Manganese promotion in cobalt-based Fischer-Tropsch catalysis

F. Morales Cano, O.L.J. Gijzeman, F.M.F. de Groot and B.M. Weckhuysen

Department of Inorganic Chemistry and Catalysis, Debye Institute, Utrecht University, Sorbonnelaan 16, 3584 CA Utrecht

ABSTRRACT

The effect of Mn addition on the catalytic performances of Fischer-Tropsch synthesis was investigated using a series of Co/TiO_2 catalysts prepared by two different preparation methods; incipient wetness impregnation (IWI) and homogeneous deposition precipitation (HDP). Mn was loaded using two different procedures in order to investigate its interaction with Co and TiO_2. Several characterization techniques, mainly XRD, XPS and TPR, were used to elucidate the Co oxidation state and dispersion and to estimate the Mn location. Fischer-Tropsch synthesis carried out at 1 bar of pressure showed an improvement of the catalytic performance in the Mn-promoted HDP catalyst, whereas no promotion effect was found in Mn-promoted IWI catalyst. This difference can be explained by a different Co-Mn interaction.

1. INTRODUCTION

The transformation process from syngas to hydrocarbons; i.e., Fischer-Tropsch synthesis (FTS) is gaining more and more importance due to the need for e.g. high purity diesel fuels. Overall process efficiency requires catalysts with high volume productivity, low deactivation rates, and high chain growth probability values (a), what leads to long chain hydrocarbons as the main product stream. Co-based catalysts are the most selective towards long chain hydrocarbons (mainly paraffins) what make them the catalysts of choice for low temperature FTS. In addition, water-gas shift reaction does not occur to a high extent on Co^0 [1], what means that Co-based catalysts are suitable when a rich H_2/CO feed of syngas is used e.g. from natural gas.

The use of other metals in small amounts, have been investigated over the last decades with the aim of enhancing the catalytic performances of Co-based catalysts. Several noble metals, such as Ru and Re, have been reported to enhance the Co reducibility and hence, to increase the catalytic activity [2, 3].

Other positive effects that can be achieved by using promoter elements are e.g. the inhibition of carbon deposition on Co^0 and a decrease of Co sintering what leads to the improvement of catalyst stability and a decrease of deactivation rates during FTS [4, 5]. The use of Mn as promoter for Co-based FTS catalysts can be found in the patent literature as well [6], but its exact role is unclear. In order to obtain a promotion effect, it is important to achieve a co-promotor interaction in the catalyst precursor so that a synergistic effect can be obtained [7, 8].

In the present work, four Co/TiO_2 catalysts were prepared, characterized and tested in FTS reaction in order to evaluate the promotion effect of Mn and the influence of the preparation method on the final catalytic performances. In this way, a structure-activity relationship could be approached.

2. EXPERIMENTAL

2.1. Catalyst preparation

Degussa P25 titania (surface area of 45 m^2/g, pore volume of 0.5 cm^3/g) was used as support for the preparation of cobalt FTS catalysts (Table 1). Two catalysts were prepared by incipient wetness impregnation (IWI) using aqueous solutions of cobalt nitrate and a mixture of cobalt and manganese nitrates (IWI-Co and IWI-CoMn). For this preparation method the support was pressed in pellets and sieved (0.21-0.50 mm) prior to impregnation. The other two samples were prepared by homogeneous deposition precipitation (HDP) method and the manganese was loaded after calcination by the IWI method (HDP-Co and HDP-CoMn). All catalysts were calcined at 400 °C in air for 4 hours and finally reduced at 400 °C in a H_2 flow for 6 hours followed by passivation.

2.2. Catalyst characterization

Catalyst samples were characterized using X-ray diffraction (XRD) and X-ray photoelectron spectroscopy (XPS) techniques before and after reduction. Powder XRD measurements were performed using an ENRAF-NONIUS XRD system equipped with a curved position-sensitive INEL detector and applying a Co $K\alpha_1$ radiation source (λ = 1.78897 Å). The XPS data were obtained with a Vacuum Generators XPS system, using a CLAM-2 hemispherical analyzer for electron detection. Non-monochromatic Al (Kα) X-ray radiation was used, employing an anode current of 20 mA at 10 KeV. The binding energies obtained were corrected for charge shifts using Ti $2p_{3/2}$ = 458.5 eV as reference. In addition, reduction experiments were carried out by temperature programmed reduction (TPR) of calcined samples using a tubular quartz reactor flushed with 5 % H_2/Ar flow and raising the temperature at the constant rate of 10°C/min. The content of H_2 in the outflowing gas was monitored with a thermo-conductivity detector.

