INVESTIGATION OF PROMOTING EFFECTS OF MANGANESE OXIDE ON CARBON NANOFIBERS SUPPORTED COBALT CATALYSTS FOR FISCHER-TROPSCH SYNTHESIS

The effects of the addition of MnO to a carbon nanofibers supported cobalt catalyst were studied. The original sample, cobalt loading 9.5 wt% and 8% cobalt dispersion, was promoted by impregnation with small amounts of MnO (0.03, 0.1, 0.3, 0.6 and 1.1 wt%). XPS and STEM-EELS showed MnO to be associated with Co both in the dried and in the reduced catalyst. In the drying step MnO was deposited on the passivated cobalt particles due to the tendency of both metals to form stable mixed compounds. After reduction the MnO remained close to the cobalt particles, as the support material lacked sites with significant interaction with MnO. The promoter suppressed both the hydrogen chemisorption uptake and the cobalt reducibility even with the lowest MnO loading. At 1 bar large improvements in the selectivity towards C$_{5+}$ products (from 31 to 45 wt%) were found with MnO loadings of 0.3 wt% and higher. At 20 bar the addition of only 0.03 wt% MnO improved the C$_{5+}$ selectivity from 74 to 78 wt%, but larger amounts decreased the selectivity to 52 wt% at 1.1 wt% MnO. The surface specific activity (TOF) first increased with MnO loading from 26 to 60·10$^{-3}$ s$^{-1}$ for 0.3 wt% MnO while it decreased, probably as a consequence of too high coverage of the Co surface, at MnO loadings >0.3 wt%. From product analysis (paraffin-olefin ratio) it appears that a major role of MnO involves moderation of hydrogenation reactions.
Chapter 4

Introduction

In the Fischer-Tropsch (FT) reaction synthesis gas (CO/H\textsubscript{2}) is catalytically converted into hydrocarbons via surface polymerization. By using synthesis gas produced from natural gas, coal or biomass transportation fuels can be obtained from feedstocks other than crude oil. The quality of the products formed in combination with a non-crude oil feedstock support the FT process to play a crucial role in the energy supply to society in the coming decades.

Supported cobalt catalysts are well known for their activity and selectivity in the FT reaction [1]. The catalysts are often promoted with small amounts of noble metals to decrease the reduction temperature and to increase the activity [2-4]. To achieve better selectivities towards long chain products special metal oxides can be added [4-7]. In this chapter we investigate the influence of manganese oxide on carbon nanofibers supported cobalt catalysts. MnO is reported to be a promoter for cobalt-based FT catalysts in both academic and patent literature. Originally, most research was devoted to cobalt on MnO\textsubscript{2} supports and to systems with mixed oxides of cobalt and manganese [8-12]. All of these systems have relatively high manganese loadings. Recently, MnO promoter effects on cobalt catalysts supported on oxidic carriers have been investigated [13-20]. The promoting effect of MnO is suggested to originate from a lower degree of reduction of cobalt [12,13,20]. In all cases also a metal oxide was used as support material, which lowers the cobalt reducibility as well, thus complicating the analysis. Therefore, we decided to reduce support effects by using an inert carrier, viz. carbon nanofibers (CNF). This is a novel graphitic support material with promising applications, also as support for FT catalysts [21,22]. Recently, we showed with XPS and STEM-EELS that in Co/CNF catalysts promoted with MnO the promoter is present only in the vicinity of the cobalt particles and not elsewhere on the support [23]. The objective of this chapter is to provide comprehensive characterization and to investigate systematically at low and high pressure the catalytic effects of the manganese loading on Co/CNF catalysts. Catalysts with Co/Mn molar ratios varying from 11 to 431 were prepared and characterized by acid-base titration, H\textsubscript{2} chemisorption, STEM-EELS, TEM, TPR, XPS and XRD, while Fischer-Tropsch catalysis experiments were carried out in fixed bed reactors both at atmospheric pressure and at 20 bar.
Experimental session

Catalyst preparation

Carbon nanofibers of the fishbone-type with an average diameter of about 30 nm were grown from synthesis gas using an earlier described method [24]. Purification comprised refluxing in 1M KOH and adsorption sites were created by refluxing the CNF in concentrated HNO₃, as described by Toebes et al. [25]. After washing and drying at 120 ºC CNF with a BET surface area of 160 m²/g and a bulk density of 0.50 g/ml were obtained.

Cobalt was loaded on the activated CNF by incipient-wetness impregnation (pore volume 0.56 ml/g) of a solution containing 0.97 g/ml Co(NO₃)₂·6H₂O (Acros p.a.) resulting in a loading of 9.5 wt% cobalt in the final catalyst. The catalyst precursor was dried in air at 120 ºC for 18 h and subsequently reduced at 350 ºC for 2 h in a flow of 10% H₂/He. After passivation in a 1 vol‰ oxygen flow at room temperature the sample coded Co/CNF was obtained.

