MASTER THESIS

Structure-performance relationships of cobalt supported on carbon materials in the Fischer-Tropsch synthesis

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Abstract

Fischer-Tropsch synthesis over supported cobalt catalysts is an important industrial process for the conversion of synthesis gas to hydrocarbons. Although enormous efforts have yet been devoted to understand the fundamental aspects of the Fischer-Tropsch synthesis, the influence of the support structure still remains subject of debate. This is largely caused by poorly reported synthesis procedures and reaction conditions, which makes reproducibility and mutual comparison difficult. In this research, mesoporous carbon supports with well-defined ordered pore structures were synthesized. These carbon materials ruled out effects induced by variations in pore size and mixed metal-support phases. Thereby, quantitative analysis of the results and visualization with electron microscopy was facilitated. After examination of the catalyst synthesis procedure, it was found that defects in the carbon structure and oxygen functionalities on the carbon surface could serve as anchoring points and prevent undesired particle growth during catalysis. Confinement of cobalt nanoparticles in support pores was also found to be a powerful tool for preparing stable catalysts. Two phenomena had to be considered when pore confinement was used to stabilize cobalt nanoparticles during catalysis. Firstly, the pores should be large enough to enclose at least 6 nm sized cobalt particles. Smaller particles mainly produced methane, which is a valueless Fischer-Tropsch synthesis product. Secondly, pore blocking should be considered. Especially when pores are only accesible from two sides, pore blocking could shield part of the active metal species from reactants, resulting in low catalytic activity. When cobalt nanoparticles were insufficiently stabilized by the support material, particle growth occurred. If this happened to a large extent, the amount of catalytically active sites decreased, resulting in lower catalytic activity. Carbon-supported cobalt catalysts seemed to display two different particle growth mechanisms. Ostwald ripening was proposed when cobalt nanoparticles had initially a bi- or multimodal size distribution. Migration and coalescence was proposed when cobalt particles were uniformly sized. Finally, a true understanding of structure-performance relationships will provide rational catalyst design and ultimately the development of highly active, selective, and stable catalysts, both for fundamental research and large-scale industrial processes.

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List of Abbreviations

2D	Two-dimensional
3D	Three-dimensional
ACSA	Atomic cross section area
ASF	Anderson-Schulz-Flory
BET	Brunauer-Emmett-Teller
BF	Bright field
BJH	Barrett-Joyner-Halenda
BOE	Barrel of Oil Equivalent
CA	Carbon aerogel
СВ	Carbon black
CDC	Carbide-derived carbon
CMK-3	Carbon Mesostructured by KAIST-3
CMK-8	Carbon Mesostructured by KAIST-8
CNFs	Carbon nanofibers
CNTs	Carbon nanotubes
Со	Cobalt
CTY	Cobalt-time yield
DF	Dark field
EDX	Energy dispersive X-ray spectroscopy
EXAFS	Extended X-ray absorption fine structure
Fe	Iron
FID	Flame ionization detector
FT	Fischer-Tropsch
FTS	Fischer-Tropsch synthesis
FWHM	Full width at half maximum
GC	Gas chromatography
GJ	Gigajoules
GTL	Gas-to-Liquids technology
H ₂ -TPR	Hydrogen temperature programmed reduction
HAADF	High-angle annular dark-field
HTFT	High-temperature Fischer-Tropsch
IWI	Incipient wetness impregnation

KAIST	Korean Institute of Science and Technology
KIT-6	Korea Institute of Technology-6
LTFT	Low-temperature Fischer-Tropsch
MC	Migration and coalescence
MSA	Metallic surface area
NASDAQ	National Association of Securities Dealers Automated Quotations
\mathbf{N}_{AV}	Avogadro constant (6.022 x 10^{23} mol ⁻¹)
n.d.	not determined
NOMC	Non-ordered mesoporous carbon
NP(s)	Nanoparticle(s)
OM-CDC	Ordered mesoporous carbide-derived carbon
OMC	Ordered mesoporous carbon
OPEC	Organization of the Petroleum Exporting Countries
OR	Ostwald ripening
PEO	polyethylene oxide
PPO	polypropylene oxide
PSD	Pore size distribution
RT	Room temperature
SBA-15	Santa Barbara Amorphous-15
SSA	Specific surface area
STM	Scanning tunneling microscopy
STY	Space-time yield
STEM	Scanning transmission electron microscopy
TEM	Transmission electron microscopy
TEOS	Tetraethyl orthosilicate
TCD	Thermal conductivity detector
TGA-MS	Thermographimetric analysis/mass spectrometry
TOF	Turnover frequency
TOS	Time on stream
WGS	Water-gas shift
WTY	Weight-time yield
XANES	X-ray absorption near edge structure
XRD	X-ray diffraction

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Chapter 1

Introduction

1.1 An alternative for crude oil

The world's fuel and chemical production is currently to a large extent based on crude oil. In 2014 4.2 billion tons were extracted and processed worldwide.¹ However, the reserves of crude oil are slowly becoming depleted and the urge for alternatives is increasing. Because of that, the production of synthesis gas, a mixture of CO and H₂, and its conversion to a range of fuels and chemicals becomes economically more viable.² Synthesis gas can be obtained from the combustion of biomass, natural gas, or coal. The conversion of synthesis gas to fuels and chemicals is also known as the Fischer-Tropsch (FT) process, which offers a potential alternative for the depletion of crude oil reserves.³

Fischer-Tropsch Synthesis (FTS) is a heterogeneous catalytic process for the conversion of synthesis gas into clean hydrocarbon fuels and valuable chemicals. It is worthwhile to mention that there has been a renewed scientific interest in this process, which is mainly due to:

- (i) The costs and availability of crude oil. Currently, the crude oil prices are around U.S.\$45 *per* barrel according to the NASDAQ Stock Market. Besides, the crude oil prices are expected to rise to U.S.\$55 *per* barrel in 2017 according to the NASDAQ forecast. This predicted increase is based on the decision of Organization of the Petroleum Exporting Countries (OPEC) to limit the production of crude oil after a long period of unrestrained output.⁴ Hence, it is expected that the interest in alternatives for crude oil will continue to increase in the future.
- (ii) Stricter environmental laws regarding pollution. Diesel fuels derived from crude oil are contaminated with sulfur, nitrogen and aromatics, that cause pollutant emission from the engine. On the contrary, the clean FTS diesel fuels contain virtually no heteroatoms and aromatics, resulting in reduced pollutant emissions.⁵ Moreover, diesel fuels produced with FTS exhibit outstanding properties compared to diesel fuels derived from crude oil, such as a very high cetane number.
- (iii) The large amount of natural gas reserves available compared to the reserves of crude oil. The production of synthesis gas from natural gas accounts for over 60% of the total cost of the overall FT process. Currently, the prices of natural gas are U.S.\$2.6 per Gigajoules (GJ)

and in 2016 these prices have varied between U.S.\$2.5 and U.S.\$3.5 *per* GJ according to the NASDAQ. In order to compare prices of natural gas and crude oil, the term "Barrel of Oil Equivalent" (BOE) is used. This term expresses the energy content of a barrel of oil, which is 6.1 GJ.⁶ In terms of energy cost, the average production price for crude oil from natural gas is U.S.\$18 *per* barrel in 2016. Additionally, we should take into consideration that the thermal efficiency of a Gas-to-Liquid (GTL) facility is about 65%.⁷ Hence, the prices of crude oil should be well above U.S.\$28 *per* barrel to make the GTL process economically viable. The minimum price *per* barrel excludes the additional costs of capital, operating costs and the costs of catalyst production. This illustrates that any carbon source being used must be available at low cost in order for the FT process to be economically viable.⁸ The different technologies available to generate synthesis gas are discussed elsewhere.⁹

1.2 Fischer-Tropsch Synthesis in general

FTS can be visualized as a surfacecatalyzed polymerization process with CH_x monomers, which are formed by hydrogenation of adsorbed CO. This leads to the production of hydrocarbons with a broad range of chain lengths and functionalities.¹¹ The carbon number distribution of the product can be described by the Anderson-Schulz-Flory (ASF) polymerization model. According to this model, the chain growth probability (α) depends on the reaction conditions and the catalyst, but is assumed to be independent of the carbon chain length. ¹⁰ α can be determined by constructing ASF plots. Either the weight fraction or the mole fraction of a certain hydrocarbon fragment is divided by



Figure 1.1. Calculated hydrocarbon distributions for varying chain growth probability α . Reproduced from Ref.¹⁰

its carbon number and the natural logarithm of this value is plotted against the carbon number. The slope of the ASF plot is then proportional to $ln(\alpha)$. Hydrocarbon distributions can be calculated from different values of α as shown in **Fig. 1.1**. More detailed information and relevant equations for the calculation of α values can be found in scientific literature.^{10,12,13}

FTS is a highly exothermic process (see eqn 1.1) and it follows from thermodynamics that the water-gas shift (WGS) reaction occurs simultaneously (see eqn 1.2). This reaction is an equilibrium in which CO and H₂O are converted into CO₂ and H₂ byproducts. The FT process generally includes a reaction to produce n-paraffins (eqn. 1.3) and another reaction to produce α -olefins (eqn. 1.4).¹⁴ Besides those two types of products, FTS also produces alcohols,

aldehydes, acids and aromatic compounds in various amounts.¹⁵ The most commonly used catalysts for FTS are those based on cobalt (Co) or iron (Fe). The first is used for the production of higher paraffins, while the latter exhibits a selectivity towards lower olefins.

$$CO + 2 H_2 \rightarrow -CH_2 - + H_2O \quad \triangle H^0 = -165 \text{ kJ} \cdot \text{mol}^{-1}$$
 (1.1)

$$CO + H_2O \rightleftharpoons H_2 + CO_2 \qquad \triangle H^0 = -42 \text{ kJ} \cdot \text{mol}^{-1}$$
(1.2)

$$n \operatorname{CO} + (2n+1) \operatorname{H}_2 \to \operatorname{C}_n \operatorname{H}_{2n+2} + n \operatorname{H}_2 \operatorname{O} \quad \text{paraffins}$$
(1.3)

$$n \operatorname{CO} + 2n \operatorname{H}_2 \to \operatorname{C}_n \operatorname{H}_{2n} + n \operatorname{H}_2 \operatorname{O} \qquad \text{olefins} \qquad (1.4)$$

From an industrial viewpoint it is most viable to maximize the value of the chain growth probability (α) during FTS in order to produce long chain waxes. Subsequently, hydrocracking can be performed in order to give a maximum yield of products in the diesel distillate range (C₉-C₂₂).¹⁶

The overall process includes three important steps: Conversion of carbon feedstock to synthesis gas, conversion of synthesis gas into long-chain hydrocarbon products and hydrocracking of the long-chain hydrocarbons. A detailed scheme of the relevant steps in the overall FT process, including synthesis gas production from natural gas and hydrocracking, is given in **Fig. 1.2**.



Figure 1.2. Flow chart of the relevant steps in the overall Fischer-Tropsch process. Reproduced from Ref.⁸

1.2.1 Operating modes and reactor design

The FTS can be operated in low-temperature modes and in high-temperature modes. High temperatures generally lead to increased methane formation, enhanced carbon deposition on the catalyst and decrease of the average molecular weight of the products.¹⁷ In low-temperature modes generally a lower catalytic activity is observed compared to high-temperature modes.¹⁸

Low-temperature Fischer-Tropsch (LTFT) synthesis is operated in a temperature range of 200-240°C with iron or cobalt catalysts.² LTFT aims on the production of long-chain hydrocarbons, such as wax, diesel and naphta. The reaction system includes three phases: Solid (catalyst), liquid (heavy hydrocarbons) and gas (reactants, steam and light hydrocarbons). The reactors that are used can either be slurry phase reactors or (multitubular) fixed bed reactors.¹⁹

High-temperature Fischer-Tropsch (HTFT) synthesis on the other hand is operated in a temperature range of 300-350°C with iron catalysts.² Cobalt catalysts are not used in HTFT synthesis because of their high methane production at elevated temperatures. HTFT aims on the production of gasoline and light olefins and the reaction system includes two phases: Solid (catalyst) and gas (hydrocarbons). The reactors that are used can either be circulating fluid bed reactors or fixed fluid bed reactors.¹⁹



Figure 1.3. Overview of FT reactors. Reproduced from Ref.²⁰

FTS is an exothermic process and therefore it has a relatively high potential for sintering of catalytically active metal nanoparticles (NPs). Sintering leads to a decrease of active metallic surface area and thereby to deactivation of the catalyst. This process is thermodynamically driven by the surface free energy minimization of small particles. Excessive heat enhances this energetically favorable process. Isothermal conditions are important and the reactor system should thus be chosen with care. Fixed bed reactors may have poor heat transfer rates, especially in the gas-solid mode, since the gaseous phase has low heat conductivity and the heat removal capacity is therefore low. This could lead to temperature gradients in the reactor and even "hot spots" may arise in the catalyst. The variation of temperature in both the reactor and the catalyst itself could affect the results of FTS. On the laboratory scale, desired isothermal conditions can be optimized by diluting the catalyst with a smaller inert solid, such as SiC, while keeping all the other parameters unvaried.²¹ Another precaution that could be taken, is to choose support materials with high heat conductivity.

Moving bed reactors, such as slurry phase and fluidized bed reactors, have a much higher heat removal capability and therefore a higher reactor capacity compared to fixed bed reactors. However, the movement of the catalyst bed can have an undesired influence on the particle size, known as attrition.²⁰ Microchannel reactors have been developed with the aim to combine the best of both fixed and moving bed reactors. The catalyst bed is stationary and the very small tube diameter enhances the heat removal capability.²² An overview of the reactor types can be found in **Fig. 1.3**. More details regarding the development of these reactors can be found in scientific literature.^{2,17,19,23}

1.2.2 Reaction mechanism

In 1926 the carbide mechanism was formulated by Fischer and Tropsch.²⁴ This mechanism assumes dissociative chemisorption of H₂ and CO, followed by the formation of a metal carbide and hydrogenation of the chemisorbed carbon producing CH₂ monomers. Chain growth proceeds stepwise by insertion of CH₂ monomers in the alkyl chains. Chain termination can occur either by β -H abstraction or hydrogenation. The former process leads to production of α -olefins, while the latter produces n-paraffins. The overall scheme is depicted in **Fig. 1.4**.



Figure 1.4. Overall scheme of the carbide mechanism. Reproduced from Ref.²⁵

In the 1950s it was recognized that the carbide mechanism was not consistent with thermodynamic data for the formation of FT products by direct hydrogenation of carbides at the FTS reaction temperatures.²⁶ Another flaw of the carbide mechanism was that it did not account for the oxygenates that were formed during FTS. A new mechanism, the oxygenate mechanism, was therefore developed by Storch et al. in 1951^{27} and gained general acceptance. According to this mechanism CO is chemisorbed and reacts with adsorbed H₂ to form adsorbed hydroxyl carbenes, =CH(OH), which can grow by a combination of condensation and water elimination steps using adjacent groups.²⁸ Chain termination occurs via different pathways to form paraffins, olefins or oxygenates. The overall scheme is depicted in **Fig. 1.5**.



Figure 1.5. Overall scheme of the oxygenate mechanism. Reproduced from Ref.²⁵

In the 1970s Pichler and Schulz proposed a CO insertion mechanism. In this mechanism chain growth proceeds via direct insertion of a CO molecule into a carbon-metal bond, which is produced by hydrogenation of a surface carbonyl group.²⁹ Chain termination could occur via numerous routes including desorption, hydrogenation and insertion of oxygenated species.³⁰ The overall scheme is depicted in **Fig. 1.6**.



Figure 1.6. Overall scheme of the CO insertion mechanism. Reproduced from Ref.²⁵

Since then, several other mechanisms have been proposed and this matter still remains a controversial issue among scientists.^{8,31} A detailed discussion on the FT mechanism is beyond the scope of this thesis. Nevertheless, several articles and review papers are available on the topic for the interested reader.^{2,11,17,25,30}

1.3 Fischer-Tropsch synthesis catalysts

The FTS mechanism is complicated, since numerous reactions can occur simultaneously. The surface of a FT catalyst is very heterogeneous. It follows that many active intermediate species are likely to be present and may be involved in chain growth and termination.³⁰

Depending on what kind of products are desired, a catalyst can be chosen. The Group VIII metals ruthenium, iron, cobalt and nickel are the most active metals for the hydrogenation of carbon monoxide.²¹ However, a disadvantage of nickel is that it produces mainly methane under practical reaction conditions. Ruthenium is also less applied on industrial scale, because it is scarce and very expensive. Consequently, iron- and cobalt-based catalysts are most suitable for industrial applications. The first is mainly used to produce lower olefins under HTFT conditions, while the latter exhibits a higher selectivity towards higher paraffins under LTFT conditions.³² Cobalt-based catalysts are more active per weight of metal, more stable towards deactivation by water, less active for the competing WGS reaction, and produce less oxygenates than iron-based catalysts.³³ Due to the low activity for the WGS reaction, cobalt catalysts are unable to significantly alter the amount of H₂ during FTS. Therefore, they can only operate at a narrow range of $H_2/CO \approx 2$, whereas iron catalysts can produce hydrocarbons at a broader range of H₂/CO ratios. Iron catalysts are more appropriate for conversion of biomass-derived synthesis gas, which has a relatively low H₂/CO ratio.²¹ Studies on the parameters affecting the selectivity and the kinetics of the FTS reaction are a direct consequence of its complexity. Understanding these parameters is of key importance for improving existing FTS processes. From an industrial viewpoint it is most viable to maximize the hydrocarbon product chain length and to perform hydrocracking after FTS. Based on the average weight of the FTS products, cobalt catalysts are usually preferred for the synthesis of long-chain paraffins. The remainder of this thesis will therefore exclusively focus on cobalt FTS.

1.3.1 Catalytic performance

Key parameters for evaluating the performance of cobalt FTS catalysts are activity, selectivity and stability. The catalytic performance can be influenced in various ways. For example by altering the catalyst preparation method, changing the cobalt loading or using different support materials. The role of the support material still remains subject of debate³¹ and will therefore be the main focus of this project. The support material controls several factors, that directly influence the catalytic performance. Not only metal-support interactions play a role, but also the pore size, pore texture and specific surface area are key factors.

The catalyst activity can be reported in various manners. The relevant activity expressions are listed in **Table 1.1**. Cobalt FTS catalysts aim to produce long-chain waxes and the selectivity is therefore reported as C_{5+} selectivity. This is the selectivity towards products that contain five or more carbon atoms in the hydrocarbon chains. Besides, it is conventional to report the C_1 selectivity. Methane formation should be minimized during FTS, as it is an invaluable product.

Expression	Formula	Description
CO conver-	CO [1 -1] CO [1 -1]	Percentage of CO molecules con-
conv	$\frac{\text{CO}_{\text{in}}[\text{mL·s}^{-1}] - \text{CO}_{\text{out}}[\text{mL·s}^{-1}]}{\text{CO}_{\text{in}}[\text{mL·s}^{-1}]} \cdot 100\%$	verted [%]
Space-time yield (STY)	$\frac{\mathrm{CO_{in}[mol \cdot s^{-1}]} \cdot \frac{\mathrm{CO_{conv}[\%]}}{100}}{\mathrm{V_{cat}[m^3]}}$	Moles of CO converted <i>per</i> unit volume <i>per</i> second. High bulk densities favor the STY. $[mol_{CO} \cdot m^{-3} \cdot s^{-1}]$
Weight- time yield (WTY)	$\frac{CO_{in}[mol \cdot s^{-1}] \cdot \frac{CO_{conv}[\%]}{100}}{m_{cat}[g]}$	Moles of CO converted <i>per</i> gram of catalyst <i>per</i> second. $[mol_{CO} \cdot g_{cat}^{-1} \cdot s^{-1}]$
Cobalt- time yield (CTY)	$\frac{\mathrm{CO}_{in}[\mathrm{mL}\cdot\mathrm{s}^{-1}]\cdot\mathrm{CO}\mathrm{conv}[\%]}{\mathrm{m}_{cat}[\mathrm{g}]\cdot\mathrm{Co}\ \mathrm{loading}[\mathrm{wt}.\%]\cdot\mathrm{V}_{m}[\mathrm{mL}\cdot\mathrm{mol}^{-1}]}$	Moles of CO converted <i>per</i> gram cobalt <i>per</i> second. High cobalt dispersions and reducibility fa- vor the CTY. $[mol_{CO} \cdot g_{Co}^{-1} \cdot s^{-1}]$
Turnover frequency (TOF)	$\frac{\mathrm{CTY}\cdot\mathrm{ACSA^a}~\mathrm{Co}[\mathrm{m}^2]\cdot~\mathrm{N}^b_{AV}[\mathrm{mol}^{-1}]}{\mathrm{MSA^c}[\mathrm{m}^2\mathrm{g}_{\mathrm{Co}}^{-1}]}$	Moles of CO converted <i>per</i> cobalt surface atom <i>per</i> second. The TOF represents the intrinsic ac- tivity of an active site. $[s^{-1}]$

Table 1.1. Overview of FTS activity expressions.

^a ACSA: Atomic cross section area

^b N_{AV} : Avogadro constant

^c MSA: Metallic surface area

Additionally, stability represents an important factor for the process economics. Noble metals, including cobalt, are generally available at high costs, which demand an enduring catalyst lifetime in order to make the FTS process economically viable.³⁴ It is therefore desirable to understand the deactivation mechanisms and to minimize their consequences. The various catalyst deactivation mechanisms as reported in literature³⁵ are listed below. Due to the complex nature of FTS it remains difficult to appoint the true cause of deactivation and in reality different mechanisms might occur simultaneously.



Figure 1.7. The two main sintering mechanisms: Coalescence and Ostwald ripening.

- Sintering or particle growth is induced by the high chemical potential and the high surface free energy of small metal species.³⁶ Sintering is especially prominent at elevated temperatures and occurs predominantly via two mechanisms: Migration and coalescence (MC) or Ostwald ripening (OR) (see **Fig. 1.7**). MC occurs when two metal NPs agglomerate to form one larger particle. Metal NPs should have large interparticle distances in order to minimize MC by increasing the energy barrier for migration. OR is the dissociation of atoms or molecules with a net flux from small to large particles, resulting in the formation of larger particles. Metal NPs should be uniformly sized in order to minimize OR by minimizing the net flux of atoms or molecules.³⁷ Minimization of both MC and OR can be achieved by dispersing metal NPs accros a suitable support material.
- Re-oxidation of active metallic cobalt is caused by the presence of water during FTS. It has been shown with calculations that re-oxidation under typical FT conditions is only possible when the cobalt crystallite size is below 5 nm in diameter.^{11,38} In contradiction, further reduction of cobalt oxide species during FTS has been proposed as well. These ambivalent results emphasize the simultaneous importance of catalyst preparation methods, support materials and experimental conditions.
- Carbidization of cobalt species has been reported by *in situ* and XRD studies. Carbidization seems to be reversible upon mild hydrogen treatments.
- Coke formation on the catalyst surface affects the activity due to diffusion inhibition and pore plugging. The carbon species may accumulate to form more stable species, which can physically block the support surface or chemisorb on catalytically active sites.
- Reconstruction of the cobalt surface occurs under FTS reaction conditions. The driving force for this process is the minimization of the surface free energy. The newly formed surface may be less active in the FTS.
- Formation of mixed cobalt-support species, which are hardly reducible. This phenomenon depends strongly on the support material that is used.
- Attrition is the fragmentation of catalyst particles. This is particularly applicable to fluid bed reactors.
- Poisoning by sulfur impurities and possibly nitrogen contaminants in the feedstock. Sulphur species in the form of H₂S or COS can block the catalytically active sites.

