nm are not stable on this particular type of TiO_2 , so it is questionable whether it would be worthwhile to target nanoparticles smaller than 12 nm for this catalyst.

Third, an effect of NC shape on FT performance was observed. Lower FT activity was obtained with disk-shaped than with spherical Co-NC, which was tentatively ascribed to increased exposure of hcp (0001) facets on the disks. Remarkably, the disk shape of the NC

endured the harsh FT conditions for over 100 h. This means that, in principle, other shapes have the potential to improve FT performance, provided that the exposure of more active facets is favored.

The advanced studies that can be performed with NC-based catalysts are not limited to the examples described in this thesis. Other interesting cobalt structure–FT performance studies could be performed using pre-formed NC, such as investigating promoter effects through precisely controlling the amount and location of promoters, or investigating catalyst stability and NC growth mechanisms through synthesis of a catalyst with a bimodal NC size distribution from mixed batches of NC. In addition, this approach could be extended in an analogous manner to other cobalt-catalyzed reactions or to NC of related metals.

In addition to model studies with Co-NC, we investigated the interplay between metal nanoparticles and supports in more detail. From a literature survey, it was concluded that tuning of metal-support interactions can lead to up to 15 times enhancement of productivity. In addition, we found that ROR treatments doubled the activity of cobalt on reducible supports by mitigating TiO_x - or NbO_x -overlayer coverage. This could be interesting from an application point of view, because it would allow process intensification using a relatively straightforward pre-treatment and the effect seems stable, at least during the 100 h that were investigated here.

Overall, the potential of Co-NC as model catalysts for FT as well as regulation of metal-support interactions for enhanced catalytic performance have been explored. The conclusions from the work described herein could lead to improved catalytic performance through rational catalyst design.

Chapter 8b

Nederlandse samenvatting

Samenvatting

Heterogene katalyse is een essentiële technologie voor de productie van brandstoffen en chemicaliën. Naar verwachting zal de vraag naar fossiele brandstoffen, en in het bijzonder vloeibare brandstoffen voor transport, de komende jaren toenemen terwijl restricties op CO₂-emmissies waarschijnlijk een serieuze beperking voor de productie zullen vormen. Het zogenaamde ‘gas-to-liquids’ (GTL) proces heeft de potentie om de netto CO₂-voetafdruk van vloeibare brandstoffen te reduceren en ultraschone brandstoffen te produceren als bijkomend voordeel.

De Fischer-Tropschsynthese (FT), d.w.z. de gekatalyseerde omzetting van CO en H₂ tot lange koolwaterstofketens, is een belangrijke component van GTL. Kobaltdeeltjes van enkele nanometers groot op een dragermateriaal worden vaak gebruikt als katalysator voor FT en de structuur van de nanodeeltjes kan hun katalytische prestaties sterk beïnvloeden. Effecten van de grootte en kristalstructuur van de kobaltnanodeeltjes zijn bijvoorbeeld al gerapporteerd.

Verdere studies naar de relaties tussen kobaltstructuur en FT-prestaties zouden gefaciliteerd kunnen worden met goed gedefinieerde modelkatalysatoren op basis van kobaltnanokristallen (Co-NC), bereid m.b.v. colloïdale technieken. Deze aanpak biedt in principe controle over de grootte, vorm en samenstelling van de Co-NC. De navolgende bevestiging van de Co-NC aan een dragermateriaal en activering zijn echter even belangrijk voor de toepassing als katalysator, maar hier is nog relatief weinig onderzoek aan gedaan voor onedele metalen. Het doel van het in dit proefschrift beschreven onderzoek is het bestuderen van de bereiding van modelkatalysatoren op basis van Co-NC en hun toepassing in FT om de relatie tussen kobaltstructuur en katalytische prestaties te onderzoeken.

In **Hoofdstuk 2** hebben we het effect van oxidatieve behandelingen van Co-NC op hun bevestiging aan koolstofnanobuisjes (CNT) en activering voor FT onderzocht. Bevestiging van ϵ -kobaltnanokristallen resulteerde in clustering van de NC en lage activiteit. Na oxidatie van de NC tot CoO bij lage temperatuur werden de NC uniform bevestigd aan de CNT. De liganden werden gemakkelijk verwijderd tijdens *in situ* reductie en hoge activiteit werd verkregen. Het was zelfs mogelijk om een op NC gebaseerde kobaltkatalysator volledig te activeren voor FT met behulp van deze milde procedure. Oxidatie tot Co₃O₄ bij hoge temperatuur leidde tot meer deeltjesgroei tijdens *in situ* reductie of FT en dus was de katalytische activiteit lager. Een zware oxidatieve behandeling was dus onnodig en zelf contraproductief. Milde oxidatie bij lage temperatuur genoot derhalve de voorkeur als behandeling voor de bevestiging en activering van de katalysatoren op basis van Co-NC.