Subsequently, manganese was loaded on six portions of Co/CNF using incipient wetness impregnation with aqueous solutions of Mn(NO₃)₂·4H₂O (Acros p.a.) with different concentrations. A reference sample coded CoH was prepared by impregnation with a diluted HNO₃ solution (pH 5) in order to reveal any effects caused by the new preparation step. The catalysts loaded with manganese are coded Co431Mn, Co95Mn, Co39Mn, Co19Mn and Co11Mn, the numbers indicating the cobalt to manganese atomic ratio (table 1). All catalyst precursors were dried in air at 120 ºC for 18 h.

Catalyst characterization

The number of acidic groups prior to loading the support with cobalt or manganese was determined by titration [25]. Amounts of 50 mg treated and untreated CNF were suspended in a 25 ml solution of 0.1 M NaCl and 0.1 M oxalic acid in demineralized water.

Table 1. Composition, H₂ uptake and calculated cobalt dispersion of the samples under investigation.

<table>
<thead>
<tr>
<th>Sample</th>
<th>Co (wt%)</th>
<th>MnO (wt%)</th>
<th>H₂ uptake (mmol/g)</th>
<th>Dispersion (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>CoH</td>
<td>9.5</td>
<td>-</td>
<td>0.063</td>
<td>7.8</td>
</tr>
<tr>
<td>Co431Mn</td>
<td>9.5</td>
<td>0.028</td>
<td>0.063</td>
<td>7.8</td>
</tr>
<tr>
<td>Co95Mn</td>
<td>9.5</td>
<td>0.13</td>
<td>0.054</td>
<td>6.7</td>
</tr>
<tr>
<td>Co39Mn</td>
<td>9.5</td>
<td>0.30</td>
<td>0.051</td>
<td>6.4</td>
</tr>
<tr>
<td>Co19Mn</td>
<td>9.5</td>
<td>0.63</td>
<td>0.053</td>
<td>6.6</td>
</tr>
<tr>
<td>Co11Mn</td>
<td>9.4</td>
<td>1.1</td>
<td>0.052</td>
<td>6.5</td>
</tr>
</tbody>
</table>
(pH=3.0). Under continuous stirring 10 mM NaOH was added dropwise with a rate of 0.05 ml/min until the final pH of 10 was reached. During the titration the pH was monitored with a pH electrode. The difference in amount of NaOH needed to reach pH 7 with the blank and the sample is reported in mmol/g.

Powder X-ray diffraction (XRD) patterns were measured using an Enraf-Nonius CPS 120 powder diffraction apparatus with Co Kα radiation (\( \lambda = 1.789 \) Å).

Temperature programmed reductions were executed with an Autochem 2920 instrument from Micromeritics. Typically 0.1 g sample was after drying reduced in a flow of 50 ml/min 5%H₂/Ar, the temperature was increased with 5 °C/min from room temperature to 750 °C.

XPS measurements were performed on a Thermo VG Scientific XPS system using non-monochromatic Mg (Kα) radiation. The XPS apparatus was equipped with a reaction chamber where samples could be reduced in situ. The samples CoH and Co11Mn were measured both after drying and after in situ reduction at 350 °C for 2 h, the other samples were only measured after drying. The pass energy of the analyser was set at 70 eV. Charging effects were minimal with shifts of at most 0.2 eV. The C peak at 284.2 eV was used as a reference to correct for the charging of the samples. The escape-depth of photoelectrons generated is small (~1.5 nm), which, if surface area of the support and metal loading are known, allows to evaluate particle sizes. From the quantitative Co/C and Mn/C ratios particle sizes for cobalt and manganese oxide were calculated using the model for hemi-spherical particle shapes [26-28].

Hydrogen chemisorption measurements were carried out using a Micromeritics ASAP 2010C. Before each measurement the sample was dried in vacuum at 120 °C overnight and reduced for 2 h in flowing H₂ at 350 °C with a heating rate of 5 °C/min. After reduction the samples were evacuated at that temperature for 30 minutes. The H₂-adsorption isotherms were measured at 150 °C [29]. The H/Co ratios at zero pressure were found by extrapolation of the linear part of the isotherm. Calculations were made using the total amount of hydrogen adsorbed assuming complete reduction and a stoichiometry of 1 hydrogen atom per cobalt surface atom [29].

The dried catalyst precursors and the reduced catalysts were examined with transmission electron microscopy (TEM) in a FEI Tecnai12 or in a FEI Technai20F. TEM samples were crushed and subsequently suspended in ethanol under ultrasonic vibration. A drop of this suspension was loaded onto a holey carbon film on a copper TEM grid.
Promoting effects of manganese oxide

The sample with the highest manganese loading was examined in a dedicated aberration corrected scanning transmission electron microscope (STEM), VG HB501, equipped with a Nion Mark II Cs corrector and a Gatan Enfina spectrometer to obtain energy electron loss spectroscopy (EELS) spectra. High Angle Annular Dark Field (HAADF) images were acquired at an acceptance angle of 70-210 mrad. A 2 s dwell time per spectrum was used, resulting for a 30*35 pixel image in an acquisition time of 45 min. We measured 14 full images and 8 line-scans, each taken on different parts of the specimen.

