Reversible and Irreversible Changes in Co Fischer-Tropsch Catalysts During Synthesis

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Introduction

With the resurgent interest in Fischer-Tropsch catalysis, it is important to understand any catalyst changes that can occur during the synthesis. In this presentation we report on three intrinsic modes of deactivation that have been observed in studies of experimental supported Co catalysts. These include reversible surface oxidation, irreversible mixed metal oxide formation, and cobalt particle growth. Techniques to monitor these changes are presented as well as some hypotheses regarding the mechanisms that are responsible for them.

Materials and Methods

The major techniques that were employed in this study include TGA analysis, chemisorption, TEM analyses, including sample treatment in a dedicated ex-situ reactor cell that allowed inert transfer of treated samples into the TEM to reexamine previously viewed areas, as well as fixed bed and slurry reactor tests.

Results and Discussion

Fischer-Tropsch catalysts contain at least one redox active component which during the synthesis reaction is subjected to variable redox as well as hydrothermal conditions. This combination can create support and metal motion during synthesis. In catalysts that have not been engineered to mitigate this problem, there can be substantial deactivation due to changes in the cobalt particle size and interaction with the support. Our results clearly show the importance of nanoscale homogeneity (i.e. homogeneous Co nanoscale decoration of the support maximizing Co-Co interparticle separation) to minimize the extent of agglomeration during long runs. Agglomeration can occur when cobalt particles approach a critical distance of each other. The presence of water exacerabates this problem as cobalt oxide or hydroxide intermediates wet and spread on the support. Two predominant growth mechanisms can occur: coalescence and Ostwald ripening. Coalescence results from the physical mating of two Co crystallites, whereas Ostwald ripening involves atomic transport. The Ostwald atomic migration mechanism on supported metallic catalysts creates a distribution with both larger and smaller particles, with the latter disappearing with time. Our TEM results (see Figure 1) clearly indicate that coalescence is the predominant mechanism. Cobalt can also be removed from the active reaction manifold if its oxide combines with the support to form irreducible mixed metal oxide phases.

Significance

Mitigation of deactivation is an important aspect of operating Fischer-Tropsch catalysts in long term commercial runs. From the type of studies presented here, we have been able to learn the nature of the deactivation mechanisms and how to limit their impact on our catalyst and process.

Figure 1. TEM image of two cobalt particles during coalescence.