

Cobalt supported on carbon nanofibers – a promising novel Fischer-Tropsch catalyst

G. L. Bezemer, A. van Laak, A. J. van Dillen and K. P. de Jong

Department of Inorganic Chemistry and Catalysis,
Utrecht University, Sorbonnelaan 16, 3584 CA Utrecht, The Netherlands

ABSTRACT

The potential of carbon nanofibers supported cobalt catalysts for the Fischer-Tropsch reaction is shown. Using the wet impregnation method cobalt on carbon nanofiber catalysts were prepared with cobalt loadings varying from 5 to 12 wt%. The cobalt particle size of the catalysts varied with increasing loading from 3 to 13 nm. Cobalt particles were localized both at the external and at the internal surface of the fibers. The activity at 1 bar syngas varied with increasing loading from 0.71 to $1.71 \cdot 10^{-5} \text{ mol}_{\text{CO}} \cdot \text{g}_{\text{Co}}^{-1} \cdot \text{s}^{-1}$. This might indicate that smaller particles are less active in the Fischer-Tropsch reaction, but may also be provoked by different fractions of cobalt present inside the fibers. Stable activity of $225 \text{ g}_{\text{CH}_2} \cdot \text{l}_{\text{cat}}^{-1} \cdot \text{h}^{-1}$ for 400 h was obtained at pressures of 28-42 bar syngas. A C_{5+} selectivity of 86 wt% was found, which is remarkably high for an unpromoted catalyst.

1. INTRODUCTION

In the Fischer-Tropsch (FT) reaction synthesis gas (CO/H_2) is converted into hydrocarbons. By using synthesis gas produced from natural gas, coal or biomass, transportation fuels can be produced from feedstocks other than crude oil. Currently the FT process is commercially operated by several companies.

Cobalt is well known for its activity in the FT reaction. Almost all research on cobalt catalysts has been devoted to oxidic supports such as Al_2O_3 , SiO_2 or TiO_2 . A drawback of oxidic supports is that cobalt may react with the support to irreducible mixed compounds during either synthesis or catalysis [1]. Due to this reactivity FT synthesis using cobalt particles smaller than 4 nm has not been reported on oxidic supports [2,3].

To circumvent the problem of cobalt reacting with the support the use of carbon as support has been explored [4,5]. However the carbon materials used

were not very pure and ill defined. Therefore it may be advantageous to explore graphitic carbon as a support material. Carbon nanofibers (CNF) is a very promising, novel graphitic support material with a potential use in many applications [6]. It consists of interwoven fibers of graphitic carbon from a high purity, a high mechanical strength and a high chemical inertness. The use of CNF for the FT reaction has been reported by van Steen *et al.* who studied copper and potassium promoted iron catalysts [7]. Here, we report on the interesting catalytic properties of Co/CNF prepared by wet impregnation. In a first attempt to study this system we varied the cobalt loading from 5 to 12 wt%.

2. EXPERIMENTAL

2.1 Catalyst preparation

Carbon nanofibers of the fishbone-type with a diameter of about 30 nm were grown out of synthesis gas using an earlier described method [8]. After growth impurities were removed by successively refluxing the sample in KOH [1 M] and in concentrated HNO₃. By treatment in HNO₃ the polarity of the surface is significantly increased due to the introduction of oxygen-containing surface groups. Due to the breaking up of the fibers resulting from oxidation of defect rich regions, the inner tubes are further opened [9,10]. Furthermore, the surface groups act as sites of interaction with the metal precursor.

Cobalt was deposited on thus activated CNF using a wet-impregnation method adapted from Reuel *et al.* [4]. In a flask the required amount of Co(NO₃)₂·6H₂O dissolved in 10 ml toluene/ethanol (2:1 v/v) was added to 1.0 g of CNF. Under continuous stirring the solvent was evaporated at ambient temperature applying a dynamic vacuum. The catalyst precursors were dried at 60 °C in air and subsequently reduced in a pure hydrogen flow (200 ml/min) at 300 °C for two hours. The samples were carefully passivated at 150 °C using a CO₂/N₂ flow (1:5 v/v). Catalysts with cobalt loadings of 5, 8 and 11.9 wt% were prepared, further denoted as Co5, Co8 and Co12.