Catalytic testing

Catalysts were tested at atmospheric pressure and at high pressure. The measurements at 1 bar were carried out at 220 °C using CO/H₂ (1/2 v/v) after a reduction treatment at 350 °C for 2 h in hydrogen. Typically 30 mg of catalyst particles (0.5-1.0 mm) was diluted with 200 mg SiC particles (0.2 mm) to achieve isothermal plug-flow conditions. Selectivities of the catalysts were established at a CO-conversion of 2%, which was achieved by tailoring the space velocity. For the high-pressure measurements 0.25 g catalyst (150-212 µm) was diluted with 0.5-0.7 g SiC. Catalysts were also reduced in hydrogen at 350 °C for 2 h and the catalytic data were obtained at 220 °C and a pressure of 20 bar using a flow of CO/H₂/N₂ (33/66/6). The space velocity was adjusted to maximize CO conversions at around 60%. Reported catalytic data were obtained after three days of operation. Values for catalyst deactivation were based on the decrease of activity from day 1 to day 3 and are reported as percentage of activity per day.

Results and Discussion

Titration

The activated carbon nanofibers used as support contained initially 0.15 mmol acidic groups per gram. MnO was loaded on the Co/CNF after a reduction treatment at 350 °C for 2 h. Unfortunately, the remaining amount of acidic groups on Co/CNF could not be measured directly as the presence of cobalt interfered. Therefore, a sample of the original oxidized, un-loaded CNF batch was reduced in H₂ at 350 °C and was subsequently titrated. This sample contained only 0.06 mmol/g, which is an upper limit for the acid sites in Co/CNF that can serve as anchoring groups for the manganese. Despite of this decrease in acidic surface groups we noticed that the carbon nanofibers were still hydrophilic as wetting by water occurred smoothly.
XRD

XRD patterns of the unpromoted reduced and passivated Co/CNF together with dried CoH and dried Co11Mn are shown in figure 1. The starting material Co/CNF showed in addition to the graphite diffraction lines also contributions from CoO and metallic Co. The graphite diffraction lines are present at 30, 51, 63 and 95 °2θ while the diffractions at 43 and 77 °2θ are indicative for CoO. Line broadening analysis of the 43 °2θ diffraction resulted in a domain size of 3 nm for CoO. The main diffraction line for metallic cobalt is present at 52 °2θ and coincides with graphite contributions and three more metallic lines are found at 61, 91 and 114 °2θ, characteristic for fcc cobalt. Although hcp is the most stable structure for bulk cobalt up to the transition temperature of 416 °C, small cobalt particles are reported to have the fcc structure [29,30]. The presence of CoO domains of 3 nm together with metallic Co in the sample demonstrates that reoxidation during the passivation treatment was not complete but probably resulted in the formation of a shell of cobalt oxide surrounding a metallic core.

Both the dried CoH sample and Co11Mn, as a representative example of the promoted catalysts, showed distinct diffractions typical for $\text{Co}_3\text{O}_4$. No diffraction lines other than those of CNF or $\text{Co}_3\text{O}_4$ were observed. Apparently during impregnation and drying cobalt originally present in Co/CNF as CoO and Co metal was oxidized to $\text{Co}_3\text{O}_4$. The formation of $\text{Co}_3\text{O}_4$ was also observed in the dried MnO promoted samples. For Co11Mn no additional diffractions originating from manganese compounds are observed, probably because the manganese loading was too small (figure 1).

TPR

Temperature programmed reduction profiles of the dried samples given in figure 2 show four distinct reduction peaks around 175, 240, 340 and 475 °C. The first one at 175 °C, which increases with the manganese loading, can be ascribed to reduction and
decomposition of nitrates [29]. The peak area of the second peak at 240 ºC is unaffected by the manganese loading. This peak is stemming from the reduction of Co$^{3+}$ to Co$^{2+}$ showing that Co$_3$O$_4$ is present in the dried catalyst precursors, as was found with XRD. We used peak fitting to get an estimation of the peak areas of the Co$^{3+}$ reduction peak at 240 ºC and the Co$^{2+}$ reduction peak at 340 ºC in CoH. From the ratio of the peaks it could be concluded that indeed in the dried samples all cobalt is present as Co$_3$O$_4$.

Interestingly, the Co$^{2+}$ to Co$^{0}$ reduction found at 340 ºC is influenced by the presence of MnO. CoH and the catalysts with MnO loading up to 0.30 wt% MnO have similar peak areas, but going to higher manganese loadings the intensity of the peak for the CoO reduction decreases, which indicates a strong interaction between CoO and MnO. The run-up of the broad peak around 475 ºC makes quantitative identification difficult, but assuming similar peak shapes with peak fitting we obtained peak area ratios higher than 1:3 for CoH and the three catalysts with lowest manganese loading, suggesting complete reduction. However, the samples with higher manganese loading have a broadened reduction peak, which makes quantitative analysis impossible. Taking into account the shift of the CoO reduction peak to higher temperatures, it is possible that some cobalt will remain unreduced after the reduction treatment (350 ºC, 2 h) prior to H$_2$ chemisorption, in situ XPS, and catalytic testing.