In **Hoofdstuk 3** hebben we de impact van oxidatie van de drager bestaande uit CNT op de structuur en prestaties van kobaltkatalysatoren in FT onderzocht. Goed gedefinieerde modelkatalysatoren op CNT en geoxideerde CNT (oxCNT) met 10 gew.% kobaltbelading werden gesynthetiseerd door bevestiging van 6 nm colloïdale CoO-NC. De CoO-NC op onbehandelde CNT werden volledig gereduceerd tot Co-NC en groeiden tot 11 nm tijdens reductie. Dit in tegenstelling tot oxCNT, waar slechts ~50 % CoO-reductie werd waargenomen en de NC 7 nm bleven, wat duidde op een sterkere metaal-dragerinteractie met oxCNT. Co-NC/CNT waren uitzonderlijk actief in FT met een omzettingsfrequentie

(TOF) van $150 \cdot 10^{-3} \text{ s}^{-1}$ en relatief stabiel. Ter vergelijking, de TOF op oxCNT was slechts $63 \cdot 10^{-3} \text{ s}^{-1}$ en de katalysator deactiveerde sterker. Met behulp van *in situ* XRD bleek oxidatie van CNT te resulteren in 32 % minder kristallijn, metallisch kobalt, wat samenviel met een 35 % lagere initiële TOF. De sterkere deactivering van Co-NC op geoxideerde CNT kon niet worden verklaard door deeltjesgroei, herstructurering van de NC, of oxidatie van Co tijdens FT, waardoor een verhoogde afzetting van koolstofhoudende verbindingen als een mogelijke oorzaak overbleef.

In **Hoofdstuk 4** hebben we de bereiding van Co-NC op TiO_2 en SiO_2 als dragermateriaal onderzocht en hun katalytische prestaties in FT bestudeerd. Co-NC van 3-12 nm werden gesynthetiseerd met een hete-injectiemethode, geoxideerd bij lage temperatuur om magnetische interacties te beperken en vervolgens bevestigd aan TiO_2 of SiO_2 . De katalytische activiteit van de meeste TiO_2 -gedragen monsters kwam overeen met die van een Co/ TiO_2 monster bereid d.m.v. impregnatie van kobaltnitraat, waaruit bleek dat relevante data verkregen werd met deze modelkatalysatoren. De op kobaltgewicht gebaseerde activiteit van 3 nm Co-NC op TiO_2 was vijfmaal lager dan verwacht en dit werd gedeeltelijk toegeschreven aan verlies van kobalt aan de drager. Verder groeiden de kobaltdeeltjes op TiO_2 en de 3 nm Co-NC op SiO_2 tijdens reductie en FT, terwijl 6 en 9 nm Co-NC op SiO_2 stabiel waren. We stelden voor dat de interactie tussen Co(O) en TiO_2 verantwoordelijk was voor de verminderde stabiliteit van de Co-NC.

In **Hoofdstuk 5** hebben we de synthese van schijfvormige Co-NC, hun bevestiging aan een drager en het effect van hun anisotropie op FT onderzocht. Schijfvormige Co-NC met een hexagonale dichtste pakking (hdp) werden gelijktijdig gesynthetiseerd met bolvormige NC met de ϵ -kobaltstructuur. Na oxidatie tot CoO werden deze NC afgezet op SiO_2 met een laag specifiek oppervlak. Elektronenmicroscopische analyse toonde aan dat numeriek 66 % van de afgezette CoO-NC schijven en 34 % bollen waren. Na *in situ* reductie van de CoO-NC tot Co was de FT-activiteit van de katalysator met schijven slechts de helft van die van de katalysator met enkel bolvormige Co-NC. Interessant is dat de katalysatoren stabiel waren de grootte en vorm van de NC zelfs voor de schijfvormige Co-NC behouden bleef. XPS wees uit dat de meeste amineliganen werden verwijderd tijdens activering/FT en *in situ* XRD onthulde dat de kristalstructuur van beide katalysatoren tijdens FT vergelijkbaar was, nl. polykristallijne Co-NC met kristaldomeinen van 3-5 nm en ongeveer 65 % hdp Co en 21-32 % Co met kubische dichtste pakking. Op basis van deze experimenten stellen we voorlopig voor dat het veranderen van bolvormige naar schijfvormige Co-NC de FT-activiteit verlaagde door een toename van de relatieve hoeveelheid hdp (0001)-facetten.

In **Hoofdstuk 6** hebben we een overzicht gepresenteerd van de recente literatuur over het reguleren van metaal-dragerinteractie (MSI), met focus op strategieën om de katalytische prestaties te verhogen. Dit onderwerp heeft de afgelopen jaren veel aandacht gekregen, maar een systematische rationalisatie van het veld ontbreekt vanwege de grote diversiteit in katalysatoren, reacties en MSI-modificatiestrategieën. In dit hoofdstuk hebben we de recente vooruitgang in MSI-modificatiestrategieën om de katalytische prestaties voor verschillende reacties te verhogen behandeld en gecategoriseerd. Verder hebben we recent gerapporteerde productiviteitsverhogingen in C_1 -chemie als gevolg van MSI-regulatie gekwantificeerd. Onze analyse wees uit dat tot vijftienmaal

productiviteitsverhoging is bereikt en dat MSI een grote impact heeft voor metaalnanodeeltjes kleiner dan 4 nm.

In **Hoofdstuk 7** hebben we reductie-oxidatie-reductie (ROR) behandelingen onderzocht als methode om de metaal-dragerinteractie in gedragen kobaltkatalysatoren te reguleren om zo hun FT-prestaties te verhogen. Reductie van kobaltoxide op reduceerbare (TiO_2 en Nb_2O_5) en onreduceerbare ($\alpha\text{-Al}_2\text{O}_3$) metaaloxiden gevolgd door gecontroleerde oxidatie leidde tot holle kobaltoxidedeeltjes via het Kirkendall-effect. Een tweede reductie resulteerde in een verdubbeling van de H_2 -opname voor de TiO_2 - en Nb_2O_5 -gedragen monsters en een afname voor het $\alpha\text{-Al}_2\text{O}_3$ -gedragen monster. Dit effect werd toegeschreven aan modulatie van de metaal-dragerinteractie in plaats van herverdeling van het kobalt. De gemodificeerde metaal-dragerinteractie verdubbelde de katalytische FT-activiteit van Co op TiO_2 en Nb_2O_5 , terwijl de activiteit van Co op $\alpha\text{-Al}_2\text{O}_3$ licht afnam. De toename in activiteit werd veroorzaakt door meer toegankelijke kobaltoppervlaktes zoals bleek uit de constante TOF, terwijl het volledige promotie-effect van de TiO_x - of NbO_x -verbindingen behouden bleef. Het efficiëntere gebruik van het kobalt- en dragergrensvlak leidde tot uitzonderlijk actieve FT-katalysatoren.

