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Priority Communication

Fischer–Tropsch synthesis: Cobalt particle size and support effects on intrinsic activity and product distribution

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ABSTRACT

The influence of cobalt particle size in the range 3 to 18 nm on the Fischer–Tropsch synthesis intrinsic activity and product distribution was investigated over 26 alumina (γ-Al_2O_3 and α-Al_2O_3) supported catalysts. A volcano-like curve was obtained for the γ-Al_2O_3 based catalysts when the C_{5+} selectivity was plotted as a function of the particle size. The maximum selectivity was located at 7–8 nm. This is the first time an optimum particle size has been identified. An apparent optimum size was also discovered for the series of α-Al_2O_3 based catalysts. Interestingly, the C_{5+} selectivity of the α-Al_2O_3 based catalysts was higher than the selectivity of the γ-Al_2O_3 based catalysts at all particle sizes. Thus, the selectivity is related both to the particle size and the support. No relation was observed between the cobalt particle size and the cobalt site-time yield.

1. Introduction

Modern Fischer–Tropsch technology aims at converting synthesis gas into long-chain hydrocarbons (i.e. C_{5+} hydrocarbons). Supported cobalt was, from an early stage, considered to be a favourable material for this purpose. However, despite the early discovery, the publication rate on these catalysts has never been as high as it is today. The impact of cobalt dispersion and support on the catalytic performance are two particularly hot topics.

Bezemer et al. [1] recently reported a strong influence of the cobalt particle size on both the cobalt site-time yield and the C_{5+} selectivity for a total of five supported catalysts. Carbon nanofibers were chosen as support materials because of their weak interactions with cobalt. Although inert supports may be advantageous in model systems, most commercial catalysts will likely consist of cobalt placed on a porous metal oxide support. Thus, in the quest for development of improved cobalt catalysts, it is especially important to acquire knowledge of the metal oxide supported catalysts.

At conditions favouring chain-growth, cobalt site-time yields have traditionally been considered independent of both cobalt dispersion and support identity. Iglesia [2], for instance, found constant site-time yield for the particle size range 10–210 nm for catalyst systems based on Al_2O_3, SiO_2, and TiO_2. Later, Lok [3] confirmed that the findings of Iglesia [2] were also valid at higher cobalt dispersions. Lok [3] obtained cobalt metal particle sizes of 3 nm on γ-Al_2O_3 using the so-called high dispersion cobalt (HDC) synthesis method. In contrast, Bezemer et al. [1] found a positive correlation between the particle size and the site-time yield in the particle size range 3 to 8 nm for cobalt supported on carbon nanofibers. However, exactly the same curve is obtained if the particle size is replaced by the cobalt loading on the *x*-axis. The site-time yield was constant above 8 nm. In qualitative agreement with Bezemer et al. [1], Martínez and Prieto [4] recently observed that the site-time yield increased by almost two orders of magnitude when the particle size increased from 4.1 to 11 nm on surface-protected delaminated ITQ-2 zeolites.

The metal oxide support and the cobalt particle size may of course also influence the product distribution. In fact, Storsæter et al. [5] observed significant variations in selectivity for cobalt on different supports (γ-Al_2O_3, SiO_2, and TiO_2). Furthermore, Saib et al. [6] reported a strong influence of the support pore size on the C_{5+} selectivity although the support in all cases was silica. Similarly, we [7] recently found a strong, positive correlation between the pore sizes of 13 γ-Al_2O_3 supported cobalt catalysts and the selectivity. Iglesia [2] attributed his observed differences in selectivity for cobalt on pure and modified Al_2O_3, SiO_2, and TiO_2 only to the variations in the extent of α-olefin re-adsorption. The sup-

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port and the cobalt dispersion were not considered to influence the probability of intrinsic chain-growth on cobalt surfaces. The dispersion varied in the range of 0.45 to 9.5%, corresponding to a particle size range from 10 to 210 nm if cobalt oxide can be completely reduced to metal. Shi and Davis [8], however, reported that the re-incorporation of α-olefin products as chain initiators does not have a major impact on the product distribution. Bezemer et al. [1] recently extended the investigation of Iglesia [2] to the particle size regime below 10 nm. Interestingly, there was a positive correlation between the particle size and the selectivity in the particle size range 3 to 8 nm. Above 8 nm, the selectivity did not change. It should be mentioned that the values were recorded at different temperatures (483 and 523 K) and CO conversion levels (13–84%) and that both these variables impact the product distribution.

