Highly-dispersed Cobalt Fischer-Tropsch Catalysts

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Introduction
The economy of the Fischer-Tropsch process is critically dependent on the effectiveness of the cobalt catalysts. Therefore, the design of the catalysts has focused on methods to improve the cobalt utilisation by optimising metal crystallite size, improving reducibility or increasing stability. Iglesia [1] and others have shown that the Fischer-Tropsch synthesis rate increases linearly with increasing dispersion, irrespective of the chemical identity of the underlying support, at least in the dispersion range 0 - 0.12. Earlier dispersion and support effects reported were explained to be mostly due to incomplete reduction and/or re-oxidation. Very high dispersions have been reported to reoxidise at typical FT conditions and it has been suggested that catalyst productivity can be increased by catalysts that maintain cobalt dispersion at or near an optimum of 0.15, especially at high cobalt loadings [1]. We report here on the newly developed so-called HDC (high-dispersion cobalt) catalysts [2,3] which show dispersions close to the desired 0.10-0.15 even at high metal loadings of up to 50% cobalt in the reduced state.

Results and discussion
The classical method for making cobalt catalysts is by incipient wetness impregnation using an aqueous cobalt nitrate solution at low pH. At low pH there is only modest interaction between the positively charged alumina carrier and the similarly positively charged cobalt cations. Hence cobalt is deposited as relatively large clusters of crystallites. Though this method leads to good catalysts, dispersion is mostly only 0.05-0.10, i.e. lower than the postulated optimum of 0.15. In addition, it is rather difficult to realise high dispersion at high metal loadings. We have developed a method for producing cobalt catalysts with dispersions at, or close to the reported optimum dispersion of 0.15. Moreover, these catalysts can be prepared at high cobalt loading thus increasing the effectiveness of the FT catalyst. A feature of the process is that the cobalt is deposited at high pH thus realising a firm anchoring of the cobalt cation onto the now negatively charged support. This leads to a very even and uniform distribution of cobalt across the surface which is expected to reduce the thermodynamic driving force for particle migration and sintering and hence should result in increased stability. In addition, stabilised supports can be used thus further contributing to stability through a reduced tendency for wasteful cobalt aluminate formation. The high metal loading not only leads to high weight or volume activity, but also to favourable cobalt/alumina ratios which again, should reduce the tendency for inactivation by cobalt aluminate formation through oxidation of the cobalt.

A range of oxidic catalysts was prepared differing in cobalt content up to 42 wt% (50% in the reduced state). Activities of the reduced catalysts appeared to be linearly
proportional to cobalt surface area per g catalyst as measured by hydrogen chemisorption confirming that the findings by Iglesia [1] and others are also valid for higher cobalt dispersions and loadings.

In-situ XRD showed that the reduction occurs in discrete steps: at first a reduction of Co$_3$O$_4$ to CoO followed by the reduction of CoO to the metallic state. Though the cobalt crystallites clearly grow when raising temperature, they are remarkably stable and only slowly lose dispersion, suggesting a very effective metal support interaction. This is surprising as the reducibility of the catalysts is close to 100% showing that only low amounts of cobalt are sacrificed for metal-support interaction.

Crystallite size of Cobalt HDC catalyst (23% cobalt) during reduction

![Crystallite size vs Temperature](image)

The data on the crystallite size distribution indicate that the main mechanism of growth at higher temperatures is by crystallite coalescence rather than "Ostwald type" ripening. This metal crystallite growth appeared to develop as a bimodal distribution.

References