Afsluitende opmerkingen

Het eerste doel was een methode te ontwikkelen voor het bereiden van gedragen model-kobaltkatalysatoren die relevant zijn voor de Fischer-Tropsch synthese. Oxidatie van gesynthetiseerde Co-NC bij kamertemperatuur werd geïdentificeerd als meest geschikte behandeling voor een uniforme verdeling van de Co-NC over een drager en efficiënte activering, terwijl de impact op de eigenschappen van de Co-NC geminimaliseerd werd. In de hoofdstukken 2 tot en met 5 hebben we de veelzijdigheid van deze aanpak gedemonstreerd, aangezien deze werd toegepast om Co-NC op CNT, zowel onbehandeld als geoxideerd, en op de oxidische dragers, TiO_2 en SiO_2 , te bereiden. Het grootste nadeel van deze benadering voor de synthese van modelkatalysatoren is het onvermijdelijke verlies van controle over de kristalstructuur van het metaal als gevolg van oxidatie. We verwachten dat deze strategie van opzettelijke oxidatie van gesynthetiseerde nanokristallen (NC) bij lage temperatuur om magnetische interacties en de daaruit volgende clustering van NC te omzeilen nuttig zou kunnen zijn om ook NC van andere ferromagnetische metalen uniform te bevestigen aan dragers.

Momenteel zijn deze op NC-gebaseerde katalysatoren vooral geschikt voor modelstudies en niet voor industriële toepassing vanwege hun typisch delicate en dure syntheseprocedure. Zeer weinig op NC-gebaseerde katalysatoren zijn daarom commercieel verkrijgbaar. De relevantie voor de industrie zit hem echter in de inzichten die mogelijk kunnen worden verkregen uit de modelstudies die nu kunnen worden uitgevoerd. Verschillende voorbeelden van dergelijke studies zijn gepresenteerd in dit proefschrift, waarin de gesynthetiseerde op NC-gebaseerde katalysatoren worden gebruikt om structuur-prestatie-relaties vast te stellen.

Ten eerste versterkten functionele groepen en defecten op CNT de metaal-dragerinteractie en maakten ze de katalysatoren beter bestand tegen deeltjesgroei, maar ze verlaagden tegelijkertijd de intrinsieke katalytische activiteit en selectiviteit door het

verminderen van de hoeveelheid kristallijn kobalt en het verhogen van de deactiveringssnelheid. Opmerkelijk genoeg was de activiteit van Co-NC op onbehandelde CNT uitzonderlijk hoog met een TOF van $150 \cdot 10^{-3} \text{ s}^{-1}$. Desondanks blijven er vragen onbeantwoord, zoals het type zuurstofbevattende functionele groepen op CNT, de locatie van het amorfe kobalt en de oorzaak van de waargenomen deactivering op oxCNT. Als het begrip van deze metaal-dragerinteracties vordert, kan het hopelijk worden geëxtrapoleerd om optimale grensvlakken te ontwerpen op industrieel relevantere dragers.

Ten tweede waren Co-NC op SiO_2 beter bestand tegen deeltjesgroei dan op TiO_2 . De deeltjesgroei hing sterk af van de grootte van de NC, waarbij 3 nm Co-NC minder stabiel waren dan 6 nm Co-NC en Co-NC van alle grootten op TiO_2 uiteindelijk groeiden tot ongeveer 12 nm. De implicatie van deze waarneming is dat kobaltdeltjes kleiner dan 12 nm niet stabiel zijn op dit specifieke type TiO_2 , dus is het de vraag of het de moeite waard is om streven naar nanodeeltjes kleiner dan 12 nm voor dit type katalysator.

Ten derde werd een effect van NC-vorm op FT-prestaties waargenomen. Lagere FT-activiteit werd verkregen met schijfvormige dan met bolvormige Co-NC en dit werd voorlopig toegeschreven aan verhoogde blootstelling van hdp (0001)-facetten op de schijven. Opmerkelijk is dat de schijfvorm van de Co-NC de FT-omstandigheden langer dan 100 uur heeft doorstaan. Dit betekent dat in principe andere vormen het potentieel hebben om FT-prestaties te verhogen, als tenminste actievere facetten blootgesteld worden.

De geavanceerde studies die uitgevoerd kunnen worden met op NC-gebaseerde katalysatoren zijn niet beperkt tot de voorbeelden die in dit proefschrift zijn beschreven. Andere interessante kobaltstructuur-FT-prestatiestudies kunnen worden uitgevoerd met behulp van NC, zoals het onderzoeken van promotoreffecten door de hoeveelheid en locatie van de promotors nauwkeurig te controleren, of het onderzoeken van katalysatorstabiliteit en groeimechanismen van NC door de bereiding van een katalysator met een bimodale NC-groottedistributie van gemengde partijen NC. Bovendien kan deze benadering op analoge wijze worden uitgebreid naar andere door kobalt gekatalyseerde reacties of naar NC van verwante metalen.