To summarise, the effect of cobalt dispersion and support on the Fischer–Tropsch synthesis performance is still not well established for supported cobalt catalysts. In this contribution, we investigate the effect of both these variables in a systematic and rigorous manner. A total of 22 γ-Al_2O_3 and four α-Al_2O_3 supported catalysts with different cobalt particle sizes were exposed to exactly the same reaction conditions. By using such a systematic approach, we were able to show that both the cobalt particle size and the support influence the C_{5+} selectivity. In contrast, we did not observe any correlation between cobalt particle size and the cobalt site-time yield.

2. Experimental

A total of 26 catalysts were prepared by one-step incipient wetness impregnation of γ-Al_2O_3 or α-Al_2O_3 with different cobalt nitrate solutions (water, ethylene glycol (EG), diethylene glycol (DEG), or mixtures of these). In some cases, perrhenic acid was added to the impregnation solution as a rhenium precursor. The cobalt loading was 12, 20, or 30 wt% and the rhenium loading 0 or 0.5 wt%. After impregnation, the catalysts were dried at 383 K for 3 h and calcined at 573 K for 16 h. The same Sasol GmbH Puralox type γ-Al_2O_3 was used for all the samples. It is low in sodium (26 ppm), an element which has a known effect on the chain-growth probability of cobalt catalysts [7]. The α-Al_2O_3 support was produced by calcination of the γ-Al_2O_3 support at 1413 K for 10 h.

Nitrogen adsorption–desorption isotherms were measured on a Micromeritics TriStar 3000 instrument at 77 K. The surface area was calculated from the Brunauer–Emmett–Teller (BET) equation, while the total pore volume and the average pore size were found applying the Barrett–Joyner–Halenda (BJH) method.

X-ray diffraction patterns were recorded at ambient temperature on a Siemens D5005 X-ray diffractometer using Cu$K\alpha$ radiation. The crystallite size of Co_3O_4 was determined by performing a full profile pattern fit using TopasP and an instrument resolution function.

Transmission electron microscopy (TEM) was used to visualise the distribution of the cobalt in a number of substrates. Samples were prepared by embedding non-reduced catalysts in resin and preparing slices of nominal 50 nm thickness using a Richert Jung Ultracut E ultramicrotome. TEM was performed using a JEOL 2010F instrument operating at 200 kV.

X-ray photoelectron spectroscopy (XPS) was performed in a KRATOS AXIS ULTRA^{DLD} using monochromatic Al$K\alpha$ radiation ($h\nu = 1486.6$ eV), as well as achromatic Mg$K\alpha$ radiation ($h\nu = 1253.6$ eV), at 15 kV and 10 mA. For the survey and high resolution scans, pass energies of 160 and 20 eV were used, respectively.

Oxygen titration was performed on a Micromeritics AutoChem II 2920 unit. The catalysts were first reduced *in situ* in H_2 at 623 K for 16 h. A series of oxygen pulses were then passed through the catalyst at 673 K. The degree of reduction (DOR) was calculated assuming that all cobalt in metallic form were oxidised to Co_3O_4.