The last broad reduction peak with a maximum around 475 ºC can be ascribed to some gasification of CNF to methane, as GC analysis demonstrated. The higher the manganese loading on the catalysts, the lower the gasification peak. The TPR pattern of the support (data not shown) has the support reduction peak around 600 ºC, which indicates that metallic cobalt acts as a catalyst probably by the spill-over of hydrogen atoms. Now from figure 2 it can be concluded that the addition of manganese to the catalyst lowers the gasification peak area. This indicates that either cobalt does not reduce

\begin{figure}[h]
\centering
\includegraphics[width=\textwidth]{figure2.png}
\caption{TPR profiles of the dried samples, normalized on cobalt intake.}
\end{figure}
completely at 475 °C, which is rather unlikely, or that MnO remains associated with the metallic cobalt particles, thus reducing the cobalt surface area available for catalytic gasification of carbon.

XPS

The Co\textsubscript{2p} spectra, normalized on the carbon 1s peak area are shown in figure 3 for the dried CoH and the three catalysts with the highest manganese loadings: Co39Mn, Co19Mn and Co11Mn. Distinct peaks stemming from 2p\textsubscript{3/2} at 780.0 eV and 2p\textsubscript{1/2} at 795.4 eV can be seen for CoH, characteristic for Co\textsubscript{3}O\textsubscript{4}. For the sample with the highest MnO loading, Co11Mn, both peaks are shifted to significantly higher binding energies, i.e. 780.9 and 797.2 eV, which indicates that a different cobalt compound is present at the surface of the cobalt particles. The mixed spinel of cobalt and manganese oxide and CoO both have a binding energy similar to the observed values [31]. In the samples Co19Mn and Co39Mn some broadening of the cobalt peak is observed but not the distinct shift to higher binding energy as observed for Co11Mn, which might be explained by the lower Mn loadings that were not sufficient to lead to mixed spinel formation.

In table 2 the Co/C, Mn/Co and Mn/C atomic ratios as measured by XPS are given. The cobalt particle size in CoH was calculated from the Co/C ratio to be 11 nm. The loading of MnO on the samples resulted in a small but distinct lowering of the Co/C atomic ratio, as we found before [23]. The atomic ratio of Co/C decreased from 0.022 to 0.018 going from CoH to Co11Mn (table 2). This decrease of the Co/C could be explained if the cobalt particle size would increase from 11 to 15 nm going from CoH to Co11Mn. In our TEM analysis, however, we did not find any indication of larger cobalt particle sizes related to the presence of MnO. An alternative explanation would be the coverage of cobalt(oxide) by MnO. From the STEM-EELS measurements (vide infra) we found that manganese and cobalt are super positioned. The mean escape depth of the

![Figure 3. Co 2p XPS region of dried CoH and the three catalysts with highest MnO loading. Spectra have been normalized to carbon 1s.](image-url)
Promoting effects of manganese oxide

Table 2. Atomic ratios of four dried catalysts as obtained with XPS.

<table>
<thead>
<tr>
<th>Sample</th>
<th>Co/C</th>
<th>Mn/Co</th>
<th>Mn/C</th>
</tr>
</thead>
<tbody>
<tr>
<td>CoH</td>
<td>0.022</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>Co39Mn</td>
<td>0.020</td>
<td>0.08</td>
<td>0.0017</td>
</tr>
<tr>
<td>Co19Mn</td>
<td>0.021</td>
<td>0.16</td>
<td>0.0036</td>
</tr>
<tr>
<td>Co11Mn</td>
<td>0.018</td>
<td>0.32</td>
<td>0.0059</td>
</tr>
</tbody>
</table>

generated photo-electrons through MnO is only 1.2 nm. This implies that the coverage of cobalt(oxide) by small amounts of MnO can significantly reduce the amount of photo-electrons that reach the detector. Consequently, the present decrease in Co/C ratio can be explained very well by coverage of the cobalt oxide particles with MnO.

The Mn/C atomic ratios obtained from XPS (table 2) were more than three times higher than the overall Mn/C ratio, which shows that MnO is highly dispersed on the samples. For Co11Mn we obtained from XPS a MnO particle size of 0.6 nm, assuming a hemi-spherical shape, or 0.4 nm for spherical particles. XPS is not able to discriminate between these options, but anyhow we can conclude from these data that MnO is highly dispersed in Co11Mn, and as discussed above, most likely (partly) located on top of the cobalt(oxide) particles. For Co19Mn and Co39Mn we found using the Mn/C ratios even smaller MnO particle sizes of 0.3-0.4 nm, which shows that the size of the MnO particles is affected by the loading.

