Toward Three-Dimensional Nanoengineering of Heterogeneous Catalysts

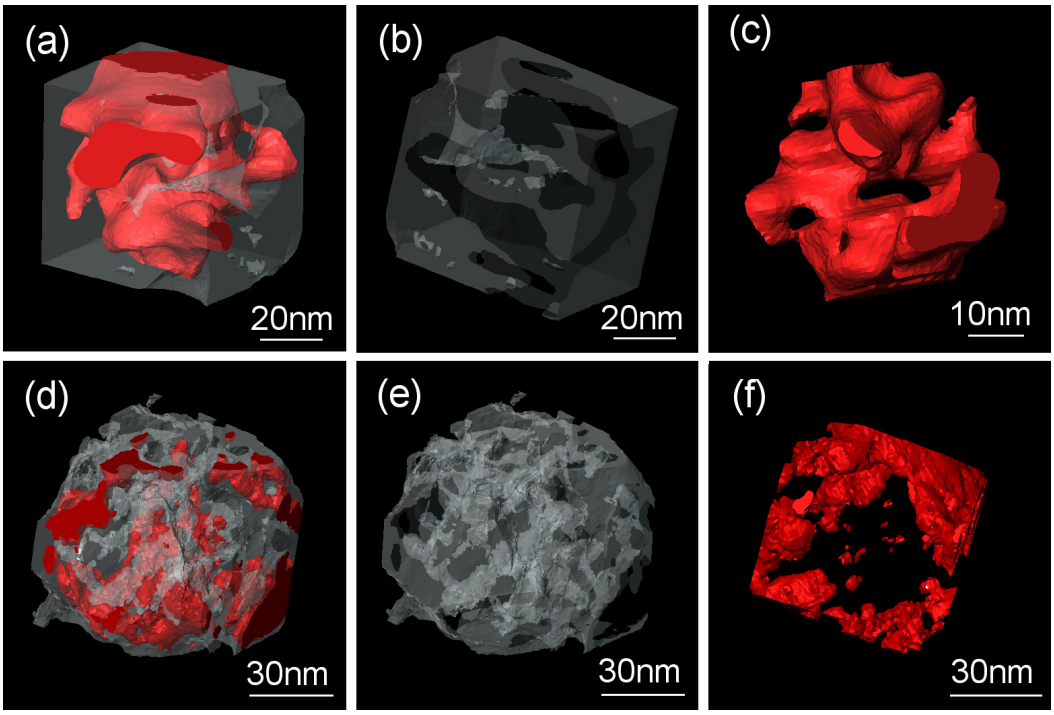

Figure 1: 3-D reconstructions of the two catalysts. (a)-(c) shows the Co_3O_4/γ-alumina system, and (d)-(f) shows the Co_3O_4/Ni-aluminate/α-alumina system. (a) shows the Co_3O_4 in red and the γ-alumina in semi-transparent grey. (b) shows only the alumina, rotated 180° with respect to (a). The darker grey areas indicate the porous regions in which the cobalt oxide resides. (c) shows that agglomerates of the cobalt oxide particles are also very porous. (d) shows Co_3O_4 in red on a Ni-aluminate cluster in semi-transparent grey. (e) shows only the highly porous Ni-aluminate and (f) shows that despite this porosity, the cobalt oxide chooses to stay primarily on the surface and form "nanocages."

3-D nanoscale structures correlate with higher selectivity of catalysts

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The Fischer-Tropsch (FT) process is a key industrial process that has a long history of commercial development and application in the conversion of coal and natural gas to clean hydrocarbon fuel. The importance of FT technology is emphasized by increasing crude oil prices, the need to diversify energy sources with minimum environmental impact, and explore sustainable sources such as biomass. As such, FT catalysts are widely studied by oil companies, labs, and universities around the world. FT catalysts based on cobalt particles on a porous alumina support provide high activity and selectivity to long chain paraffins, low-water-gas shift activity, and economic viability in converting a variety of hydrocarbon sources to fuel and petrochemical products.

To optimize the efficiency of these catalysts and the FT process, a fundamental understanding of the their size, shape, and distribution, and their relation to catalytic activity/selectivity must be obtained on the nanoscale. Standard methods for measuring particle size and dispersion, such as chemisorption and X-ray diffraction (XRD), generate average microscopic properties and give little direct information. In contrast, the transmission electron microscope (TEM) is a powerful tool for the direct study of the catalyst particles on the nano and atomic scale. However, since cobalt oxide particles are known to aggregate in three-dimensions, a simple two-dimensional TEM image is not sufficient to completely describe their structure. Advances in electron tomography in the scanning transmission electron microscope (STEM) now enable reliable and quantifiable three-dimensional reconstructions of inorganic materials to be achieved with a spatial resolution approaching 1nm[3]. Here we apply this technique to two Re promoted

FT catalyst systems: 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 α-alumina impregnated with 5% Ni. The heat treatment and addition of Ni in this latter system acts to strengthen the support and thus provides superior mechanical properties. The materials were studied in their unreduced condition so that Co is present in the form of Co_3O_4. The C_5+ selectivity of the second system is greater than the first by ~5%, and while this appears moderate, the difference will be of clear significance in a commercial system.

The first and less selective catalyst is shown in Figure 1(a-c). In this system, the cobalt oxide enters the highly porous γ-alumina support and completely fills the pores, forming an interlocking catalyst/support structure. Even in a reduced state, this morphology is expected to yield very little physical space for reactions to take place. In the second and more selective system (Figure 1(d-f)), the cobalt oxide preferentially sits solely on the Ni-aluminate (which in turn connects to α-alumina pieces, not shown in this figure), and does not penetrate the pores at all, instead forming nanocages. This unexpected Co_3O_4 distribution provides a more open local environment for reactions to take place, and we believe that the higher selectivity of this catalyst system over the other correlates with the 3-D nanocage morphology and its selection of the Ni-aluminate support over γ-alumina. This powerful 3-D information gives us direct insight into the nanoscale differences between catalyst systems that are invisible to bulk property measurements.

The ability to understand and optimize parameters that influence specific properties, such as selectivity, is of tremendous potential for the future design of heterogeneous catalysts that play a key role in the management of energy supply for hydrocarbon production with a positive environmental impact. We are also using these powerful 3-D techniques to study a variety of complex nanomaterials, such as porous nanoparticles made of Pd, Pt, Au, C, and C nanotubes with applications in hydrogen and electrical energy storage, and multi-shell semiconductor nanowires with applications in optoelectronic nanodevices.

Reference:

"Toward Three-Dimensional Nanoengineering of Heterogeneous Catalysts," I. Arslan, J. C. Walmsley, E. Rytter, E. Bergene, and P. A. Midgley, *Journal of the American Chemical Society,* **130 (17)**, 5716-5719 (2008).

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