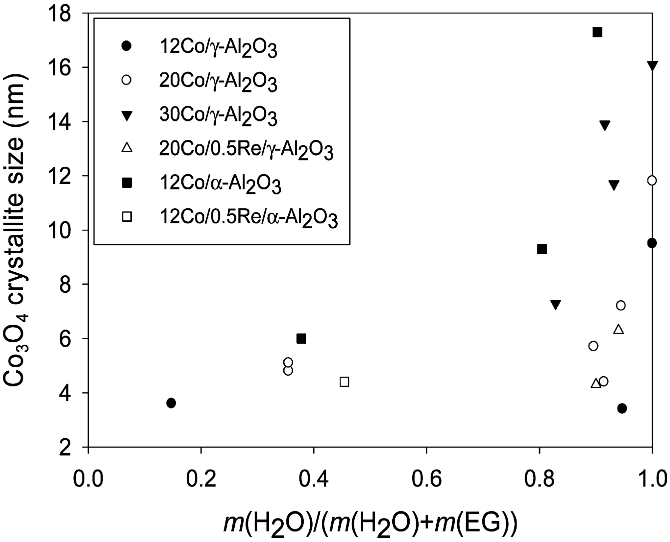

Fig. 1. Effect of water mass fraction of impregnation solvent on the post calcination Co_3O_4 crystallite size. The experimental error ($\pm 2\sigma$) for the crystallite size is ±0.5 nm.

Hydrogen adsorption isotherms were recorded on a Micromeritics ASAP 2010C unit at 313 K. The samples were reduced *in situ* in flowing H_2 at 623 K for 16 h. The adsorption isotherm was recorded in the pressure interval 15 to 500 mm Hg. In order to calculate the cobalt dispersion (D), it was assumed that two cobalt surface atoms were covered by one hydrogen molecule. The cobalt particle size ($d(Co^0)$) was calculated from:

$$d(Co^0)(nm) = \big(96/D(\%)\big) \cdot \mathrm{DOR}. \qquad (1)$$

Fischer–Tropsch synthesis was done in fixed-bed reactors at 483 K, 20 bar, and $H_2/CO = 2.1$. The samples were pre-reduced, *in situ*, in H_2 at 623 for 16 h at atmospheric pressure. The space velocity was varied to give CO conversion levels between 15 and 50% during Fischer–Tropsch synthesis. The cobalt site-time yield was calculated from the cobalt-time yield measured after 100 h on stream and the cobalt dispersion was measured *ex situ* by hydrogen chemisorption. The C_{5+} selectivity was calculated at 43–46% CO conversion for all catalysts. Olefin/paraffin ratios were calculated at the same conversion levels.

3. Results and discussion

Two different aluminas were used as supports, namely γ-Al_2O_3 and α-Al_2O_3. The surface area of the γ-Al_2O_3 supported catalysts ranged from 103 to 162 m^2/g, the pore volume from 0.38 to 0.60 cm^3/g, and the average pore diameter from 10.3 to 12.4 nm. The physical parameters of the α-Al_2O_3 supported catalysts were very different from the γ-Al_2O_3 based catalysts. The surface area varied from 12 to 22 m^2/g while the pore volumes and the pore diameters were located in the intervals 0.04–0.11 cm^3/g and 12–20 nm, respectively.

As shown in Fig. 1, we were able to tailor the post calcination Co_3O_4 crystallite size between 3.4 and 17 nm by varying the water concentration of the impregnation solvent, the cobalt loading, and the alumina support. However, at relatively high concentrations of EG ($m(H_2O)/(m(H_2O) + m(EG)) < 0.8$), the crystallites were small in size (4–6 nm), irrespective of cobalt loading or alumina support. Most likely, the glycol acted primarily as a surfactant, thereby increasing the wetting ability of the cobalt salt solutions. Above $m(H_2O)/(m(H_2O) + m(EG)) > 0.8$, on the other hand, the crystallite size was influenced by cobalt loading and alumina support. Specifically, the crystallite size increased with cobalt loading. Also, larger