2.2 Catalyst Characterization

The reduced and passivated catalysts were characterised using SEM, TEM, XPS and XRD. SEM was performed using a Philips XL30 FEG apparatus. TEM images were obtained using a Philips Tecnai-20 FEG TEM operated at 200 kV. XPS data were obtained with a Vacuum Generators XPS system using-monochromatic Al K_α radiation. XRD measurements were performed with a Nonius PDS 120 powder diffractometer system using Co K_{α1} radiation ($\lambda=1.78897 \text{ \AA}$).

2.3 Catalytic testing

The FT measurements were carried out at 220 °C and at 1 bar CO/H₂ (1:2 v/v). A high GHSV (3500 h⁻¹) was used in combination with line tracing at 130 °C to prevent product condensation. Typically 50 mg of catalyst particles (0.5-1.0 mm) was diluted with 500 mg SiC (0.2 mm) to achieve isothermal plug-flow conditions. Hydrocarbon products (C₁-C₁₆) were analysed with an FID on a Varian 3800 GC with a fused silica CP-Sil 5CB column. Selectivities of the catalysts were compared at the same CO-conversion (2%), which was achieved by tailoring the GHSV. A linear relation between GHSV and CO-conversion was found.

The catalyst loaded with 11.9 wt% cobalt was also tested at a pressure of 28-42 bar, which is closer to conditions used in industry. After re-reduction the catalyst was tested at 214 °C using a GHSV of 1700 h⁻¹ for 400 h.

3. RESULTS AND DISCUSSION

3.1 Characterization of the catalysts

The bulk density of the purified CNF was approximately 0.64 g/ml with a pore volume of 0.40 ml/g. The material obtained consisted of fibers of graphitic carbon with a diameter of about 30 nm and a specific surface area of 150 m²/g. The fibers are interwoven and form skeins with meso- and macropores. The 3D structure of the support bodies with long interwoven fibers inside the CNF skein is clearly shown (Fig. 1).

The catalysts were further studied using XRD. With XRD characteristic graphite diffractions were found (30, 50, 64 and 95 ° 2θ) together with cobalt oxide reflections (43 and 73 ° 2θ) as can be seen in Fig. 2. By applying the Scherrer equation on the line width at 43 ° 2θ the cobalt particle size was calculated. The particle sizes, which are given in Table 1, increased from 3 to 13 nm with increasing cobalt loading.

Particle sizes were also measured using TEM. Representative images of Co5 and Co8 are shown in Fig. 3 and Fig. 4. Small particles are visible on the fibers

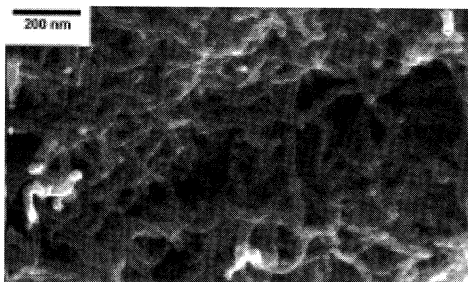


Fig. 1. SEM micrograph of purified CNF

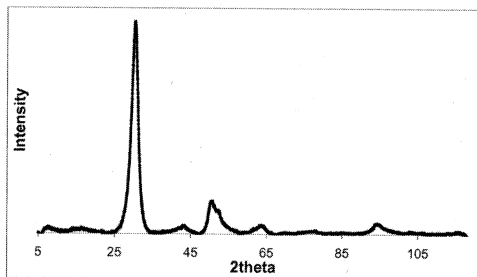


Fig. 2. XRD spectrum of Co5

Table 1

Properties of catalysts studied

Name	Co loading Co/C (at/at)	TEM (nm)	XRD (nm)	XPS (Co/C)	Act. (CTY)	TOF	α	CH ₄ (wt%)
Co5	0.0107	3-4	3	0.0016	0.71	1.3	0.61	46
Co8	0.0177	4-7	6	0.0275	1.60	5.9	0.62	41
Co12	0.0272	-	13	0.0344	1.71	13.6	0.62	39

XPS = Co/C atomic ratio

TOF = $10^{-3} \cdot s^{-1}$ CTY = $10^{-5} \text{ mol}_{\text{Co}} \cdot \text{g}_{\text{Co}}^{-1} \cdot \text{s}^{-1}$

and with EDX it was confirmed that they consist of cobalt and cobalt oxide. Particle sizes found with TEM confirmed the XRD results (Table 1).