Naast modelstudies met Co-NC hebben we het samenspel tussen metaalnanodeeltjes en dragers onderzocht. Uit een literatuuronderzoek werd geconcludeerd dat regulering van de metaal-dragerinteractie tot vijftienmaal productiviteitsverhoging kan leiden. Bovendien ontdekten we dat ROR-behandelingen de FT-activiteit van kobalt op reduceerbare dragers verdubbelden door de bedekking door TiO_x - of NbO_x -verbindingen te verminderen. Dit kan interessant zijn voor de toepassing, omdat het procesintensificatie mogelijk maakt met behulp van een relatief eenvoudige voorbehandeling en het effect stabiel lijkt, in ieder geval gedurende de 100 uur die hier zijn onderzocht.

In het algemeen is het potentieel van Co-NC als modelkatalysatoren voor FT onderzocht alsook de regulering van metaal-dragerinteracties voor verbeterde katalytische prestaties. De conclusies van het hier beschreven werk kunnen leiden tot verbeterde katalytische prestaties door rationeel katalysatorontwerp.

Appendices

Appendix A

Electron diffraction of Co- and CoO-NC

Electron diffraction was performed on NC both untreated and after LT-oxidation. The electron diffraction pattern of the untreated NC was measured under cryo conditions using the TU/e CryoTitan microscope and the LT-oxidized NC under regular conditions using the Tecnai 12 microscope. The assignment of the diffraction pattern to a specific cobalt phase is given in Table A1.

Figure A1. Electron diffraction pattern of CoO-NC.

Table A1. Experimental d-spacing values for Co- and CoO-NC and reported values for the reference materials. Only the d-spacings with a relative intensity above 10 % are given.

Co-NC	ϵ -Co reference ¹	ϵ -Co reference ¹	CoO-NC	CoO reference ²	CoO reference ²
d (Å)	d (Å)	<i>h k l</i>	d (Å)	d (Å)	<i>h k l</i>
2.07	2.04	2 2 1	2.52	2.46	1 1 1
1.95	1.94	3 1 0	2.18	2.13	2 0 0
1.89	1.85	3 1 1	1.52	1.51	2 2 0
1.23	1.2	5 1 0	1.26	1.28	3 1 1
-	1.13	5 2 0	1.04	1.23	2 2 2

TEM of Co1/CNT

Figure A2. TEM image of Co1/CNT after drying and exposure to air.

XRD of Co/CNT Catalysts

Figure A3. XRD patterns of pristine CNT and the Co/CNT catalysts after various oxidative treatments.

Particle Size Analysis of Co2/CNT and Co3/CNT

Figure A4. Particle size distributions of Co2/CNT (red) and Co3/CNT (blue).

TGA of Co3/CNT

Figure A5. Combined TGA and MS results of Co3/CNT in 25 vol% H₂ with a heating ramp of 10 °C·min⁻¹.

Fischer-Tropsch Synthesis Activity

Figure A6. Cobalt time yield during the first 100 h time-on-stream at 20 bar, 220 °C, H₂/CO = 2 v/v, GHSV = 2350–7850 h⁻¹

Spent Catalysts

Figure A7. TEM analysis of the spent catalysts. TEM images of the spent catalysts of a Co1/CNT, b Co2/CNT and c Co3/CNT after more than 100 h TOS and the cobalt particle size distributions of the fresh (open fill) and spent (solid fill) of d Co2/CNT and e Co3/CNT.

Reported Turnover Frequencies

The turnover frequencies that were used as a comparison were recalculated from publications by Herranz et al.³ and by Delgado et al.⁴ Their catalysts, testing conditions and units to express the TOF differed from ours, which made recalculation necessary. The results of which are given in Table A2.

Herranz et al. synthesized CoO–NC using a similar $\text{Co}_2(\text{CO})_8$ decomposition method as reported here, but in the presence of both oleic acid and trioctylphosphine oxide (TOPO) as surfactants. The NC were deposited on silica with a BET surface area of $300 \text{ m}^2\cdot\text{g}^{-1}$. The catalytic tests were performed under methanation conditions at 1 bar, 240°C and $\text{H}_2/\text{CO}/\text{Ar} = 3/10/20 \text{ v/v/v}$. The TOF values were derived from Figure 5, in which the TOF was defined as the number of CO molecules converted per number of Co atoms at the surface per second. According to the unit indicated, the values should be multiplied by a factor 10^3 , but the resulting TOF would be unrealistically high and lead to CO conversion levels of 10^5 – $10^6 \%$. Rather, we assumed the multiplication factor to be 10^{-3} . The TOF at 220°C was derived from the values TOF at 240°C . To this end, the Arrhenius equation and the experimentally determined activation energy ($105 \text{ kJ}\cdot\text{mol}^{-1}$) were used to correct for the temperature difference. Unfortunately, it is not straightforward to correct for the effect of different reaction pressures and feed compositions. Especially at higher pressure, approximately a twofold increase in TOF can be expected.⁵

The NC by Delgado et al. were prepared through reduction of cobalt chloride by sodium borohydride as a reducing agent in the presence of polyvinylpyrrolidone (PVP) as surfactant. Subsequently, the NC were emplaced on TiO_2 P25. The applied FT conditions were 20 bar, 240°C and $\text{H}_2/\text{CO} = 2 \text{ v/v}$ and the TOF values were reported in mol CO converted per mol Co surface atoms per hour. These values were first divided by $3600 \text{ s}\cdot\text{h}^{-1}$ to obtain a TOF per second and afterwards recalculated for a reaction temperature of 220°C using again the Arrhenius equation. A typical activation energy of $100 \text{ kJ}\cdot\text{mol}^{-1}$ was assumed.

