Highly dispersed silica supported cobalt catalysts for Fischer-Tropsch synthesis

Johan P. den Breejen, Jelle R.A. Sietsma, Petra E. de Jongh, A. Jos van Dillen,
Johannes H. Bitter and Krijn P. de Jong*
Inorganic Chemistry and Catalysis, Utrecht University, NL-3508 TB Utrecht (The Netherlands)
*k.p.dejong@chem.uu.nl.

Introduction

In the Fischer-Tropsch (FT) reaction, CO and H_2 are converted into hydrocarbons using preferably a supported cobalt catalyst. The importance of a high cobalt dispersion for FT catalysts was put forward recently, using a cobalt on carbon nanofiber catalyst. It was demonstrated that 6-8 nm cobalt particles were most effective for the FT reaction [1].

On oxidic supports, the synthesis of readily reducable catalysts with high dispersion is a real challenge. While preparing small cobalt particles, the interaction with the support has to be taken into account. Whereas a strong interaction with the support can lead to poorly reducible species, a weak interaction will lead to sintering of small particles during calcination, reduction or FT synthesis. [2].

Using a recent finding by our group [3], we are able to synthesize small supported cobalt oxide crystallites via a facile route. This includes a change in calcination gas from air to NO in He. This calcination method was used in the current study to prepare FT catalysts with small cobalt oxide particle sizes. Here we report on the large effects of the reduction temperature on the FT activity of these catalysts.

Materials and Methods

The cobalt on silica catalyst was prepared via incipient wetness impregnation. A silica support (Grace-Davison Davicat silica gel) was impregnated with an aqueous cobalt nitrate solution, to achieve a cobalt loading of 18 wt%. The catalysts were dried by heating from room temperature (RT) to 70 ºC with a heating rate of 1 ºC min^{-1}, maintaining this temperature for 12 h. The calcination (NC) was performed with a stream of 1%vol NO in He, with a total space velocity of 1 l min^{-1} g_{cat}^{-1}. The samples were heated from RT to 450 ºC with a heating rate of 1 ºC min^{-1} and kept at this temperature for 4 h. For comparison, the catalyst was also calcined with air (AC) under similar conditions. Another catalyst was used as-dried and (*in-situ*) direct reduction (DR) prior to FT catalysis.

The Fischer-Tropsch reaction was performed at 220 ºC at 1 bar and H_2/CO ratio of 2 (v/v). Prior to the measurements, the catalysts were *in-situ* reduced at various temperatures, ranging from 300 to 600 ºC, for 2 h, with a heating rate of 5 ºC min^{-1} and a flow of 33% H_2 in He (60 ml/min). Typically, 20 mg catalyst was diluted with 200 mg SiC (200 µm) to achieve isothermal plugflow conditions. Online product gas analysis (C_1-C_{20}) was performed using a Gas Chromatograph (GC) to determine the selectivity (wt%) towards C_1 (methane) and C_{5+}-hydrocarbons.

The conversion was kept at 2% by tailoring the space velocity. Reported catalytic data are obtained after at least 16 hours of operation.

Results and Discussion

In Figure 1, the activity in Cobalt-Time-Yield, CTY (10^{-5} mol CO g_{Co}^{-1} s^{-1}) has been plotted as function of the reduction temperature. As can be observed, the activity increased as the reduction temperature was increased to 450 ºC. At higher reduction temperatures, the activity of the AC and DR catalyst levels off and decreased at too high reduction temperatures. On the contrary, the NC catalyst activity was enhanced with a maximum value at 550 ºC.

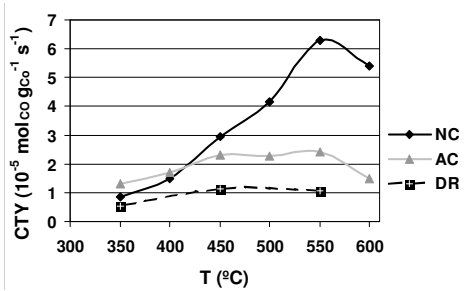

Figure 1. FT activity as function of the reduction temperature

These trends can be tentatively ascribed to both a difference in reduction degree and a difference in particle size. Since the average Co_3O_4 crystallite size, as determined with XRD (Scherrer), is much larger for the AC catalyst compared to the NC catalyst (11 and 4 nm respectively), the reduction of the AC catalyst is expected to proceed faster. That means that a further increase in reduction temperature beyond 450 ºC has limited effect on the reduction degree, and thus activity. For the small particles of the NC catalyst, a higher reduction temperature was needed because of an increased interaction with the support. The significantly higher activity for the small particles reduced at high temperatures, compared to the large particles of the AC catalyst, again shows an effect of particle size in the FT reaction, although the optimum particle size seems to be somewhat lower (4-5 nm) than on CNF material. At too high reduction temperatures (600 ºC), sintering probably caused a decrease in activity for all catalysts.

In the full paper, more details about the degree of reduction will be provided.

Significance

A highly active Co/SiO_2 catalyst is prepared via a novel calcination method. We succeeded in making a catalyst with a small Co particle size (4-5 nm) which could be obtained after a high temperature reduction and displays an efficient cobalt usage.

References

1. Bezemer, G.L., Bitter, J.H., Kuipers, H.P.C.E., Oosterbeek, H., Holewijn, J.E., Xu, X..D., Kapteijn, F., van Dillen, A.J., de Jong, K.P., *J. Am. Chem. Soc.* 128, 3956 (2006).
2. Soled, S.L., Iglesia, E., Fiato, R.A., Baumgartner, J.E., Vroman, H., Miseo, S., *Top. Catal.* 26, 101 (2003).
3. Sietsma, J.R.A., van Dillen, A.J., de Jongh, P.E., de Jong, K.P., Patent application, GB0515887.6 (2005).