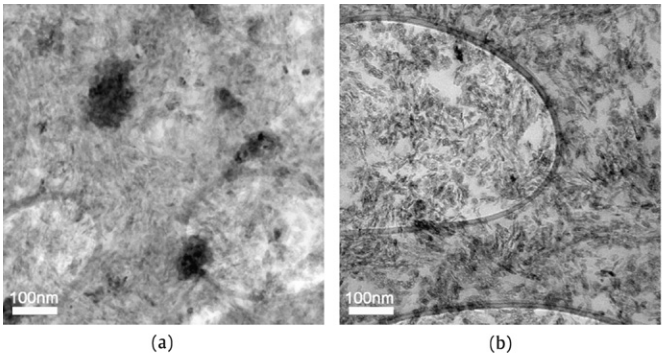

Fig. 2. Examples of TEM images. (a) Microstructure of 12Co/γ-Al_2O_3 (H_2O), (b) microstructure of 12Co/γ-Al_2O_3 (EG).

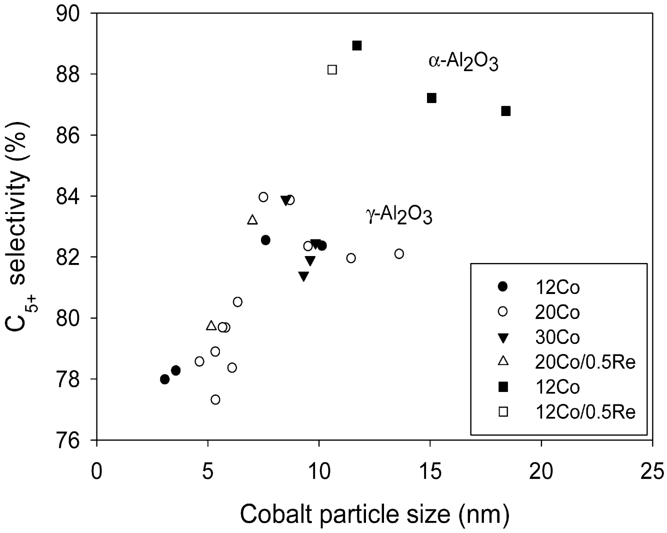

Fig. 3. Relationship between the cobalt particle size and the C_{5+} selectivity. The experimental error ($\pm 2\sigma$) for the particle size and selectivity is ±0.5 nm and 0.5%, respectively.

crystallites were formed in α-Al_2O_3 than in γ-Al_2O_3. To conclude, by making use of an organic solvent, we were able to vary the Co_3O_4 crystallite size independently of the physical parameters of the starting supports. This allows an independent study of the effect of particle size on the Fischer–Tropsch synthesis performance for a metal oxide based catalyst system.

The choice of solvent did not only impact the size, but also the distribution of the Co_3O_4 crystallites. TEM images (Fig. 2) revealed that while Co_3O_4 appeared in aggregates with dimensions above 100 nm when pure water was used as solvent, the aggregates were absent when ethylene glycol was used as solvent. These scenarios were observed on both γ-Al_2O_3 and α-Al_2O_3. In Fig. 2a, the aggregates show dark contrast relative to the support. In Fig. 2b, the sample was significantly thinner than in Fig. 2a, aggregates were not present and more detailed analysis confirmed that the Co_3O_4 was more uniformly distributed in the support. Images (not shown) were also collected for an aqueous/EG solvent sample. The pattern of Co_3O_4 distribution lay between that seen for the pure water and pure ethylene glycol based catalysts. Thus, the degree of aggregation is related to the water concentration of the solvent.

Oxygen titration of the pre-reduced catalysts was used to calculate the amount of reducible cobalt. The degree of reduction varied between 16 and 89%. The smallest cobalt particles were the most difficult to reduce. Since reduction was not complete, the degree of reduction was taken into account when the cobalt metal particle size was calculated (Eq. (1)).