The influence of manganese on the cobalt oxidation state after reduction was also investigated with XPS. The Co$\text{2p}$ spectra before and after reduction of CoH and Co11Mn are given in figure 4. For CoH the Co$\text{2p}$ binding energies shifted from 780.0 and 795.4 eV in the dried sample to 778.2 eV and 793.5 eV in the reduced sample, values that are indicative of metallic cobalt. After reduction a shoulder remained at the oxidic position showing that not all cobalt was reduced. For the promoted sample Co11Mn the peak

![Figure 4. Co 2p XPS region before (black) and after reduction (grey) for CoH and Co11Mn, spectra have been normalized to carbon 1s.](image)
maximums did not shift after reduction, although significant shoulders at the metallic cobalt positions were formed. This shows that the outer layer of the cobalt particles in Co11Mn was mainly oxidic, while in CoH the majority of cobalt atoms probed were reduced. The higher oxidation state of cobalt due to the presence of MnO, is in line with the TPR results where the influence of MnO on the cobalt reduction was pronounced. The atomic ratios between Co, C and Mn did not change upon reduction showing the absence of significant restructuring of the phases leading to changes in their dispersion. This makes it likely that Co and Mn remained closely associated after the reduction treatment.

\[H_2\text{chemisorption}\]

The hydrogen uptake data and the calculated apparent dispersions of the catalysts are given in table 1. It was not possible to obtain the actual degree of reduction of cobalt as back titration with oxygen interfered with the oxidation of the support material. Therefore, we assumed complete reduction, which, as mentioned in the discussion on the TPR patterns, might not be valid for the two samples with the highest MnO loadings. Consequently, the actual dispersion of these samples could be higher than the values reported. For the unpromoted sample CoH we found a cobalt dispersion of 7.8%, which corresponds to an average cobalt particle size of 12 nm [29] that is close to the result of 11 nm found with XPS. The addition of 0.028 wt% MnO resulted in the same cobalt dispersion, but addition of higher amounts of manganese lowered the cobalt dispersion to the lowest value of 6.4%. The presence of manganese oxide on the cobalt surface may decrease the hydrogen chemisorption uptake in two different ways. The coverage of cobalt atoms at the surface by MnO decreases the amount of sites that are probed with chemisorption. It is also possible that MnO decreases the ultimate degree of reduction of cobalt, which also decreases the hydrogen uptake.

![Figure 5. Schematic representation of the location of MnO on the cobalt catalysts. Until Co39Mn we find MnO mainly present as monolayers on Co, for higher loadings MnO forms multi-layers and is also found on the CNF support, still in close contact with the Co particles.](image-url)
From table 1 it is clear that the exposed cobalt surface as probed by hydrogen chemisorption did not decrease further for MnO loadings higher than 0.30 wt%. The particle size for MnO calculated from quantitative XPS for Co39Mn was 0.3-0.4 nm, which is about the height of a monolayer of MnO. For low MnO loadings we therefore expect MnO to be mainly present as monolayer patches on the cobalt particles.

For higher MnO loadings monolayer coverage of the cobalt surface by MnO is unlikely. It was calculated that the Mn loading of Co11Mn is equivalent to an MnO-monolayer over the cobalt surface, which would block all the sites present for hydrogen chemisorption. But the amount of H\textsubscript{2} chemisorbed was still 80% of that of the unpromoted catalyst, from which we can conclude that for this loading of MnO the promoter is not exclusively present as a monolayer on the cobalt metal. From quantitative XPS for Co11Mn MnO particle sizes between 0.4 and 0.6 nm were obtained, which correspond to approximately two times the thickness of a monolayer. Therefore, we propose that at higher MnO loadings a significant part of MnO is located on the CNF surface in the close vicinity of the cobalt particles. The development of the MnO structure with increasing loading has been depicted in figure 5.

**TEM**

TEM was used to measure the particle size distribution in the original reduced and passivated Co/CNF sample. The majority of the particles observed had sizes around 8 nm. In figure 6 small cobalt(oxide) particles can be observed supported on the carbon nanofibers. The small particles displayed low contrast with the graphite support, which

![Figure 6. TEM image of original Co/CNF catalyst showing the interwoven carbon nanofibers structure of the support with small supported cobalt particles with low contrast.](image-url)
indicates that they have been oxidized. Indeed, in the high resolution image depicted in figure 7 the d-spacing (0.21 nm) confirms the presence of CoO. Also some larger particles were present with sizes up to 25 nm, thus shifting the average particle size towards the value (12 nm) obtained from H$_2$ chemisorption.

**STEM-EELS**

Scanning transmission electron microscopy (STEM) measurements combined with electron energy loss spectroscopy (EELS) were performed to gain more insight into the location of manganese and cobalt both before and after the reduction treatment. We studied the sample with the highest manganese loading, Co11Mn. In figure 8A a representative dark field image is shown together with the areal densities of carbon, cobalt, manganese and oxygen of the dried sample. In the dark field image an individual carbon nanofiber is depicted on which the several brighter spots are visible. By comparing the dark field image with the elemental mappings it can be concluded that these brighter spots in dark field, with sizes varying from 4-14 nm, comprise of both cobalt oxide and manganese oxide. Also the elemental mappings and the bright field image shown in figure 8B suggest that the particles contain both metals, however, the 8 nm-sized particle in the lower left corner does not appear in the manganese mapping. This indicates that although manganese is always associated with cobalt, the opposite is not true. Mixed particles, however, prevailed; in total we detected 54 mixed particles and only 2 monometallic cobalt oxide particles.
Figure 8. STEM-EELS images of dried Co11Mn, from left to right: the HAADF (A) or bright field image (B) and the C, Co, Mn and O areal densities, derived from the EELS signals for two parts (A,B) of the specimen.

