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Using Ex-situ TEM to Understand the Effect of Different Oxidative Environments on Small Metal Particle Morphology

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Metal particle oxidation is an important factor in catalysis. Water-induced oxidation is well-known to occur during Fischer-Tropsch synthesis (FTS) and can lead to deactivation [1-4]. Air oxidation/reduction treatments are observed to increase the initial activity in FT catalysts [5,6]. Thus, oxidation can either lead to significant deactivation [1-4] or to improved activity [5,6]. Several ex-situ TEM studies were undertaken to reveal the effects of these different oxidation environments on the metal particle morphology in an experimental supported Co-based FTS catalyst.

In all cases, catalyst was prepared for TEM by crushing it into fines using an agate mortar and pestle. The fines were dusted onto a 200 mesh, holey-alumina-coated TEM grid. The grid was transferred into a specially designed ex-situ reactor where it was treated and then moved via an inert transfer protocol into a Philips CM200F for examination [7]. Metal particles were imaged in the bright field (BF) TEM mode at an accelerating voltage of 200 kV, and areas of interest were "mapped" so that the <u>same</u> metal particles could be re-examined subsequent to each reactor treatment.

In the case of the dry (lab) air oxidation, the material was given an initial 400 °C, 4 h treatment under H_2. The reduction was followed by a 350 °C, 3 h air oxidation. Examination of the reduced material revealed distinct Co metal particles on the support (Figure 1a). Similar to previous observations [8-10] the air oxidation treatment resulted in the formation of torus-shaped structures (Figure 1b). This hollow dome morphology results from diffusion rate differences between the cobalt and the oxygen ions at elevated temperatures.

The effect of a water (steam)-based oxidation was studied next. The experimental catalyst was first reduced in the reactor (1.2 MPa H_2, 400 °C, 8 h) and then held under FTS conditions (2 MPa H_2:CO ~2.1:1, 215 °C) for 1 h. The gas hourly space velocity (GHSV) was specifically controlled to create high CO conversion (high water partial pressure) conditions around the TEM grid. The TEM grid was then given a low temperature reduction (1.2 MPa H_2, 215 °C, 4 h) followed by another 1 h FTS treatment.

Significant morphological changes accompanied the water-based oxidation (Figures 2a-2c). Instead of forming the torus presented during a dry air oxidation, a metal oxide/hydroxide species developed. This species wet the support so effectively that it was essentially "invisible". However, subsequent re-reduction of the metal oxide/hydroxide resulted in distinct metal particles. It is the spreading of this oxide/hydroxide species that is well-known to allow adjacent metal particles to "reach" each other and ultimately coalesce resulting in deactivation during FTS [4].

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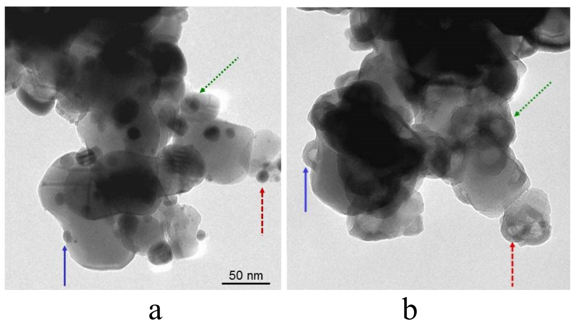

Figure 1. BF TEM images showing supported: (a) metal and (b) metal oxide particles subsequent to dry (lab) air oxidation. Arrows locate same crystallite in each image.

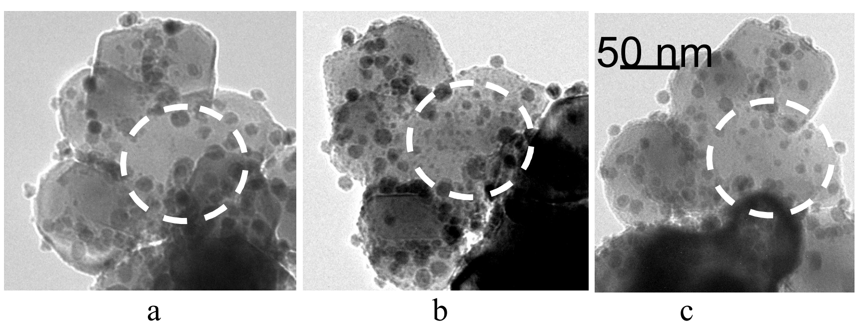

Figure 2. BF TEM images showing supported metal after: (a) 1 h on FTS, (b) reduction treatment, and (c) 1 h on FTS. Circled area locates same region in each image.

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