1.3.2 Catalyst support material

Transition metals are catalytically active due to their electronic configurations, that enable them to temporarily exchange electrons with reacting species. The valence shells of transition metals are partially filled d-orbitals. The electrons in the d-orbitals of transition metal catalysts are easily lost and gained. The catalytic properties of metallic particles are significantly enhanced upon down-sizing to the nanoscale, ³⁶ since the chemical potential of metal atoms in a NP is inversely proportional to the radius of that metal NP. Transition metal NPs display activity in

the catalysis of numerous industrially relevant processes. This activity is largely dominated by the available metallic surface area.

The FTS reaction is classified as sympathetic structure sensitive by using the classification of Che and Bennett.³⁹ This means that the TOF increases with particle size and, sometimes, it also shows a maximum at intermediate particle size. Sympathetic structure sensitivity originates from the dissociation of the triple C-O bond. The dissociation of this strong bond requires an ensemble of surface metal atoms arranged as a step on the surface, also referred to as the B5 site (see **Fig. 1.8**).

Drawbacks that arise in the use of metal



Figure 1.8. Top (*a*) and side (b) view of the pentacoordinated B5 site which occurs at the step where (100) and (111) planes intersect. Image adapted from Ref.³⁴

NPs are the high chemical potential and the high surface free energy of the small metal particles. Due to these properties, metal NPs are prone to particle growth. This leads to a decrease in available metallic surface area and therefore results in a lower catalytic activity. In order to prepare active, selective and stable catalysts, metal NPs should be dispersed across a suitable support material.

Very recently, it was found that the type of interaction between cobalt NPs and the support material is of the utmost importance to the catalytic properties of cobalt FTS catalysts.³¹ Due to the complex reaction network of FTS, elucidating the true role of the support material on catalytic performance provokes discussions and confusion among scientists. Different aspects, such as the cobalt particle size effect, FTS reaction mechanism and catalyst deactivation mechanism may be interrelated and influence both each other and the catalytic properties. It becomes even more complicated when we take into consideration that the amount of active sites changes with the physical and chemical environment of the catalyst. Active sites may be blocked by adsorbed species⁴⁰ or the cobalt surface may rearrange⁴¹ upon exposure to high temperatures and reductive gases. Hence, the true role of the support material on catalytic performance still remains subject of debate.

This is illustrated by an educative example: The cobalt particle size effect. This effect describes the general observation that cobalt particles below a certain critical size, display both a lower TOF and a higher methane selectivity compared to cobalt particles above that critical size.^{42,43} Research groups all over the world have attempted to reveal the origin of this effect. However, the origin has been described inconsistently in scientific literature. In 2009, Den Breejen *et al.* had attributed it to both blockage of edge/corner sites and a lower intrinsic activity on the terraces.⁴³ At the same time, Prieto *et al.* had connected the effect to surface reconstruction towards more open crystal planes and/or defect sites.⁴¹ Then, in 2010 Yang *et al.* had related the effect to blockage of active sites by adsorbed C and O species on the catalyst surface.⁴⁰ Even more contradictory results were obtained by Wang *et al.*, who reported in 2011 that FTS is in general structure insensitive and that no intrinsic particle size effect was observed. They had asscribed the apparent particle size effect to cobalt oxidation during FTS for small cobalt crystallites.⁴⁴ The conflicting results implicate that observations depend critically on measurement techniques and conditions. Moreover, the observations might even be support

dependent.

The influence of the support structure on FTS performance has been studied already by Lesaint *et al.* in 2008 with mesoporous alumina and it was concluded that the support plays an important role in catalytic performance, as it influences several factors.⁴⁵ However, the surface of an oxidic support, such as alumina, silica or titania is terminated by hydroxyl groups. These surface groups can facilitate strong metal-support interactions, which decrease the reducibility of the metal. Moreover, the strong interactions complicate the analysis of the results due to induced electronic effects. Carbon would be more suitable for studying the true influence of the support structure on catalytic performance. Different from oxidic supports, the carbon surface is not or only marginally terminated by hydroxyl surface groups. Consequently, undesired mixed metal-support phases are not formed when carbon is used as a support material⁴⁶ and effects caused by these undesired phases can be ruled out during the analysis of the results.

It is known from literature that carbon-supported catalysts with average cobalt particle sizes close to an optimum value of 6-8 nm, favor the shift of the FTS reaction towards the desired paraffins. Larger particles display a lower TOF and smaller particles display both a lower TOF and a lower C_{5+} selectivity.⁴² Carbon support material is an excellent candidate for enhancing catalytic performance,⁴⁷ since it expells the co-produced water and heat. The formation of "hot spots" can be avoided due to the good thermal conductivity properties of carbons. Furthermore, carbon materials have a higher surface area, which aids to disperse the catalytic NPs and increase the number of active sites. It was also found that carbon support reduces the metal-support interactions and enhances the metal oxide reduction.⁴⁶ A problem that might arise with carbon support material, is the sintering of metallic cobalt species. It is known from literature that carbon supports generally interact weakly with metal NPs due to the lack of anchoring points on the carbon surface.^{48,49}

Cage-type mesoporous carbon materials in which cobalt can be confined have been selected as catalyst support for this research. Nanosized metal particles confined in the cages of wellordered mesopores are known to reveal unexpectedly high selectivity or conversion due to the enhanced adsorption and the increased local density of the reactants.⁵⁰ Besides, it has been demonstrated that cobalt confined in mesoporous materials with narrow pore size distribution (PSD) did not experience sintering, even after FTS.^{50–52} Ordered mesoporous carbons (OMCs) are preferred over other porous carbons for their high surface areas, well-interconnected pores and controllable pore sizes.⁵³ Well-defined ordered structures facilitate visualization and quantitative analysis of the results by excluding effects induced by variations in pore length or diameter.⁵⁴ A true understanding of the influence of the support structure on catalytic performance will provide opportunities for the development of active, selective and stable FT catalysts, both for fundamental research and large-scale industrial processes.

1.3.3 Nanocasting

Cage-type mesoporous carbon materials can be prepared *via* the nanocasting technique as reported by Ryoo et al.^{55,56} Nanocasting is a method for synthesizing nanostructured porous materials with well-defined pore structures and controllable pore sizes. This technique uses a mold with relevant structures on the length scale of nanometers. The void of the mold is filled with a precursor and the mold is removed afterwards. Hence, a negative replica of the mold

remains. The nanocasting pathway involves three main steps (see **Fig. 1.9**): i) formation of the template; ii) the casting step with target precursor, which includes the conversion of the precursor to the desired product; and iii) removal of the template.⁵⁶



Figure 1.9. Schematic illustration of the nanocasting pathway. Reproduced from ref.⁵⁶

Templates with a controllable morphology and structure are desired. One of the most versatile hard templates is ordered mesoporous silica, since it can be prepared in various morphologies. Consequently, silica materials will be used as templates throughout this study. Two different silica templates will be synthesized by the soft-templating method as described in literature.^{55,56} Additionally, commercially available fumed silica will be used. Fumed silica consists of microscopic droplets of amorphous silica. The bulk density of the white powder is extremely low and the surface area is high. The specific surface area decreases



*Figure 1.10. Schematic representation of the fumed silica synthesis. Adapted from Ref.*⁵⁷

with increasing silica particle size. It is produced from flame hydrolysis of vaporized SiCl₄ at 1000°C (see **Fig. 1.10**).⁵⁷ The supplier Evonik sells it under the trade name Aerosil. Another requirement for the template is that is has to be removed without affecting the replica. For silica templates, leaching is the most common option to remove the template.

The replica material can be introduced in the pore system of the template in the form of a precursor. Subsequently, the precursor has to be converted to the final material. The precursor must be able to enter the template structure, so it should be gaseous, highly soluble or liquid at moderate conditions. Conversion to the desired composition should not change the chemical properties of the template and induce only a minor decrease in precursor volume. Sucrose was found to be a suitable carbon precursor and could be converted to carbon through a carbonization process.⁵⁵ Sucrose does not react chemically with the silica template and decomposes to carbon during the conversion step. Moveover, an interesting possibility is the direct creation of additional functional surface groups during the nanocasting process. Alternatively, surface functionalities can be created by a post-synthesis treatment.⁵⁶

Another post-synthesis modification is widening of existing pores or creation of additional pores. Hence, materials with at least two pore systems of different size are created. These

materials, consisting of structural elements that have a structure themselves, are called "hierarchical". The two major processes for the introduction of porosity are physical and chemical activation. Physical activation uses gaseous oxidation agents, such as CO_2 or gaseous H_2O . The principle is based on the etching of carbon atoms from the framework by the formation of CO. Activation with CO_2 yields the formation of additional micro- and macropores, while activation with H_2O rather yields narrow pores. On the other hand, chemical activation uses inorganic dehydration agents, such as KOH or $ZnCl_2$. The resulting carbon materials exhibit well-defined porosity compared to materials prepared with physical activation.

However, both physical and chemical activation do not yield materials with very narrowly distributed pores. The carbidederived carbon (CDC) method is an alternative for the generation of micropores. With this method, (semi-)metal carbides are synthesized and treated with chlorine at high temperatures. The chlorine treatment removes the (semi-)metal in the form of a metal chloride and yields the carbide-derived carbon material. If ordered mexoporous silicon carbide is subjected to the chlorine treatment, ordered mesoporous CDC (OM-CDC) with combined micro- and mesopores can be obtained (see **Fig. 1.11**).

Carbon nanotubes (CNTs) are used as a reference support in this research. CNTs consist of rolled graphene sheets.⁵⁹ Graphene is a 2D carbon nanomaterial that consists of a single graphite layer of sp² hybridized carbon atoms. In this structure,



Figure 1.11. Schematic structure of OM-CDC materials. Image adapted from Ref.⁵⁸

benzene rings are connected to form a planar honeycomb-type arrangement of atoms with delocalized double bonds.⁶⁰ CNTs and carbon nanofibers (CNFs) have already been studied extensively and the cobalt FTS catalytic performance has been demonstrated in earlier research.^{14,42,46,61}

1.4 Research questions

In order to establish a relationship between support structure and catalytic performance, five separate research questions were formulated:

- 1. How does the carbonization temperature of the support material influence the catalytic performance?
- 2. How does the catalyst preparation method influence the catalytic performance?
- 3. What kind of surface functionalities are desired for preparing stable catalysts?
- 4. How does the pore geometry of the support material influence the catalytic performance?
- 5. How does the pore size of the support material influence the catalytic performance?

Regarding the approach, ordered mesoporous carbon support material will be synthesized. The influence of the carbon-silica composite carbonization temperature on the support properties will be investigated first. Then, the catalyst preparation method will be examined. This

includes the synthesis conditions, the drying step, and the calcination step. Furthermore, different surface functionalities will be introduced post-synthesis on the support material. After examination of the preparation method, the influence of the pore geometry and pore size on catalytic performance will be investigated. It will be attempted to answer these research questions through the employment of different characterization techniques and catalytic tests. The experimental methods that were used in this study will be described in **Chapter 2**. Then, **Chapter 3** focusses on research question 1,2 and 3. Furthermore, question 4 and 5 will be elaborated in **Chapter 4** and **Chapter 5** respectively. Moreover, a summary, general discussion, and comparison to literature will be provided in **Chapter 6**. Last, an outlook will be provided in **Chapter 7**.

Chapter 2

Experimental

The experimental methods that were used in this research will be described in this chapter. First, the support syntheses will be described in **Section 2.2**. This section is subdivided in two groups: Subsection 2.2.1 about the silica templates that were used for nanocasting and subsections 2.2.2 - 2.2.6 about the carbon support materials. Then, the catalyst preparation and characterization methods will be described in **Section 2.3** and **2.4** respectively. The two aforementioned sections will also briefly describe the theoretical background of the catalyst preparation and characterization methods. Finally, details will be provided about catalytic testing in **Section 2.5**.

2.1 Chemicals

Detailed information on the chemicals that were employed during the synthesis of support materials and catalysts is listed in **Table 2.1**.

Chemical	Formula	Purity	Supplier
Aerosil 90	SiO ₂	$\sim 100\%$	Evonik
Aerosil 380	SiO ₂	$\sim 100\%$	Evonik
N-butanol	C ₄ H ₉ OH	99%	Sigma-Aldrich
Calcium chloride	CaCl ₂	$\sim 100\%$	Sigma-Aldrich
Cobalt (II) nitrate hexahydrate	$Co(NO_3)_2 \cdot 6H_2O$	99%	Sigma-Aldrich
Ethanol	C ₂ H ₅ OH	99%	VWR
Hydrochloric acid solution	HC1	37wt.% in H ₂ O	Merck
Hydrofluoric acid solution	HF	37wt.% in H ₂ O	Sigma-Aldrich
P123	EO ₂₀ PO ₇₀ EO ₂₀	$\sim 100\%$	Sigma-Aldrich
Sucrose	$C_{12}H_{22}O_{11}$	99%	Roth
Sulfuric acid	H_2SO_4	99%	Sigma-Aldrich
Tetraethyl orthosilicate (TEOS)	$Si(C_2H_5O)_4$	98%	Sigma-Aldrich
Isopropanol	(CH ₃) ₂ CHOH	99%	Sigma-Aldrich

Table 2.1. Overview of the chemicals that were used.

2.2 Support material synthesis

2.2.1 Silica templates

Hexagonally ordered mesoporous silica (SBA-15)

Hexagonally ordered mesoporous SBA-15 was synthesized by dissolving 24.1 g triblock copolymer P123 in a solution of 400 g deionized water and 12.7 g HCl (37%) in a 1000 mL polypropylene bottle. The resulting solution was left to dissolve P123 overnight at 35°C under magnetic stirring. Then, 47.4 g of TEOS was added and the solution was left under magnetic stirring for 24 h. Subsequently, the white suspension was hydrothermally treated at 130°C for 24 h in a a Teflon-lined autoclave. After cooling to room temperature, the solid product was recovered by washing with a 1500 mL deionized water/ethanol solution (1:1 by volume) and static drying at 60°C. The compound was calcined in a muffle furnace at 550°C for 6 h with a heating rate of 4.4°C/min to remove the remaining structure-directing agent.

Cubic ordered mesoporous silica (KIT-6)

Cubic ordered mesoporous KIT-6 was synthesized by dissolving 11.1 g triblock co-polymer P123 in a solution of 400 g deionized water and 21.9 g HCl (37%) in a 1000 mL polypropylene bottle. P123 was left to dissolve overnight at 35°C under magnetic stirring. Then, 11.1 g *n*-butanol was added and the solution was left under magnetic stirring for 1 h at 35°C. Next, 23.8 g TEOS was added and the solution was left under magnetic stirring for 24 h at 35°C. The subsequent annealing, washing, drying, and calcination steps are identical to the SBA-15 synthesis.

Fumed silica

Commercially available Aerosil 90 and Aerosil 380 were used. These are hydrophilic fumed silicas with a specific surface of 90 m²/g and 380 m²/g respectively.

2.2.2 Ordered mesoporous carbons

CMK-3

CMK-3 is a negative replica of SBA-15 with 2D hexagonally ordered mesopores. To synthesize CMK-3, a solution of 2.5 g sucrose, 10 mL deionized water, and 280 mg H_2SO_4 was used as a carbon precursor. Wet impregnation was carried out with 2.0 g SBA-15 and the aforementioned solution in a porcelain dish. The sucrose was polymerized by heating the mixture in air at 100°C for 6 h and then with 1°C/min heated to 160°C for 6 h. Subsequently, wet impregnation was carried out a second time with a carbon precursor: A solution of 1.6 g sucrose, 10 mL deionized water, and 180 mg H_2SO_4 . The resulting mixture was heated again with the aforementioned temperature program. Carbonization was performed under a 60 mL/min N_2 flow in a tubular furnace. The sample was heated to 500, 900, or 1300°C with 2°C/min for 2 h. The resulting carbon/SBA-15 composite was dissolved in 250 mL $H_2O/EtOH/HF$ solution (1:1:1 by volume) in a closed polypropylene bottle and left overnight to dissolve the silica. After filtration and

washing with large amounts of ethanol, the product was left to dry at room temperature. The F^- ions in the filtrate were deactivated with a saturated CaCl₂ solution in water. The resulting carbon materials were labeled as CMK3-500, CMK3-900 and CMK3-1300, depending on the carbonization temperature.

CMK-8

CMK-8 is a negative replica of KIT-6 with 3D cubic ordered mesopores. The synthesis of CMK-8 is identical to CMK-3 synthesis, except that KIT-6 is used as a hard template instead of SBA-15.

2.2.3 Non-ordered mesoporous carbons

To synthesize non-ordered mesoporous carbons (NOMCs), 2.0 g of SiO₂ NPs, either Aerosil 90 or Aerosil 380, were dispersed in 30 mL deionized water and a solution of 2.0 g sucrose in 10 mL deionized water with 4 droplets H_2SO_4 . The sucrose was polymerized by heating in air at 100°C for 3 h and then with 1°C/min to 160°C for 3 h. The carbonization and silica dissolution procedure are identical to CMK-3 synthesis. The resulting carbon materials were labeled as MC90 and MC380, depending on the type of Aerosil that they originate from.

2.2.4 Hierarchical carbons

Carbon aerogel (CA) with large mesopores and macropores was physically activated with CO₂ to create additional micro- and macropores. Furthermore, the CDC method was used to create ordered mesoporous carbide-derived carbon (OM-CDC). The detailed synthesis procedure can be found in literature.^{58,62} Besides, a commercially available carbon black (CB) with the trade name Printex was used for comparison.

2.2.5 Carbon nanotubes

Carbon nanotubes (CNTs) were used as a reference support in this research. The properties of the pristine material used and details about the synthesis procedure and mechanism can be found elsewhere.^{63,64}

2.2.6 Surface functionalization

Oxygen-containing functional groups were introduced post-synthetically on the carbon surface by a partial oxidation treatment. CMK-3 was heated in static air with 1.6°C/min to 400°C for 1 h in a porcelain dish.

Nitrogen-containing functional groups were introduced by an ammonia treatment on partially oxidized CMK-3. The CMK-3 material was spread out on an alumina boat, which was put in a tube furnace. First, the furnace was flushed for about 15 minutes with high N_2 flow (1600 mL/min). Then, the gas flow was changed to NH₃. After flushing for 10 minutes with 450 mL/min, the sample was heated with 6.3°C/min to 400°C for 5 h in 250 mL/min NH₃.

2.3 Catalyst preparation

2.3.1 Incipient wetness impregnation

Catalysts were prepared via incipient wetness impregnation (IWI). In this method the dry porous material is impregnated with an amount of precursor solution equal to the pore volume. The precursor solution contains the main element of the active phase and a suitable solvent. During the impregnation step the precursor solution is added dropwise under stirring in order to homogeneously cover the support material.⁴⁹ In this study the precursor solution consists of Co(NO₃)₂·6 H₂O dissolved in ethanol. Ethanol was used as a solvent to increase the wetting of the hydrophobic carbon powder. The Co(NO₃)₂·6 H₂O concentration in the precursor solutions was based on the pore volume of the carbon support materials, as determined by nitrogen physisorption to achieve a cobalt loading of approximately 10 wt.% for all the catalysts. The metallic cobalt (Co^0) weight loading was calculated for all catalysts with eqn. 2.1. This weight loading is essential to determine crucial properties, such as cobalt particle size and metallic surface area. The cobalt oxide weight loading was calculated either with eqn. 2.2 or with eqn. 2.3. Eqn. 2.2 assumes CoO after calcination and eqn. 2.3 assumes Co_3O_4 after calcination. The cobalt oxide weight loading is essential for loading reactors with an amount of catalyst, that contains cobalt oxides prior to reduction. Regarding the impregnation conditions, two parameters were varied during this study. First, the temperature of the support and the precursor was either around 0°C or room temperature. Furthermore, impregnation was either performed under static vacuum with the intention to clear the pores and create sufficient capillary suction or at ambient pressure.

$$\frac{m_{cobalt}}{m_{cobalt} + m_{support}} \cdot 100 \% \qquad \text{cobalt wt.\%} \qquad (2.1)$$

$$\frac{m_{cobalt}}{m_{CoO} + m_{support}} \cdot 100 \% \qquad \text{cobalt wt.\%} \qquad (2.2)$$

$$\frac{m_{cobalt}}{m_{Co_3O_4} + m_{support}} \cdot 100 \% \qquad \text{cobalt wt.\%} \qquad (2.3)$$

2.3.2 Drying and calcination

Drying leads to formation of a metal nitrate salt inside the pores of the support. Upon solvent removal, the precursor concentration reaches saturation and crystallization occurs. In this study most of the impregnated support materials were dried under static air at 60°C overnight. One catalyst was dried in a fluidized bed reactor under a 50 mL/min N₂ flow at 70°C for 3 h with a heating rate of 1°C/min.

Usually calcination is performed after drying to convert the formed cobalt nitrate salt into cobalt oxide NPs by thermal decomposition of the salt anion. The conditions of this procedure have been found to be critical for producing catalysts with favorable properties.⁴⁹ Officially,

the term calcination applies to heat treatments in air. However, this term is also used for heat treatment in an inert gas atmosphere, such as N_2 . For silica-supported cobalt catalysts it was found that calcination in N_2 leads to a more homogeneous metal distribution compared to calcination in air.⁶⁵ Furthermore, the calcination temperature should be high enough to decompose the metal salt, but low enough to restrict particle mobility in order to prevent metal redistribution and sintering. Since the anchoring of metal NPs on a carbon support is not very robust, the calcination temperature should be relatively low compared to calcination of metal NPs on oxide supports.

In this research sieve fractions (75-212 μ m) were prepared of the dried catalysts. The sieve fraction was calcined under 100 mL/min N₂ flow in a fixed bed reactor at 250°C, 200°C or 140°C for 4 h with a heating rate of 2.0°C/min, 1.5°C/min or 1.0°C/min respectively.

After calcination, all catalysts were labeled in the form of Co/x-y-z. Were x represents the support material and y the carbonization temperature. Z represents optional alterations in different parameters, such as surface treatment, impregnation method, drying method, or calcination temperature. If no z is mentioned in the label, pristine carbons were used and impregnation was performed under static vacuum at 0°C (denoted in **Table 2.2** as vacuum/0°C). Drying was performed in static air at 60°C, except for the sample denoted as Co/CMK3-900-RTF, which was dried in a fluidized bed reactor for 3 h @70°C under N₂ flow. An overview of the catalysts can be found in **Table 2.2**. The Co⁰ weight loadings are theoretical values calculated with eqn. 2.1.

Catalyst label	Surface	Co ⁰ wt.%	Impregnation	Calcination
	treatment			
Co/CNT	-	9.01	Vacuum/0°C	250°C
Co/CMK3-500	-	10.9	Vacuum/0°C	250°C
Co/CMK3-900	-	10.6	Vacuum/0°C	250°C
Co/CMK3-1300	-	10.4	Vacuum/0°C	250°C
Co/CMK3-900-RT	-	10.4	Air/RT	250°C
Co/CMK3-900-RT3	-	3.33	Air/RT	250°C
Co/CMK3-900-RTF	-	9.88	Air/RT	250°C
Co/CMK3-900-200	-	10.3	Air/RT	200°C
Co/CMK3-900-140	-	11.3	Air/RT	140°C
Co/CMK3-900-OX	Oxidizing	11.9	Air/RT	200°C
Co/CMK3-900-AM	Ammonia	12.8	Air/RT	200°C
Co/CMK8-900-250	-	10.9	Vacuum/0°C	250°C
Co/CMK8-900-RT	-	10.5	Air/RT	250°C
Co/CMK8-900-200	-	10.3	Air/RT	200°C
Co/CB	-	14.8	Air/RT	250°C
Co/MC90-900	-	10.8	Vacuum/0°C	250°C
Co/MC380-900	-	10.4	Vacuum/0°C	250°C
Co/CA-900	-	11.1	Vacuum/0°C	250°C
Co/OMCDC	-	10.3	Vacuum/0°C	250°C

Table 2.2. Overview of the catalysts employed during this research.