Figure 9. STEM-EELS of reduced Co11Mn, from left to right: the HAADF image and the C, Co, Mn and O areal densities as derived from the EELS signals for two parts (A,B) of the specimen.
The Mn patches have slightly different shapes than the Co particles, which suggests that Mn is covering Co, a conclusion that was also drawn from the presented XPS data. These findings are in line with literature results showing that mixed oxides of cobalt and manganese are sometimes found to be surface enriched in manganese [32]. Moreover, this larger size for the MnO particles strongly suggests that part of the promoter is present on the CNF support, although closely associated with Co.

Figure 9 shows the HAADF image and the elemental mappings with high resolution of two different single particles after reduction and passivation. The elemental mappings of cobalt, manganese and oxygen in figure 9A correlate, so it can be concluded that after the reduction treatment cobalt, manganese and oxygen remained associated. However, closer examination shows that cobalt matches with the particles imaged by HAADF, whereas the manganese mapping is non-continuous, pointing towards segregation on atomic scale. Segregation is also seen in figure 9B where the upper left part of the particle contains only cobalt oxide whereas the other parts consist of both cobalt- and manganese oxide. This indicates that during the reduction of cobalt oxide MnO was partly redistributed over the cobalt metal surface. These findings agree with the results of XPS and H_2 chemisorption that indicate free metallic Co surface next to MnO coverage.

Catalysis

The steady state performance of the catalysts at 1 bar after 48 h is given in figure 10 and in table 3. The presence of MnO both influenced the activity and the selectivity of the catalysts. Upon manganese loading the C_{5+} selectivity increased from 31 to 45 wt% mainly at the expense of methane formation which decreased from 36 to 23 wt%. We note that C_{5+} selectivity increased markedly up to Co39Mn, but did not improve further.

![Figure 10](image_url)
Table 3. FTS catalytic performances at 1 bar, 220 °C.

<table>
<thead>
<tr>
<th>Sample</th>
<th>Activity</th>
<th>TOF ($10^{-3}$ s$^{-1}$)</th>
<th>C$_1$ (wt%)</th>
<th>C$_{5+}$ (wt%)</th>
<th>alpha</th>
</tr>
</thead>
<tbody>
<tr>
<td>CoH</td>
<td>1.8</td>
<td>14</td>
<td>36</td>
<td>31</td>
<td>0.60</td>
</tr>
<tr>
<td>Co431Mn</td>
<td>1.7</td>
<td>13</td>
<td>32</td>
<td>36</td>
<td>0.63</td>
</tr>
<tr>
<td>Co95Mn</td>
<td>1.8</td>
<td>17</td>
<td>28</td>
<td>41</td>
<td>0.65</td>
</tr>
<tr>
<td>Co39Mn</td>
<td>1.6</td>
<td>16</td>
<td>25</td>
<td>45</td>
<td>0.67</td>
</tr>
<tr>
<td>Co19Mn</td>
<td>1.4</td>
<td>13</td>
<td>25</td>
<td>44</td>
<td>0.66</td>
</tr>
<tr>
<td>Co11Mn</td>
<td>1.2</td>
<td>11</td>
<td>23</td>
<td>45</td>
<td>0.67</td>
</tr>
</tbody>
</table>

Activity: $10^{-5}$ mol CO s$^{-1}$ g$^{-1}$ Co

with higher Mn loadings. Figure 11 plots the product distribution for CoH and Co11Mn is plotted. It is clear that the catalysts display ASF kinetics and the chain growth probabilities can be derived from the linear part of the plot. An increase of alpha from 0.60 to 0.67 was found going from the unpromoted to the highest loaded sample with a similar trend as with the methane and C$_{5+}$ selectivities.

The activity of the catalysts at 1 bar decreased upon loading of MnO from 1.78 to 1.17 $10^{-5}$ mol$_{CO}$/g$_{Co}$·s$^{-1}$ but the samples Co431Mn and Co95Mn showed no decrease in activity yet. This shows that small amounts of MnO on the catalyst improve the selectivity without hampering the activity. This is even more interesting as we found a decrease in the hydrogen chemisorption uptake for Co95Mn of 15% compared to the reference sample (CoH). The activity normalized on the cobalt surface area, the turn-over frequency (TOF), increased from 14 to $17\cdot10^{-3}$ s$^{-1}$ going from CoH to Co95Mn. Also Co39Mn showed a higher TOF than the unpromoted sample. Minor amounts of MnO on the surface of cobalt therefore result in higher TOF values for the remaining sites. The TOF values mentioned are, however, based on the exposed cobalt surface area in the reduced samples prior to catalytic operation. As the actual cobalt catalyst is created in situ, the observed differences in TOF can also be related with changes to the catalyst under

![Figure 11. ASF plot for CoH and Co11Mn showing the influence of MnO on the chain growth probability and the product distribution at 1 bar.](image-url)
reaction conditions [33]. We could not measure the hydrogen chemisorption after catalytic operation and consequently report these apparent TOF values.

