

Performance of supported Co catalysts for Fischer-Tropsch synthesis

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Introduction

Fischer-Tropsch synthesis aims at converting syngas into high quality diesel. The syngas may be produced from different C-containing feedstocks i.e. natural gas, oil, coal or biomass. Syngas from natural gas has a higher H₂/CO ratio than syngas derived from coal or biomass, but the H₂/CO ratio may be adjusted by the water-gas shift (WGS) reaction either by a separate catalytic unit or by using a FT catalyst with WGS activity. Cobalt is considered the most favourable catalyst for the synthesis of long-chain hydrocarbons from natural gas-based syngas due to its high activity and selectivity to long chain hydrocarbons and relatively slow deactivation [1].

Cobalt site-time yields have usually been considered independent of both cobalt dispersion and the nature of the support. However, it has been shown recently that for Co supported on carbon nanotubes, a positive correlation exists between the Co particle size and the site-time yield for Co particles provided that the particles are less than 6-7 nm [2, 3]. For Co supported on Al₂O₃ the results are not so unambiguous and a recent study did not report any relation between the Co particle size and the alumina support [4]. For small Co particles supported on Al₂O₃ the extent of reduction is relatively low, but this is taken into account when calculating the site-time yield.

Experimental evidence shows that the C₅⁺ selectivity depends on the particle size, on the support material and of course on the reaction conditions [1, 5]. It is known that the addition of steam to the feed results in an increased C₅⁺ selectivity [5]. The use of promoters has also an influence on the C₅⁺ selectivity and Re gives in most cases an increase in the selectivity of C₅⁺ [1]. However, the effect of Co dispersion and the support on the performance of Fischer-Tropsch synthesis catalysts is still far from being well established and the present work deals with a systematic study of the behaviour of catalysts with different particle sizes and of different structural parameters of the support.

Co catalysts deactivate during use and several mechanisms have been proposed including sintering, carbon formation and possibly Co oxidation. As will be shown, the rate of deactivation also depends on the Co dispersion and on the nature of the support material. For slurry type reactors the mechanical strength of the catalyst particle is also very important.

Materials and Methods

Catalysts containing 12 or 20 wt% Co were prepared by one-step incipient wetness impregnation of the supports with aqueous solutions Co(NO₃)₂·6H₂O. HReO₄ was added to the impregnation solution in cases where Re was used as promoter. Catalysts with different Co particle sizes were also prepared using different cobalt nitrate solutions containing water, ethylene glycol and diethylene glycol. Fischer-Tropsch synthesis was performed in a fixed-bed

reactor (10 mm i.d.) at 483 K and 20 bar using 1 g catalyst diluted with inert particles. The catalysts were sieved to catalyst particle sizes between 53 and 90 µm. The samples were reduced *in situ* in H₂ and 1 bar while the temperature was increased at 1 K/min to 623 K. The system was then pressurized to 20 bar and synthesis gas (H₂:CO=2:1) was introduced to the reactor. Heavy hydrocarbons (waxes) were collected in a heated trap and liquid products were removed in a cold trap. The effluent gaseous products were analysed using a GC equipped with TC and FID detectors. Details of the experimental setup are given elsewhere [1, 5].

Results and Discussion

In order to study the effect of the particle size and the support material on the catalytic performance of supported Co catalysts, several different series have been prepared including Co supported on alumina with different structural properties and Co supported on one specific alumina. For all the catalysts the particle size has been varied. It is assumed based on testing, that the use of ethylene/diethylene glycol does not influence the catalytic behaviour of Co. The results are also compared with Co model catalysts and with previous results for Co supported on SiO₂ and TiO₂ [5]. All these experiments are carried out in the same equipment and at the same condition. Since the C₅⁺ selectivity for the FT synthesis depends on the conversion, the experiment results are therefore compared at constant conversion (40 – 45 %).

H₂ chemisorption was used to determine the Co dispersion and in combination with O₂ titration the Co particle size was calculated. The Co particle size was also compared with XRD and TEM data. The particle size is determined before the experiments were carried out and an understanding of what happens during reduction/reaction is important when comparing results from different studies. Wax makes characterization of used catalysts difficult.

The experiments clearly show that the C₅⁺ selectivity depends on the structure of the alumina. α -alumina always gives substantial higher C₅⁺ selectivity than γ -alumina irrespective of the Co particle size. The selectivity of C₅⁺ on γ -alumina increases with increasing particle size up to about 10 nm and then the selectivity remains almost constant for particle sizes up to 20 nm (range of particle sizes studied). In fact, the results could indicate that a maximum in the C₅⁺ selectivity exists and for γ -alumina this corresponds to a particle size of 10 nm

Significance

Selectivity is a key issue in modern Fischer-Tropsch catalysis and the understanding of the parameters determining the selectivity on oxidic supports is important from a scientific as well as from an industrial point of view. It is also a key issue to relate the parameters giving high selectivity to catalyst activity (turnover frequency) and to catalyst deactivation.

References

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