The significant discrepancy between the TOF reported here and those reported previously for LT- or non-oxidized NC-based catalysts was remarkable, because those catalysts were rather comparable to ours, in particular the discussed Co/ SiO_2 catalysts. Although the cause was not established, the most significant difference appeared to be in the choice of surfactants. Only oleic acid was used as a surfactant in our NC synthesis, whereas also TOPO was used by Herranz et al. TOPO reportedly poisons the catalytic activity in CO_2 hydrogenation⁶ and therefore, a similar poisoning effect could have occurred as well in FT. In the case of Delgado et al., boron from the reducing agent, NaBH_4 , remained in the catalysts and probably affected the catalytic performance considerably.

Table A2. Turnover frequencies reported in literature for LT- or non-oxidized NC-based catalysts. The TOF were converted to the same units and to the same reaction temperatures.

Herranz et al. ³			Delgado et al. ⁴			
Average particle diameter (nm)	TOF at 240 °C (10 ⁻³ s ⁻¹)	TOF at 220 °C (10 ⁻³ s ⁻¹)	Average particle diameter (nm)	TOF at 240 °C (h ⁻¹)	TOF at 240 °C (10 ⁻³ s ⁻¹)	TOF at 220 °C (10 ⁻³ s ⁻¹)
3.0	0.6	0.2	1.8	19	5.1	2.0
4.2	0.8	0.3	2.6	13	3.5	1.4
4.6	1.0	0.4	5.2	6.6	1.8	0.7
5.3	0.8	0.3	7.0	2.1	0.6	0.2
10	1.9	0.7	–	–	–	–

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Appendix B

Methods

In situ XRD quantitative phase analysis

In situ XRD results were analyzed by Rietveld refinement using Bruker TOPAS v5.0 software. A LaB_6 standard reference material (660c) from the National Institute of Standards and Technology was measured and fitted using the fundamental parameters approach to determine the emission profile and instrument details. The K-emission profile of Mo was refined to $K_{\alpha 1}$ emission of 0.708856 Å and $K_{\alpha 2}$ emission of 0.712992 Å, while simultaneously refining a 4th order Chebyshev polynomial background, tube tails, cylindrical 2θ correction (Sabine), and sample displacement and tilt. The obtained emission profile and instrument details were applied in the analysis of all samples.

The bare supports, CNT and oxCNT, were measured at ambient conditions to establish the contribution of the support as well as the background. The XRD profile was fitted between 9 and 35 ° 2θ using a 5th order Chebyshev polynomial background. The CNT and oxCNT structures were experimentally determined by refining a graphite structure (ICDD PDF-4+2016, PDF 04-014-0362) through tuning of the lattice parameters within ± 0.06 Å, crystallite size (Gaussian) and strain (Lorentzian), and preferential orientations in the [111] and [011] directions using the March-Dollase model. The amorphous phase was modelled using two pseudo-Voigt peaks around 10.3 and 21.5 ° 2θ . Simultaneously, cylindrical 2θ correction (Sabine) and sample displacement and tilt were refined.

The XRD patterns of the catalysts were fitted using the determined (ox)CNT and amorphous phase contributions in combination with identified cobalt phases obtained from the ICDD PDF-4+2016 database, i.e. hcp Co (PDF 04-001-3273), fcc Co (PDF 04-001-2681) and CoO (PDF 04-001-8626). The structures of (ox)CNT and the amorphous phase were fixed, leaving only the possibility for scaling. For the Co phases, the lattice parameters were constrained by ± 0.05 Å, although for most phases variations of ± 0.02 Å were obtained. Size broadening was described using Lorentzian functions, while strain broadening was not included in the analysis, as that did not improve the quality of the fit. For hcp Co, preferred orientations in the [100] and [001] directions were also refined using the March-Dollase model. We tentatively propose that this is because of an hcp-fcc intergrowth phase that needs to be taken into account (see results and discussion in the main text). The average crystallite size was determined as the volume weighted mean column length, derived from the integral peak breadth using a crystallite shape factor (k) of 1. A 5th order Chebyshev polynomial background, cylindrical 2θ correction (Sabine) and sample displacement and tilt were refined together with the (ox)CNT contribution and the Co and amorphous phases.

Results

Figure B1. N₂-physorption isotherms of CNT and oxCNT.

Figure B2. Particle size distributions derived from TEM of the as-prepared samples (brown), the reduced samples (aqua) and spent samples (orange) together with the fitted lognormal distributions. The particle size distributions are given for **a** Co-NC/CNT and **b** Co-NC/oxCNT. Particles >20 nm (if present) were not taken into account for the lognormal distributions.

Figure B3. High-resolution TEM results after reduction and passivation of **a** Co-NC/CNT and **b** Co-NC/oxCNT.

Figure B4. C_{5+} -selectivity of the two catalysts during 100 h on stream at 20 bar, 220 °C, $H_2/CO = 2$, GHSV = 5950–8900 h^{-1} .

Figure B5. TEM images after >100 h FT and passivation of **a** Co-NC/CNT and **b** Co-NC/oxCNT.

Figure B6. Rietveld Refinement results and diffraction patterns of Co-NC/CNT and Co-NC/oxCNT obtained with *in situ* XRD during FT between 32 and 42 h on stream at 10 bar, 220 °C and $\text{H}_2/\text{CO} = 2 \text{ v/v}$. Five scans of 2 h were accumulated and no change in the diffraction patterns was apparent over the course of the reaction. Reference patterns of the bare supports were measured at ambient conditions and refined.

