Stability of CO hydrogenation catalysts studied in-situ

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Abstract: Like any other catalytic reaction, the cobalt-based Fischer-Tropsch CO hydrogenation is plagued by a number of deactivation processes. Oxidation and sintering are two of the main ones and these have been studied at reaction conditions using an in-situ magnetometer and a number of model catalysts with well defined crystallite sizes. The roles of CO and water on these deactivation pathways could be clearly identified.

Keywords: Fischer-Tropsch, in-situ magnetometer, cobalt, deactivation.

1. Introduction

Supported cobalt crystallites in the nanometer range are applied industrially in the Fischer-Tropsch synthesis (FTS) [1] and have been reported to show a very different resistance with regard to deactivation compared to larger cobalt particles [2,3]. This observation has been attributed to differences in surface energy [2]. The Fischer-Tropsch (FT) product water is reported to have a severe effect on the deactivation of cobalt-based FT catalysts [1-8]. Three mechanisms have been proposed in literature (see figure 1): oxidation of metallic cobalt to FT inactive cobalt oxide [2,4,7], hydrothermal sintering of cobalt particles resulting in a loss of specific surface area [6,8], and formation of FT inactive cobalt-support compounds [5,7].

2. Experimental

An *in situ* magnetometer at the University of Cape Town [3,7-9] was specifically designed for research on such phase transformations in FT catalysts under fully relevant working conditions for the FTS. These phase changes can be identifies via changes of magnetic properties, e.g. from ferromagnetic to anti-ferromagnetic species in the event of metallic cobalt forming oxidic cobalt species. Furthermore, the special magnetic properties of nanoparticles allow for a qualitative and, in some cases even, quantitative analysis of crystallite size changes. Cobalt oxide nanoparticles were prepared separately allowing the application of powerful techniques for the controlled synthesis of well-defined nanoparticles with narrow size distributions. These well-defined nanoparticles were subsequently supported, reduced and tested under various conditions. A series of model catalysts consisting of nanoparticles with well-defined average sizes ranging from 3 to 10 nm on Al_2O_3 or SiO_2 was exposed to different ratios of the partial pressures of the FT product H_2O to H_2 and/or syngas [3,7].

3. Results and discussion

Co-feeding of H_2O with synthesis gas mimics high FT conversion levels while the actual CO conversion was below 10%. Both model catalyst systems displayed a size-dependent oxidation behaviour with smaller nanoparticles being less stable than larger ones [3,7] as predicted for the oxidation to CoO [2]. However, the formation of cobalt-support compounds, namely cobalt aluminates and silicates, was underlying [7].

In addition to these metal oxides, solid carbon spheres were utilised as a support in order to limit the formation of metal-support compounds. The effect of CO and H_2O on the deactivating Co oxidation reaction was tested in H_2O-rich environments simulating high FT conversion levels. The reactant CO was identified as the major oxygen source during water-induced oxidation of cobalt to cobalt oxide, while the oxidation of Co by H_2O-derived oxygen is seemingly kinetically hindered.

Lastly, another newly developed Co/C model catalyst with well-defined cobalt nanoparticles on exfoliated graphite has been developed for testing the stability of well-defined monodisperse Co nanoparticles in H_2O-

rich atmospheres. A hypothesised inter-connection between hydrothermal sintering and oxidation [6] of cobalt nanoparticles was captured *in situ*. Utilisation of non-functionalised carbon as support material allowed for the monitoring of the sintering process as the pristine carbon provides limited stabilisation due to weak metal-support interactions.

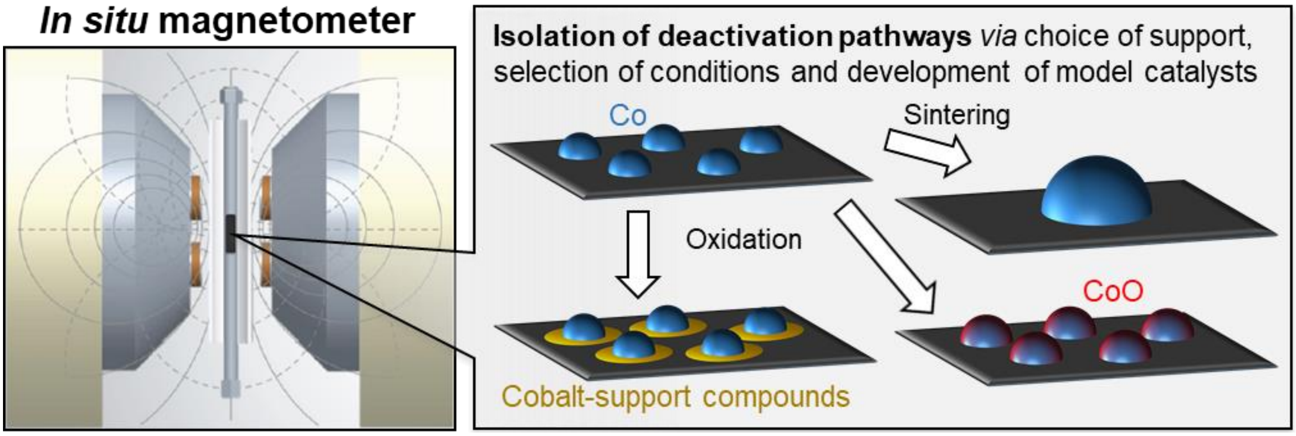

Figure 1. Characterisation of deactivation mechanisms of cobalt-based Fischer-Tropsch model catalysts under high conversion levels utilising an *in situ* magnetometer.

4. Conclusions

Deactivation of cobalt based catalysts strongly depends on reaction conditions during the Fischer-Tropsch synthesis. Importantly, there appears to be an interplay between carbon monoxide and water regarding catalyst stability.

References

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