

COBALT SUPPORTED ON CARBON NANOFIBERS- A NOVEL FISCHER-TROPSCH CATALYST

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Introduction

In the Fischer-Tropsch (FT) reaction synthesis gas (CO/H₂) is catalytically 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. This is a major advantage with rising fuel demands and environmental constraints. The FT process yields a mixture of mainly long straight chain paraffins, ditto 1-olefins, and water as a by-product. In a second step the hydrocarbons are hydrocracked and yield middle distillates as products. These products are completely free from sulphur, nitrogen and aromatics and burn considerably better than conventional diesel. The quality of the products formed in combination with a non-crude oil feedstock ensures the FT process to play a crucial role in the energy supply of the coming decades.

Supported cobalt is well known for its activity in the FT reaction. However, almost all research on FT cobalt catalysts is confined to cobalt on oxidic supports. A drawback of these supports is their reactivity towards cobalt(II), which results in the formation of irreducible mixed compounds during preparation or catalysis [(1)]. To overcome these problems of cobalt the use of carbon as support has been explored [(2,3)]. However, the carbon materials used were ill defined and not very pure. Therefore we decided to use carbon nanofibers (CNF) as a support. CNF is a novel graphitic support material with a potential use in many applications [(4)]. It consists of skeins of interwoven fibers of graphitic carbon from a high purity and a high mechanical strength. The use of CNF for the FT reaction has been reported by van Steen *et al.* who studied copper and potassium promoted iron catalysts [(5)]. Here, we report on the interesting catalytic properties of differently loaded (5-12 wt%) Co/CNF catalysts prepared by wet impregnation [(6)].

Experimental

Activated CNF were prepared using a literature method [(7)]. Cobalt was deposited on the fibers using a wet impregnation method adapted from Reuel *et al.* [(3)]. Catalysts with cobalt loadings of 5, 8 and 12 wt%, further denoted as Co5, Co8 and Co12, were

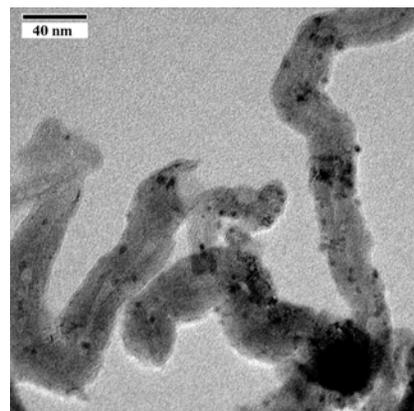


Fig. 1. TEM image of Co5, small cobalt particles are visible on the fibers.

prepared. Catalyst precursors were reduced in hydrogen at 300 °C for two hours and subsequently passivated at 150 °C using CO₂. The catalysts were characterized with XRD and TEM. FT measurements were carried out at 220 °C and at 1 bar CO/H₂ (1:2) using a high GHSV (at least 3500 h⁻¹) to prevent product condensation. Selectivities of the catalysts were compared at the same CO-conversion, which was achieved by tailoring the GHSV. Sample Co12 was also tested at a pressure of 28-42 bar, which is closer to conditions used in industry. After a re-reduction the catalyst was tested at 214 °C using a GHSV of 1700 h⁻¹ for 400 h.

Results and Discussion

With XRD it was found that cobalt particle sizes increase with increasing loading from 3 to 13 nm (table 1). TEM studies confirmed this result. A representative TEM image of Co5 depicted in figure 1 shows 3-4 nm cobalt particles nicely

dispersed over different fibers. All three catalysts displayed ASF kinetics with a chain growth probability (α) of 0.61 or 0.62. The methane selectivity varied from 46 to 39 wt% going from Co5 to Co12. The activity of the catalysts at 1 bar, normalized on the loading (CTY) showed a more than twofold increase going from the lowest to the highest loading. 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 figure 2. However this interpretation should be handled with care; it cannot be excluded that other parameters are of importance too. So more research is needed to find out the cause of this correlation.

Sample Co12, the catalyst with the highest activity at 1 bar was also tested at pressures closer to commercial operation conditions. The catalyst showed a stable activity during 400 h of operation. At a weight-time-yield of 225 g_{CH₂}·g_{cat}⁻¹·h⁻¹ the C₅₊ selectivity was as high as 86 wt%. This demonstrates the potential of Co/CNF catalysts for the FT reaction.

Conclusions

Co/CNF catalysts with small cobalt particles well dispersed on carbon nanofibers were synthesized. Stable activity of 225 g_{CH₂}·g_{cat}⁻¹·h⁻¹ for 400 h was obtained at pressures of 28-42 bar syngas. A C₅₊ selectivity of 86 wt% was found, which is remarkably high for an unpromoted system. These results demonstrate that CNF is a very promising

Table 1. Properties of the catalysts studied.

Nam e	TEM (nm)	XRD (nm)	Act. (CTY)	TOF	α	CH ₄ (wt%)
Co5	3-4	3	0.71	1.3	0.61	46
Co8	4-7	6	1.60	5.9	0.62	41
Co12	-	13	1.71	13.6	0.62	39

CTY = 10⁻⁵ mol_{CO}·g_{Co}⁻¹·s⁻¹ TOF = 10⁻³·s⁻¹

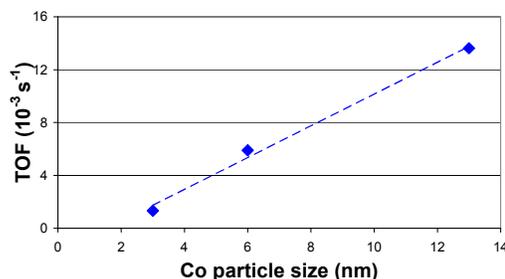


Fig. 2. Relation between cobalt particle size and TOF.

support for Fischer-Tropsch catalysts.

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

References

- [1] van Berge PJ, van de Loosdrecht J, Barradas S, van der Kraan AM. Oxidation of cobalt based Fischer-Tropsch catalysts as a deactivation mechanism. *Catal. Today* 2000;58:321-34.
- [2] Moreno-Castilla C, Carrasco-Marin F. Cobalt Catalysts Supported on Activated Carbons - Preparation and Behavior in the Hydrogenation of Carbon Oxides. *J. Chem. Soc.-Faraday Trans.* 1995;91:3519-24.
- [3] Reuel RC, Bartholomew CH. Effects of support and dispersion on the carbon monoxide hydrogenation activity/selectivity properties of cobalt. *J. Catal.* 1984;85:78-88.
- [4] de Jong KP, Geus JW. Carbon nanofibers: Catalytic synthesis and applications. *Catalysis Reviews-Science and Engineering* 2000;42:481-510.
- [5] van Steen E, Prinsloo FF. Comparison of preparation methods for carbon nanotubes supported iron Fischer-Tropsch catalysts. *Catal. Today* 2002;71:327-34.
- [6] Bezemer GL, van Laak A, van Dillen AJ, de Jong KP. *Stud. Surf. Sci. Catal.* accepted.
- [7] Toebes ML, Bitter JH, van Dillen AJ, de Jong KP. Impact of the structure and reactivity of nickel particles on the catalytic growth of carbon nanofibers. *Catalysis Today* 2002;76:33-42.