Figure B7. Diffraction patterns of **a** Co-NC/CNT and **b** Co-NC/oxCNT obtained with *in situ* XRD after reduction, measured at 1 bar, 180 °C and 25 vol% H₂ in He flow, and during FT between 32 and 42 h on stream at 10 bar, 220 °C and H₂/CO = 2 v/v.

Appendix C

Figure C1. Schematic illustration of the catalyst synthesis procedure.

Figure C2. Histograms and lognormal distributions of Co-NC that were later attached to SiO₂.

Figure C3. N₂-physisorption isotherms of the bare supports, TiO₂ and SiO₂.

Table C1. N₂-physisorption results of the bare supports, TiO₂ and SiO₂.

Support	S _A _{BET} (m ² ·g ⁻¹)	Pore volume (mL·g ⁻¹) ^a
TiO ₂ P25	53	0.31
SiO ₂ Aerosil OX50	43	0.14

^a Determined at P/P₀ = 0.995

Figure C4. TEM analysis of pristine IWI-Co/TiO₂ after heat treatment in N₂. TEM image (left) with the arrows indicating several Co₃O₄ particles and the corresponding histogram and lognormal distribution (right).

Figure C5. Deconvolution of the TPR profiles of the Co/TiO₂ samples. Three Gaussian contributions (dashed colored lines) were combined to give the overall fit (black solid line) to the experimental data (solid colored lines).

Figure C6. Cobalt-weight-based activity of the SiO₂-supported Co-NC against time-on-stream. FT was performed at 20 bar, 220 °C, 2 H₂/CO (v/v), GHSV = 1500–10750 h⁻¹ and X_{CO} = 15–30 %.

Figure C7. Overview of the samples after catalysis. HAADF-STEM-EDX of spent Co/TiO₂ samples are in the left column (Co in red) and TEM of the SiO₂-supported samples is in the right column. **a** Co₃/TiO₂, **b** Co₃/SiO₂, **c** Co₆/TiO₂, **d** Co₆/SiO₂, **e** Co₁₂/TiO₂, **f** Co₉/SiO₂ and **g** IWI-Co/TiO₂.

Figure C8. Quantification of the cobalt content in the support of the reduced Co/TiO₂ samples. HAADF-STEM-EDX map of **a** Co₃/TiO₂ and **c** Co₃/SiO₂ both after reduction (Co in red) and **b,d** the same location with only the Co signal from EDX, respectively. Parts of the samples without any visible particles are highlighted as Area #1.

The cobalt content in the support was determined using the ratio between the Co, O and Ti/Si signals in the highlighted area obtained by quantification of the EDX spectra using FEI Velox software. The same was done for the complete field of view and gave the total Co content, so both in the support and in the NC. The difference between the two represented the amount of Co residing in the NC. The results of multiple EDX maps (4–13) was averaged.

Figure C9. Diffractogram of reduced and passivated IWI-Co/TiO₂ as measured by XRD. The expected diffractions for TiO₂ in the anatase and rutile phase are provided. No cobalt phases were apparent.

Figure C10. Thermodynamic equilibrium composition calculations on the formation of mixed metal-support compounds of Co/TiO₂ (left) and Co/SiO₂ (right). Equilibrium calculations based on the Gibbs free energy were performed with HSC Chemistry 7.1 software using 1 kmol CoO(s), 100 kmol TiO₂(s) or SiO₂(s) and 100 kmol H₂(g) as starting compounds and a constant number of atoms and pressure (1 bar). All available solid Co, CoO_x, Ti, TiO_x and TiH_x and mixed Co-TiO_x species in the database (or the Si analogues) were included as possible reaction products together with gaseous H₂, H₂O and O₂. A large excess of H₂ and TiO₂ or SiO₂ with respect to CoO was selected to keep the partial pressure of H₂O formed upon reduction of CoO low, in line with the experimental conditions during reduction in a plug flow reactor.

Based on these calculations, it is thermodynamically possible to form small amounts of cobalt titanates in a reducing environment at the relevant temperatures, whilst cobalt silicates are not stable under the same conditions. N.B. H₂ and the supports are outside of the scale of the plots.

Figure C11. Effect of ligand removal on the particle growth in Co₃/TiO₂ (left) and Co₃/SiO₂ (right). The histograms and lognormal distributions are shown for the catalysts in the pristine, spent and cleaned and then spent state. Ligands were removed by plasma cleaning for 8 h prior to reduction and catalysis. No effect was observed on the particle size after catalysis on TiO₂ but it did reduce the sintering in Co₃/SiO₂.

Figure C12. Sintering behavior of IWI-Co/TiO₂ after >100 h on stream at 20 bar, 220 °C, 2 H₂/CO. The histograms and lognormal distributions of the IWI-Co/TiO₂ before (left) and after catalysis (right) are shown together with the histograms and lognormal distributions for the NC-based Co6/TiO₂ and Co12/TiO₂ samples as comparison.

Figure C13. Effect of prolonged reduction on the particle growth in Co12/TiO₂. The histograms and lognormal distributions are shown for Co12/TiO₂ in the pristine state and after reduction at 350 °C for 8 and 16 h. Prolonged reduction did not influence the final particle size.

Figure C14. The size evolution of individual Co-NC in Co12/TiO₂ during reduction. a HAADF-STEM and c HAADF-STEM-EDX images of pristine Co12/TiO₂. b HAADF-STEM and d HAADF-STEM-EDX images of the same locations after reduction at 350 °C for 8 h. Co is depicted in red. The highlighted area contains two particles that disintegrated during reduction and formed multiple smaller particles.

