Reaction dependent particle size effects in carbon supported cobalt catalysts

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Introduction

Particle size effects in nanocatalysis are of growing interest. For both supported and unsupported particles (*e.g.* colloids) various examples are known where the catalytic performance was proven to be dependent on particle size and shape.[1-3] A growing number of studies are conducted to understand the nature of these effects, which is increasingly facilitated by well defined preparation routes, support materials, surface science studies and *ab-initio* calculations. A major challenge in studying particle size effects is the increased reactivity of smaller particles towards the support. The use of carbon supports and especially graphite like carbon nanofibers (CNF) is expected to alleviate this problem and allows an undisturbed study of particle size effects.

Here the effects of Co particle sizes are investigated for Fischer Tropsch synthesis and ethanol-steam reforming. A decrease in Co particle is accompanied with a relative increase in the amount of uncoordinated surface sites, which is likely to have a significant impact on catalysis. The two target reactions were chosen since different types of bond are involved in the rate determining step i.e. π-bond activation of CO for FT synthesis and C-C σ-bond activation for ethanol-stream reforming.[3]

For the Fischer-Tropsch (FT) reaction it has been shown that Co-particles smaller than 6-8 nm were less active per accessible site as compared to larger particles.[4, 5] The origin of the lower activity and selectivity of small Co particles is a longstanding scientific question. In order to reveal details of this origin we made use of steady-state isotopic transient kinetic analysis (SSITKA) which reveals surface coverages and residence times of carbon, oxygen and hydrogen containing intermediates and reactants.[6] Co/CNF catalysts with cobalt particle sizes ranging from 2.6 to 16 nm were used. It is shown that the higher number of edges and corners on smaller particles resulted in a higher amount of irreversibly bonded CO, thus blocking of sites, and that the remaining terrace sites were less active for the FT reaction.

For the ethanol steam reforming the reversed was observed i.e., a high number of under coordinated sites is beneficial for activity and even more pronounced for stability.
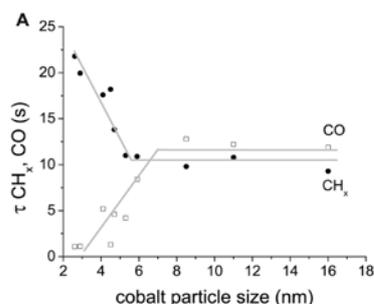
Experimental

Cobalt catalysts were prepared via incipient wetness impregnation. Cobalt particle sizes in a range of 2.6 to 16 nm were obtained by varying the cobalt loading (1-22 wt%), cobalt precursor (cobalt nitrate or cobalt acetate) or solvent (water or ethanol).[5] The impregnated catalyst precursors were dried overnight at 120 °C. Next, the catalysts were reduced at 350 °C under a flow of 30% $H_2/N2$, and subsequently passivated using a diluted (0.1 vol%) oxygen flow.

The SSITKA apparatus used in this study has been described before.[8] To perform an experiment, typically 100 mg of catalyst (90-150 μm) was diluted with 200 mg SiC (75-150 μm) and loaded in a plug flow microreactor. An *in-situ* reduction was performed under a flow of 10 mL.min⁻¹ H_2 at 350 °C (heating rate of 5 °C.min⁻¹) and 1 bar for 2 h. Subsequently, the reactor was cooled to 170 °C under the H_2 flow. At this temperature, the flow was switched to syngas ($^{12}CO/H_2/Ar$ = 1.5/15/33.5 mL.min⁻¹) and the pressure was increased to 1.85 bar. The temperature was raised to 210 °C and the reaction was performed for at least 15 h prior to a SSITKA experiment. Then a switch was made to labelled syngas (the label either being ^{13}CO or D_2) and the products were analyzed by mass spectrometry. The back-switch to unlabled gases was used to calculate residence times and surface coverages.

The ethanol steam reforming (SR) was performed in a fixed-bed reactor at 1 bar, 500 °C. Typically 2.5 - 20 mg of Co/CNF catalyst, diluted with 60 mg SiC, was reduced, *in situ*, at 350 °C for 2 h in a flow of 30 mL.min⁻¹ H_2. Next, the hydrogen was purged with N_2 at 500 °C for 30 min, after which a steam/ethanol mixture was introduced in a 3.0 molar ratio (60 mL.min⁻¹) to perform the SR reaction. To obtain the required H_2O/ethanol molar ratios, two separate N_2 flows of 30 mL.min⁻¹ were passed through heated saturators containing either water or ethanol.

Fig. 1 CH$_x$ and CO residence times as function of the Co particle size.