2.4 Characterization

In this section the techniques used to characterize the support materials and the resulting catalysts will be discussed. The theoretical background will be explained briefly, the purposes will be mentioned, and the settings will be described. First, nitrogen physisorption will be discussed in **Section 2.4.1**. Next, Raman spectroscopy will be discussed in **Section 2.4.2**. Then, thermogravimetric analysis under nitrogen and X-ray diffraction (XRD) will be discussed in **Section 2.4.3** and **2.4.4** respectively. Furthermore, electron microscopy (EM) will be discussed in **Section 2.4.5**. The last techniques that will be discussed in **Section 2.4.6** and **2.4.7** respectively are hydrogen chemisorption and hydrogen temperature programmed reduction (H₂-TPR).

2.4.1 Nitrogen physisorption

Nitrogen physisorption is used to determine the specific surface area of support materials. Furthermore, the technique provides information on the pore volume and pore dimensions based on a weak, non-dissociative interaction of N_2 molecules with the support surface. The amount of adsorbed molecules is measured to determine the specific surface area of the support. The pore volume is essential to carry out incipient wetness impregnation. From the catalyst viewpoint, N_2 physisorption was used to analyze if there was any pore blocking after support impregnation. Pore blocking is indicated by a decrease in SSA and pore volume.

Nitrogen physisorption isotherms were measured at -196°C (the boiling point of liquid nitrogen) on a Micromeritics TriStar 3000 instrument. Before the measurements, samples were dried at 150°C under flowing nitrogen. Specific surface areas (SSAs) were calculated using the multi-point BET method ($0.05 < p/p_0 < 0.25$). Furthermore, the pore volumes (V_{pore}), pore size distributions (PSDs), and average pore diameters were determined by the BJH method by using the adsorption branches of the isotherms.

2.4.2 Raman spectroscopy

Raman spectroscopy gives information about the vibrational modes of a system and can be used as a tool for the characterization of carbon allotropes. The Raman spectra contain information about the atomic structure and the electronic properties.^{66,67} This technique is particularly useful for graphene, the building block for sp² carbon allotropes. Graphene consists of one atomic layer of sp² bonded carbon atoms arranged as a honeycomb. Materials with multiple graphene layers are called graphite or graphitic.⁶⁰ The carbon materials synthesized *via* the nanocasting procedure have a defective graphite structure and are amorphous. Such materials exhibit two broad Raman peaks centered around 1360 and 1600 cm⁻¹, corresponding to the disorder-induced D-band and the G-band of graphitic carbon, respectively.⁶⁸ The first originates from breathing modes of sp² atoms in aromatic rings (see



Figure 2.1. The breathing modes of sp² hybridized carbon atoms in aromatic rings.

Fig. 2.1), while the latter is assigned to bond stretching of sp² pairs in both rings and chains.⁶⁷ The breathing modes, however, are symmetry forbidden in defect–free bulk graphite and only

Raman active in the presence of defects and disorder.⁶⁹ The D-band intensity is proportional to the number of six-fold sp² carbon rings and its full width at half maximum (FWHM) is related to the ordering and size distribution of sp² rings. The presence of rings other than six-fold increases the width of the D-band. It follows that both the ratio between the intensities of the D-band and the G-band (I_D/I_G) and the width of the D-band at FWHM can be used to determine the degree of graphitization in amorphous carbon materials.

The actual Raman spectroscopy measurements were carried out on a Renishaw Invia Raman microscope working at 532 nm excitation wavelength. The spectra were deconvoluted by assuming mixed Gaussian/Lorentzian peaks to describe the D- and G-bands. The fit was performed by using Origin Pro 2015.

2.4.3 Thermogravimetric analysis under nitrogen

Thermogravimetric analysis/mass spectrometry (TGA-MS) under nitrogen was used to analyze the surface functionalities of the support material and to confirm the presence of postsynthetically introduced functional groups. From a catalyst viewpoint, this technique was used to analyze the cobalt nitrate precursor decomposition during calcination under N₂ flow. The measurements were performed with a Perkin Elmer Pyris 1 TGA instrument. Approximately 10 mg of material was used and the analyses were done with a mass spectrometer. The starting temperature was 50°C and the samples were heated to 800°C with a heating rate of 5°C/min. The samples were held under 10 mL/min nitrogen flow during the analysis.

2.4.4 X-ray diffraction

X-ray Diffraction (XRD) is a bulk technique that utilizes the diffraction of X-rays by the electron density of a material. In this study, it was applied to identify the cobalt crystalline phases and to determine the average crystallite size. The width of a diffraction peak can be related to the average crystallite size (d) *via* the Scherrer equation (2.4):

$$d = \frac{K \cdot \lambda}{\beta \cdot \cos\theta} \qquad \qquad \text{Scherrer equation} \qquad (2.4)$$

where K is the shape factor, λ the X-ray wavelength, β the full-width at half-maximum (FWHM) of a diffraction peak, and θ is the scattering angle of the considered Bragg reflection. Alternatively, the peak width can be expressed as the integral width, which is the area under the diffraction peak divided by the peak maximum.²¹

It is important to take into consideration that broadening XRD peaks could not only be related to the crystallite size, but also to the presence of strained and imperfect crystals. In that case, the Scherrer equation would yield crystallite sizes that are much smaller than the real sizes. Furthermore, cobalt particles could exist of multiple crystalline domains. Hence, the calculated value for d might deviate severely from values obtained with nanoscale techniques, such as electron microscopy.

XRD patterns were recorded with a Bruker AXS D2 Phaser, using Co $K\alpha_{1,2}$ radiation with $\lambda = 1.79026$ Å and K = 0.89. In order to obtain a good diffraction signal, the surface of the calcined catalyst in the sample holder was flattened as much as possible. The diffraction

patterns were collected in a range of $30^{\circ}-60^{\circ} 2\theta$ with an increment of $0.05^{\circ} 2\theta$. The integration time *per* measurement point was 5 seconds in general. The sample holder was rotated at 15 rotations *per* minute. The cobalt crystalline phases where qualitatively determined with the Eva2 software. XRD peaks associated with Co₃O₄ are 36.5° , 43° , and $52^{\circ} 2\theta$ and associated with CoO are 42.5° and $49.5^{\circ} 2\theta$. It follows that the absence or the presence of a peak at 36.5° can be used to distinguish between Co₃O₄ and CoO. However, the peak at 36.5° could be overruled by the noise from amorphous carbon. Hence, the position of the peak around $50^{\circ} 2\theta$ was used to quantify the volume-averaged Co₃O₄ or CoO crystallite sizes. Quantitative analysis was performed *via* a line broadening analysis by a fitting procedure in the Topas5 software. This program determines the volume-averaged crystallite size with the Scherrer equation based on the integral peak width.

The particle size of Co⁰ can be calculated from a Co₃O₄ crystallite according to eqn. 2.5.⁷⁰ CoO crystals adopt the rock salt structure with a lattice constant of 4.2615 Å.⁷¹ The crystal unit cell contains 4 cobalt atoms and 4 oxygen atoms. A 1.35 Å covalent radius of cobalt is estimated, considering low spin and high spin cases.⁷² Then, the volume fraction of cobalt atoms can be calculated by eqn. 2.6 and the estimated size of Co⁰ by eqn. 2.7.

$$d(Co^{0}) = 0.75 \cdot d(Co_{3}O_{4}) \qquad \text{estimated size } Co^{0} \qquad (2.5)$$

$$\frac{V_{Co}}{V_{CoO}} = 4 \cdot \frac{\frac{4\pi}{3} \cdot (1.35)^3}{(4.2615)^3} = 0.532$$
 volume ratio Co in CoO (2.6)

$$d(\text{Co}^0) = \sqrt[3]{0.532} \cdot d(\text{CoO}) = 0.810 \cdot d(\text{CoO}) \quad \text{estimated size Co}^0 \tag{2.7}$$

2.4.5 Electron microscopy

Transmission electron microscopy (TEM) provides images of the cobalt NPs on the support material. These images are generated in transmission, meaning that electrons in a beam are passing through the sample. TEM is also an essential tool to get an impression of the homogeneity of a sample and to determine the particle size. There are two different imaging modes in TEM: Bright field (BF) and dark field (DF). BF relies on the directly transmitted electron beam and DF uses the diffracted electron beam. Whether BF or DF should be used depends on the desired information. For instance, with BF the mass-thickness contributes strongly to the image, whereas with DF the image is sensitive to crystallinity.

Scanning transmission electron microscopy (STEM) uses a small electron beam to scan across the sample and a sub-Ångstrom spatial resolution can be obtained. STEM relies on absorption contrast, which is directly related to the atomic number of elements present.

Energy dispersive X-ray spectroscopy (EDX) also uses a small electron beam to scan across the sample. Different from STEM, the X-rays reflected by the sample are detected. These X-rays provide elemental analysis.
For TEM measurements, catalysts were suspended in isopropanol and ultrasonically dispersed. Drops of the dispersions were applied on a copper grid. A FEI Tecnai 12 transmission electron microscope, operated at 120 kV, was used to investigate the samples. Several images with different magnifications were recorded and saved.

High-angle annular dark-field (HAADF) scanning transmission electron microscopy (STEM) imaging and EDX analysis were performed on a FEI Talos F200X transmission electron microscope, operated at 200 kV and equipped with a high-brightness field emission gun (X-FEG) and a Super-X G2 EDX detector. The same copper grids as mentioned above were used for this instrument.

The particle size analysis was performed by randomly measuring 200 to 300 particles (N) from several images with the assistance of the iTEM software. Histograms were constructed in Microsoft Excel 2010 with the number-averaged particle diameter (d_N). The metallic surface area is of the utmost important for the catalytic performance. Hence, the surface-averaged particle sizes were calculated. First, the surface area of all individual particles was calculated with eqn. 2.8, assuming spherical particles. Then, the average particle surface area ($A_{average}$) was calculated in Microsoft Excel 2010. This value was recalculated to an average particle diameter with eqn. 2.9. Additionally, the standard deviation (σ) of d_N was calculated with Microsoft Excel 2010 and the relative uncertainty (ϵ) was calculated with eqn. 2.10. More details about the basic principles of particle size analysis can be found in scientific literature.⁷³

$$A = \pi \cdot d_{N}^{2} \qquad \text{surface area (nm2)} \qquad (2.8)$$

$$d_{\text{average}} = \sqrt{\frac{A_{\text{average}}}{\pi}} \qquad \text{particle size (nm)} \qquad (2.9)$$

$$\epsilon = \frac{\sigma}{d_{N}} \cdot 100\% \qquad \text{relative uncertainty (%)} \qquad (2.10)$$

2.4.6 Hydrogen chemisorption

Hydrogen chemisorption provides information on the cobalt metallic surface area and the amount of cobalt surface sites. The technique is based on dissociative adsorption of H_2 molecules. Dissociation of H_2 is required to correlate the amount of surface sites to the amount of H_2 molecules adsorbed. The metallic surface area is determined by measuring the amount of adsorbed H_2 and using the area occupied *per* adsorbed molecule.

Hydrogen chemisorption was carried out with a Micromeritics Autochem ASAP 2020C. 100 mg calcined catalyst was dried under He flow at 120°C for 2 h and then reduced for 2 h in flowing H₂ at 350°C with a heating rate of 5°C/min. After evacuation, the hydrogen adsorption isotherms were measured at 150°C. Extrapolating the linear part of the isotherm gives the total amount of adsorbed H₂ when the cobalt surface is saturated. Subsequently, the H/Co atomic ratios at zero pressure can be determined. The particle sizes and metal dispersions were estimated, while assuming spherical geometry for cobalt particles, complete reduction and an H/Co adsorption stoichiometry of 1. For estimating the particle sizes (d) eqn. 2.11 was used and for estimating the metal dispersions (%D) eqn. 2.12 was used. W denotes the weight percentage of metallic cobalt and X is the total hydrogen uptake in μ mol/g_{cat}.⁷⁴

$$d = \frac{81.6 \cdot W}{X}$$
 particle size (nm) (2.11)
$$\%D = \frac{1.179 \cdot X}{W}$$
 dispersion (%) (2.12)

2.4.7 Hydrogen temperature-programmed reduction

Hydrogen temperature-programmed reduction (H_2 -TPR) provides information about the reducibility of cobalt oxides in a catalyst. The technique uses the uptake of probe molecule H_2 to study the reducibility of the catalyst by increasing the reaction temperature.

 H_2 -TPR was carried out with a Micromeritics Autochem II 2920 Chemisorption Analyzer. The hydrogen consumption was quantified with a thermal conductivity detector (TCD). Typically, 55-65 mg of the calcined catalysts was heated up to 350°C with a heating rate of 5°C/min and held at that temperature for 2 h. Then, heating continued up to 800°C with 5°C/min. The gas atmosphere was a mixture of 5 vol% H_2 in Ar flowing with 50 mL/min throughout the whole temperature program. Prior to heating, the samples were dried at 100°C for 1 h under flowing Ar.

2.5 Catalysis

2.5.1 Reduction under hydrogen

Reduction under hydrogen was performed on a Flowrence (Avantium) 16 parallel reactor unit. The reduced catalysts were used for analysis and visualization of particle growth with electron microscopy. Each stainless steel reactor was loaded with 10 to 20 mg catalyst and 100 mg SiC. All catalysts were dried for 2 h at 100°C under He flow. Then, the catalysts reduced at 350°C for 8 h in 25 vol% H₂ in He with a heating rate of 1°C/min. The catalysts were cooled to 180°C with 3°C/min. Subsequently, the gas flow was changed to He only for cooling to room temperature. Subsequently, the catalysts were passivated using a diluted (0.1 vol%) oxygen flow.

2.5.2 Low pressure Fischer-Tropsch synthesis

Low pressure Fischer-Tropsch synthesis at 1 bar pressure was performed in a laboratory scale fixed bed reactor. A high GHSV ($3500 h^{-1}$) was used in combination with line tracing at 130° C to prevent product condensation. Typically 200 mg SiC ($200-400 \mu$ m) was mixed with 20 mg calcined catalyst ($75-212 \mu$ m) and put in a U-shaped glass reactor. Reduction was performed in 50 vol% H₂ in Ar (20 and 40 mL/min respectively) at 350° C for 2h with a heating rate of 300° C/h. After reduction, the catalysts were cooled down to 220° C with 300° C/h. FTS

was performed at 220°C in 50 vol% CO in H₂ (4 and 8 mL/min respectively). Hydrocarbon products (C_1 - C_{18}) were analyzed with a flame ionization detector (FID) on a Varian 3800 gas chromatograph (GC) with a fused silica CP-Sil 5 CB column. Typically, the CO conversions were 0-3% and the results were reported for 15-20 h time on stream. Important quantities, such as CTY, TOF and selectivities, were calculated with Microsoft Excel 2010. The TOF was based on the metallic surface area as calculated from hydrogen chemisorption. The C₅₊ selectivity is reported as the selectivity towards C₅-C₁₈.

2.5.3 High pressure Fischer-Tropsch synthesis

Fischer-Tropsch synthesis was performed on a Flowrence (Avantium) 16 parallel reactor unit. Each stainless steel reactor was loaded with 20 to 50 mg catalyst (75-212 μ m) mixed with 100 mg SiC (200-400 μ m). The catalyst bed volume was 200 μ L throughout. Although, the cobalt weight loadings were similar for each catalyst, the activities could be omnifarious. This anticipation was already verified with low pressure Fischer-Tropsch synthesis prior to high pressure Fischer-Tropsch synthesis. Thus, the amounts of catalyst were varied in order to obtain CO conversions between 10 and 40%. All catalysts were reduced in situ in 25 vol% H₂ in He at 350°C for 8 h with a heating rate of 1°C/min. Afterwards, the reactors were cooled down to 180°C at which the pressure was increased to 20 bar under H₂. Then, the feed was changed to a H_2/CO ratio of 2.0 with 5 vol% He. After 1 h, the temperature was increased to a reaction temperature of 220°C with a heating rate of 1°C/min. The products were analyzed using online GC (Agilent 2890A). The permanent gases were separated on a ShinCarbon ST (#19043) column and quantified against He as an internal standard using a TCD detector. CO conversions were calculated with eqn. 2.13. Hydrocarbons (C_1-C_9) were separated on an Agilent J&W PoraBOND Q column, detected with an FID detector, and quantified against the TCD signal of the internal standard He. The selectivities towards lower hydrocarbon fractions (S_{CX}) were calculated from the converted CO according to eqn. 2.14. The C_{5+} selectivity (S_{C5+}) was calculated from the yields to lower hydrocarbons according to eqn. 2.15. The gas hourly space velocity (GHSV) was initially 2000 h^{-1} . In some catalytic runs, the conversion was increased after 100 h on-stream. This was achieved by decreasing the GHSV to 1000 h^{-1} , aiming to report the performance of all catalysts at 10-40% conversion and eliminating effects of conversion on selectivity. Activities reported as CTY were based on the metallic cobalt weight loading and the catalyst mass. The TOF was based on the metallic surface area as determined by hydrogen chemisorption. At the end of a catalytic run, the waxes in the pores of the catalysts were stripped off for 12 h under H_2 flow at 200°C. Subsequently, the reactors were cooled down to room temperature under a flow of Ar. When removing the catalysts from the reactors, these were exposed to air prior to further characterization by (S)TEM.

$$X_{CO} = \frac{mol_{CO,in} - mol_{CO,out}}{mol_{CO,in}} \cdot 100\%$$
CO conversion (%) (2.13)

$$S_{CX} = \frac{Y_{CX}}{\text{mol}_{CO,\text{in}} - \text{mol}_{CO,\text{out}}} \cdot 100\% \qquad \qquad C_1 - C_9 \text{ selectivity (\%)} \quad (2.14)$$

$$S_{C5+} = (1 - S_{C1-C4}) \cdot 100\%$$
 C₅₊ selectivity (%) (2.15)

Furthermore, catalytic runs were used to verify if there were any diffusion limitations in the catalysts. This was achieved by increasing the temperature stepwise after 100 h on-stream. In every step, the temperature was increased with 10° C relative to the previous step and left at that temperature for 10 h. Consequently, Arrhenius plots could be constructed with the different reaction rates (k) at each temperature. From the plots, the pre-exponential factor (A) and the activation energy (E_{*a*}) could be determined for each catalyst, which are indicators of the active sites and diffusion limitations, respectively.

Chapter 3

Results and discussion: Support synthesis and catalyst preparation

In this chapter the preparation method of OMC-supported cobalt FTS catalysts will be examined and optimized. CMK-3 with 2D hexagonally ordered mesopores and *p6mm* symmetry (see **Fig. 3.1**) was used as a support material throughout this chapter. CNTs are used as a reference support material. First, the support properties and catalytic performance of cobalt supported on CMK-3 carbonized at different temperatures will be discussed in **Section 3.1**. Then, the results regarding the catalyst preparation will be elaborated in **Section 3.2**. This includes the influence of impregnation, drying, calcination, and surface functionalities on catalytic performance.



Figure 3.1. Schematic representation of CMK-3 structure and synthesis.

3.1 Support synthesis: CMK-3

3.1.1 Textural properties and mesostructure

The textural properties of the as-synthesized support materials were characterized by nitrogen physisorption and are summarized in **Table 3.1**. According to the porosity data in **Table 3.1**, changing the carbonization temperature resulted in a slight change in the textural properties. CMK3-900 displayed the largest surface area, pore volume, and mesopore size. Hence, it was expected that 900°C would be the optimum carbonization temperature in order to create a suitable support material. The CMK-3 and CNTs isotherms (see **Fig. 3.2A**) were of type IV according to the IUPAC classification.⁷⁵ For CMK-3, a sharp capillary condensation took place at the relative pressure 0.4-0.6, indicating the presence of uniform mesopores. For CNTs, capillary condensation in the mesopores took place at the relative pressure 0.9, indicating that the mesopores in CNTs were larger than in CMK-3. The shapes of the CMK-3 and CNT hysteresis loops indicated the presence of cylindrical mesopores with open ends at both sides. The uniform mesopores in CMK-3 were further corroborated by the narrow pore size distribution, scaled to the primary axis in **Fig. 3.2B**. The pore size distribution for CNTs, scaled to the secondary axis in **Fig. 3.2B**, was broad.

Sample	$S_{BET} (m^2 \cdot g^{-1})$	Total pore volume	Micropore volume	Average
		$(\mathrm{cm}^3 \cdot \mathrm{g}^{-1})$	$(\mathrm{cm}^3 \cdot \mathrm{g}^{-1})$	$d_{\rm meso}$ (nm)
CMK3-500	1178	1.00	0.04	2.5
CMK3-900	1271	1.45	0.07	4.3
CMK3-1300	1240	1.32	0.05	4.0
CNTs	190.1	1.35	0.01	31

Table 3.1. Porosity data of CMK-3 carbonized at different temperatures and CNTs.



Figure 3.2. A) Nitrogen adsorption/desorption isotherms and B) BJH pore size distributions calculated from the adsorption branches of CMK3-900 and CNTs.

3.1.2 Degree of graphitization

The degree of graphitization was determined with Raman spectroscopy. All CMK-3 materials exhibited two Raman peaks around 1360 and 1600 cm⁻¹, respectively corresponding to the D-band and the G-band (see **Fig. 3.3**). The D-band originated from breathing modes of sp² atoms in aromatic rings, whereas the G-band was assigned to bond stretching of sp² pairs in both rings and chains.⁶⁷ As explained in **Section 2.4.2**, the I_D/I_G ratio and the FWHM of the D-band can be used as a measure for the degree of graphitization. The raman spectrum of CMK3-500 in **Fig. 3.3A** displayed a lower I_D/I_G ratio and a wider D-band compared to the raman spectrum of CMK3-1300 in **Fig. 3.3B**. Both **Fig. 3.3** and **Table 3.2** indicated that the degree of graphitization increased with increasing carbonization temperature. This correlated well with what was reported in scientific literature.⁶⁸



Figure 3.3. Raman spectra with corresponding fitting curves for CMK-3 carbonized at A) 500°C and B) 1300°C.

Table 3.2. I_D/I_G ratio and FWHM	of the D-band	for CMK-3	carbonized at di	fferent tem	peratures
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Sample	I_D/I_G	FWHM D-band (cm ⁻¹)	
CMK3-500	0.70	256	
CMK3-900	0.95	133	
CMK3-1300	1.00	79	

3.1.3 Oxygen-containing surface groups

TGA-MS under nitrogen was used to determine the amount of oxygen-containing surface groups on the carbon support materials. Heat treatment in flowing N₂ induced a change in the sample weight, as depicted in **Fig. 3.4A**. Below 150°C, weight loss was associated with the release of adsorbed water and the weight loss for CMK-3 between 150 and 450°C was attributed to the removal of oxygen-containing surface groups. The prominent weight loss of CMK3-500 above 450°C was assigned to the carbonization of sucrose, which resulted in desorption of *e.g.*, CH₄ and CO. Further carbonization occured for CMK3-500 due to incomplete carbonization at 500°C during synthesis.

Additionally, the evolution of CO_2 during heat treatment under N_2 flow was monitored by an online mass spectrometer (MS). Desorption of CO_2 indicated the presence of oxygencontaining surface groups. **Fig. 3.4B** clearly showed that the amount of oxygen-containing surface groups was comparable for CMK3-900 and CMK3-1300. On the contrary, the CMK3-500 surface desorbed more CO_2 compared to CMK-3 carbonized at higher temperatures, which indicated the presence of more oxygen-containing surface groups. On CNTs, the amount of oxygen-containing surface groups was larger compared to CMK3-500. Also the oxygen functionalities on CNTs were more stable compared to CMK3-500, since CO_2 desorption only became significant above 400°C.