Loading of higher amounts than 0.13 wt% MnO resulted in a decrease in activity. This decrease in activity showed the same trend as the decrease in dispersion obtained from H$_2$ chemisorption but was stronger. This resulted in a 35% lower TOF going from Co95Mn to Co11Mn. This clearly indicates that sites, which are present for H$_2$ chemisorption, are not one-to-one active for the FT reaction, but it rather shows that ensembles of cobalt sites are needed. This is comparable with our previous preliminary results on the cobalt particle size effect in FT catalysis where cobalt particles smaller than 12 nm were less active and exhibited far lower TOF values [22].

Another interesting feature of the MnO promoted catalysts is the change from paraffin-rich to olefin-rich products. In figure 12 the paraffin over olefin ratio is shown for the linear products for carbon numbers 2 to 8. The P/O ratio at all carbon numbers systematically decreased with the MnO loadings on the samples. The impact of addition of only 0.03 wt% MnO is again pronounced with a decrease of octane/octene ratio from 11 to 8. In the paraffin to olefin ratio the trade-off between the primary hydrogenation activity and the C-C coupling activity of the catalyst is manifested. As the hydrogenation activity of the catalysts decreases, more long-chain products will be formed as well as products that contain more olefins, which is the case for MnO promoted catalysts. A main role of the MnO promoter at 1 bar is therefore the moderation of the hydrogenation activity of the metallic cobalt.

Catalytic performances measured at 20 bar, which is a condition more relevant for industrial application, are reported in table 4. The loading of MnO on the catalysts influenced both the activity and the selectivity of the catalysts. The cobalt specific activity

![Figure 12](image_url)
Table 4. FTS catalytic performances at 20 bar, 220 °C.

<table>
<thead>
<tr>
<th>Sample</th>
<th>Activity (10^(-5) mol CO·s⁻¹·g⁻¹Co)</th>
<th>Deactivation (%/day)</th>
<th>TOF (10^(-3) s⁻¹)</th>
<th>C₁ (wt%)</th>
<th>C₅⁺ (wt%)</th>
<th>alpha</th>
</tr>
</thead>
<tbody>
<tr>
<td>CoH</td>
<td>4.1</td>
<td>7</td>
<td>26</td>
<td>18</td>
<td>74</td>
<td>0.91</td>
</tr>
<tr>
<td>Co431Mn</td>
<td>5.1</td>
<td>6</td>
<td>37</td>
<td>14</td>
<td>78</td>
<td>0.89</td>
</tr>
<tr>
<td>Co95Mn</td>
<td>6.8</td>
<td>3</td>
<td>60</td>
<td>15</td>
<td>77</td>
<td>0.89</td>
</tr>
<tr>
<td>Co39Mn</td>
<td>5.8</td>
<td>3</td>
<td>54</td>
<td>20</td>
<td>66</td>
<td>0.86</td>
</tr>
<tr>
<td>Co11Mn</td>
<td>2.7</td>
<td>7</td>
<td>25</td>
<td>21</td>
<td>52</td>
<td>0.85</td>
</tr>
</tbody>
</table>

Activity: 10^(-5) mol CO s⁻¹ g⁻¹Co

Increased from 4.1 to 6.8·10^(-5) mol_CO g_Co⁻¹ s⁻¹ going from the unpromoted catalyst to Co95Mn. The addition of higher amounts of MnO caused a rapid decrease in activity to 2.7·10^(-5) mol_CO g_Co⁻¹ s⁻¹ for Co11Mn. The differences in the TOF, also plotted in figure 13, were even larger and varied from 26 to 60·10^(-3) s⁻¹ between CoH and Co95Mn. Interestingly similar TOF values were found for the un-promoted catalyst and the over-promoted catalyst. The catalysts deactivated with 4-7% of their activity per day, values that gradually declined in time. Meanwhile, stable selectivities were found. The addition of small amounts of MnO was beneficial for catalyst stability. The relative periods of time-on-stream in this study do not allow firm conclusions on the influence of MnO on the stability of the catalysts.

The methane selectivity of the catalysts varied from 14 to 21 wt%. Addition of only 0.03 wt% MnO resulted in a decrease in methane make from 18 to 14 wt%, but the addition of higher amounts of MnO caused progressively higher methane selectivities up to 21 wt%. Upon manganese loading the C₅⁺ selectivity first increased from 74 to 78 wt% for Co431Mn, before it decreased to 52 wt% for Co11Mn. Also at 20 bar, the promoted catalysts contained more olefins, whilst the chain growth probability decreased continuously upon the addition of MnO from 0.91 to 0.85. It is known that the selectivity...
of catalysts in the FT reaction can vary largely with reaction conditions [33,34]. However, the presented data were measured at the same conditions and similar CO-conversions, which allows to study the influence of MnO as a promoter within this series.

