Improved Fischer-Tropsch catalysts guided by learnings from deactivation studies

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Abstract: Catalyst deactivation is an important problem in Fischer-Tropsch catalysis during long term commercial runs. This presentation will focus on our understanding of the main deactivation pathways during Fischer-Tropsch synthesis and our learnings on how to design a catalyst to help mitigate deactivation.
Keywords: Catalyst deactivation, Fischer-Tropsch, Supported Co catalysts.

1. Introduction

Deactivation of supported Co Fischer-Tropsch catalysts remains an important although somewhat controversial subject, as multiple deactivation mechanisms have been proposed [1, 2]. We are particularly focused on the deactivation pathways that cannot be reversed by simply re-reducing the catalyst. From our results, taken from multi-month runs in slurry bubble column reactors, we conclude that formation of refractory non-reducible mixed oxides and agglomeration of cobalt crystallites are the two factors primarily responsible for long term irreversible deactivation [3]. We do not see a loss of activity from carbon formation. In this paper, we focus primarily on the problem of cobalt crystallite growth and provide a geometrically based phase diagram that should help guide preparation of catalysts that will have less Co agglomeration. Our experimental data indicates that coalescence is the predominant growth mechanism and that nano-scale homogeneity of cobalt crystallites on the support dramatically influences the degree of coalescence. The geometric model described here attempts to quantitatively relate the physical properties of the support [surface area, pore size and pore volume] with the size and distribution of Co crystallites on both fresh and deactivated catalysts. As Co crystallites grow, the distance between them increases until they reach a critical state of separation where the growth slows down dramatically. Once we understand the parameters describing that state, we can attempt to create a similar Co-Co separation in fresh catalysts by adjusting support surface area, pore size, and pore volume, as well as cobalt loading and dispersion. We assume that if we prepare a fresh catalyst with Co-Co spacing similar to those in pseudo-equilibrated catalysts, then we can remove the driving force for agglomeration. We model the pseudo-equilibrated state from a geometric perspective using the experimentally determined Co particle size distributions from bubble column pilot plant runs that have lasted for 6 months or longer. We also discuss approaches to synthesize more uniformly distribute cobalt particle distributions, particularly by controlled the stages of cobalt nitrate decomposition.

2. Experimental

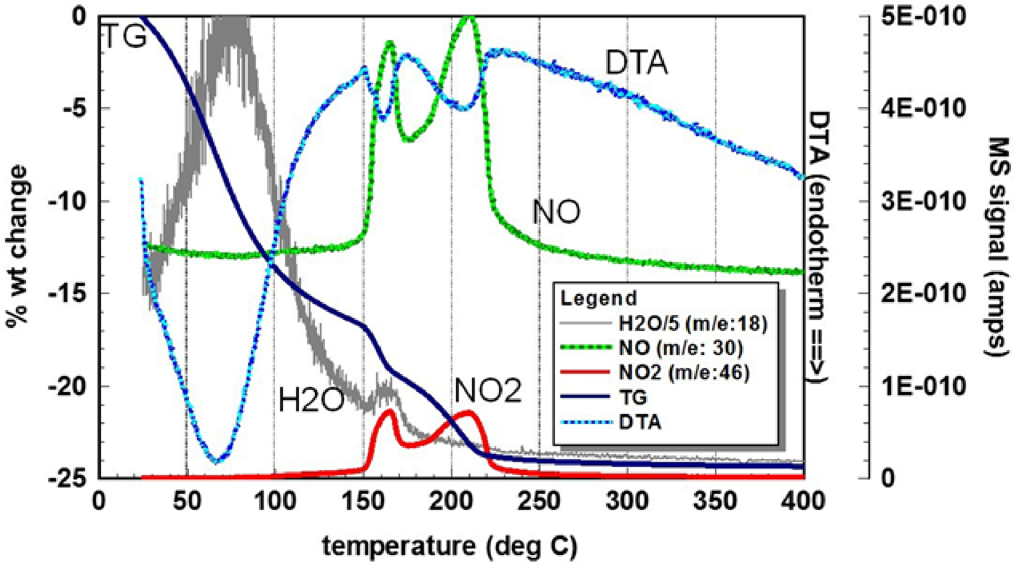
The major techniques that were employed in this study include TGA analysis, chemisorption, and TEM analyses, including sample treatment in a dedicated ex-situ reactor cell that allows inert transfer of treated samples into the TEM to reexamine previously viewed areas, as well as fixed bed and slurry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

3. Results and discussion

As a first approximation, we visualize the growth process as occurring on a two-dimensional support surface, with particles agglomerating when they approach a critical distance of each other. We do this by defining a virtual Co particle with this critical distance equal to a fixed multiple of its actual radius. We visualize that during water-induced oxidation, oxidized cobalt particles interact with and wet the support surface more thoroughly, thereby increasing their effective radius. As particles approach their neighbors they come into contact with those at a critical distance. We use actual Co particle size TEM distributions, factor in known support characteristics (surface area, pore volume) and assume coalescence occurs when Co-Co distances are less than a critical amount. We determine the critical distances from measured Co particle size distributions of pilot plant deactivated samples. In selecting parameters that give Co-Co spacing greater than the critical distance on fresh catalysts, we are also constrained to avoid small particles that will easily oxidize and to keep the cobalt particles substantially smaller than the pore size of the support. We will share preparation phase diagrams with different surface area and pore diameters.

One of the key remaining research challenges involves learning how to reproducibly and homogeneously place the Co particles uniformly on supports. We show two approaches. The first involves use of organic chelating agents to affect the size and nanoscale uniformity. The second involves changing the decomposition kinetics and environment during cobalt nitrate decomposition as shown in Figure l below.

Figure 1. Decomposition of impregnated Co nitrate solution in air.



4. Conclusions

Mitigation of deactivation is an important aspect of operating Fischer-Tropsch catalysts in long term commercial runs. Learning the design principles for catalyst preparation can help accomplish this.

References

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