Appendix D

Methods

In situ XRD quantitative phase analysis

The diffractograms from *in situ* XRD were analyzed by Rietveld refinement using Bruker TOPAS v5.0 software. First, a LaB₆ standard reference material (660c) from the National Institute of Standards and Technology was measured and fitted using the fundamental parameters approach to determine the emission profile and instrument details. The K-emission profile of Mo was refined to K_{α1} emission of 0.708856 Å and K_{α2} emission of 0.712992 Å, while simultaneously refining a 4th order Chebyshev polynomial background, tube tails, cylindrical 2θ correction (Sabine), and sample displacement and tilt. The obtained emission profile and instrument details were applied in the analysis of all samples.

The bare support was measured to establish the contribution of the support as well as the background from the sample holder, e.g. the borosilicate capillary and quartz wool. The XRD profile was fitted between 7 and 37.5 ° 2θ using a 4th order Chebyshev polynomial background and 8 pseudo-Voigt peaks. Simultaneously, cylindrical 2θ correction (Sabine) and sample displacement and tilt were refined.

The XRD patterns of the catalysts were fitted using the determined SiO₂ contribution in combination with identified cobalt phases obtained from the ICDD PDF-4+2016 database, i.e. hcp Co (PDF 04-001-3273), fcc Co (PDF 04-001-2681) and CoO (PDF 04-001-8626). The SiO₂ contribution was predominantly fixed, leaving only the possibility for scaling. For the Co phases, the lattice parameters were constrained by ±0.05 Å, although for most phases variations of ±0.02 Å were obtained. Size broadening was described using Lorentzian functions, while strain broadening was not included in the analysis, because that did not improve the quality of the fit. For hcp Co, preferred orientations in the [100] and [001] directions were also refined using the March-Dollase model. We tentatively propose that this is because of an hcp-fcc intergrowth phase that needs to be taken into account (see results and discussion in the main text). The average crystallite size was determined as the volume weighted mean column length, derived from the integral peak breadth using a crystallite shape factor (k) of 1. A 4th order Chebyshev polynomial background, cylindrical 2θ correction (Sabine) and sample displacement and tilt were refined together with the SiO₂ contribution and the Co phases.

Results

Figure D1. TEM image of the precipitate from magnetic separation directly after the synthesis of disk-shaped and spherical Co-NC. The rounded, high-contrast particles were classified as spherical NC and the low-contrast and elongated, high-contrast NC were classified as disk-shaped Co-NC.

Figure D2. Size distributions of 100 disk-shaped Co-NC. Histogram of **a** the diameter, **b** the height and **c** the resulting aspect ratio of the Co-NC.

Figure D3. Tilting series of a TEM sample with disk-shaped and spherical CoO-NC between -50 and 50° with an interval of 10° .

Figure D4. TEM analysis of the diameter of 100 disk-shaped and 100 spherical Co-NC before and after tilting the TEM sample by 50°. **a** the diameter at 50° plotted against the diameter of the same NC at 0° with the diagonal dashed line indicating an unchanged diameter. **b** Histogram of the diameter at 50° (d_{50}) over the diameter at 0° (d_0).

Figure D5. Illustration of the predicted projection length of a Co-NC disk tilted by 50°. The theoretical projection length at 50° was calculated as $x = \cos(50^\circ) \cdot d + \cos(40^\circ) \cdot h$.

Figure D6. Intensity profile obtained by radially averaging and background correcting the SAED pattern from the inset of Figure 5.2a. The peak at $d = 2.19 \text{ \AA}$ could be assigned exclusively to hcp cobalt. The following reference diffraction patterns were obtained from the PDF-4+ 2016 database: fcc Co (00-015-0806), hcp Co (01-071-4652), ϵ Co (04-017-5578), CoO (00-042-1300), Co_3O_4 (00-042-1467)

Figure D7. High-resolution TEM under cryogenic conditions of as-synthesized disk-shaped and spherical Co-NC with little to no solvent present. **a** TEM image with in the framed area an 11 nm, high-contrast NC that was classified as spherical. **b** Fourier transform of the highlighted area. The lack of hexagonal symmetry together with the obtained lattice spacings (2.14, 1.93 and 1.70 $\text{\AA}$) indicated that the particle consisted of ϵ -cobalt.

Figure D8. TEM images of a batch of mixture of disk-shaped and spherical Co-NC attached to SiO₂. The Co underwent only one precipitation-redispersion cycle after synthesis and were attached to SiO₂ afterwards. **a** and **b** are two images of this sample showing inhomogeneous distribution of the Co-NC.

Figure D9. Fischer-Tropsch synthesis results of Co-D/SiO₂ and Co-S/SiO₂ at 20 bar, 220 °C and H₂/CO = 2 v/v. **a** C₅₊-selectivity as a function of time-on-stream and **b** ASF product distribution averaged between 80-100 h on stream. The trendlines fitted to the solid filled datapoints (C₄-C₇) were used to determine α .

Figure D10. XPS survey scans of the catalysts in the pristine and spent state and a bare SiO₂ reference. The spent catalysts were measured after 100 h FT and subsequent passivation. The data was offset with $1 \cdot 10^5$ CPS increment at 0 eV binding energy. The regions of interest are labelled.