Hydrogen chemisorption data were used to calculate cobalt dispersion and, in combination with oxygen titration data, to estimate the cobalt metal particle size. While the Co_3O_4 crystallite size ranged from 3.4 to 17 nm, the cobalt metal particle size varied from 3.1 to 18 nm.

Fischer–Tropsch synthesis was done at 483 K, 20 bar, and $H_2/CO = 2.1$. Before measurement, the catalysts were sieved to catalyst particle sizes between 53 and 90 µm. This size regime ensures absence of reactant diffusion limitations [7,9].

By using the cobalt-time yield measured after 100 h on stream and the cobalt dispersion measured *ex situ* by hydrogen chemisorption as basis, the cobalt site-time yield varied only between 31 and 63×10^{-3} s^{-1}. Furthermore, the relatively small variations in site-time yield could not be correlated with the cobalt particle size. In contrast, Bezemer et al. [1] observed that the site-time yield increased by a factor of more than 20 when the particle size increased from 3 to 16 nm. The increase was two orders of magnitude for Martínez and Prieto [4] when the particle size increased from 4 to 11 nm. The reason for the discrepancy between the present investigation and the two above mentioned investigations is not clear.

As it is known that the CO conversion level influences the selectivity, the C_{5+} selectivity was calculated at the same conversion for all catalysts. As shown in Fig. 3, the cobalt particle size is related to the selectivity. For the series of γ-Al_2O_3 supported catalysts, the selectivity increased sharply with increasing particle size up to about 7 nm. Remarkably, there was an apparent optimum particle size for the selectivity at approximately 8 nm. As shown in Fig. 3, the selectivity was constant for particles larger than 9–10 nm. The C_{5+} selectivity was directly correlated to the CH_4 and C_2–C_4 selectivity. Thus, a minimum CH_4 and C_2–C_4 selectivity was also recorded at 8 nm.

XPS was used to investigate whether any remaining organic solvent in some samples could be partly responsible of the results shown in Fig. 3. Two catalysts which were prepared using different solvents (H_2O and H_2O/EG (10:1)) and exhibited different C_{5+} selectivity (81.9 and 83.9%) were selected for study. However, the XPS spectra of the two catalysts were identical. On basis of the absence of any apparent contribution in the XPS spectrum at the relevant binding energy of 282.5 eV [10], the presence of cobalt carbide can most probably can be excluded. Furthermore, there was no obvious trend between the degree of reduction and C_{5+} selectivity. Finally, note that the variations in selectivity in Fig. 3 were obtained on a series of γ-Al_2O_3 based catalysts characterised by only small variations in pore diameter. Thus, the pore diameter in itself had no bearing on the C_{5+} selectivity.

Bezemer et al. [1] also observed that a minimum cobalt particle size is necessary to give high C_{5+} selectivity. The authors pointed out that the Fischer–Tropsch reaction comprises a large number of elementary steps, such as dissociation, hydrogenation, and insertion. Bezemer et al. [1] speculated that on small crystallites (i.e. <8 nm), the domains that combine the different sites are not stable or they contain a non-optimum ratio of the different sites. The results in Fig. 3 are consistent with the speculations by Bezemer et al. [1].

Fig. 4 shows a positive correlation between the C_3 olefin/paraffin ratio and the C_{5+} selectivity for cobalt supported on γ-Al_2O_3. Thus, a large extent of α-olefin re-adsorption cannot explain the high C_{5+} selectivity and vice versa. Instead, we propose a reaction scheme where the selectivity can be explained solely by the propagation-to-termination probability of the primary reactions, i.e. hydrogen abstraction to olefins and hydrogenation to paraffins. In fact, two volcano-like curves were obtained when the individual propene and propane selectivity was plotted as a function of the cobalt particle size. Analogous to the volcano-like curve in Fig. 3, these curves had their *minimum* propene and propane selectivity at 8 nm. However, the relative variations in propane selectivity were