Oxygen-containing surface groups can serve as anchoring point for metal NPs.⁷⁶ Hence, it was expected that the presence of these groups would be beneficial for preparing stable catalysts with high dispersion of catalytically active metal NPs. An increase in metal dispersion will inevitably lead to a decrease in average NP size. However, a very high dispersion of metal NPs is not necessarily the holy grail in cobalt FTS. It was already demonstrated that cobalt NPs below 6-8 nm displayed a lower TOF and a lower C_{5+} selectivity compared to larger cobalt NPs.⁴² Hence, the influence of oxygen-containing groups on FTS catalytic performance should not be misinterpreted. A high metal dispersion is desired for preparing stable catalysts, but the cobalt NPs should not be smaller than 6-8 nm. For the CMK-3 materials, the highest cobalt dispersion was expected on CMK3-500.



Figure 3.4. Results from TGA-MS under nitrogen for CMK-3 materials carbonized at different temperatures and CNTs. A) The residual masses and B) the CO_2 evolution were both plotted against the temperature.

3.1.4 Characterization of calcined catalysts

The nature of cobalt species on CMK-3 and CNTs

XRD was used to determine the cobalt crystalline phases and the volume-averaged crystallite size after calcination. The XRD patterns of the pristine CMK3-900 support and Co/CMK3-900 are shown in **Fig. 3.5A**. The amorphous CMK-3 supports made it rather difficult to identify

from the XRD patterns which crystalline phases were present. The absence or the presence of a peak at $36.5^{\circ} 2\theta$ could be used to distinguish between Co_3O_4 and CoO. However, the peak at $36.5^{\circ} 2\theta$ could be overruled by the noise from amorphous carbon. XRD peaks at $49.5^{\circ} 2\theta$ are associated with CoO and peaks at $52^{\circ} 2\theta$ with Co_3O_4 . The peak at $49.5^{\circ} 2\theta$ indicated that CoO was the predominant crystalline phase on CMK-3 materials. The XRD patterns of the pristine CNT support and Co/CNT are shown in **Fig. 3.5B**. For Co/CNT the peak at $36.5^{\circ} 2\theta$, which indicated Co_3O_4 as the predominant crystalline phase, was clearly visible. In all cases the peak between 42° and $43^{\circ} 2\theta$ was used to calculate the volume-averaged crystallite size based on the integral peak width. Additionally, the corresponding Co^0 crystallite sizes were estimated for a comparison with hydrogen chemisorption results that will follow. The resulting values for Co/CNT and the three Co/CMK-3 catalysts are shown in **Table 3.3**. On CNTs, the average crystallite size was larger compared to CMK-3 materials.



Figure 3.5. XRD patterns of A) Co/CMK3-900 and B) Co/CNT. The pristine supports are displayed in black.

Table 3.3. Crystallite sizes of Co_3O_4 , CoO and Co⁰ from XRD for cobalt supported on CMK-3 materials and CNTs.

Catalyst	Crystalline phase	Crystallite size (nm)	Crystallite size Co ⁰ (nm)
Co/CNT	Co ₃ O ₄	5.8	4.4
Co/CMK3-500	CoO	1.6	1.3
Co/CMK3-900	CoO	1.4	1.1
Co/CMK3-1300	CoO	1.9	1.5

Support-assisted reduction

CoO was the predominant crystalline phase in the CMK-3 materials after calcination. During calcination, the cobalt nitrate precursor decomposed and cobalt oxides were formed. Oxygen atoms from the cobalt oxides can be accepted by carbon atoms. Thereby, mobile metallic cobalt is formed. By exposure to air after calcination, metallic cobalt re-oxidized predominantly into CoO. It was reported previously that OMCs enabled reduction of cobalt oxides into metallic cobalt in inert atmospheres.^{50,77} This behaviour was caused by the partial rehybridization from sp² to sp³ and the pyramidalization of the carbon atoms in curved aromatic systems. This led

to weakening of the metal oxide bond strength and facilitated reduction of metal oxides at low temperatures.⁷⁸ However, complete reduction of Co_3O_4 did not occur for Co/CNT during calcination. The support-assisted reduction of the Co/CMK-3 catalysts could be ascribed to the defective graphite structure of CMK-3 materials. The carbon atoms could act as reducing agents and accept oxygen from the cobalt oxides. Thereby, support-assisted reduction may be facilitated already at 250°C in a N₂ atmosphere. A drawback of support-assisted reduction is that sintering could already occur during calcination. Especially with cobalt crystallites below the pore diameter of CMK-3. These small crystallites are not properly confined in the pores and could easily move around.

Morphology and particle size distribution

HAADF-STEM investigations (**Fig. 3.6**) showed that the size and the dispersion of cobalt NPs within the pore systems was significantly different for CMK-3 carbonized at different temperatures. For Co/CMK3-500 (**Fig. 3.6AB**) only small and well-dispersed cobalt NPs (2-3 nm) were observed. For Co/CMK3-900 (**Fig. 3.6CD**) two distinct types of cobalt NPs were observed: Small NPs (2-3 nm) inside the pore system and large cobalt particles (~200 nm) on the external surface of CMK-3 particles. The same was observed for Co/CMK3-1300 (**Fig. 3.6EF**) and even more large cobalt particles (>200 nm) seemed to be present in Co/CMK3-1300 compared to Co/CMK3-900. It should be noted that the average cobalt crystallite sizes on CMK-3 materials determined with XRD were 1.4-1.9 nm (see **Table 3.3**), which indicated that cobalt particles could consist of multiple crystalline domains. Furthermore, **Fig. 3.6E** showed that the pore framework of CMK3-1300 was partially enlarged and destroyed, which could be attributed either to the high carbonization temperature or to the calcination procedure.

Additionally, HAADF-STEM images were employed to evaluate the particle size distributions. A histogram was constructed (see **Fig. 3.7**) with the number-averaged particle diameters, obtained by randomly measuring 200 to 300 particles. The quantitative particle size analysis correlated well with the qualitative information from the HAADF-STEM images in **Fig. 3.6**. The bimodal distributions of Co/CMK3-900 and Co/CMK3-1300 yielded very large standard deviations and relative uncertainties. Hence, the surface-averaged particle sizes were only calculated for cobalt particles of 6 nm or smaller and can be found in **Table 3.4**. The surfaceaveraged particle sizes below 6 nm were comparable for the CMK-3 materials. It was evaluated previously with XRD that the cobalt crystalline phase in CMK-3 after calcination was CoO. Hence, the Co⁰ particle sizes were calculated with eqn. 2.7 for comparison with hydrogen chemisorption that will follow.



Figure 3.6. HAADF-STEM images of (A,B) Co/CMK3-500, (C,D) Co/CMK3-900, and (E,F) Co/CMK3-1300 after calcination under nitrogen at 250°C.



Figure 3.7. HAADF-STEM particle size analysis of cobalt NPs supported on CMK-3 materials with different carbonization temperatures.

Table 3.4. HAADF-STEM particle size analysis of cobalt supported on CMK-3 with different carbonization temperatures.

Catalyst	CoO particle size (nm)	Relative uncertainty	Co ⁰ particle size (nm)
		(%)	
Co/CMK3-500	2.8 ± 0.5	19	2.3 ± 0.4
Co/CMK3-900	3.1 ± 0.7	23	2.5 ± 0.6
Co/CMK3-1300	2.8 ± 0.7	26	2.3 ± 0.6

EDX elemental mapping of Co/CMK3-900 (see **Fig. 3.8**) confirmed that cobalt NPs were indeed present inside the CMK-3 pores and that the distribution of cobalt NPs was not completely homogeneous. However, it should be noted that EDX elemental mapping yields two dimensional images of three dimensional particles. The images do not give any information on the thickness of the CMK-3 particle, but rather display a distorted representation of reality.



Figure 3.8. EDX elemental mapping TEM images at the edge of a CMK3-900 particle. A) Carbon is depicted in green and B) cobalt is depicted in red.

3.1.5 Characterization of reduced catalysts

Metallic surface area and cobalt particle size

Hydrogen chemisorption was performed in order to evaluate the cobalt particle sizes, metallic surface areas, and dispersions after reduction on CNTs and CMK-3 materials with different degrees of graphitization. The values obtained for Co/CNT were in accordance with values reported in literature.⁷⁹ The values obtained for Co/CMK-3 (see **Table 3.5**) were significantly different from the HAADF-STEM particle size analysis. For Co/CMK3-900 and Co/CMK3-1300 the Co⁰ particle sizes estimated by hydrogen chemisorption were 10 and 17 nm, respectively. These values are averages from the 2-3 nm cobalt NPs in the CMK-3 pores system and the large cobalt particles on the CMK-3 external surface. However, for Co/CMK3-500 hydrogen chemisorption yielded a 7.5 nm Co⁰ particle size, which is larger compared to HAADF-STEM. It might be that HAADF-STEM failed to show the bimodal size distribution for Co/CMK3-500, since it is a nanoscale characterization technique and only shows a very small part of the catalyst.

Catalyst	Metallic surface area	Co^0 particle size (nm)	Dispersion (%)
5	$(\mathrm{m}^2 \cdot \mathrm{g}_{metal}^{-1})$	1	1 ()
Co/CNT	68.2	8.2	12
Co/CMK3-500	99.8	7.5	13
Co/CMK3-900	74.7	10	9.5
Co/CMK3-1300	42.4	17	5.6

Table 3.5. Metallic surface areas, average cobalt particle sizes, and dispersions of cobalt supported on CNTs and CMK-3 materials determined with hydrogen chemisorption.

The particle sizes obtained by HAADF-STEM and hydrogen chemisorption were much larger than the crystallite sizes from XRD. This arised from particles consisting of several crystalline domains. Furthermore, the particle sizes from hydrogen chemisorption were based on adsorption of H_2 . Thus, especially from a catalysis viewpoint, the metallic surface areas and particle sizes obtained with hydrogen chemisorption are more relevant for this study than the XRD crystallite sizes.

Particle aggregation during reduction

Bright field TEM was used to analyze the morphology and cobalt distribution of the reduced catalysts. **Fig. 3.9C-F** clearly showed that cobalt particle aggregation had occured for Co/CMK3-900 and Co/CMK3-1300 during reduction. On the contrary, TEM images of Co/CMK3-500 (see **Fig. 3.9AB**) showed no particle aggregation. The difference between Co/CMK3-500 and the other two catalysts could be attributed to difference in the oxygen-containing surface groups. As TGA-MS under nitrogen had demonstrated previously (see **Section 3.1.3**), CMK3-500 contained more oxygen functionalities compared to CMK3-900 and CMK3-1300. These surface groups served as anchoring sites for cobalt NPs and thereby prevented particle aggregation.



Figure 3.9. Bright field TEM images of (A,B) Co/CMK3-500, (C,D) Co/CMK3-900, and (E,F) Co/CMK3-1300 after reduction under hydrogen at 350°C for 8 h. 37

3.1.6 Catalytic performance of cobalt supported on CMK-3 and CNTs

Low pressure Fischer-Tropsch synthesis

Low pressure FTS was performed to evaluate and compare the catalytic performance of the CMK-3 and CNTs supported catalysts at 220°C and 1 bar. The activities, reported as CTY, are plotted against the TOS in Fig. 3.10 and the overall results are displayed in Table 3.6. Co/CNT showed a higher activity and C_{5+} selectivity than all the CMK-3 supported catalysts. Nevertheless, it should be noted that both the activities (see Fig. 3.10) and C_{5+} selectivities (see Fig. A.1AB in Appendix A) for Co/CNT decreased significantly over time, whereas for the CMK-3 supported catalysts these two parameters remained constant. This observation could be explained by comparing TEM images from the catalysts after reduction and after FTS at 1 bar. For Co/CNT, Fig. 3.11AB indicated cobalt particle growth afer FTS at 1 bar. For Co/CMK3-900, Fig. 3.11CD showed the same cobalt aggregates after reduction and FTS at 1 bar. No significant particle growth was observed for the CMK-3 supported catalysts after FTS at 1 bar, which explained the constant activities and selectivities. Co/CMK3-900 displayed the highest TOF of all CMK-3 supported catalysts. The lower TOF for Co/CMK3-500 is likely caused by the cobalt particle size effect. As indicated previously during the catalyst characterization, Co/CMK3-500 mainly contains 2-3 nm cobalt NPs, which are below the optimum size of 6-8 nm.⁴² All CMK-3 supported catalysts displayed relatively low C_{5+} selectivities.

It was considered that CMK-3 supported catalysts could have suffered from diffusion limitations due to CMK-3 pore system, which was only accesible from two sides. In order to analyze this phenomenon, the temperature was increased stepwise for Co/CMK3-1300 during FTS at 1 bar (data not shown). With the varying reaction rates obtained at different temperatures, an Arrhenius plot was constructed. The activation energy could be deducted from the ramp of this plot. The apparent activation energy was 98 kJ·mol⁻¹, which was similar to values reported in literature for cobalt FTS catalysts that did not suffer from diffusion limitations. 40,44,80 This indicated that diffusion limitations were absent in Co/CMK3-1300, as the apparent activation energy would be half the true activation energy for intraparticle diffusion limitations. 81



Figure 3.10. CTY during FTS at 220°C and 1 bar plotted against the TOS for CO conversions between 0 and 3% for Co/CMK3-500, Co/CMK3-900, Co/CMK3-1300, and Co/CNT. The H_2 /CO ratio was 2:1 and the GHSV 3500 h^{-1} .

Table 3.6. Results from FTS at 220°C and 1 bar reported from 15-20 h time on stream and CO conversions between 0 and 3% for Co/CMK3-500, Co/CMK3-900, Co/CMK3-1300, and Co/CNT. The H_2 /CO ratio was 2:1 and the GHSV 3500 h^{-1} .

Catalyst	CTY (10^{-5} mol)	TOF (10^{-3})	CH ₄ selectivity (%)	C_{5+} selectivity (%)
	$\text{CO} \cdot g_{\text{Co}}^{-1} \cdot \text{s}^{-1}))$	s^{-1})		
Co/CNT	3.4	20	38	35
Co/CMK3-500	1.0	3.8	55	19
Co/CMK3-900	1.0	5.1	63	15
Co/CMK3-1300	0.3	2.4	75	6.1



Figure 3.11. Bright field TEM images of A) Co/CNT after reduction under hydrogen at 350°C for 8 h, B) Co/CNT after FTS at 1 bar for 40 h TOS, C) Co/CMK3-900 after reduction under hydrogen at 350°C for 8 h, and D) Co/CMK3-900 after FTS at 1 bar for 40 h TOS.

High pressure Fischer-Tropsch synthesis

High pressure FTS was performed to evaluate and compare the catalytic performance of the CMK-3 and CNTs catalysts at 220°C and 20 bar. The activities, reported as CTY, are plotted against the TOS for the CMK-3 and CNTs supported catalysts in **Fig. 3.12**. The GHSV was initially 2000 h⁻¹, but was lowered to 1000 h⁻¹ after 10 h TOS in order to report catalytic performance at CO conversions between 10 and 20 % for all catalysts. Different from FTS at 1 bar, Co/CMK3-900 and Co/CMK3-1300 had completely deactivated after 10 h TOS. Hence, their selectivities and long-term stability could not be evaluated. The TOFs and selectivities for Co/CNT and Co/CMK3-500 are displayed in **Table 3.7**. Co/CMK3-500 showed a relatively high CH₄ and low C₅₊ selectivity. The higher methane selectivity for Co/CMK3-500 compared

to Co/CNT could be attributed to the cobalt particle size effect. HAADF-STEM showed cobalt NPs of 2-3 nm after reduction, which were below the optimum value of 6-8 nm.⁴²

Regarding the long-term stability, CO conversion decreased from 49% to 33% for Co/CNT and from 13% to 11% for Co/CMK3-500 in the interval 10-100 h TOS. The better stability of Co/CMK3-500 was attributed to its ordered pore structure and high SSA which were likely to benefit the catalyst stability. This effect would even be more prominent at higher space velocities.⁸²

Additionally, after 100 h TOS the temperature was increased stepwise in order to check for diffusion limitations. This could not be checked for Co/CMK3-900 and Co/CMK3-1300, since these catalysts had completely deactivated after 10 h TOS. Arrhenius plots were constructed for Co/CNT and Co/CMK3-500 and the apparent activation energies were 97 kJ·mol⁻¹ and 98 kJ·mol⁻¹ respectively. This indicated that diffusion limitations were absent for both catalysts (see also **Section 3.1.6**).



Figure 3.12. CTY during FTS at 220°C, 20 bar, and H_2 /CO ratio 2:1 plotted against the TOS for CO conversions between 10 and 20% for Co/CMK3-500, Co/CMK3-900, Co/CMK3-1300, and Co/CNT. The GHSV was 2000 h^{-1} in the first 10 h TOS and 1000 h^{-1} from 10-150 h TOS. After 100 h TOS the temperature was increased stepwise to check for diffusion limitations.

Catalyst	CTY (10^{-5} mol)	TOF (10^{-3})	CH_4 selectivity (%)	C ₅₊ selectivity (%)
-	$\text{CO} \cdot g_{\text{Co}}^{-1} \cdot \text{s}^{-1}))$	s^{-1})		-
Co/CNT	15	139	10	81
Co/CMK3-500	1.8	20.4	36	51

Table 3.7. Results from FTS at 220°C, 20 bar, and H_2 /CO ratio 2:1 reported from 10-100 h TOS at GHSV = 1000 h^{-1} and CO conversions between 10 and 20% for Co/CMK3-500, Co/CMK3-900, Co/CMK3-1300, and Co/CNT.

3.1.7 Particle agglomeration during catalysis

In order to investigate why and how Co/CMK3-900 and Co/CMK3-1300 had deactivated during FTS at 20 bar, HAADF-STEM was used to analyze the spent catalysts. Co/CMK3-1300, the least active catalyst, was also analyzed with EDX elemental mapping in order to obtain insights on the deactivation.

HAADF-STEM analysis of the spent catalysts in **Fig. 3.13** showed a clear difference between active Co/CMK3-500 and deactivated Co/CMK3-1300. The cobalt NPs in Co/CMK3-500 were still located in the CMK-3 pores and homogeneously distributed (see **Fig. 3.13AB**), whereas the cobalt NPs in Co/CMK3-1300 had migrated to the CMK-3 external surface and grown to very large cobalt particles with a multimodal size distribution (see **Fig. 3.13CD**). This was supported by the particle size analysis of the spent Co/CMK3-1300 catalyst, which can be found in **Appendix B**. The cobalt NPs that had already formed aggregates after reduction, agglomerated during FTS at 20 bar. The stability of Co/CMK3-500 could be attributed to the presence of oxygen-containing surface groups, which served as anchoring points for cobalt NPs and thereby prevented particle growth.

Fig. 3.14 shows EDX elemental mapping TEM images of Co/CMK3-1300. Initially, it was considered that cobalt carbides could have been formed during FTS at 20 bar due to the defective graphite structure of CMK-3 materials. However, **Fig. 3.14A** shows a close up of an agglomerate, which consists of metallic cobalt (red) surrounded by an oxide layer (blue). The oxide layer was likely caused due to exposure to air before characterization with (S)TEM. Formation of an oxide layer around metallic cobalt during FTS is in contradiction with thermodynamic calculations reported in literature, which showed that cobalt NPs could only re-oxidize when they are below 5 nm in diameter.^{11,38} These calculations also showed that formation of an oxide layer around a metallic core is thermodynamically unstable. However, the contribution of support interactions and possible surface reconstruction under FTS conditions were not taken into consideration.³⁵ The cobalt oxide agglomerates in Co/CMK3-1300 were apparently stabilized on the external surface of CMK-3 particles.

Fig. 3.14B shows a close up of the empty CMK-3 pores. An additional EDX elemental mapping TEM image, showing cobalt, oxygen, and carbon, can be found in Appendix C. The EDX analysis showed that metallic cobalt had migrated completely out of the CMK-3 pores during FTS at 20 bar. Migration of cobalt supported on alumina over macroscopic distances has been observed in earlier research and was attributed to high temperature effects or low H_2/CO ratios and low gas flow rates.^{83,84} Partial oxidation induced by water and diffusion of cobalt particles has been proposed as particle growth mechanism.⁸⁵ Migration of cobalt supported on silica over macroscopic distances was attributed to entrainment of cobalt NPs by

reaction products at high CO conversions of 65%.⁸⁶ In this study, migration of cobalt supported on carbon over macroscopic distances was observed at low CO conversions of 10-20%. This migration was therefore not likely to be caused by entrainment of cobalt NPs, but rather by a combination of high temperature and pressure, lacking anchoring points for cobalt NPs on the CMK-3 surface, and poor confinement of cobalt NPs in the CMK-3 pores. Tentatively, OR is proposed as the main particle growth mechanism in carbon-supported cobalt FTS catalysts with a distinct bi- or multimodal cobalt particle size distribution after calcination. A schematic representation of particle growth is depicted in Fig. 3.15. Both the multimodal cobalt particle size distribution after catalysis shown in Fig. 3.13D and the presence of agglomerates rather than aggregates on the CMK-3 external surface supported the OR mechanism. The multimodal cobalt particle size distribution indicated a net flux of cobalt atoms or clusters from small to larger cobalt particles during FTS at 20 bar. Consequently, larger particles grew at the expense of small ones. Nevertheless, it is not excluded that the MC mechanism could have taken place simultaneously. Recently, Xaba et al.⁸⁷ found evidence with HAADF-STEM EDX that OR and MC could occur simultaneously for cobalt supported on titania during FTS. In situ TEM or in situ scanning tunneling microscopy (STM) could be used to draw conclusions on the cobalt particle growth mechanism. These techniques could provide insights on the atomic scale.^{88,89}



Figure 3.13. HAADF-STEM images of (A,B) Co/CMK3-500 and (C,D) Co/CMK3-1300 after FTS at 20 bar for 150 h TOS.



Figure 3.14. EDX elemental mapping TEM images of Co/CMK3-1300 after FTS at 20 bar for 150 h TOS. A) Cobalt is depicted in red, oxygen in blue, and B) carbon in green.

It was reported in literature that waterinduced re-oxidation of carbon-supported cobalt FTS catalysts was inhibited due to carbon's hydrophobic nature.⁴⁷ However, in this study it could not be excluded that reoxidation had occurred during FTS at 20 bar. The cobalt NPs had migrated completely out of the CMK-3 pores during FTS and were located on the external surface of CMK-3 particles. Cobalt particles on the CMK-3 external surface were easily accesible to water molecules and could be prone to waterinduced re-oxidation. Thermodynamic calculations have shown that cobalt NPs could only re-oxidize during FTS when they are below 5 nm in diameter, ^{11,38} but support interactions and possible surface reconstruction were not taken into consideration. Experiments with co-feeding water during catalytic runs are needed to confirm or deny waterinduced re-oxidation. The spent catalysts should be analyzed with X-ray absorption near edge structure (XANES). XANES is very



Figure 3.15. Schematic representation of cobalt particle growth when cobalt NPs are not uniformly sized. A) Co/CMK3-900 and Co/CMK3-1300 before FTS at 20 bar and B) Co/CMK3-900 and Co/CMK3-1300 after FTS at 20 bar for 150 h TOS and exposure to air.

promising for this, because quantitative results on the degree of reduction can be obtained without removing the FT waxes covering the catalyst.³⁵ Hence, exposure of the cobalt particles to air is prevented and can be ruled out during analysis.