TEM images show that the fibers are not solid, but have an inner core with a diameter of approximately 8 nm. Fig. 3 indicates that a significant part of the cobalt particles is localized in the inner tube because a string of particles follows the course of the fiber core. Upon tilting the fiber along its axis during TEM analysis, these particles are not moved, which proves their location in the inner tube. This phenomenon was most pronounced with Co5. The deposition of cobalt and other metals inside carbon nanotubes using wet impregnation techniques has been reported earlier [11,12]. To our best knowledge, this is the first report on cobalt particles deposited in the central tube of carbon nanofibers.

Quantitative XPS was used to further study the amount of cobalt present in the inner core of the fibers. XPS is a surface sensitive technique with an escape depth of the photo-electrons for graphite of 2-3 nm, so cobalt loaded inside the

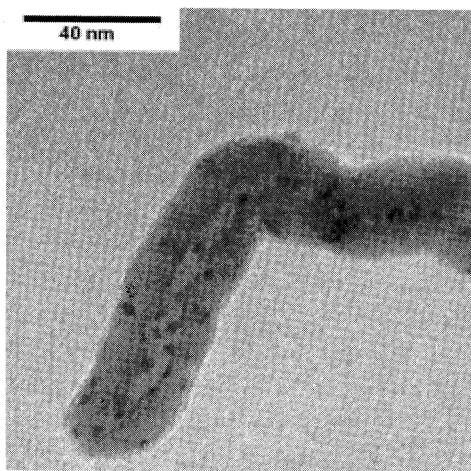


Fig. 3. TEM image of Co5, small cobalt particles are visible in and on the CNF.

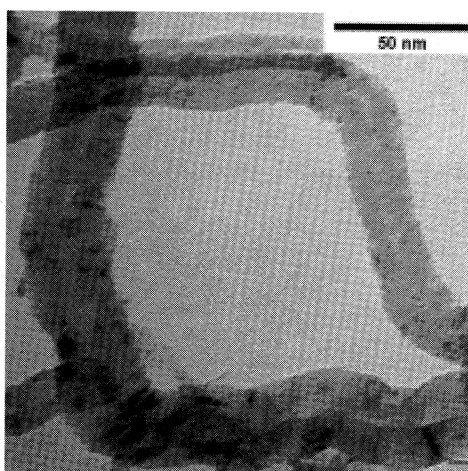


Fig. 4. TEM image of Co8, small cobalt particles are visible on the CNF.

fibers is hidden for the XPS technique. The areas of the carbon and the cobalt peak were used to calculate the Co/C ratios shown in Table 1. For Co5 this ratio is far lower than the actual loading, but also for Co8 and Co12 a higher ratio would be expected if particle sizes were taken into account. From XPS results it may be concluded that the larger the Co loading, the lower the fraction inside the tubes.

3.2 Catalytic testing

The performance of the catalysts at 1 bar is given in Table 1. The catalysts displayed ASF kinetics, with a methane selectivity varying from 46 for the lowest to 39 wt% for the highest loading. The C_{5+} selectivities varied from 29 to 34 wt%. In Fig. 5 the ASF plot of Co12 is shown. The chain growth probability (α) of the three catalysts turned out to be virtually the same: 0.61 or 0.62. After an initial deactivation of at most 30% the catalysts displayed stable activities for 70 h, which indicates that the CNF support is not gasified during catalytic operation. The activity at 1 bar, normalised on the cobalt loading (CTY), exhibited a more than two-fold increase going from the lowest to the highest loaded catalyst.

The TOF values were calculated using XRD data on the particle size and the measured CTY. A linear relation between the cobalt particle size and the TOF was found: an increase of the cobalt particle size coincides with an increase of the TOF. This relation is plotted in Fig. 6. However, this interpretation should be handled with care; it can not be excluded that this correlation is brought about, or at least affected due to the presence of a loading dependent part of the Co particles in the inner tubes of the fibers. So more research is needed to find out the cause of this correlation.