Figure D11. *In situ* XRD profiles and Rietveld refinement results of the Co-NC/SiO₂ during Fischer-Tropsch synthesis. The bare SiO₂ support was measured under ambient conditions as a reference. The diffractograms were obtained over the first 18 h on stream at 10 bar, 220 °C and H₂/CO = 2 v/v by accumulating six scans of 3 h. No change in the XRD patterns was observed over the course of the reaction.

Appendix E

Figure E1. Additional electron microscopy images of the TiO_2 -supported samples upon reduction-oxidation-reduction treatments. STEM-HAADF combined with EDX mapping of Co/ TiO_2 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- TiO_2); **e, f, g, h** samples after reduction at 350 °C and oxidation at 200 °C (RO200- TiO_2); **i, j, k, l** samples after reduction at 350 °C, oxidation at 200 °C and reduction at 220 °C (RO200R- TiO_2) and passivation.

Figure E2. Additional electron microscopy images of the Nb₂O₅-supported samples upon reduction-oxidation-reduction treatments. STEM-HAADF combined with EDX mapping of Co/Nb₂O₅ 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-Nb₂O₅); **e, f, g, h** samples after reduction at 350 °C and oxidation at 200 °C (RO200-Nb₂O₅); **i, j, k, l** samples after reduction at 350 °C, oxidation at 200 °C and reduction at 220 °C (RO200R-Nb₂O₅) and passivation.

Figure E3. 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.

Table E1. 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/ α -Al ₂ O ₃	6.0

Figure E4. 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 E2. The degree of cobalt reduction 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 E5. 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 E6. Cobalt-weight-based activity over time-on-stream. Cobalt-weight-based catalytic activity of Co/TiO₂, Co/Nb₂O₅ and Co/Al₂O₃ 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 E3. Summary of the catalytic performance at 20 bar, 220 °C and H₂/CO = 2 V/V. The reported data was averaged over three data points between 90–100 h on stream.

Sample	GHSV (h ⁻¹)	CO conv. (%)	Cobalt– Time– Yield ^a	TOF (s ⁻¹)	Selectivity (%)		
					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
α-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

^a in 10⁻⁵ mol_{CO}·g_{Co}⁻¹·s⁻¹

Figure E7. 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 $\text{H}_2/\text{CO} = 2 \text{ V/V}$ in all cases, except ref.⁹ where $\text{H}_2/\text{CO} = 1 \text{ V/V}$. 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 E4. Lewis acidity of various metal oxides. Data was obtained from ref¹⁴

Formal oxidation state of the cation (N _M)	Formula of the corresponding metal oxide	Lewis acid character (N _M –2δ _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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In preparation.

van Deelen, T. W., Yoshida, H., Oord, R., Zečević, J., Weckhuysen, B. M. & de Jong, K. P. Cobalt nanocrystals on carbon nanotubes in the Fischer-Tropsch synthesis: the impact of support oxidation.

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Presentations

Oral presentations

van Deelen, T. W. & de Jong, K. P. Cobalt Nanocrystals as Model Catalysts for the Fischer-Tropsch Synthesis.

12th Natural Gas Conversion Symposium, San Antonio, TX, US (June 2019)

van Deelen, T. W. & de Jong, K. P. Assembly and Activation of Cobalt Nanocrystal Catalysts for the Fischer-Tropsch Synthesis.

13th European Congress on Catalysis, Florence, Italy (August 2017)

van Deelen, T. W. & de Jong, K. P. Assembly and Activation of Cobalt Nanocrystal Catalysts for the Fischer-Tropsch Synthesis.

25th North American Catalysis Society Meeting, Denver, CO, US (June 2017)

van Deelen, T. W. & de Jong, K. P. Assembly and Activation of Cobalt Nanocrystal Catalysts for the Fischer-Tropsch Synthesis.

18th Netherlands Catalysis and Chemistry Conference (NCCC), Noordwijkerhout, The Netherlands (April 2017)

Poster presentations

van Deelen, T. W., Nijhuis, J. J., Krans, N. A., Zečević, J. & de Jong, K. P. Support-Dependent Growth of Cobalt Nanocrystals Applied as Fischer-Tropsch Catalysts

19th Netherlands Catalysis and Chemistry Conference (NCCC), Noordwijkerhout, The Netherlands (April 2018)

van Deelen, T. W., Su, H., Sommerdijk, N. A. J. M. & de Jong, K. P. Supported Cobalt Colloids as Model Catalysts in the Fischer-Tropsch Synthesis

17th Netherlands Catalysis and Chemistry Conference (NCCC), Noordwijkerhout, The Netherlands (April 2016)

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Curriculum vitae

Tom van Deelen was born on December 9, 1991 in Soest, The Netherlands. After completing his pre-university education at the Johan van Oldenbarnevelt Gymnasium in Amersfoort in 2009, he studied chemistry at Utrecht University and obtained a bachelor degree in 2012. He continued his education at Utrecht University and graduated from the master program 'Nanomaterials: Chemistry and Physics' in 2014. His main research project was entitled 'Niobia-Promoted Co/CNT Catalysts for the Fischer-Tropsch Synthesis' and was supervised by dr.

Arjan den Otter and prof. Krijn de Jong. In addition, he worked on the synthesis of novel hydroprocessing catalysts during an industrial internship at Albemarle in Amsterdam under supervision of dr. Jana Juan-Alcañiz and dr. Jaap Bergwerff

In 2014, Tom started a PhD research project on the application of colloidal cobalt nanocrystals in the synthesis of supported cobalt catalysts for the Fischer-Tropsch synthesis in the Inorganic Chemistry and Catalysis group at Utrecht University under supervision of prof. Krijn de Jong. The results of this research are described in this thesis.