3.2 Catalyst preparation

3.2.1 Impregnation and drying

Several phenomena possibly occuring during impregnation were considered to find the reason for the inhomogeneous cobalt distribution in CMK-3 supported catalysts. First, the distribution of cobalt ions on the support after impregnation could be affected by electrostatic interactions.²¹ It was known from literature that the point of zero charge (PZC) for graphitic carbon is 4-5 and for oxidized carbon 2-4.⁹⁰ At pH values below the PZC, the support surface is positively charged; at pH values higher than the PZC, the support surface is negatively charged. If the impregnating cobalt nitrate solution has a pH below the PZC, the carbon support surface will be positively charged. Consequently, repulsion between the carbon surface and the Co²⁺ ions might lead to inhomogeneous cobalt distribution in the resulting catalyst. At pH values higher than the PZC, the carbon support surface will be negatively charged and positively charged cobalt ions are distributed more homogeneously. Consequently, the pH of the cobalt nitrate solutions was considered. This pH value turned out to be 3-4, which is relatively low. Hence, cation adsorption could be limited at these conditions (pH < PZC) due to the repulsion between positively charged cobalt cations and the positively charged carbon surface.

Furthermore, it was suspected that impregnation under static vacuum caused too fast evaporation of the ethanol precursor solvent. Consequently, the cobalt nitrate concentration had suddenly exceeded supersaturation and precipitation had occurred before the precursor solution was homogeneously distributed over the support pores. This resulted in an inhomogeneous distribution of cobalt NPs in the catalyst (see Fig. 3.8). Static vacuum was even unneccesary during impregnation, since the 2-3 nm CMK-3 pores could facilitate sufficient capillary forces. On the contrary, carbon materials with larger pores, such as CNTs, might require static vacuum during impregnation in order to increase capillary suction and force the precursor solution to enter the pore system. In order to prevent too fast evaporation of ethanol, CMK-3-900 impregnation was carried out dropwise at ambient pressure in a mortar. The HAADF-STEM images in Fig. 3.16AB showed the multimodal cobalt particle size distribution in Co/CMK3-900 after impregnation under vacuum, whereas Fig. 3.16CD showed a more uniform particle size distribution in Co/CMK3-900 after impregnation at ambient pressure (Co/CMK3-900-RT). Furthermore, the ordered mesostructure of CMK-3 seemed to be partially destroyed in Co/CMK3-900-RT. The same phenomenon was observed previously for Co/CMK3-900 and Co/CMK3-1300 impregnated under vacuum (see Appendix D) and could be attributed to the calcination treatment.

Additionally, drying in static air was known to be a possible cause of particle agglomeration.⁹¹ The liquid precursor could allow for mobility and redistribution, resulting in an inhomogeneous distribution of active species. In order to analyze whether the drying step had affected the cobalt distribution, one Co/CMK3-900 sample was dried at 70°C with a heating rate of 1°C/min for 3 h under 50 mL/min N₂ flow in a fluidized bed reactor (Co/CMK3-900-RTF). A difference was observed with HAADF-STEM between the conventionally dried catalysts (**Fig. 3.16A-D**) and the fluidized bed dried catalyst (**Fig. 3.16EF**). Fluidized bed drying clearly led to a homogeneous cobalt distribution with uniformly sized particles.



Figure 3.16. HAADF-STEM images of the calcined catalysts (A,B) Co/CMK3-900, (C,D) Co/CMK3-900-RT, and (E,F) Co/CMK3-900-RTF. 47

Particle aggregation during reduction

Bright field TEM was used to analyze the morphology and cobalt distribution of the reduced catalysts. **Fig. 3.17AB** showed that particle aggregation had occured for Co/CMK3-900-RT. However, the amount of aggregates seemed to be smaller compared to Co/CMK3-900 prepared under static vacuum (see **Fig. 3.9CD**) and the primary cobalt particles were smaller in size. **Fig. 3.17CD** showed that particle aggregation had hardly occured for Co/CMK-3-RTF. **Fig. 3.17C** showed the only aggregate that was found in this sample.



Figure 3.17. Bright field TEM images of (A,B) Co/CMK3-900-RT and (C,D) Co/CMK3-900-RTF after reduction under hydrogen at 350°C for 8 h.

3.2.2 Catalytic performance: Impregnation and drying

Low pressure Fischer-Tropsch synthesis

Low pressure FTS was performed to evaluate and compare the catalytic performance of the CMK-3 supported catalysts after changing the impregnation and drying method. The activities, reported as CTY, are plotted against the TOS in **Fig. 3.18** and the overall results are displayed in **Table 3.8**. By changing the impregnation method, both the activities and the selectivities of Co/CMK3-900-RT had improved compared to Co/CMK3-900. Co/CMK3-900-RT3, with 3.33 wt.% Co⁰, displayed a comparable activity to Co/CMK3-900. The cobalt was apparently more efficiently distributed in Co/CMK3-900-RT3, which could have been caused by changing the impregnation method and/or lowering the cobalt weight loading. Nevertheless, the CH₄ selectivities were still higher than 50% for all CMK-3 supported catalysts, which was attributed to the 2-3 nm cobalt particles in the CMK-3 pores. Co/CNT still displayed a higher activity and C₅₊ selectivity than all the CMK-3 supported catalysts, which could be attributed to the larger cobalt particle size on CNTs compared to CMK-3. Besides, the vast open space in between the CNTs may have benefitted adsorption and diffusion processes in the Co/CNT catalyst.

Remarkably, Co/CMK3-900-RTF displayed a high deactivation over time. Tentatively, the following explanation is proposed: Co/CMK3-900-RTF contained predominantly homogeneously distributed 2-3 nm cobalt NPs after calcination (see Fig. 3.16EF). These small NPs were prone to sintering due to their high chemical potential and surface free energy. The NPs were uniformly sized and sintering was unlikely to proceed *via* the OR mechanism, as proposed previously for catalysts with a multimodal cobalt particle size distribution after calcination. However, the NPs were closely packed in the CMK-3 pores and the interparticle spacing was therefore small. Consequently, sintering on the nanoscale occured *via* the MC mechanism. The particle growth was supported by a 15% decrease in CH₄ selectivity and a 15% increase in C_{5+} selectivity from 1 to 45 h TOS (see Fig. A.1C in Appendix A). Besides the increase in C_{5+} selectivity, it was expected that growth of the 2-3 nm cobalt NPs, would be accompanied by an increase in activity. However, the activity actually decreased and a possible explanation for this could be that the cobalt NPs grew until they blocked the CMK-3 pores. Blocking of the CMK-3 pores shielded part of the cobalt surface from reactants and thereby decreased the activity. It should also be considered that the cobalt NPs in Co/CMK3-900-RTF were below 5 $\,$ nm in diameter and could have re-oxidized during FTS. Furthermore, the CO conversion had decreased over time and that this could possibly have induced the increase in C_{5+} selectivity. To obtain more insights on the deactivation of Co/CMK3-900-RTF, the spent catalyst should be analyzed with N_2 physisorption to check for pore blocking. Re-oxidation during FTS could be confirmed or denied with XANES measurements on the spent catalyst.



Figure 3.18. CTY during FTS at 220°C and 1 bar plotted against the TOS for CO conversions between 0 and 3% for Co/CNT, Co/CMK3-900, Co/CMK3-900-RT, Co/CMK3-900-RT3, and Co/CMK3-900-RTF. The H_2 /CO ratio was 2:1 and the GHSV 3500 h⁻¹.

Table 3.8. Results from FTS at 220°C and 1 bar reported from 15-20 h time on stream and CO conversions between 0 and 3% for Co/CNT, Co/CMK3-900, Co/CMK3-900-RT, Co/CMK3-900-RT3, and Co/CMK3-900-RTF. The H_2 /CO ratio was 2:1 and the GHSV 3500 h⁻¹.

Catalyst	CTY (10^{-5} mol)	CH ₄ selectivity (%)	C ₅₊ selectivity (%)
	$\text{CO} \cdot g_{\text{Co}}^{-1} \cdot \text{s}^{-1}))$		
Co/CNT	3.4	38	35
Co/CMK3-900	1.0	63	15
Co/CMK3-900-RT	1.5	58	19
Co/CMK3-900-RT3	1.0	58	19
Co/CMK3-900-RTF	0.8	52	24

High-pressure Fischer-Tropsch synthesis

High pressure (20 bar) FTS was performed to evaluate and compare the catalytic performance of the CMK-3 supported catalysts after changing the impregnation and drying method. The activities, reported as CTY, for Co/CMK3-900-RT, Co/CMK3-900-RT3, and Co/CMK3-900-RTF

plotted against the TOS are shown in **Fig. 3.19**. Co/CMK3-900 was added as a reference. The GHSV was 2000 h^{-1} from 1 to 100 h TOS and was decreased to 1000 h^{-1} after 100 h TOS in order to report catalytic performance at CO conversions between 10 and 20% for all catalysts.

The overall results are displayed in **Table 3.9** and Co/CMK3-500 was added as a reference. The activity of Co/CMK3-900-RT was higher compared to Co/CMK3-500 and the activity of Co/CMK3-900-RTF was similar to Co/CMK3-500. The C₅₊ selectivities for Co/CMK3-900-RT and Co/CMK3-900-RTF were 50% and 23%, respectively. The CH₄ selectivity was 39% for Co/CMK3-900-RT and 61% for Co/CMK3-900-RTF. The difference in selectivities was attributed to the predominant presence of 2-3 nm sized cobalt NPs in Co/CMK3-900-RTF. Regarding the long-term stability, the activities for both catalysts remained constant over time. Similar to FTS at 1 bar, Co/CNT still displayed a higher activity and C₅₊ selectivity than all the CMK-3 supported catalysts. To obtain a more complete analysis of the catalytic data, the activity *per* cobalt surface atom for Co/CMK3-900-RT and Co/CMK3-900-RTF (TOF) should be determined. Characterization with hydrogen chemisorption would yield the metallic surface areas, which could be used to determine the TOFs.

Co/CMK3-900-RT3, a CMK-3 supported catalyst with 3.33 wt.% Co⁰, deactivated rapidly in the first 10 h TOS and its activity fluctuated severely. The selectivities could not be reported because of the low and severely fluctuating CO conversion. Due to the low cobalt weight loading, the cobalt NPs might not have been sufficiently confined in the CMK-3 pores and were therefore prone to sintering at 20 bar. Characterization of the calcined, reduced, and spent catalyst with TEM are needed to confirm or deny this hypothesis.



Figure 3.19. CTY during FTS at 220°C, 20 bar, and H_2 /CO ratio 2:1 plotted against the TOS for CO conversions between 10 and 20% for Co/CNT, Co/CMK3-900, Co/CMK3-900-RT, Co/CMK3-900-RT3, and Co/CMK3-900-RTF. The GHSV was 2000 h^{-1} in the first 100 h TOS and 1000 h^{-1} from 100-150 h TOS.

Table 3.9. Results from FTS at 220°C, 20 bar, and H_2/CO ratio 2:1 reported at GHSV = 1000 h^{-1} and CO conversions between 10 and 20% for Co/CNT, Co/CMK3-900, Co/CMK3-900-RT, Co/CMK3-900-RT3, and Co/CMK3-900-RTF.

Catalyst	CTY (10^{-5} mol)	CH_4 selectivity (%)	C ₅₊ selectivity (%)
	$\text{CO} \cdot g_{\text{Co}}^{-1} \cdot \text{s}^{-1}))$		
Co/CNT	15	10	81
Co/CMK3-500	1.8	36	51
Co/CMK3-900-RT	2.5	39	50
Co/CMK3-900-RTF	1.5	61	23

Spent catalysts

Analysis of the catalysts after FTS at 20 bar with bright field TEM (see Fig 3.20AB) showed a significant difference in cobalt distribution over the CMK-3 support for Co/CMK3-900-RT compared to the deactivated Co/CMK3-900 and Co/CMK3-1300 catalysts (see Fig 3.13CD). In the deactivated catalysts the cobalt NPs had migrated completely to the CMK-3 external surface, whereas in Co/CMK3-900-RT there were still cobalt NPs located in the CMK-3 pores. Nevertheless, cobalt particle growth had occured in Co/CMK3-900-RT. Some cobalt NPs had even grown larger than the CMK-3 pores and thereby partially destroyed the CMK-3 framework. Besides, some cobalt NPs had grown into rod-like particles. This indicated either that the CMK-3 pores forced cobalt NPs to grow in a certain direction or that growth occurred preferably on a specific crystalline facet. Because the cobalt particles in Co/CMK3-900-RT were similar in size after FTS at 20 bar, OR was unlikely to be the particle growth mechanism in this catalyst. Tentatively, MC is proposed as the main particle growth mechanism when cobalt NPs are uniformly sized after calcination, as in Co/CMK3-900-RT. Evidence for this mechanism was found in bright field TEM images after FTS at 20 bar. In Fig. 3.21 the spots where cobalt NPs had coalesced were indicated with red arrows. A schematic representation of this mechanism is depicted in Fig. 3.22AB. Alternatively, Hansen et al.⁸⁹ interpreted metal particles exceeding the pore size as evidence of the OR mechanism. It is also not excluded that both MC and OR could occur simultaneously. As discussed previously, in situ TEM or in situ STM could be used to draw conclusions on the cobalt particle growth mechanism.

In Co/CNT the cobalt NPs were located on the CNTs and surrounded by a vast open space in between the CNTs, whereas in Co/CMK3-900-RT the cobalt NPs were confined in the CMK-3 pores. In Co/CNT, cobalt NPs could grow unlimited, which eventually led to catalyst deactivation. On the other hand, cobalt particle growth in Co/CMK3-900-RT did not necessarily lead to catalyst deactivation, since growth was limited by the CMK-3 pores.

In Co/CMK3-900-RTF, the cobalt NPs were well-dispersed and homogeneously distributed after calcination. The cobalt NPs were still likely to grow to some extent during reduction. After reduction, the cobalt NPs may have been rigidly confined in the CMK-3 pores and hence migrated to a smaller extent compared to the cobalt NPs in Co/CMK3-900-RT. This was supported by the TEM images of Co/CMK3-RTF after reduction in **Fig. 3.17CD**, which showed virtually no aggregation. The TEM images after FTS at 20 bar in **Fig. 3.20CD** indicated that particle growth did occur, but to a smaller extent compared to Co/CMK3-900-RT. The relatively

small cobalt NPs in **Fig. 3.20CD** also explained the high methane selectivity of this catalyst. Additionally, some CMK-3 pores could be blocked by cobalt NPs and consequently part of the cobalt would not available for reactants. A schematic representation of this phenomenon is depicted in **Fig. 3.22CD**. It is not excluded that the mechanism depicted in **Fig. 3.22AB** also occured in Co/CMK3-900-RTF. To confirm or deny pore blocking, N₂ physisorption measurements could be carried out on the reduced Co/CMK3-900-RTF catalyst.



Figure 3.20. Bright field TEM images of (A,B) Co/CMK3-900-RT, (C,D) Co/CMK3-RTF after FTS at 20 bar for 150 h TOS.



Figure 3.21. Bright field TEM image of Co/CMK3-900-RT after FTS at 20 bar for 150 h TOS. The spots where cobalt NPs had coalesced were indicated with red arrows.



Figure 3.22. Schematic representation of migration and coalescence as the predominant particle growth mechanism when cobalt NPs are uniformly sized. (*A*,*B*) CMK-3 framework destruction due to particle growth and (*C*,*D*) CMK-3 pore blocking due to rigid confinement of cobalt NPs.

Additionally, the cobalt particle size distribution from TEM images of spent catalysts in **Fig. 3.23** showed that the cobalt NPs in Co/CMK3-900-RTF were mainly below the optimum size of 6-8 nm. The inset added to **Fig. 3.23** displays the FTS activity, reported as CTY, of carbon-supported cobalt catalyst with respect to the cobalt particle size.⁴² The activity decreases rapidly for cobalt NPs below 6 nm. From this it could be concluded that the cobalt NPs in Co/CMK3-900-RTF were too small for FTS and that fluidized-bed drying is not suitable for preparing CMK-3 supported cobalt FTS catalysts.



Figure 3.23. TEM particle size analysis of Co/CMK3-900-RT and Co/CMK3-900-RTF after FTS at 220°C and 20 bar for 150 h TOS. The inset displays the FTS activity of carbon-supported catalysts ($220^{\circ}C$, $H_2/CO = 2$, 1 bar), reported as CTY, with respect to the cobalt particle size and is adapted from Ref.⁴²

3.2.3 Calcination temperature

Another factor that influenced the cobalt distribution in the catalyst was the calcination treatment. It was known from literature that anchoring of metal NPs on carbon support is not very robust.⁷⁶ Hence, mobile species could be formed during calcination at elevated temperatures. Consequently, particle aggregation or agglomeration could occur. It was suspected that calcination at 250°C may have been too severe and may have resulted in complete reduction of cobalt oxides and undesired cobalt particle mobility. This was supported by support-assisted reduction of cobalt supported on CMK-3 (see also **Section 3.1.4**). The uncalcined Co/CMK3-900 catalyst, impregnated at ambient pressure, was investigated with TGA-MS under nitrogen to obtain more information on the influence of the calcination treatment. **Fig. 3.24** showed that the cobalt nitrate precursor was already completely decomposed at 200°C, which proved that calcination at 250°C was indeed too severe. The light blue and dark blue line in **Fig. 3.24** are the MS signals for NO and NO₂ respectively, which are decomposition products of the cobalt nitrate precursor. The MS signal for CO₂ was also plotted in **Fig. 3.24**. The CO₂ fragment was already observed at low temperatures. Two peaks arose at 100°C and 130°C. This could be the decomposition of oxygen-containing surface groups or could be induced by decomposition of the cobalt nitrate precursor. Between 200°C and 250°C the CO₂ signal increased, which suggested support-assisted reduction. The MS signal for CO was also observed at low temperatures (data not shown).



Figure 3.24. The evolution of CO_2 , NO and NO_2 for Co/CMK3-900 in a nitrogen atmosphere at increasing temperature, monitored by online MS. All signals were normalized to their highest ion current. The inset displays the relative mass loss of the catalyst with respect to the temperature.

Tentatively, two mechanisms are proposed to take place during calcination at 250°C to form either CO₂ or CO. First, cobalt nitrate decomposed in Co₃O₄, NO and NO₂ already during the heating step. Then, support-assisted Co₃O₄ reduction took place. Oxygen atoms from Co₃O₄ bound to defects in CMK-3 (see eqn. 3.1) and the remaining cobalt and oxygen atoms were rearranged as CoO. Subsequently, support-assisted CoO reduction occured, meaning that oxygen atoms were released from the CoO lattice and cobalt atoms were rearranged into Co⁰. The released oxygen atoms were energetically active and could easily react with carbon atoms to yield CO₂ (see eqn. 3.2 and 3.3). Alternatively, oxygen atoms from Co₃O₄ could react directly with CMK-3 to form CoO and CO (see eqn. 3.4). Then, CoO released oxygen again to form Co⁰ and more CO (see eqn. 3.5). It was not clear which of the two proposed mechanisms was predominant and they may even have occurred simultaneously. More experiments with variations in different parameters, such as heating ramp and temperature, could be performed in order to draw conclusions on the support-assisted reduction mechanism.

$$\text{Co}_3\text{O}_4/\text{CMK} - 3 \rightarrow 3\text{CoO/CMK} - 3 - \text{O}$$
 (3.1)

$$3$$
CoO/CMK $- 3 - O \rightarrow 3$ Co⁰/CMK $- 3 + 2$ CO₂ (3.2)

$$2\text{CoO/CMK} - 3 \rightarrow 2\text{Co}^0/\text{CMK} - 3 + 2\text{CO}_2$$
(3.3)

$$\text{Co}_3\text{O}_4/\text{CMK} - 3 \rightarrow 3\text{CoO}/\text{CMK} - 3 + \text{CO}$$
 (3.4)

$$3$$
CoO/CMK $- 3 \rightarrow 3$ Co⁰/CMK $- 3 + 3$ CO (3.5)

Regardless of the mechanism, formation of mobile Co^0 species during calcination was undesired. Mobile Co^0 species could sinter to form large, less active cobalt particles. Besides, formation of CO or CO_2 molecules during support-assisted reduction weakened or even partially destroyed the CMK-3 framework, since carbon atoms were released from the framework during this process. Hence, because of the calcination temperature impact, it was recommended to calcine CMK-3 supported catalysts at 200°C instead of 250°C to prevent undesired formation of mobile Co^0 species and CMK-3 framework destruction.

The nature of cobalt species after Co/CMK3-900 calcination at 200°C

Co/CMK3-900 was impregnated at ambient pressure at room temperature, dried statically at 60°C and calcined under N₂ flow at 200°C (Co/CMK3-900-200). XRD was used to determine the cobalt crystalline phases and the volume-averaged crystallite size.

The XRD patterns (see **Fig. 3.25**) demonstrated that Co_3O_4 was the predominant cobalt phase in CMK-3 after calcination at 200°C. Co/CMK-3 did not show support-assisted reduction during calcination at 200°C. It was expected that mobile metallic cobalt was not formed and sintering did not occur. Furthermore, the cobalt volume-averaged crystallite size increased from 1.4 to 2.8 nm for catalyst calcination at 200°C compared to calcination at 250°C (see **Table 3.10**). The Co/CMK3-900-200 cobalt crystallite size was closer to the CMK-3 pore size (~ 4 nm) compared to the Co/CMK3-900 crystallite size. This may enhance the confinement effect and reduce sintering during reduction under hydrogen and FTS reaction conditions. Alternatively, the larger crystallite size for Co/CMK3-900-200 could be ascribed to monocrystalline cobalt NPs in this catalyst versus polycrystalline cobalt NPs in Co/CMK3-900. Metallic cobalt was formed during calcination at 250°C, which re-oxidized possibly to polycrystalline cobalt NPs during exposure to air. The observed crystallite size for Co/CMK3-900 would therefore be smaller than the cobalt particle size, since cobalt NPs consisted of multiple crystalline domains. The estimated Co⁰ volume-averaged crystallite sizes are also displayed in **Table 3.10** for a comparison with hydrogen chemisorption results that will follow.



Figure 3.25. XRD patterns of Co/CMK3-900-200 and Co/CMK3-900. Co_3O_4 is the predominant cobalt crystalline phase after calcination at 200°C and CoO is the predominant phase after calcination at 250°C, as indicated by the peak positions around 50° 2 θ and the emerging peak at 36.5° 2 θ for Co/CMK3-900-200.

Table 3.10. Crystallite sizes of Co_3O_4 , CoO and Co^0 from XRD for cobalt on CMK-3 calcined at 200 and 250°C.

Catalyst	Crystalline phase	Crystallite size (nm)	Crystallite size Co ⁰ (nm)
Co/CMK3-900	CoO	1.4	1.1
Co/CMK3-900-200	Co_3O_4	2.8	2.1
Morphology after calcination at 200°C

Bright field TEM analysis (see **Fig. 3.26**) demonstrated that the CMK-3 framework was not destroyed during calcination at 200°C. Cobalt particles were homogeneously distributed over the CMK-3 pores. As displayed in **Fig. 3.26B** a bimodal particle size distribution was still observed. However, the frequency and the size of the large cobalt particles seemed to be lower compared to the catalyst calcined at 250°C. Although, it should be noted that TEM is a nanoscale technique and only shows a very small fraction of the catalyst.



Figure 3.26. Bright field TEM images of Co/CMK3-900-200.