Comparison of the catalytic data obtained at 1 bar and at 20 bar shows both similarities and large differences. At both conditions the TOF increased upon the loading of MnO, however, the 20% increase at 1 bar was modest compared to the 130% increase at 20 bar. From work on single crystals it is known that metal oxides can increase the specific activity for CO hydrogenation and that addition of too large amounts of the promoting element causes a decrease in TOF [35,36], confirming the trend in our data. Also operating at high pressures promoted catalysts can have higher turn-over rates with, for instance, a three-fold increase of TOF for Ru promoted cobalt catalysts [37]. The larger influence of MnO on the specific activity at 20 bar could be related to the more severe conditions at high pressure. For example, the presence of MnO in combination with cobalt surface reconstruction might create more sites on the catalyst that are active in chain growth. However, more research is needed to verify this hypothesis.

The trends in chain growth probability were completely different: an increase from 0.60 to 0.67 at 1 bar vs. a decrease from 0.91 to 0.85 at 20 bar. Related to these changes in chain growth probability we found a clear optimum in C\textsubscript{5+} selectivity at 20 bar, while at 1 bar it remained high, also at high MnO loadings. The influence of MnO loading on selectivity at 1 bar is most probably related with the initially very low C\textsubscript{5+} selectivity due to the high hydrogen coverage on the catalyst surface [38]. The addition of MnO may have decreased the hydrogen coverage on the catalyst, hereby increasing the C\textsubscript{5+} selectivity. For the 20 bar experiments the catalyst surface is already largely covered with CO resulting in a high C\textsubscript{5+} selectivity even for the un-promoted catalyst. The role of the promoter is now more delicate and over-promotion causes lower selectivity towards desired products [12].

**Association of Mn with Co**

The data presented so far show that small amounts of manganese have a significant influence on the cobalt reducibility and dispersion (TPR and H\textsubscript{2} chemisorption) and that MnO is present closely associated with the cobalt(oxide) particles in the dried and in the reduced samples (XPS and STEM-EELS). Now the question arises why manganese is only present associated with cobalt and is not located elsewhere on the CNF surface. Two explanations can be brought forward to answer the question. The first one addresses the number of available sites for anchoring the manganese during preparation, the second deals with the extent of interaction with sites on CoO and sites on carbon, respectively.
From the titration experiment we know that the reduction treatment of the support material diminishes the number of acidic groups to only 0.06 mmol per gram sample. The partly oxidized cobalt particles, however, account for a three times higher amount of oxygen surface groups in the sample. Assuming similar occupancies this would result in the majority of manganese located on top of cobalt oxide.

In the second explanation the presence of manganese oxide on top of the cobalt oxide particles is ascribed to the higher extent of interaction of MnO with CoO than with carbon. Co and Mn have similar ionic radii and readily form stable mixed oxides \([32,39]\). As we did not detect any manganese located on the CNF support, which is not expected with an equal distribution over the support oxygen groups and the cobalt oxide (\textit{vide supra}), the most probable reason for the presence of manganese on top of cobalt in the dried catalyst is the high extent of interaction between cobalt and manganese oxide. However, during the reduction treatment the cobalt particles become metallic, which diminishes the interaction with MnO. In their study on MnO promotion in Co/TiO\(_2\) catalysts, Morales \textit{et al.} observed the migration of MnO away from the cobalt to the support during the reduction step \([19]\). In our case MnO did not interact with the inert graphite surface (e.g. Mn carbides were not observed in XPS), thus favoring the presence of the promoter close to the cobalt particles. This is the most important reason why CNF is our support of choice to study promoter effects in FT catalysis.

**Conclusion**

In this chapter we have shows that carbon nanofibers provide a suitable support to study the manganese oxide promotion effect in cobalt based FT catalysis, as interference of support effects is minimized. Cobalt properties can therefore be influenced by the addition of MnO loadings as low as 0.03 wt\%. With XPS and STEM-EELS we show that manganese is present closely associated with cobalt both in the catalyst precursor and in the final catalyst. We demonstrate that manganese retarded the cobalt reduction and \textit{in situ} XPS showed that the surface of the cobalt is more oxidic when MnO is added to the catalysts. Catalytic performances were affected differently at tests at 1 bar and at 20 bar. At 1 bar the chain growth probability increased and simultaneously the product distribution shifted towards olefinic products at increasing MnO loading. This shows that the presence of MnO moderates the hydrogenation activity of the catalysts. Interestingly, at 1 bar the TOF increased 20\% upon loading with small amounts of manganese (0.13 wt\% MnO). In the experiments at 20 bar \(C_5^+\) selectivity first increased from 74 to 78 wt\% at 0.03 wt\% MnO, before it decreased to 52 wt\% for 1.1 wt\% MnO. The TOF increased
with at most 130% at 0.13 wt% MnO that nicely shows this promoter can favourably affect both activity and selectivity, depending on concentration and test conditions.

References
