

3-D Quantification of Heterogeneous Catalysts

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Introduction

The Fischer–Tropsch (FT) process is commonly used to convert synthesis gas to clean hydrocarbon fuel [1]. The importance of the technology is increasing as crude oil prices remain unstable, and the global research market demands new and renewable sources of energy with minimum environmental impact. Despite the large research efforts, surprisingly little is known about the morphology of the catalyst particles on the nanoscale, the detailed interaction with their support, the pore structure of the support and how these affect the catalytic activity and selectivity.

In order for the FT process to become more mainstream and efficient, we must understand these morphological structures and interactions on a fundamental level. To measure particle sizes and distributions, standard techniques are usually employed such as chemisorption and X-ray diffraction (XRD). However, these techniques are only useful for information on the microscale, and are not sensitive to anything occurring on the nanoscale where the important catalytic interactions take place. For higher resolution analysis, conventional transmission electron microscopy (TEM) is usually used to analyze the atomic structure and interfaces of catalysts with their supports. Unfortunately, this still only provides two dimensional (2-D) information of an intrinsically three dimensional (3-D) nanoscale material, and therefore limits the structure-property understanding of these complex materials.

Materials and Methods

Here we use electron tomography in the scanning transmission electron microscope (STEM) [2] to elucidate the 3-D morphology of FT catalysts with a resolution of ~1nm in all three spatial dimensions. A series of images are taken in the STEM, typically in one degree increments, over a tilt range of usually +70 to -70, although the higher the tilt range and the larger the number of images, the better the 3-D resolution. These images are then aligned and reconstructed using commercially available reconstruction algorithms (such as those in Insept 3D), and displayed using visualization software (such as Amira).

We apply this technique to two Re promoted FT catalyst systems [3] prepared in slightly different ways. The first is a 20 wt % Co/0.5 wt % Re catalyst on a high surface area γ -alumina substrate and the second is a 12 wt % Co/0.5 wt % Re catalyst on a heat-treated substrate of γ -alumina impregnated with 5% Ni. The phases present in the heat-treated support are α -alumina (Al_2O_3), and Ni-aluminate (NiAl_2O_4). The Co is studied in its unreduced form as Co_3O_4 .

Results and Discussion

Figure 1 illustrates the two systems. Figure 1 (a-b) shows the cobalt oxide in a γ -alumina support and (c-d) show the cobalt oxide in an α -alumina/Ni-aluminate support. In the first system, the cobalt oxide enters the highly porous γ -alumina support and fills the pores, forming an interlocking catalyst/support structure. In the second system, the cobalt oxide preferentially chooses to sit solely on the Ni-aluminate (which in turn connects to α -alumina pieces), and does not penetrate the pores very much, instead forming nanocages. This unexpected Co_3O_4 distribution undoubtedly provides a more open local environment for reactions to take place, and we believe that the influence of this nanostructure must be taken into account in understanding the higher C_5^+ selectivity relative to the first sample [4]. 3-D quantification of the two systems will be presented.

Significance

The STEM tomography technique allows us to make quantitative measurements in 3-D, at the nanoscale, and specifically at the site of the catalyst which is much more precise than most standard microscale chemical measurements that are not sensitive to the locations of the catalyst and their immediate environments.

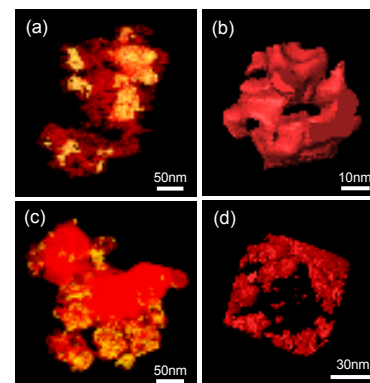


Figure 1. Two catalyst systems with different supports. The first system (a-b) forms an interlocking structure with its support with no free surface area. The second catalyst (c-d) is more selective and this may be attributed to its unique nanocage morphology (d) that allows larger surface area for reactions to take place.

References

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