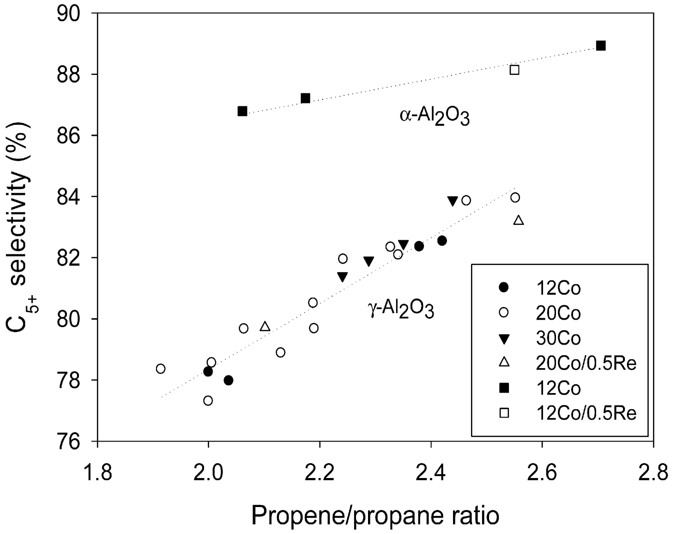

Fig. 4. Relation between the C_3 olefin/paraffin ratio and the C_{5+} selectivity. The experimental error (±2σ) for the olefin/paraffin ratio and selectivity is ±0.05 and 0.5%, respectively.

somewhat larger than the variations in propene selectivity. The correlation between the olefin/paraffin ratio and the C_{5+} selectivity (Fig. 4) indicates that the activities of the termination reactions hydrogenation and hydrogen abstraction change concurrently with the activity of secondary α-olefin hydrogenation.

Fischer–Tropsch synthesis was also performed for four α-Al_2O_3 based catalysts. As shown in Fig. 3, these catalysts also exhibited a maximum in C_{5+} selectivity at a certain particle size. Thus, a volcano-like curve might exist for this support as well. Interestingly, the selectivity of the α-Al_2O_3 supported catalysts was significantly higher than the selectivity of the γ-Al_2O_3 supported counterparts at all experimentally studied particle sizes. Based on these data, we speculate that separate volcano curves exist for all supported cobalt catalyst systems. The choice of support, however, will influence the C_{5+} selectivity levels, i.e. the vertical position in Fig. 3. To conclude, it is clear that the C_{5+} selectivity is not only related to the cobalt particle size, but also to the choice of support. It should also be mentioned that no correlation was found between the cobalt aggregate size and the selectivity. In fact, cobalt oxide was present as single crystallites or in very small aggregates for the most selective α-Al_2O_3 based catalyst and the least selective γ-Al_2O_3 support catalyst.

The variations in selectivity between the γ-Al_2O_3 and α-Al_2O_3 based catalysts cannot be explained in terms of diffusion effects. In fact, the data of Bezemer et al. [1] and the present investigation indicate that the product distribution is affected similarly by the particle size whether cobalt is located inside porous metal oxide supports or readily accessible on inert materials (e.g. carbon nanofibers). Rytter et al. [9] also excluded diffusion effects as playing a major role for the product distribution. Instead, we believe the difference in selectivity between the γ-Al_2O_3 and α-Al_2O_3 supported catalysts is related to the chemical properties of the Al_2O_3 surfaces. To test this hypothesis, the product selectivity of equally sized cobalt particles placed on different alumina phases will be evaluated and this work is in progress.

As shown in Fig. 4, there is a separate relationship between the olefin/paraffin ratio and the C_{5+} selectivity for the α-Al_2O_3 based catalysts. The variation in olefin/paraffin ratio may be explained by the olefin hydrogenation activity. Finally, we propose that all catalytic supports have a positive correlation between the olefin/paraffin ratio and C_{5+} selectivity. However, the vertical position in Fig. 4 will vary for each catalyst system.

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