Table 1
Overview of Co catalysts prepared together with their metal loadings.

Sample code	Wt % Co	Wt % Mn	Preparation procedure
IWI-Co	11.5	0	IWI of Co
IWI-CoMn	11.2	1.2	IWI of Co and Mn
HDP-Co	7.5	0	HDP of Co
HDP-CoMn	7.5	2	HDP of Co + IWI of Mn

2.3. Catalytic testing

Prior to catalytic tests the samples were reduced at 300 °C for 1 hour. FTS reaction was carried out using a plug flow reactor in which the catalysts were diluted in SiC. The reaction was carried out at 1 bar of pressure, 220 °C and H_2/CO ratio of 2 (GHSV= $8100 \ h^{-1}$). The products composition was analyzed on-line with a gas Chromatograph equipped with a fused silica column of 50 meters length and a flame ionization detector.

3. RESULTS AND DISCUSSION

3.1. X-ray diffraction

XRD patterns of the calcined catalysts showed the presence of crystalline Co_3O_4 structure. Approximate Co_3O_4 particle sizes were obtained using the line broadening of diffraction peaks. The values were found to be around 13 nm for HDP catalysts and around 18 nm for IWI catalysts (Table 2). However, the catalysts prepared by the HDP method showed very low intensity diffraction peaks of cobalt species and this made it impossible to determine the particle sizes accurately. This is probably due to the presence of very small particles in amorphous state, which were not visible with XRD, and due to the lower cobalt loading contained in these catalysts. After reduction a low intensity peak due to Co^0 (HCP) was detected in the IWI catalysts, which might be the signal of only some % of the Co content due to the presence of unreduced Co in some amorphous oxidic state. The HDP reduced catalysts did not show any Co signals in XRD due to a small particle distribution.

3.2. X-ray photoelectron spectroscopy

The presence of the Co_3O_4 structure in all calcined samples was confirmed by XPS where the binding energies of $Co2p_{3/2}$ in all samples were close to 779.8 eV. The Co/Ti ratios reflected higher dispersions achieved by the HDP method since both samples prepared by this method gave higher values (Table 2). In both type of promoted catalysts Mn seemed to be already highly dispersed over the TiO_2 or on top of Co_3O_4 as revealed by the high Mn/Co ratios. This high Mn dispersion might be due to a high metal-support interaction [9]. It has also been reported that under certain conditions some metal ions can diffuse into the TiO_2 lattice forming very stable compounds [10].

Table 2
XRD and XPS results obtained for the calcined and reduced Co/TiO_2 catalysts.

Sample	Co_3O_4 size[a] (nm)	Co^0 size[b] (nm)	Co/Ti ratio[a]	Mn/Co ratio[a]	Co/Ti ratio[b]	Mn/Co ratio[b]
IWI-Co	17.8	12.2	0.15	0	0.23	0
IWI-CoMn	18.1	9.2	0.10	0.57	0.21	0.38
HDP-Co	13.5	-	0.28	0	0.24	0
HDP-CoMn	-	-	0.24	0.58	0.22	0.75

"After calcination, after reduction.

Measurements of all reduced samples detected CoO as the main compound present since the catalysts were passivated. Co^{2+} oxidation state can be identified by the shake-up features present at slightly higher binding energies than the maximum and by an increase of the difference in binding energy between the $Co2p_{3/2}$ and $Co2p_{1/2}$ peaks.

After reduction, Co/Ti ratios increased in the IWI catalysts what suggests that Co was spreading over the support, whereas in the HDP catalysts the Co/Ti ratio remained similar with no significant changes in dispersion. With regard to the Mn, the Mn/Co ratio decreased for the IWI-CoMn catalyst after reduction (from 0.57 to 0.38) due to an increase of the Co signal. Hence, the Mn would be already spread over the TiO_2 before reduction without any close interaction with Co. In the HDP-CoMn catalyst a large increase of the Mn/Co ratio (from 0.58 to 0.75) was obtained after reduction whereas the Co/Ti ratio did not change much. Thus, this increase of the Mn signal might be due to a migration of Mn particles from the top of the cobalt particles towards the support as soon as Co_3O_4 is being reduced to Co^0. After reduction the Mn remains in the oxidic state as MnO [11], which can interact with the cobalt particles as long as these are not totally reduced.