Pore blocking after calcination at 200°C

After calcination at 200°C the apparent SSA and pore volume had decreased to about half the values of the pristine CMK-3 support. Furthermore, the hysteresis loop had moved to a lower region of relative pressure, as depicted in Fig. 3.27A. These phenomena were not observed for CNTs (data not shown) or CNFs after catalyst preparation.⁹² Possible explanations for these phenomena were pore blocking by cobalt particles or a carbothermal reaction of the carbon framework during the catalyst preparation. The latter was unlikely due to the inert nature of carbon support material and the low calcination temperature. However, it was observed previously that part of the CMK-3 framework had collapsed after catalyst calcination at 250°C (see **Appendix D**). Pore blocking seemed to be a more likely explanation for the decrease in SSA and pore volume. The large downshift of the hysteresis loop after impregnation suggested that part of the pores were not available for the N₂ probe molecules. This was further supported by the BJH pore size analyses in Fig. 3.27B, which showed a lower differential pore volume for the catalyst compared to the pristine support. However, the well-defined mesoporosity seemed to be preserved after catalyst preparation, as indicated by the shape of the hysteresis and the narrow pore size distribution. This suggested that some pores were completely blocked, while other pores remained accesible for N₂ probe molecules.

We should be careful with preliminary conclusions on the influence of pore blocking on catalysis. It has to be considered that N_2 physisorption measurements were performed when cobalt oxides were present in the catalyst. However, a reduction step is carried out prior to catalysis, which produces metallic cobalt particles that are smaller compared to cobalt oxide particles. The apparent bore blocking as indicated by N_2 physisorption measurements may thus become less important during catalysis.



Figure 3.27. A) Nitrogen adsorption/desorption isotherms and B) BJH pore size distributions calculated from the adsorption branches of CMK3-900 and Co/CMK3-900-200.

Reducibility after calcination at 200°C

The H₂-TPR profiles of calcined Co/CMK3-900-200 (red line) and Co/CNT (grey line) in **Fig. 3.28** showed the typical multi-step reduction process of Co₃O₄ NPs. This supported the observation from XRD that Co₃O₄ was present in Co/CMK3-900-200 and in Co/CNT. The first peaks at 50 minutes (T = 200-250°C) were related to the formation of CoO from Co₃O₄ species. The peaks between 60 and 90 minutes (T = 250-350°C) represented the formation of metallic cobalt from CoO. The broad peaks between 200 and 300 minutes (T \approx 500°C) were associated with methanation of the carbon support, which occurs at high temperatures under hydrogen atmosphere in the presence of cobalt NPs.⁴⁰ It should be noted that the CMK-3 support consumed more hydrogen during support methanation compared to CNTs. This was attributed to the defective graphite structure of the CMK-3 support, which could easily release carbon atoms.



Figure 3.28. Hydrogen consumption, quantified with a TCD, plotted against the time for the calcined Co/CMK3-900-200 (red) and Co/CNT (grey) catalysts. The vertical offset was 0.01 and the total hydrogen consumption was normalized to the mass and cobalt weight loading of the catalyst. The temperature was plotted against the time on the secondary axis and the blue line represents the temperature program.

3.2.4 Surface functionalities

Different surface treatments were carried out to obtain functional groups on the CMK-3 surface. CMK3-900-OX was post-synthetically oxidized to introduce oxygen-containing functionalities on the surface, such as carboxyl and phenol groups. CMK3-900-AM was treated with ammonia to introduce nitrogen-containing functionalities, such as pyrrol and amine groups. The functional groups were analyzed with TGA-MS under nitrogen. **Fig. 3.29A** displays the residual masses of the pristine functionalized materials. CMK3-900-OX released a relatively large amount of adsorbed water during the drying step, which could be attributed to the hydrophilic surface of this material. The presence of oxygen-containing and nitrogen-containing surface groups was confirmed by the MS signals of CO_2 and NO_2 , respectively. **Fig. 3.29B** displays the normalized CO_2 MS signal for CMK3-900-OX and the normalized NO_2 MS signal for CMK3-900-AM, both plotted against the temperature. The catalysts prepared from the functionalized CMK-3 materials were calcined at 200°C.



Figure 3.29. Results from TGA-MS under nitrogen for CMK-3 materials with different surface groups A) The residual masses and B) the normalized CO_2 MS signals for CMK3-900 and CMK3-900-OX and the normalized NO_2 MS signal for CMK3-900-AM were plotted against the temperature.

3.2.5 Catalytic performance: Calcination and surface functionalities

Low pressure Fischer-Tropsch synthesis

Low pressure (1 bar) FTS was performed to evaluate and compare the catalytic performance of the CMK-3 supported catalysts after changing the calcination temperature and introducing surface functionalities. The activities, reported as CTY, are plotted against the TOS in **Fig. 3.30** and the overall results are displayed in **Table 3.11**. Both the activities and the C₅₊ selectivities of CMK-3 supported catalysts were higher after decreasing the calcination temperature to 200°C and introducing oxygen functionalities. However, the CH₄ selectivities were still higher than 50% for all CMK-3 supported catalysts.

Remarkably, Co/CMK3-900-OX deactivated significantly over time. Tentatively, the following explanation is proposed: Co/CMK3-900-OX had oxygen-containing surface functionalities that anchor cobalt NPs. However, these functionalities were not stable under FTS reaction conditions and decomposed. Consequently, the cobalt NPs were no longer anchored to the support and prone to sintering. This was supported by **Fig. 3.29B**, which showed that the CO₂ MS signal increased rapidly at 300°C in a N₂ atmosphere. This indicated decomposition of oxygen-containing surface groups. A lower decomposition temperature is expected under reducing conditions and FTS reaction conditions. Sintering was expected to proceed *via* the MC mechanism, since oxygen-containing surface groups initially facilitated the formation of well-dispersed and uniformly sized cobalt NPs (see TEM images **Fig. E.1AB** in **Appendix E**).

Additionally, a CMK-3 supported catalyst was calcined at 140°C to analyze the influence of an even lower calcination temperature. From TEM images in **Fig. E.1CD** in **Appendix E** it could be deducted that the cobalt nitrate salt was not completely decomposed during calcination at 140°C. Furthermore, the cobalt nitrate and/or oxide particles were inhomogeneously

distributed over the CMK-3 particles. Fig. 3.30 showed that the activity of Co/CMK3-900-140 decreased significantly over time. This was caused by incomplete decomposition of the cobalt nitrate precursor during calcination at 140°C. Consequently, the nitrate precursor decomposed during the reduction step and/or under FTS reaction conditions. Formation of metallic cobalt in H₂ gas proceeds via several steps. The overall reaction is described by eqn. 3.6.⁹³ Decompositon of the cobalt nitrate precursor in H₂ gas could be detrimental to the catalyst for two reasons. Firstly, the decomposition product NH₃ could poison cobalt metallic sites in FTS catalysts and thereby decrease the CO conversion.⁹⁴ It is likely that NH₃ molecules specifically block low-coordinated atoms in cobalt NPs due to the high chemical potential and surface free energy of these atoms. Low-coordinated atoms are located on corners and edges of a cobalt NP and mainly produce methane. If Co/CMK3-900-140 experienced NH₃ poisoning, it is thus expected that the C_{5+} selectivity would increase and the CH_4 selectivity would decrease over time due to specific blocking of the methanation sites. From 5 to 35 h TOS, the C_{5+} selectivity increased from 15% to 29% and the CH₄ selectivity decreased from 60% to 49%. This indicated that Co/CMK3-900-140 indeed experienced NH₃ poisoning due to incomplete cobalt nitrate precursor decomposition during calcination at 140°C. To prove or deny this hypothesis, Co/CMK3-900-140 could be analyzed with TGA-MS under hydrogen. Secondly, the formation of H₂O could induce re-oxidation of metallic cobalt. However, this is unlikely when the cobalt NPs are located in the CMK-3 pores, since carbon supports are known to expell water by their hydrophobicity.⁴⁷

$$Co(NO_3)_2 + 9H_2 \rightarrow Co^0 + 2NH_3 + 6H_2O$$
 (3.6)



Figure 3.30. CTY during FTS at 220°C and 1 bar plotted against the TOS for CO conversions between 0 and 3% for Co/CNT, Co/CMK3-900, Co/CMK3-900-200, Co/CMK3-900-140, and Co/CMK3-900-OX. The H_2 /CO ratio was 2:1 and the GHSV 3500 h^{-1} .

Table 3.11. Results from FTS at 220°C and 1 bar reported from 15-20 h time on stream and CO conversions between 0 and 3% for Co/CNT, Co/CMK3-900, Co/CMK3-900-200, Co/CMK3-900-140, and Co/CMK3-900-OX. The H_2/CO ratio was 2:1 and the GHSV 3500 h^{-1} .

Catalyst	CTY (10^{-5} mol)	CH ₄ selectivity (%)	C ₅₊ selectivity (%)
-	$\text{CO} \cdot g_{\text{Co}}^{-1} \cdot \text{s}^{-1}))$		
Co/CNT	3.4	38	35
Co/CMK3-900	1.0	63	15
Co/CMK3-900-200	1.5	59	19
Co/CMK3-900-140	1.0	56	21
Co/CMK3-900-OX	1.8	56	21

High-pressure Fischer-Tropsch synthesis

High pressure (20 bar) FTS was performed to evaluate and compare the catalytic performance of the CMK-3 supported catalysts after changing the calcination temperature and introducing

surface functionalities. The activities, reported as CTY, plotted against the TOS are displayed in **Fig. 3.31** for Co/CMK3-900-200, Co/CMK3-900-140, Co/CMK3-900-OX, and Co/CMK3-900-AM. The GHSV was 2000 h⁻¹ from 1 to 100 h TOS and was decreased to 1000 h⁻¹ after 100 h TOS in order to report catalytic performance at CO conversions between 10 and 20%.

The overall results are displayed in **Table 3.12**. For Co/CMK3-900-200, the activity was comparable to Co/CMK3-900-RT. The C₅₊ selectivity for Co/CMK3-900-200 was 60%, which was 10% higher compared to Co/CMK3-900-RT. Co/CMK3-900-140 displayed a relatively low activity. This was attributed to the incomplete decomposition of the cobalt nitrate precursor during calcination at 140°C, as discussed previously in **Section 3.2.5**. The relatively high C₅₊ selectivity of 68% and low CH₄ selectivity of 26% supported the hypothesis of NH₃ poisoning proposed in **Section 3.2.5**.

The activities and C_{5+} selectivities for Co/CMK3-900-OX were similar and for Co/CMK3-900-AM slightly lower compared to Co/CMK3-900-200. The CH₄ selectivities for Co/CMK3-900-OX and Co/CMK3-900-AM were slightly higher compared to Co/CMK3-900-200. The similar CTY values for Co/CMK3-900-200 and Co/CMK3-900-OX supported the tentative explanation in **Section 3.2.5** that the oxygen-containing surface groups were not stable under reducing conditions and FTS reaction conditions. The nitrogen functionalities in Co/CMK3-900-AM were obtained by exchange with the oxygen functionalities and it was likely that the nitrogen surface groups also decomposed under reducing conditions or FTS reaction conditions. More experiments are needed to draw solid conclusions on post-synthetically introduced oxygen functionalities. Oxidation treatments with HNO₃ might introduce stable oxygen functionalities,⁵⁰ but this is still to be verified.

To obtain a more complete analysis of the catalytic data, the TOFs should be determined. Characterization with hydrogen chemisorption would yield the metallic surface areas, which could be used to calculate the TOFs. Furthermore, characterization of the reduced and spent catalysts could provide information on cobalt particle growth.



Figure 3.31. CTY during FTS at 220°C, 20 bar, and H_2 /CO ratio 2:1 plotted against the TOS for CO conversions between 10 and 20% for Co/CMK3-900, Co/CMK3-900-200, Co/CMK3-900-140, Co/CMK3-900OX, and Co/CMK3-900-AM. The GHSV was 2000 h⁻¹ in the first 100 h TOS and 1000 h⁻¹ from 100-150 h TOS.

Table 3.12. Results from FTS at 220°C, 20 bar, and H_2/CO ratio 2:1 reported at GHSV = 1000 h⁻¹ and CO conversions between 10 and 20% for Co/CMK3-900-200, Co/CMK3-900-140, Co/CMK3-900OX, and Co/CMK3-900-AM.

Catalyst	CTY (10^{-5} mol)	CH_4 selectivity (%)	C ₅₊ selectivity (%)
	$\text{CO} \cdot g_{\text{Co}}^{-1} \cdot \text{s}^{-1}))$		
Co/CMK3-900-200	2.4	32	60
Co/CMK3-900-140	0.9	26	68
Co/CMK3-900-OX	2.1	43	43
Co/CMK3-900-AM	1.6	40	48

3.3 Conclusions on support synthesis and catalyst preparation

The support synthesis conditions had a great influence on the support properties and on FTS catalytic performance. CMK-3 support material was synthesized from SBA-15 silica templates according to the nanocasting procedure. The carbonization temperature of silica/carbon composites dictated the degree of graphitization and the amount of oxygen-containing surface groups in the resulting carbon support material. Defects in the graphitic structure and oxygen surface functionalities were found to be powerful tools for preparing stable catalysts. They could both prevent severe cobalt particle growth during reduction and catalysis. However,

the oxygen functionalities introduced post-synthetically by a partial oxidation treatment in air appeared to be unstable under FTS reaction conditions. Overviews of catalytic results at 1 bar and 20 bar for all catalysts employed in this research can be found in **Appendix F** and **Appendix G**, respectively.

The impregnation, drying, and calcination conditions had to be optimized in order to prepare active CMK-3 supported catalysts. Initially, incipient wetness impregnation was carried out under static vacuum in order to clear the pores and increase capillary suction. It was found that ethanol, the precursor solvent, evaporated fast under static vacuum. Consequently, the cobalt nitrate concentration exceeded supersaturation and precipitated before the precursor solution was homogeneously distributed over the pore system. The resulting catalysts had a bior multimodal cobalt particle size distribution with nanoparticles located in the pores and large cobalt particles on the external surface of CMK-3 particles. On the contrary, impregnation at ambient pressure yielded a more homogeneous cobalt distribution and active CMK-3 supported catalysts.

Besides, the drying step strongly affected the cobalt distribution over the support material. Static drying led to an inhomogeneous cobalt distribution due to differences in local drying rates. On the other hand, fluidized-bed drying yielded a homogeneous cobalt distribution over the CMK-3 pores. The uniformly sized cobalt nanoparticles obtained after fluidized-bed drying were 2-3 nm in diameter and produced mainly methane, which is a valueless Fischer-Tropsch synthesis product. Besides, the 2-3 nm cobalt nanoparticles obtained after fluidized-bed drying may have blocked the CMK-3 pores and consequently part of the active metal species was not available to convert synthesis gas during catalysis.

Furthermore, defective graphite structures facilitated support-assisted reduction of Co_3O_4 nanoparticles during calcination at 250°C in a N_2 atmosphere. Defective graphite structures can accept oxygen atoms and subsequently release them together with a structural carbon atom as CO or CO_2 . Hence, mobile metallic cobalt nanoparticles were formed during the calcination treatment and sintering occured. An additional feature of this process was partial destruction of the carbon framework upon release of carbon atoms.

During reduction and/or catalysis, carbon-supported cobalt catalysts seemed to display two different sintering mechanisms. Ostwald ripening was proposed for catalysts with a distinct bi- or multimodal cobalt particle size distribution after calcination. Migration and coalescence was proposed for catalysts with uniformly sized cobalt particles after calcination.

Chapter 4

Results and discussion: Pore geometry

CMK-8 and CMK-3 were used to investigate the influence of the pore geometry on catalytic performance. In contrast to the 2D hexagonally ordered mesopores in CMK-3, CMK-8 has 3D cubic ordered mesopores and *Ia3d* symmetry. A schematic representation of the CMK-8 structure and synthesis is depicted in **Fig. 4.1**. The highly branched intertwined 3D channel network of CMK-8 is likely to provide more accesibility compared to CMK-3. It was reported in literature that the CMK-8 network can facilitate inclusion or diffusion throughout the pore channels without pore blocking.⁹⁵ 900°C was chosen as carbonization temperature for KIT-6/CMK-8 composites in order to rule out stabilization of cobalt NPs by surface functionalities arising from incomplete carbonization.



Figure 4.1. Schematic representation of CMK-8 structure and synthesis.

4.1 Support properties of CMK-8

4.1.1 Textural properties and mesostructure of the support

The textural properties of the as-synthesized CMK8-900 material were characterized by nitrogen physisorption and were summarized in **Table 4.1**. CMK-8 showed a high BET surface area of 1425 m² · g⁻¹, a total pore volume of 1.48 cm³ · g⁻¹, and a 4.0 nm pore diameter. These structural properties were similar to CMK-3. The CMK-8 isotherm in **Fig. 4.2A** was of type IV according to the IUPAC classification⁷⁵ and exhibited a hysteresis loop. The steep capillary condensation and the narrow pore size distribution (see **Fig. 4.2B**) indicated a high degree of structural ordering.

Sample	$S_{BET} (m^2 \cdot g^{-1})$	Total pore volume $(cm^3 \cdot g^{-1})$	Micropore volume $(cm^3 \cdot g^{-1})$	Average d _{meso} (nm)
CMK8-900	1425	1.48	0.08	4.0
CMK3-900	1271	1.45	0.07	4.3

Table 4.1. Porosity data of CMK8-900 and CMK3-900.



Figure 4.2. A) Nitrogen adsorption/desorption isotherms and B) BJH pore size distributions calculated from the adsorption branches of CMK3-900 and CMK8-900.

4.1.2 Oxygen-containing surface groups

The oxygen-containing groups on the CMK8-900 surface were evaluated with TGA-MS under nitrogen. The change in sample weight was depicted in **Fig. 4.3A**. Below 150°C the weight loss was associated with the release of adsorbed water, which was higher for CMK8-900 compared to CMK3-900. This could be attributed to the higher amount of oxygen-containing surface groups, which would facilitate a more hydrophylic surface. Between 150 and 450°C the weight loss was attributed to the removal of oxygen-containing surface groups. The higher evolution of CO₂ depicted in **Fig. 4.3B** showed that CMK8-900 contained indeed more oxygen

functionalities than CMK3-900. Based on the previously discussed results, it was expected that these functionalities would be beneficial for preparing stable catalysts with high metal dispersions.



Figure 4.3. Results from TGA-MS under nitrogen for CMK-3 and CMK-8 materials. A) The relative residual masses and B) the MS signals for the CO₂ fragment were both plotted against the temperature.

4.2 Characterization of calcined catalysts

The nature of cobalt species supported on CMK-8

The CMK-8 materials were impregnated either under static vacuum at 0°C or at ambient pressure at room temperature. All catalysts were dried statically at 60°C and calcined under N_2 flow either at 200°C or at 250°C for 4 h. XRD was used to determine the cobalt crystalline phases and the volume-averaged crystallite size.

Strikingly, the XRD analysis demonstrated that Co_3O_4 was the predominant cobalt phase in CMK-8 after calcination at 250°C and 200°C (see **Table 4.2**). CMK-8 did apparently not facilitate support-assisted reduction of cobalt during calcination at these temperatures. It was expected that mobile metallic cobalt was not formed during calcination and that sintering did not occur or to a smaller extent. The cobalt volume-averaged crystallite sizes were 2.5 and 2.6 nm for Co/CMK8-900 and Co/CMK8-900-200, respectively. The cobalt crystallite sizes on CMK-8 materials were comparable to Co/CMK3-900-200 and were closer to the CMK-8 pore size (~4 nm) compared to the Co/CMK3-900 crystallite size. This may enhance the confinement effect and reduce sintering during reduction under hydrogen and FTS reaction conditions.⁵⁰

Catalyst	Crystalline phase	Crystallite size (nm)	Crystallite size Co ⁰ (nm)
Co/CMK8-900	Co ₃ O ₄	2.5	1.9
Co/CMK8-900-200	Co_3O_4	2.6	2.0
Co/CMK3-900	CoO	1.4	1.1
Co/CMK3-900-200	Co ₃ O ₄	2.8	2.1

Table 4.2. Crystallite sizes of Co_3O_4 , CoO and Co^0 from XRD for cobalt supported on CMK-8 and CMK-3.

Morphology and particle size distribution

Bimodal cobalt particle size distributions, as previously observed for Co/CMK3-900 and Co/CMK3-900-200, were also observed for Co/CMK8-900 (see **Fig. 4.4AB**) and Co/CMK8-900-200 (see **Fig. 4.4CD**). 2-3 nm cobalt NPs were located in the CMK8-900 pores and large cobalt particles of ~200 nm were located on the CMK8-900 external surface. The particle size analysis in **Fig. 4.5** showed a comparable cobalt particle size distribution for Co/CMK8-900 and Co/CMK3-900. For Co/CMK8-900, the frequency of large cobalt particles was somewhat lower, but this could also be a local effect. The bimodal particle size distributions yielded meaningless average values. Hence, the surface-averaged particle sizes were only calculated for cobalt particles of 6 nm or smaller and can be found in **Table 4.3**. The values obtained for Co/CMK8-900 are comparable to Co/CMK3-900.



Figure 4.4. (*A*,*B*) HAADF STEM images of Co/CMK8-900 and (C,D) Bright field TEM images of Co/CMK8-900-200.



Figure 4.5. HAADF-STEM particle size analysis of cobalt supported on CMK8-900 and CMK3-900.

Catalyst	Co_3O_4 or CoO particle	Relative uncertainty	Co ⁰ particle size (nm)
	size (nm)	(%)	
Co/CMK8-900	3.1 ± 0.9	27	2.3 ± 0.6
Co/CMK3-900	3.1 ± 0.7	23	2.5 ± 0.6

Table 4.3. HAADF-STEM particle size analysis or cobalt supported on CMK-8 and CMK-3

4.2.1 Calcination temperature

The XRD results revealed that the impact of the calcination treatment was different for Co/CMK-8 compared to Co/CMK-3. In order to obtain more insights on this impact, the uncalcined Co/CMK8-900 catalyst, impregnated at ambient pressure, was analyzed with TGA-MS under nitrogen. The MS signals for NO and NO₂ in **Fig. 4.6B** indicated a higher cobalt nitrate decomposition temperature for Co/CMK8-900 compared to Co/CMK3-900 (see **Fig. 4.6A**). Two peaks emerged in **Fig. 4.6A** for the CO₂ signal of Co/CMK3-900 at 100°C and 130°C. A comparable peak pattern was observed in **Fig. 4.6B** for the CO₂ signal of Co/CMK8-900, but with peaks at 190°C and 210°C, respectively. As discussed previously, this could be the decomposition of oxygen functionalities or could be induced by decomposition of the cobalt nitrate precursor. Different from the CO₂ signal of Co/CMK3-900, the CO₂ signal for Co/CMK8-900 did not increase between 200°C and 250°C. An increase in the CO₂ signal was only observed at 630°C for Co/CMK8-900. Nevertheless, we should be careful with preliminary conclusions on the stability of the CMK-8 supported catalysts under reducing conditions or FTS reaction conditions.



Figure 4.6. The evolution of CO_2 , NO and NO_2 for uncalcined A) Co/CMK3-900 and B) Co/CMK8-900 in a nitrogen atmosphere at increasing temperature, monitored by online MS. All signals were normalized to their highest ion current. The insets display the relative mass loss of the catalyst with respect to the temperature.

It is likely that support-assisted reduction of Co_3O_4 as described previously in **Section 3.2.3** also occurs on CMK-8 materials due to the defective graphite structure. However, the CO_2 MS signal from TGA-MS analysis indicated that support-assisted reduction would only occur at a temperature of 630°C in a nitrogen atmosphere for Co/CMK8-900. The reason for this temperature difference between Co/CMK8-900 and Co/CMK3-900 was not entirely clear. Presumably, a difference in confinement in CMK-8 pores and CMK-3 pores played a role. More experiments are needed to draw solid conclusions on this phenomenon. Extended X-ray absorption fine structure (EXAFS) should be used to study the direct chemical environment of cobalt atoms in the CMK-3 and CMK-8 supported catalysts. Measurements should be performed on impregnated, dried, and calcined catalysts. It was also not excluded that the amount of oxygen functionalities and the degree of graphitization played a role.