Results and Discussion

Figure 1 shows a typical outcome, after data analysis, of the SSITKA experiments for the residence times of CO and CH$_x$ species as function of Co particle size. Clearly the CO residence time increases with decreasing particle size while for the CH$_x$ species the opposite trend was observed.

The coverage of reversible bound CO decreased from 0.4 for the larger particles and decreases to 0.2 for the smallest

particles. A similar trend was found for the adsorbed CH_x species and their coverage decreased from about 0.1 to 0.05 with decreasing Co particle size.

Additional experiments in which the amount of irreversible bound CO was determined (by studying switches from Ar to CO/Ar) indicated that coverage of the Co surface with irreversible bonded CO increased with decreasing particle size, and hardly any irreversibly bonded CO was present for large particles (>6 nm). This means that under the present conditions the cobalt surface was partly blocked with unreactive CO for small particles, thereby hampering catalysis.

Figure 2 shows the coverage of irreversibly bonded CO as function of the fractions of atoms with coordination number
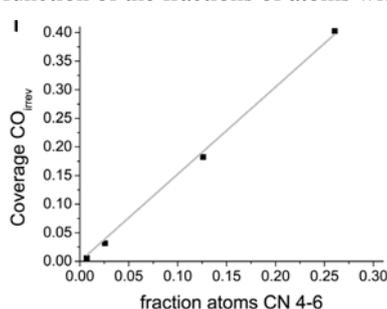
Fig. 2 Amount of irreversibly bonded CO as function of fraction Co atoms with CN 4-6

4-6.[8] Based on this result we speculate that the increase in irreversibly bonded CO for small (<6 nm) Co particles is related to the increase in coordinatively unsaturated site (cus) atoms. Thus we concluded that blocking of the edge sites by CO results in a lower activity of small Co particles (high amount of edges/corners) for FT synthesis. Moreover, from the increase in CH_x residence time it was concluded that the remaining terrace sites were also less active as compared to those of large Co particles. This might indicate that π-bond activation becomes increasingly difficult with decreasing particle size. [6]

To investigate the relevance of undercoordinated sites for other Co catalyzed reactions we studies the steam reforming of ethanol over Co/CNF catalyst with different Co
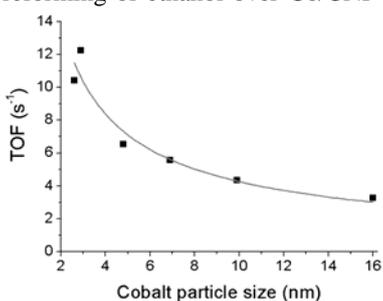
Fig. 3 Ethanol steam reforming activity (TOF) as function of Co particle size

particle sizes. Figure 3 shows the activity as function of Co-particle size. Clearly for this reaction smaller particles were more active as compared to larger ones. This is the opposite trend as that observed for the FT synthesis, which might be explained by the fact that in this reaction σ-bond activation is the rate determining step.

Though smaller particles were more active in the SR reaction, the stability of the catalyst is also influenced by particle size (figure 4). The stability was calculated as given on the right based on the differences in ethanol conversion after 0.2 and 24h where X is the ethanol conversion and assuming first-order kinetics. As can be

$$Stability = \frac{LN\,(1-X_{24h})}{LN\,(1-X_{0.2h})}$$

observed in Figure 4, a significantly higher stability was found

for the Co/CNF catalysts with small Co sizes (<4 nm) as compared to catalysts with larger sizes. This is the results of less coke formation on smaller particles as TEM analysis showed (results not shown).
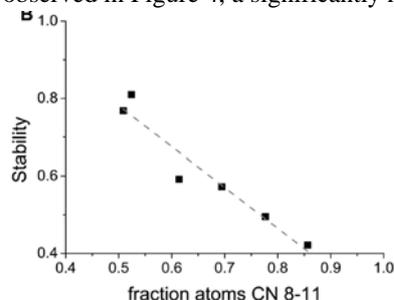
Fig. 4 Catalyst stability as function of the fraction of Co atoms with coronation number 8-11.

Conclusions

Carbon nanofibers allowed, due to their inertness, the study of Co particle size effects in Fischer Tropsch synthesis and ethanol-steam reforming. For Co particles smaller than 6 nm, a decreased TOF and increased methane selectivity has been found for FT experiments performed at 1 bar and 35 bar (H_2/CO = 2). The SSITKA results on coverages and residence indicated a.o. that the corners and edges of the Co particles were covered by irreversible bonded CO making these sites unavailable for reaction. Moreover the remaining terrace sites were less active for the reaction. On the contrary for ethanol/steam reforming the presence of edges and corners were beneficial for both activity and stability of the catalyst. These differences might be the result of different rate determining steps in both reactions. Edges and corners were shown to be beneficial for a reaction in which σ-bond breaking is rate determining.

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