A fresh amount of Co12, the catalyst with the highest CTY was also tested at pressures closer to commercial operation. The catalysts showed stable activities during 400 h of operation. At a space-time-yield of $225 \text{ g}_{\text{CH}_2} \cdot \text{l}_{\text{cat}}^{-1} \cdot \text{h}^{-1}$ the C_{5+} selectivity was as high as 86 wt%.

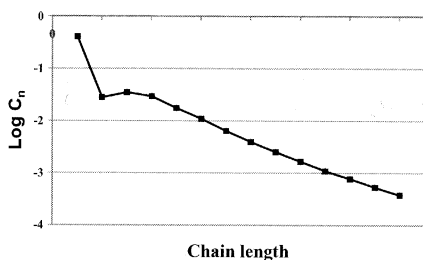


Fig. 5. ASF distribution of Co12 at 1 bar.

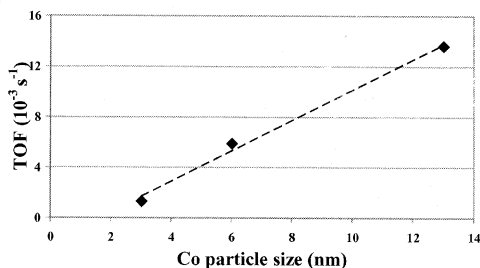


Fig. 6. Relation between cobalt particle size and TOF.

4. CONCLUSION

Co/CNF catalysts with small cobalt particles well dispersed on carbon nanofibers (CNF) were synthesized. It was shown that CNF is a very promising support material for the Fischer-Tropsch reaction. Stable activity of $225 \text{ g}_{\text{CH}_2} \cdot \text{l}_{\text{cat}}^{-1} \cdot \text{h}^{-1}$ for 400 h was obtained at pressures of 28-42 bar syngas. A C_{5+} selectivity of 86 wt% was found, which is remarkably high for an unpromoted system.

By comparing the specific activities of the catalysts at 1 bar it was found that catalysts with smaller cobalt particles showed a lower activity. Results give an indication of a cobalt particle size effect in FT, but more research is needed to exclude other possibilities, such as the different amounts of Co in the inner tube of the fibers.

ACKNOWLEDGMENTS

The authors acknowledge J.W. Geus and C. van der Spek (TEM), A. Mens (XPS), H. Holewijn and H. Oosterbeek (high pressure FT) and the financial support of Shell Global Solutions.

REFERENCES

- [1] P.J. van Berge, J. van de Loosdrecht, S. Barradas, A.M. van der Kraan, *Catal. Today*, 58 (2000) 321.
- [2] E. Iglesia, *Appl. Catal. A-Gen.*, 161 (1997) 59.
- [3] A. Barbier, A. Tuel, I. Arcon, A. Kodre, G.A. Martin, *J. Catal.*, 200 (2001) 106.
- [4] R.C. Reuel, C.H. Bartholomew, *J. Catal.*, 85 (1984) 78.
- [5] C. Morenocastilla, F. Carrascomarin, *J. Chem. Soc.-Faraday Trans.*, 91 (1995) 3519.
- [6] K.P. de Jong, J.W. Geus, *Catal. Rev.-Sci. Eng.*, 42 (2000) 481.
- [7] E. van Steen, F.F. Prinsloo, *Catal. Today*, 71 (2002) 327.
- [8] M.L. Toebes, J.H. Bitter, A.J. van Dillen, K.P. de Jong, *Catal. Today*, 76 (2002) 33.
- [9] T.G. Ros, A.J. van Dillen, J.W. Geus, D.C. Koningsberger, *Chemphyschem*, 3 (2002) 209.
- [10] M.L. Toebes, J.M.P. van Heeswijk, J.H. Bitter, A.J. van Dillen, K.P. de Jong, *Carbon* 42 (2004) 307.
- [11] S.C. Tsang, Y.K. Chen, P.J.F. Harris, M.L.H. Green, *Nature*, 372 (1994) 159.
- [12] J.P. Tessonnier, L. Pesant, C. Pham-Huu, G. Ehret, M.J. Ledoux, *Stud. Surf. Sci. Catal.*, 143 (2002) 697.