4.3 Characterization of reduced catalysts

Metallic surface area and cobalt particle size

The cobalt particle sizes, metallic surface areas, and the cobalt dispersions after reduction were analyzed with hydrogen chemisorption. The results in Table 4.4 showed relatively high metallic surface areas for cobalt supported on CMK-8. This was facilitated by the 3D channel network of CMK-8, which provided more accesibility compared to CMK-3.95 A schematic representation of the metallic surface areas available in CMK-3 and CMK-8 can be found in Fig. 4.7A and B, respectively. Co/CMK8-900-200 displayed a somewhat higher metallic surface area compared to Co/CMK8-900. It should be noted that Co/CMK8-900 was prepared under static vacuum, whereas Co/CMK8-900-200 was impregnated at ambient pressure. As discussed previously, the ethanol solvent evaporated too fast under vacuum, leading to an inhomogeneous cobalt distribution and formation of large cobalt particles. Hence, it was plausible that Co/CMK8-900 had a lower metallic surface area available compared to Co/CMK8-900-200.



Figure **4.7***. Schematic representation of the metallic surface areas available in A*) CMK-8 and B) CMK-3.

Table 4.4.	Metallic surface areas,	average cobalt	particle sizes,	and metal	dispersions of	f cobalt si	upported on
CMK-8 an	d CMK-3 determined a	with hydrogen (chemisorption.				

Catalyst	Metallic surface area	Co ⁰ particle size (nm)	Dispersion (%)
	$(m^2 \cdot g_{metal}^{-1})$		
Co/CMK8-900-200	171	4.2	23
Co/CMK8-900	141	5.7	17
Co/CMK3-900-200	96.5	7.3	13
Co/CMK3-900	74.7	10	9.5

Reducibility

Fig. 4.8 showed that the reducibility of Co/CMK8-900-200 was comparable to the reducibility of Co/CMK3-900-200. For the CMK-8 supported catalyst, a slight shift of the reduction peaks to higher temperatures was observed. A higher reduction temperature of the cobalt oxides indicated that the formation of metallic cobalt would be delayed during the reduction step. This may decrease the extent to which sintering occurs during reduction and contribute to the stability of CMK-8 supported catalysts under FTS reaction conditions. The larger hydrogen consumption of Co/CMK8-900-200 compared to Co/CMK3-900-200 at 200°C could indicate either decomposition of the cobalt nitrate precursor, which was not completely decomposed during calcination at 200°C, or the decomposition of surface functionalities.



Figure 4.8. Hydrogen consumption, quantified by a TCD, plotted against the temperature for the calcined Co/CMK8-900-200 (green) and Co/CMK3-900-200 (red) catalysts. The vertical offset was 0.04. and the total hydrogen consumption was normalized to the mass and cobalt weight loading of the catalyst. The temperature was plotted against the time on the secondary axis and the blue line represents the temperature program.

Pore blocking after calcination at 200°C

Unlike CMK-3, CMK-8 could facilitate diffusion throughout the pore channels without pore blocking due to its 3D pore network.⁹⁵ Nevertheless, it was found that the catalyst preparation procedure decreased the apparent SSA and pore volume to about half the values of the original CMK-8 support, as deducted from **Fig. 4.9A**. Pore blocking seemed to occur for Co/CMK-8-900-200 in a similar manner as for Co/CMK-3-900-200 (see **Fig. 3.27**). This was further supported by the BJH pore size analyses in **Fig. 4.9B**, which showed a decrease in differential pore volume.

This observation was in conflict with hydrogen chemisorption results in **Table 4.4**, which indicated that a very large metallic surface area was accesible in Co/CMK8-900-200. The apparent pore blocking as indicated by N₂ physisorption may have arisen from the difference in measurment conditions between N₂ physisorption and H₂ physisorption. The first was measured at -196°C, whereas the latter was conducted at 150°C. The diffusion of N₂ probe molecules was slow at -196°C, while diffusion of H₂ molecules was much faster at 150°C. Furthermore, N₂ molecules were larger compared to H₂ molecules. If cobalt NPs were confined in the pores, the N₂ molecules might be inhibited from entering the pore system, while H₂ molecules could still go in. Also it should be taken into account that hydrogen chemisorption

measured the reduced cobalt NPs, which are smaller in size compared to the cobalt oxide particles measured by N₂ physisorption.



Figure 4.9. A) Nitrogen adsorption/desorption isotherms and B) BJH pore size distributions calculated from the adsorption branches of CMK8-900 and Co/CMK8-900.

4.4 Catalytic performance of cobalt supported on CMK-8

4.4.1 Low pressure Fischer-Tropsch synthesis

The FTS activities for the CMK-8 and CMK-3 supported catalysts, reported as CTY, are plotted against the TOS in **Fig. 4.11** and the results are displayed in **Table 4.5**. A higher activity and C₅₊ selectivity was observed for CMK-8 supported catalysts compared to the CMK-3 counterpart. Co/CMK8-900 displayed a higher activity and TOF compared to Co/CMK8-900-200. The selectivities of the two CMK-8 supported catalysts were identical. The opposite was observed for Co/CMK3-900 and Co/CMK3-900-200. Co/CMK3-900 displayed a lower CTY, TOF, and C₅₊ selectivity compared to Co/CMK3-900-200. The difference between CMK-8 and CMK-3 was likely caused by the support-assisted reduction of Co₃O₄ supported on CMK-3 during calcination at 250°C.



Figure 4.10. CTY during FTS at 220°C and 1 bar plotted against the TOS for CO conversions between 0 and 3% for cobalt supported on CMK-8 and CMK-3. The H_2 /CO ratio was 2:1 and the GHSV 3500 h^{-1} .

Table 4.5. Results from FTS at 220°C and 1 bar reported from 15-20 h time on stream and CO conversions between 0 and 3% for cobalt supported on CMK-8 and CMK-3. The H_2 /CO ratio was 2:1 and the GHSV 3500 h^{-1} .

Catalyst	CTY (10^{-5} mol)	TOF (10^{-3})	CH ₄ selectivity (%)	C_{5+} selectivity (%)
	$\text{CO} \cdot g_{\text{Co}}^{-1} \cdot \text{s}^{-1}))$	s^{-1})		
Co/CMK8-900	1.7	4.9	51	25
Co/CMK8-900-200	1.3	4.0	51	25
Co/CMK3-900	1.0	5.1	63	15
Co/CMK3-900-200	1.5	6.4	59	19

4.4.2 High pressure Fischer-Tropsch synthesis

Results from FTS at 20 bar showed a relatively high CTY for Co/CMK8-900 (see **Fig. 4.11**). This could be attributed to two factors. Firstly, the 3D channel network of CMK-8 facilitated a higher metallic surface area available compared to the 2D network of CMK-3. Secondly, the oxygen functionalities on the CMK-8 surface enhanced the catalyst stability under reducing and/or FTS reaction conditions. Hence, a higher CTY was observed for Co/CMK8-900 compared to Co/CMK3-900 and Co/CMK3-900-200.

Co/CMK8-900 showed a TOF about twice as high as Co/CMK3-900-200. This indicated that a cobalt surface atom was about twice as active in Co/CMK8-900 as in Co/CMK3-900-200.

This could be attributed to a faster diffusion in the 3D channel network of CMK-8 than in the 2D network of CMK-3.

Co/CMK8-900-200 showed a lower activity and TOF compared to its Co/CMK8-900 counterpart. This is caused by incomplete decomposition of the cobalt nitrate precursor during calcination at 200°C for cobalt supported on CMK-8. As discussed previously in **Section 3.2.5**, the nitrate precursor decomposed during the reduction step prior to catalysis. If Co/CMK8-900-200 had experienced NH₃ poisoning, it was expected that the C₅₊ selectivity would be higher and the CH₄ selectivity would be lower compared to Co/CMK8-900 due to specific blocking of the methanation sites. The average C₅₊ selectivities at GHSV = 1000 h⁻¹ were 57% Co/CMK8-900-200 and 49% for Co/CMK8-900 respectively, whereas the CH₄ selectivities were 33% and 38%. The selectivities indeed indicated that Co/CMK8-900-200 had experienced NH₃ poisoning. To prove or deny this hypothesis Co/CMK8-900-200 could be analyzed with TGA-MS under hydrogen.

Additionally, after 100 h TOS the temperature was increased stepwise (not shown) in order to check for diffusion limitations in Co/CMK8-900. An Arrhenius plot was constructed and the apparent activation energy was 121 kJ·mol⁻¹. This indicated that diffusion limitations were absent (see also **Section 3.1.6**).



Figure 4.11. CTY during FTS at 220°C, 20 bar, and H_2 /CO ratio 2:1 plotted against the TOS for CO conversions between 10 and 20% for cobalt supported on CMK-8 and CMK-3. The GHSV was 2000 h⁻¹ in the first 10 h TOS and 1000 h⁻¹ from 10-150 h TOS.

Catalyst	CTY (10^{-5} mol	TOF (10^{-3})	CH ₄ selectivity (%)	C ₅₊ selectivity (%)
	$\text{CO} \cdot g_{\text{Co}}^{-1} \cdot \text{s}^{-1}))$	s^{-1})		
Co/CMK8-900	3.7	14.3	38	49
Co/CMK8-900-200	2.4	5.64	33	57
Co/CMK3-900-200	2.4	8.40	32	60

Table 4.6. Results from FTS at 220°C, 20 bar, and H_2 /CO ratio 2:1 reported at GHSV = 1000 h⁻¹ and CO conversions between 10 and 20% for cobalt supported on CMK-8 and CMK-3.

4.4.3 Spent catalyst

Cobalt particle growth appeared to be inhibited by the CMK-8 pores during FTS at 20 bar, as indicated by bright field TEM images in **Fig. 4.12**. Confinement in the CMK-8 pores could prevent particle growth *via* the MC mechanism. Confinement was supported by XRD results in **Section 4.2**, which showed that Co_3O_4 crystallites in Co/CMK8-900 were larger than CoO crystallites in Co/CMK3-900. This indicated a better confinement of cobalt NPs in the pores and possibly enhanced stability during catalysis. Oxygen functionalities could also play a role in particle growth inhibition. Results from TGA-MS under nitrogen in **Fig. 4.3** showed that CMK8-900 had more oxygen functionalities on the surface compared to CMK3-900. These functionalities could serve as anchoring points and stabilize cobalt NPs during catalysis. Hence, migration of cobalt NPs to the CMK-8 external surface was likely prevented. Additionally, results from TGA-MS under nitrogen of the uncalcined catalyst indicated that either the oxygen functionalities on the CMK3-900 surface (see **Fig. 4.6B**) were more stable compared to oxygen functionalities on the CMK3-900 surface (see **Fig. 4.6A**) and/or a higher decomposition temperature of the cobalt nitrate precursor in CMK8-900. This was represented by the shift of the CO₂ MS signal to a higher temperature for Co/CMK3-900 compared to Co/CMK3-900.



Figure 4.12. Bright field TEM images of Co/CMK8-900 after FTS at 20 bar for 150 h TOS.

4.5 **Conclusions on pore geometry**

The pore geometry had a significant influence on catalytic performance. CMK-8 was synthesized from KIT-6 silica templates according to the nanocasting procedure and the carbonization temperature was 900°C for all KIT-6/CMK-8 composites.

CMK-8 contained more oxygen functionalities on its surface compared to CMK-3 carbonized at the same temperature. These functionalities may have contributed to the stability of CMK-8 supported catalysts under reducing and/or FTS reaction conditions.

The 3D pore channels of CMK-8 facilitated a higher metallic surface area available compared to the 2D pore network of CMK-3. Hence, the CMK-8 supported catalysts displayed a higher catalytic activity compared to the CMK-3 supported catalysts.

Furthermore, CMK-8 did not facilitate support-assisted reduction of cobalt nanoparticles during calcination at 250°C in a N_2 atmosphere. This was different from the results obtained previously for CMK-3. Support-assisted reduction could still occur on CMK-8, but at higher temperatures than on CMK-3.

After catalysis, the cobalt nanoparticles were still confined in the CMK-8 pore system and had not migrated to the external surface of CMK-8 particles. The cobalt nanoparticles that were confined in the CMK-8 pores were immobilized and therefore not prone to sintering. A drawback of rigid confinement in CMK-3 pores would be pore blocking, since these pores are only accesible from two sides. It follows from rational catalyst design that CMK-8 with mesopores accesible from three dimensions offered an outcome for this problem by providing a higher metallic surface area compared to CMK-3.

Chapter 5

Results and discussion: Pore size

To investigate the influence of the pore size on catalytic performance non-ordered mesoporous carbon (NOMC) materials based on spherical silica particles and hierarchical carbons were used. The carbonization temperature for all silica/carbon composites was 900°C in order to rule out stabilization of cobalt NPs by surface functionalities arising from incomplete carbonization. A schematic representation of MC90 and MC380 synthesis can be found in **Fig. 5.1A** and **B**, respectively. Both NOMC materials have a cage-type pore structure, in which cobalt NPs can be confined. The numbers 90 and 380 represent the surface areas of the spherical silica particles in $m^2 \cdot g^{-1}$. The hierarchical carbons were either commercially available or synthesized by Dr. M. Oschatz.



Figure 5.1. Schematic representation of A) MC90-900 and B) MC380-900 structure and synthesis.

5.1 Support properties of non-ordered mesoporous and hierarchical carbons

5.1.1 Textural properties and mesostructure of the support

The textural properties of the as-synthesized NOMC materials and the as-received hierarchical carbons were characterized by nitrogen physisorption and are summarized in **Table 5.1**. The NOMC isotherms in **Fig. 5.2A** were of type IV according to the IUPAC classification⁷⁵ and exhibited hysteresis loops. **Fig. 5.2B** indicated 10-20 nm mesopores with a relatively broad pore size distribution in MC90. The MC380 isotherm and pore size distribution in **Fig. 5.2A** and **B** respectively indicated a bimodal pore size distribution. MC380 contained mesopores of about 6 nm and macropores with a broad size distribution.

The three hierarchical carbons employed during this research had different pore structures. The N₂ physisorption isotherms are displayed in **Fig. 5.2C** and the pore size distributions in **Fig. 5.2D**. CA contained large mesopores and macropores (not visible in **Fig. 5.2D**) and was physically activated with CO₂ to create additional micro- and macropores. The resulting CA material had a high SSA of 2249 m² · g⁻¹ and a large pore volume of 5.14 cm³ · g⁻¹. The pore structure of OM-CDC was similar to the CMK-3 pore structure, but the nanorods that built the main structure contained additional micropores (see also **Fig. 1.11**). OM-CDC had a high SSA of 3003 m² · g⁻¹ and a pore volume of 2.02 cm³ · g⁻¹, somewhat higher than the CMK-3 pore volume. CB was a commercially available carbon material that contained micropores and 2-20 nm mesopores with a broad size distribution (see **Fig. 5.2D**). CB had a 1100 m² · g⁻¹ SSA and a 1.98 cm³ · g⁻¹ pore volume. More details on the textural properties and mesostructure of the hierarchical carbons employed are available in literature.^{46,58,62}

Sample	$S_{BET} (m^2 \cdot g^{-1})$	Total pore volume	Micropore volume	Average
		$(\mathrm{cm}^3 \cdot \mathrm{g}^{-1})$	$(\mathrm{cm}^3 \cdot \mathrm{g}^{-1})$	d_{meso} (nm)
MC90-900	909.1	1.95	0.16	11
MC380-900	1640	4.95	0.13	12
CA	2249	5.14	0.47	9.5
OM-CDC	3003	2.02	0.15	2.0
CB	1100	1.98	0.03	10

Table 5.1. Porosity data of NOMCs and hierarchical carbons.



Figure 5.2. A) Nitrogen adsorption/desorption isotherms and B) BJH pore size distributions calculated from the adsorption branches of MC90-900 and MC380-900. C) Nitrogen adsorption/desorption isotherms and D) BJH pore size distributions calculated from the adsorption branches of CA, OM-CDC, and CB. CB was plotted against the secondary axis.

5.1.2 Oxygen-containing surface groups

The oxygen-containing surface groups of NOMCs and hierarchical carbons were evaluated with TGA-MS under nitrogen. The change in sample weight for the NOMCs and hierarchical carbons are depicted in **Fig. 5.3A** and **C**, respectively. For OM-CDC, an increase in relative residual mass was observed in **Fig. 5.3C**, which was likely a measurement error. The evolutions of CO₂ displayed in **Fig. 5.3B** showed that the NOMCs contained more oxygen functionalities compared to CMK3-900 and that these functionalities were stable up to ~400°C in a N₂ atmosphere. The CO₂ evolution in **Fig. 5.3D** showed that all hierarchical carbons contained more oxygen functionalities were stable up to ~250°C in a N₂ atmosphere, which might indicate decomposition of these functionalities under reducing and/or FTS reaction conditions. For OM-CDC the functionalities were stable up to ~400°C in a N₂ atmosphere.



Figure 5.3. Results from TGA-MS under nitrogen for NOMC materials and hierarchical carbons. A,C) The relative residual masses and B,D) the MS signals for the CO_2 fragment were both plotted against the temperature. Results for CMK3-900 were added as a reference.

5.2 Characterization of calcined catalysts

The nature of cobalt species supported on NOMCs and hierarchical carbons

The NOMCs and hierarchical carbons were impregnated under static vacuum at 0°C, except from CB, which was impregnated at ambient pressure at room temperature. All catalysts were dried statically at 60°C and calcined under N₂ flow at 250°C for 4 h. XRD was used to determine the cobalt crystalline phases and the volume-averaged crystallite sizes, as discussed previously in **Section 3.1.4**. In all catalysts Co₃O₄ was the predominant crystalline phase. The average crystallite sizes for Co/MC90-900 and Co/MC380-900 were comparable. All average crystallite sizes were larger than the size of micropores. It could be interpreted that cobalt NPs would not be located in the micropores, which were smaller than 2 nm. However, the crystallite size determined was an average and it could not be excluded that cobalt NPs were located in the micropores. 10 wt.% cobalt was likely not sufficient to obtain a confinement effect in materials with rather large mesopore sizes, such as MC90-900 and CB.

Table 5.2. Crystallite sizes of Co_3O_4 and Co^0 from XRD for cobalt supported on NOMCs and hierarchical carbons.

Catalyst	Crystalline phase	Crystallite size (nm)	Crystallite size Co ⁰ (nm)
Co/MC90-900	Co ₃ O ₄	3.3	2.5
Co/MC-380-900	Co_3O_4	3.0	2.3
Co/CA	Co_3O_4	4.0	3.0
Co/OMCDC	Co_3O_4	2.1	1.6
Co/CB	Co_3O_4	2.0	1.5
Co/CNT	Co_3O_4	5.8	4.4

Morphology and cobalt particle size of Co/MC380-900

Visualization with (S)TEM was rather difficult for cobalt supported on NOMCs, CA and CB due to the non-ordered pore structure. Bright field TEM images of Co/MC380-900 in **Fig. 5.4** either showed an inhomogeneous distribution of cobalt in the MC380-900 particles or indicated density differences in a MC380-900 particle.



Figure 5.4. Bright field TEM images of Co/MC380-900.

5.3 Characterization of reduced catalysts

The metallic surface area determined with hydrogen chemisorption in Co/MC380-900 was higher compared to Co/CMK-3-900, but lower compared to Co/CMK8-900 (see **Table 5.3**). It should be noted that Co/MC380-900 was impregnated under static vacuum and hence too

fast evaporation of the ethanol solvent could have caused a lower metal dispersion compared to impregnation at ambient pressure. A 7.2 nm Co⁰ average particle size was found for Co/MC380-900, which was higher than the 3.0 nm average crystallite size as calculated from XRD line broadening. The size difference arised from cobalt particles consisting of multiple crystalline domains.

Table 5.3. Metallic surface area, average cobalt particle size, and metal dispersion of cobalt supported on MC380 determined with hydrogen chemisorption. Co/CMK3-900 and Co/CMK8-900 were added as references.

Catalyst	Metallic surface area	Co ⁰ particle size (nm)	Dispersion (%)
-	$(m^2 \cdot g_{metal}^{-1})$	-	-
Co/MC380-900	106	7.2	14
Co/CMK3-900	74.7	10	9.5
Co/CMK8-900	141	5.7	17

5.4 Pore blocking in Co/MC380-900

As observed previously for Co/CMK3-900-200 and Co/CMK8-900-200, pore blocking also occured for Co/MC380-900 (see **Fig. 5.5**). Strikingly, the pore size distributions in **Fig. 5.5B** revealed that the macropores were not available for N_2 probe molecules, which indicated that the macropores were predominantly blocked after calcination. Specific blocking of the macropores seemed illogical, since the local drying rate would be higher in large pores compared to small pores. Hence, capillary flow phenomena would dictate that the meniscus at the drying front would recede from larger to smaller pores, entraining the dissolved precursor with it.⁹⁶



Figure 5.5. A) Nitrogen adsorption/desorption isotherms and B) BJH pore size distributions calculated from the adsorption branches of MC380-900 and Co/MC380-900.

However, the pore structure of MC380-900 was rather complex. The mesopores were negative replicas of the 6 nm A380 primary silica particles. Macropores were negative replicas of A380 silica aggregates. During the nanocasting procedure, the carbon precursor was unable to flow in between the small primary silica particles, which were the building blocks of the aggregates. Apertures in the macropores arose where other silica particles touched the aggregate. These aperatures were micropores or small mesopores and relatively narrow compared to the macropores. During the drying step the menisci receded from large to smaller pores. Consequently,



Figure 5.6. Schematic representation of A) A380 silica aggregate and B) macropore blocking in MC380-900 by a cobalt oxide plug after impregnation, static drying at 60°*C, and calcination at* 250°*C.*

the cobalt nitrate salt concentration suddenly exceeded supersaturation in the apertures, causing precipitation. A schematic representation of this phenomenon is depicted in **Fig. 5.6**. It could be argued that blocking of the apertures would vanish during calcination, since cobalt oxide particles might be smaller compared to their cobalt nitrate precursor particles. However, opening of the apertures did not occur during calcination (see **Fig. 5.5B**). This could be explained by the confinement effect, which either immobilized of cobalt oxides or retarded the decomposition of cobalt nitrate salts in the apertures. As a consequence, the apertures were still blocked after calcination and N₂ probe molecules were unable to enter the macropores during physisorption measurements. Thus, the specific blocking of the macropores could be attributed to the drying step after all, but not because of the actual volume of cobalt oxides in these pores.

5.5 Catalytic performance of cobalt supported on NOMCs and hierarchical carbons

5.5.1 Low pressure Fischer-Tropsch synthesis

The NOMC and OM-CDC supported catalysts were tested for their catalytic performance in the FTS at 1 bar. The activities, reported as CTY, are plotted against the TOS in textbfFig 5.7 and the overall results can be found in **Table 5.4**. Co/MC380-900 displayed the highest CTY and C_{5+} selectivity of all mesoporous carbons tested. Pore blocking might be eliminated during the reduction step, since metallic cobalt was smaller in size compared to cobalt oxides and cobalt nitrates. The TOFs for Co/MC380-900 and Co/CNT were comparable. This indicated that the diffusion of reactants and products in Co/MC380-900 was similar to Co/CNT. The vast open space facilitated by the macropores in MC380-900 fulfilled the same role as the open space in between the CNTs. The 6 nm mesopores in MC380-900 facilitated confinement of cobalt NPs. On the contrary, Co/MC90-900 contains 10-20 nm mesopores, which were too large to confine the cobalt NPs properly. This was supported by the 3.3 nm Co₃O₄ crystallite size as

calculated from XRD (see **Table 5.2**), which was much smaller than the MC90-900 pore size. Hence, the confinement effect was so negligible that the CTY and C_{5+} selectivity were much lower compared to Co/MC380-900.