3.3. Temperature programmed reduction
Fig. 1 shows the TPR profiles for the four catalyst precursors after calcination. Supported cobalt oxide reduction occurs in two different steps:

$$Co_3O_4 + H_2 \rightarrow 3\ CoO + H_2O$$

$$CoO + H_2 \rightarrow Co + H_2O$$
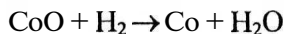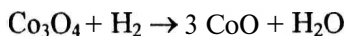
The areas of H_2-consumption peaks in all samples were in agreement with the stoichiometric of both reduction steps. For both unpromoted catalysts, the two peaks are attributed to the reduction from Co_3O_4 to CoO, which then reduces at higher temperatures to Co^0. However, in HDP-Co catalyst the second peak splitted in two maximum temperatures. This splitting is probably due to a different extent of metal-support interaction of the cobalt particles. The formation of $CoTiO_3$ has been reported to occur when small Co particles interact with TiO_2 support [12].
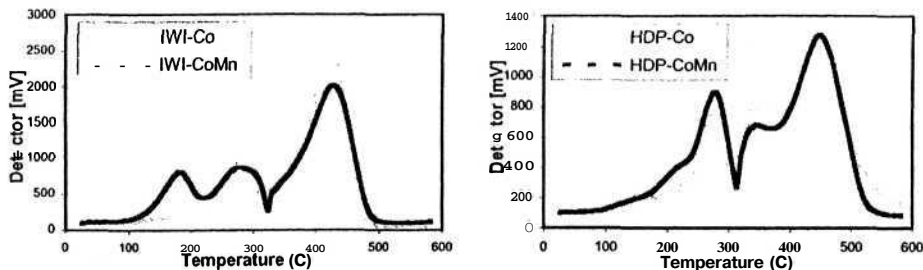
Fig 1. TPR profiles of unpromoted and **Mn-promoted Co/TiO$_2$** catalysts.

The addition of **Mn** to both types of catalysts had a different effect on the TPR profiles. In the case of the IWI-CoMn catalyst a new reduction peak appeared at lower temperatures (~180 °C) without any effect on the reduction temperature of the Co oxides since no interaction between Co and Mn is thought to take place in this sample. The new reduction peak must be due to the reduction of Mn compounds. A different effect of Mn was found in the **HDP-CoMn** catalyst. Here, the presence of Mn decreased the Co **reducibility** since there was an increase of the maximum temperature peak area. This again points towards the existence of a Co-Mn interaction in this catalyst, which depletes Co reducibillity.

3.4. Catalytic testing

CO conversion was used as a measure of catalyst activity. In the first stage of FTS reaction deactivation occurred causing a decrease of the activity until a steady state was reached in about 24 hours. During this first stage of reaction changes in selectivity were observed, increase of α values and decrease of paraffins/olefins ratios, what may be due to structural and compositional changes in the active sites [13,14]. Table 3 summarizes the catalytic performances of the **Co/TiO$_2$** catalysts under study compared at the same conversion values in order to evaluate the Mn addition.

Catalysts prepared by **IWI** showed better FTS performances since they yielded higher weight hydrocarbons. However, the presence of Mn promoter in the IWI catalyst did not enhance the catalytic performances, but in turn lowered the α values. HDP catalysts showed lower α values and higher P/O ratios than IWI catalysts. This means that the higher the **olefinic** production, the higher the chain growth probability. This is due to an increase of the **α-olefin readsorption** rate [15]. Nevertheless, the presence of Mn in HDP catalyst enhanced the catalytic performances increasing the C5+ yield and decreasing the methane formation, suggesting an influence of Mn on the Co active site. In addition, an improvement of catalytic stability was found for the Mn promoting catalyst as was revealed by the deactivation rate throughout long catalytic tests.

Table 3
Steady state FTS results for the four Co/TiO$_2$ catalysts under study.

Sample code	% CO conversion	Co-time yield $(10^3.s^{-1})$	% CH$_4$ select.	% C5+ select.	P/O Ratio	a values
IWI-Co	3.60	1.55	18.2	55.6	0.11	0.71
IWI-CoMn	3.60	1.56	19.2	51.4	0.15	0.67
HDP-Co	2.78	1.80	32.7	30.9	0.35	0.56
HDP-CoMn	2.78	1.80	22.3	43.5	0.22	0.63

4. CONCLUSIONS

It has been shown that the catalytic performances of Co/TiO$_2$ catalysts in FTS depend on the final Co phase distribution, which can be varied by using different preparation methods. The use of Mn as promoter element may lead to an improvement of the selectivity by decrease of the CH$_4$ formation and an increase of the α value. However, this promotion effect can only be achieved by using a suitable preparation procedure that leads to an appropriate Mn-Co interaction in the active catalyst. In the present work, an apparent Mn interaction in the HDP-CoMn catalyst led to a decrease of Co reducibility. This decrease of Co reducibility did not cause any loss of catalyst activity, but enhanced the selectivity towards higher hydrocarbons.

ACKNOWLEDGMENTS

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