

Materials Chemistry Seminar

*“Much ado about (almost) nothing:
supported oxide catalysts with control
at and below 1 nm”*

Although many industrially important solid catalysts are composed of simple metal oxides like titania, iron oxide, or manganese oxide, these descriptions do little to aid the researcher in identifying the active site – the particular arrangement of atoms that is responsible for bond-making and breaking – nor do they suggest opportunities for control of activity and selectivity via new catalyst design. Thus, a major area of research in the Notestein group is the control of metal oxide catalyst reactivity and selectivity by precise control over their surface structure. This talk will describe the synthesis of three classes of metal oxide catalyst, the mechanistic insights gained from the synthesis and characterization of these structures, and the enhanced catalyst performance that is enabled by this understanding.

In the first class, we seek atomic control over the size of the metal oxide cluster. Specifically, we and others have found that shrinking the active catalyst phase down to a single Fe, Ti, or Ta cation on an inert oxide like silica results in significant enhancement in catalytic oxidation rates and selectivities, relative to those of larger clusters, although it also introduces characterization challenges. Backed up by an array of spectroscopic and chemical reactivity probes, we developed several synthesis methods to ‘single-site’ catalysts, which are biased against forming large oxide clusters even when they are present at high surface densities, and thus have high productivity per total mass of catalyst.

The second example seeks to extend this control out to neighboring organic ligands for a catalyst immobilized on a surface. Anchoring a molecular catalyst is as a possible avenue control towards easier handling, but also typically results in a profound restructuring of the catalyst active site. We take inspiration from non-heme oxidase enzymes and have shown that mimetic Mn complexes become highly active oxidation catalysts when immobilized on surfaces via grafted organic acid groups. Several characterization techniques (primarily UV-visible spectroscopy and X-ray absorption spectroscopy) are employed to demonstrate that the solid catalyst contains a similar structure as in soluble model complexes, but is up to 100 times more productive in the low-temperature epoxidation of alkenes due to its improved stability.

Finally, we seek to control not only the catalyst atoms, but also the 1-2 nm of void space around the active site, much as in substituted zeolites or many enzymes. To do this we have developed a novel technique wherein a molecular template is immobilized on the catalyst surface, then atomic layer deposition (ALD) is used to grow thin oxide layers on top of the surface and around the template. Template removal introduces a size-sieving feature to the existing catalyst surface, as demonstrated by the selective photooxidation of alcohols and photoreduction of nitroarenes. Preliminary evidence points also to the ability to template small metal nanoparticle growth in these ‘nanocavities’. These sub-nm films oxide films introduce new challenges in characterization, but also introduce a new paradigm for design of all-inorganic, selective catalysts.



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12:15 pm

1315 Chemistry