For Co/OMCDC, the CTY increased over time and stabilized after 50 h TOS. This could be caused by retarded diffusion of reactants and products in the OM-CDC micropores. Furthermore, the CH₄ selectivity increased and the C₅₊ selectivity decreased, both with about 10 % in the first 50 h TOS. This could be attributed to the small cobalt NPs in the micropores, which mainly produced methane. Diffusion of reactants and products to and from these small cobalt NPs in the micropores could be limited. To confirm or deny this hypothesis, the temperature during FTS could be increased stepwise and an Arrhenius plot could be constructed. Subsequently, the activation energy, which gives information on diffusion limitations, could be calculated.



Figure 5.7. CTY during FTS at 220°C and 1 bar plotted against the TOS for CO conversions between 0 and 3% for cobalt supported on NOMCs and hierarchical carbons. The H_2/CO ratio was 2:1 and the GHSV 3500 h^{-1} .

Table 5.4. Results from FTS at 220°C and 1 bar reported from 15-20 h time on stream and CO conversions between 0 and 3% for cobalt supported on NOMCs and hierarchical carbons. The H_2/CO ratio was 2:1 and the GHSV 3500 h^{-1} .

Catalyst	CTY (10^{-5} mol	TOF (10^{-3})	CH ₄ selectivity (%)	C ₅₊ selectivity (%)
	$\text{CO} \cdot g_{\text{Co}}^{-1} \cdot \text{s}^{-1}))$	s^{-1})		
Co/MC90-900	1.0	n.d.	46	28
Co/MC380-900	3.9	15	39	39
Co/OMCDC	1.7	n.d.	41	31
Co/CMK3-900	1.0	5.1	63	15
Co/CNT	3.4	20	38	35

5.5.2 High pressure Fischer-Tropsch synthesis

Activities during FTS at 20 bar reported as CTY in Fig. 5.8 showed omnifarious results for cobalt supported on NOMCs and hierarchical carbons. First, it should be noted that the data originated from different catalytic runs. For Co/MC90-900 and Co/CA the GHSV was 2000 h^{-1} during the first 10 h TOS and then decreased to 1000 h^{-1} . After 100 h TOS the temperature was increased stepwise to check for diffusion limitations. Arrhenius plots were constructed and the apparent activation energies for Co/MC90-900 and Co/CA were 126 kJ \cdot mol⁻¹ and 115 kJ·mol⁻¹ respectively. This indicated that diffusion limitations were absent (see also Section **3.1.6**). The CH₄ and C_{5+} selectivities of Co/MC90-900 were comparable to cobalt supported on CMK materials and can be found in Table 5.5 and Appendix G, respectively. Co/CA displayed a relatively low CH_4 and high C_{5+} selectivity. The large macropores in the CA structure may have enhanced diffusion of reactants and products, while the mesopores facilitated confinement of cobalt NPs. The cobalt particles in Co/CA may have been large enough to display a lower methane selectivity compared to other catalysts. However, it should be noted that the CO conversion for Co/CA was about 7%, which may have influenced the selectivities. To obtain a more complete set of catalytic data, the TOFs for both Co/MC90-900 and Co/CA should be calculated. Hydrogen chemisorption measurements could be used to determine the metallic surface areas and calculate the TOFs.

For Co/MC380-900 the GHSV was 2000 h⁻¹ during the first 100 h TOS, resulting in CO conversions below 10% and a fluctuating CTY. After 100 h TOS the GSHV was decreased to 1000 h⁻¹ in order to obtain a CO conversion between 10 and 20%. The average CH₄ and C₅₊ selectivities were 25 and 61% respectively at GHSV = 1000 h⁻¹. Based on FTS results at 1 bar, it was initially expected that Co/MC380-900 would display a comparable catalytic performance to Co/CNT at 20 bar. However, the confinement of cobalt NPs in the MC380-900 mesopores might have been too weak to withstand 8 h reduction and was therefore negligible after the reduction step already. To investigate this, hydrogen chemisorption should be performed on Co/MC380-900 after 8h reduction at 350°C in H₂.

Different from FTS at 1 bar, Co/OMCDC had completely deactivated during FTS at 20 bar after \sim 40 h TOS. Hence, the selectivities and long-term stability were not reported. Co/OMCDC was impregnated under static vacuum. Its structure was similar to CMK-3 (see also **Fig. 1.11**) and therefore it was expected that the same phenomenon had occurred as during vacuum

impregnation of CMK3-900. The ethanol solvent had evaporated too fast and the cobalt nitrate precursor had precipitated before the liquid precursor was homogeneously distributed over the OM-CDC pore system. To verify this, calcined and spent Co/OMCDC should be analyzed with TEM.

Co/CB had also completely deactivated after ~40 h TOS, which could be attributed to two causes. Firstly, CB has 2-20 nm pores, which might not be able to confine cobalt NPs. Consequently, Co/CB was not stable during FTS. Secondly, with TGA-MS it was found that the oxygen-containing groups on the CB surface are only stable up to 250°C in a N₂ atmosphere. It was therefore likely that these functionalities decomposed under reducing and/or FTS reaction conditions and could not prevent cobalt NPs from sintering. To further investigate this, hydrogen chemisorption could be performed to analyze the metallic surface area after reduction.



Figure 5.8. CTY during FTS at 220°C, 20 bar, and H_2 /CO ratio 2:1 plotted against the TOS for CO conversions between 10 and 20% for cobalt supported on NOMCs and hierarchical carbons.

Table 5.5. Results from FTS at 220°C, 20 bar, and H_2 /CO ratio 2:1 reported at GHSV = 1000 h⁻¹ and CO conversions between 10 and 20% for cobalt supported on NOMCs and hierarchical carbons.

Catalyst	CTY (10^{-5} mol)	TOF (10^{-3})	CH ₄ selectivity (%)	C ₅₊ selectivity (%)
	$\text{CO} \cdot g_{\text{Co}}^{-1} \cdot \text{s}^{-1}))$	s^{-1})		
Co/MC90-900	2.0	n.d.	38	47
Co/MC380-900	3.8	14.2	25	61
Co/CA	1.1	n.d.	18	71
Co/CNT	15	139	10	81

5.6 Conclusions on pore size

The size of cage-type pores, in which cobalt nanoparticles could be confined, had a great influence on catalytic performance. Two factors had to be considered when cobalt nanoparticles were confined in support pores. Firstly, the pore size is crucial. Pores should be large enough to include cobalt nanoparticles of at least 6 nm in diameter. However, the confinement effect became negligible when the support pores were larger than 10 nm for 10 wt.% cobalt. Secondly, the reduction conditions should be chosen cautiously. Long reduction times were unneccesary for cobalt supported on mesoporous carbon materials and could even lead to sintering of cobalt nanoparticles.

MC380, a non-ordered mesoporous carbon material with a bimodal pore system, displayed the highest activity and C_{5+} selectivity of all catalysts tested for the Fischer-Tropsch synthesis reaction at 1 bar. MC380 was able to simultaneously confine cobalt nanoparticles in the 6 nm pores and provide accesibility for reactants *via* the macropores. However, the beneficial confinement effect was not observed during Fischer-Tropsch synthesis at 20 bar. This could be attributed either to the longer reduction time prior to Fischer-Tropsch synthesis at 20 bar or to the higher pressure. A drawback of non-ordered pore systems was that they complicated result analysis and visualization with electron microscopy.

The hierarchical carbon materials used in this study were not suitable for Fischer-Tropsch synthesis. During catalysis at 20 bar, they either displayed a low CO conversion or deactivated completely after approximately 40 hours time on stream.

Chapter 6

Summary and general discussion

The influence of the support structure on the catalytic performance of cobalt supported on carbon materials in the Fischer-Tropsch synthesis reaction was investigated. Mesoporous carbon materials were synthesized from silica templates according to the nanocasting procedure. The carbonization temperature of silica/carbon composites strongly affected the degree of graphitization and the amount of oxygen-containing surface groups in the resulting carbon support material. Defective graphite structures and oxygen-containing surface functionalities were powerful tools for preparing stable catalysts by preventing severe cobalt particle growth during reduction and catalysis. However, the oxygen functionalities introduced post-synthetically by a partial oxidation treatment in air appeared to be unstable under reducing or Fischer-Tropsch synthesis reaction conditions.

The catalyst preparation method was of the utmost important for catalytic performance. The impregnation, drying, and calcination conditions had to be optimized in order to prepare active CMK-3 supported catalysts. Initially, incipient wetness impregnation was carried out under static vacuum in order to empty the pores and increase capillary suction. Ethanol, the precursor solvent, evaporated too fast under static vacuum. Consequently, the cobalt nitrate concentration exceeded supersaturation and precipitated before the precursor solution was homogeneously distributed over the support pores. The resulting catalysts had a bi- or multimodal cobalt particle size distribution with nanoparticles located in the pores and large cobalt particles on the external surface of a CMK-3 particle. On the contrary, impregnation at ambient pressure yielded a more homogeneous cobalt distribution and active CMK-3 supported catalysts. Static vacuum was even unnecessary, since the 2-3 nm CMK-3 pores already facilitated sufficient capillary forces at ambient pressure.

The drying step strongly affected the cobalt distribution over the support material. Static drying led to an inhomogeneous cobalt distribution due to differences in local drying rates. On the other hand, fluidized-bed drying yielded a homogeneous cobalt distribution over the CMK-3 pores. The uniformly sized cobalt nanoparticles obtained after fluidized-bed drying were 2-3 nm in diameter and produced mainly methane, which is a valueless Fischer-Tropsch synthesis product. Besides, the 2-3 nm cobalt nanoparticles obtained after fluidized-bed drying may have blocked the CMK-3 pores and consequently part of the active metal species was not available to convert synthesis gas during catalysis.

During calcination at 250°C in a nitrogen atmosphere, CMK-3 facilitated support-assisted

reduction of Co_3O_4 nanoparticles. The defective graphite structures accepted oxygen atoms and subsequently released them together with a structural carbon atom as CO or CO_2 . Hence, mobile metallic cobalt nanoparticles were formed during the calcination treatment and sintering occured. An additional feature of this process was partial destruction of the carbon framework upon release of carbon atoms.

Sintering of cobalt nanoparticles occured already during reduction for 8 hours at 350°C in a hydrogen atmosphere for most catalysts. A lower temperature or shorter reduction time would be more suitable to reduce carbon-supported cobalt catalysts.

During Fischer-Tropsch synthesis, carbon-supported cobalt catalysts seemed display two different sintering mechanisms. Ostwald ripening was proposed when the cobalt particle size distribution was distinctly bi- or multimodal after calcination. Migration and coalescence was proposed when the cobalt particles were uniformly sized after calcination.

Another important tool for preparing stable catalysts was pore confinement, which could inhibit undesired particle growth. Cobalt nanoparticles that were rigidly confined in CMK-3 pores were immobilized and therefore not prone to sintering. A drawback of rigid confinement in CMK-3 pores could be pore blocking, since these pores are only accesible from two sides. It followed from rational catalyst design that another pore geometry could provide more accesibility. CMK-8, a carbon material with three-dimensional cubic ordered mesopores, offered an outcome for this problem. Additionally, a higher metallic surface area was exposed by cobalt supported on CMK-8 compared to cobalt supported on CMK-3. The higher metallic surface area induced a higher catalytic activity.

MC380, a non-ordered mesoporous carbon material with a cage-type bimodal pore system, was able to simultaneously confine cobalt nanoparticles in mesopores and provide accesibility for reactants *via* macropores. Cobalt supported on MC380 displayed the highest activity and C_{5+} selectivity of all catalysts tested for the Fischer-Tropsch synthesis reaction at 1 bar. When cage-type materials are used, the pore size should be chosen cautiously. The pore size should be large enough to enclose cobalt nanoparticles of at least 6 nm in diameter. However, if the pores are too large for the amount of cobalt that is impregnated, the confinement effect becomes negligible. A drawback of non-ordered pore systems was that they complicated result analysis and visualization with electron microscopy.

6.1 Comparison to literature

In earlier research, there was a demand for ordered pore systems to investigate the role of the support structure on catalytic performance. SBA-15 with different pore sizes was synthesized and their potential as supports for cobalt catalysts for the Fischer-Tropsch synthesis was investigated.^{14,97,98} Wang *et al.*⁹⁷ found in 2001 that cobalt supported on SBA-15 with 8.4 nm pores showed a higher CO conversion compared to cobalt supported on SBA-15 with 3.6 nm pores. Khodakov *et al.*⁹⁸ found in 2002 that cobalt supported on SBA-15 with 4.2 nm pores showed a higher CO conversion, C_{5+} selectivity, and reducibility compared to cobalt supported on SBA-15 with 2.5 nm pores. Martinez *et al.*³³ found in 2003 for their 10 wt.% Co/SBA-15 catalyst (SBA-15 with 10 nm pores) 13.2% CO conversion and 46% C_{5+} selectivity during the Fischer-Tropsch synthesis reaction at 220°C, 20 bar, and H₂/CO = 2. They also reported that
their 30 wt.% Co/SBA-15 catalyst showed a 20% higher CO conversion and C_{5+} selectivity compared to the 10 wt.% Co/SBA-15 catalyst.

However, mixed-metal support phases, which complicated analysis of the results, were formed on silica support materials. This problem could be ommitted by using carbon support materials. In this research, CMK-3 with a pore size of ~ 4 nm was synthesized from SBA-15 templates *via* the nanocasting technique. The optimized CMK-3 supported catalyst (Co/CMK3-900-200) showed a higher CO conversion and C₅₊ selectivity during the Fischer-Tropsch synthesis reaction compared to the 10 wt.% Co/SBA-15 catalyst from Martinez *et al.*³³ at similar conditions (see **Table 6.1**). The reduction conditions employed by Martinez *et al.* (hydrogen, 400°C, 10 h) were more severe than the reduction conditions in this research (hydrogen, 350°C, 8 h). Cobalt supported on silica is generally more difficult to reduce than cobalt supported on carbon. This is caused by to the mixed metal-support phases that are formed for cobalt supported on silica.¹⁴

Throughout this research, CMK-3 supported cobalt catalysts were compared with cobalt supported on CNTs. The catalytic performance found for Co/CNT was in accordance to performances reported in literature. For example, Fu *et al.*¹⁸ found 64% CO conversion and 87% C₅₊ selectivity for 20 wt.% Co/CNT during the Fischer-Tropsch synthesis reaction at 230°C, 20 bar, and H₂/CO = 2.

However, only a moderate performance was found for Co/CMK-3, as opposed to claims in literature^{18,50} (see **Table 6.1**). We should take into consideration that in both studies concerned the pristine carbon materials were treated with diluted HNO₃ to introduce oxygen functionalities prior to catalyst preparation. This could have contributed to the relatively high CO conversion and C_{5+} selectivity reported by them.

Catalyst	Co ⁰ loading	CO conver-	CH ₄ selectivity (%)	C ₅₊ selectivity (%)
	(wt.%)	sion (%)		
Co/CNT ^a	9	35	10	81
Co/CNT ^{18 b}	20	64	11	87
Co/SBA-15 ^{33 a}	10	13	28	46
Co/CMK3-900-200 ^a	10	16	59	60
Co/CMK3 ^{18 b}	20	40	15	82
Co/CMK3 ^{50 a}	20	36	11	82

Table 6.1. Comparison of Fischer-Tropsch synthesis results for cobalt supported on CNTs, SBA-15, and CMK-3 from several studies.

^a Fischer-Tropsch synthesis at 220°C, 20 bar, and $H_2/CO = 2$

^b Fischer-Tropsch synthesis at 230°C, 20 bar, and $H_2/CO = 2$

Chapter 7

Outlook

Carbon-supported cobalt catalysts for the Fischer-Tropsch synthesis have been studied in order to elucidate the role of the support structure on catalytic performance. Oxygen-containing surface functionalities can serve as anchoring points and prevent cobalt nanoparticles from severe particle growth during reduction and catalysis. However, the oxygen functionalities introduced by a post-synthesis partial oxidation in air were not stable under reducing and/or Fischer-Tropsch synthesis reaction conditions. An oxidative treatment with HNO₃ might realize the introduction of stable oxygen functionalities.^{18,50} Defects in the graphitic structure can also anchor cobalt nanoparticles strongly during the Fischer-Tropsch synthesis reaction. Defective graphite structures offer a facile outcome, since they can be created during the support synthesis procedure. Hence, tedious post-synthesis procedures are omitted. Raman spectroscopy should be used to characterize defects in carbon structures. It is crucial to gain insight in their fundamental properties and applications.

Both Ostwald ripening and migration and coalescence have been proposed as cobalt particle growth mechanisms during the Fischer-Tropsch synthesis reaction. However, more insights should be obtained on the atomic scale to draw solid conclusions on the dominating mechanism. This can be realized by using *in situ* techniques, such as *in situ* TEM or STM.

Catalyst deactivation by water-induced re-oxidation could not be excluded during this research. Co-feeding of water during catalytic runs can be used to either confirm or deny this phenomenon for carbon-supported cobalt catalysts. The spent catalysts should then be analyzed with XANES. XANES is very promising for this, because quantitative results on the degree of reduction can be obtained without removing the Fischer-Tropsch waxes covering the catalyst.³⁵ Hence, exposure of the cobalt particles to air is prevented and can be ruled out during result analysis.

Calcination of CMK-3 supported catalysts at 250°C in a nitrogen atmosphere induced support-assisted reduction of the cobalt oxide nanoparticles. Mobile metallic cobalt was formed and the carbon framework was partially destroyed upon release of carbon atoms. This complicates result analysis due to the emerge of deviating pore sizes and interpore connections. Furthermore, it is difficult to control to what extent support-assisted reduction occurs. On the contrary, support-assisted reduction might be promising for industrial applications by lowering the reduction temperature. Hence, thermal energy is saved during the Fischer-Tropsch synthesis process, which is economically beneficial and environmental friendly.

Decomposition of the cobalt nitrate precursor occured at higher temperatures on CMK-8 than on CMK-3. The reason for this temperature shift is not entirely clear. In order to investigate the direct chemical environment of cobalt atoms, EXAFS measurments should be performed on impregnated, dried, and calcined catalysts.

The CMK-8 supported catalyst calcined at 200°C and the CMK-3 supported catalyst calcined at 140°C were likely to be poisoned by ammonia. The calcination temperature was too low to decompose the cobalt nitrate precursor. Hence, the cobalt nitrates decomposed under hydrogen during the reduction step. Ammonia, a decomposition product of the nitrates, could poison methanation sites of cobalt nanoparticles. Thereby, the activity decreases and the C_{5+} selectivity increases. TGA-MS under hydrogen should be performed to confirm or deny ammonia poisoning.

Aggregation of cobalt nanoparticles supported on CMK-3 occured already during reduction for 8 hours at 350°C under hydrogen. Reduction of CMK-3 supported cobalt catalysts should be performed at relatively low temperatures and short times in order to prevent sintering of cobalt nanoparticles. Reduction at 250°C in a nitrogen atmosphere could offer an outcome for this.

Once structure-perfomance relationships in carbon-supported cobalt catalysts for the Fischer-Tropsch synthesis are fully understood, the knowledge can be applied in future research. The results obtained with carbon-supported cobalt catalysts are the foundation for expanding the research area to other support materials. Ultimately, we aim to contribute to the development of highly active, selective, and stable Fischer-Tropsch synthesis catalysts for industrial applications. Rational design of industrial catalysts offers an economically viable solution in the Fischer-Tropsch synthesis process.

Chapter 8

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Appendix A

Selectivities over time during Fischer-Tropsch synthesis at 1 bar



Figure A.1. FTS selectitivies at 1 bar for A) Co/CNT, B) Co/CMK3-900, C) Co/CMK3-900-RTF, and D) Co/CMK8-900.

Appendix **B**

TEM particle size analysis Co/CMK3-1300 spent



Figure B.1. HAADF-STEM particle size analysis of Co/CMK3-1300 before and after FTS at 220°C and 20 bar for 150 h TOS.

Appendix C

EDX Co/CMK3-1300 spent



Figure C.1. EDX elemental mapping TEM image of Co/CMK3-1300 after FTS at 20 bar for 150 h TOS. Cobalt is depicted in red, oxygen in blue, and carbon in green.

Appendix D

CMK-3 framework destruction



Figure D.1. Partially destroyed A) CMK3-900 and B) CMK3-1300 framework after impregnation under static vacuum and calcination at 250°C.

Appendix E

TEM analysis Co/CMK3-900-OX and Co/CMK3-900-140



Figure E.1. Bright field TEM images of (A,B) Co/CMK3-900-OX and (C,D) Co/CMK3-900-140.

Appendix F

Overview Fischer-Tropsch synthesis at 1 bar

Table F.1. Overview of the results from FTS at 220°C, 1 bar, and H_2 /CO ratio 2:1 reported at GHSV = 3500 h⁻¹ and CO conversions between 0 and 3%.

Catalyst	CTY (10^{-5} mol)	$TOF (10^{-3})$	CH ₄ selectivity (%)	C ₅₊ selectivity (%)
	$\text{CO} \cdot g_{\text{Co}}^{-1} \cdot s^{-1}))$	$s^{-1})$		
Co/CNT	34	20	38	35
Co/CMK3-500	1.0	3.8	55	19
Co/CMK3-900	1.0	5.1	63	15
Co/CMK3-1300	0.3	2.4	75	6.1
Co/CMK3-900-RT	1.5	n.d.	58	19
Co/CMK3-900-RT3	1.0	n.d.	58	19
Co/CMK3-900-RTF	0.8	n.d.	52	24
Co/CMK3-900-200	1.5	6.4	59	19
Co/CMK3-900-140	1.0	n.d.	56	21
Co/CMK3-900-OX	1.8	n.d.	56	21
Co/CMK8-900	1.7	4.9	51	25
Co/CMK8-900-200	1.3	4.0	51	25
Co/MC90-900	1.0	n.d.	46	28
Co/MC380-900	3.9	15	39	39
Co/OMCDC	1.7	n.d.	41	31

Appendix G

Overview Fischer-Tropsch synthesis at 20 bar

Table G.1. Overview of the results from FTS at 220°C, 20 bar, and H_2 /CO ratio 2:1 reported at GHSV = 1000 h^{-1} and CO conversions between 10 and 20%.

Catalyst	CTY (10^{-5} mol)	$TOF (10^{-3})$	CH ₄ selectivity (%)	C ₅₊ selectivity (%)
	$\text{CO} \cdot g_{\text{Co}}^{-1} \cdot \text{s}^{-1}))$	s^{-1})		
Co/CNT	15	139	10	81
Co/CMK3-500	1.8	20.4	36	51
Co/CMK3-900-RT	2.5	n.d.	39	50
Co/CMK3-900-RTF	1.5	n.d.	61	23
Co/CMK3-900-200	2.4	8.40	32	60
Co/CMK3-900-140	0.9	n.d.	26	68
Co/CMK3-900-OX	2.1	n.d.	43	43
Co/CMK3-900-AM	1.6	n.d.	40	48
Co/CMK8-900	3.6	14.3	38	49
Co/CMK8-900-200	2.4	5.64	33	57
Co/MC90-900	2.0	n.d.	38	47
Co/MC380-900	3.8	14.2	25	61
Co/CA	1.1	n.d.	18	71

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