



presents a seminar by

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entitled

The Homogenization of Heterogeneous Catalysis: Reactivity of Single Sites on Surfaces That Have No Parallel in Solution

Friday, 5 December 2014

At 9:00 am

Coolbaugh Hall, Room 219

For full seminar schedule, please visit http://chemistry.mines.edu/seminar_F14.html

My research group uses synthetic control of organic-inorganic interfaces on the molecular level in order to design and enhance catalysis on surfaces. My presentation exemplifies our approach within the context of two areas.

The first of these deals with the role of surface OH defects as weak-acid catalyst sites that work cooperatively with adsorbed/chemisorbed sites on the surface. Using such weak-acid sites on surfaces, my research group designed catalysts for the depolymerization of biomass polymers, consisting of glucan (derived from crystalline cellulose component of biomass) and xylan (derived from hemicellulose component of biomass). We demonstrated that cooperativity between OH defect sites and glycosidic oxygens of chemisorbed polysaccharides on inorganic-oxide surfaces activated the chemisorbed polysaccharides for hydrolysis. Next, we applied this to the synthesis of a more practical catalyst for biomass-polymer depolymerization, consisting of mesoporous carbon nanoparticles (MCN) with phenolic and carboxylic weak-acid sites. Our MCN catalyst depolymerizes adsorbed xylan and glucan at mild buffered pH conditions, where close contact and cooperativity between polysaccharide and carbon surface is enforced via the strong tendency of the polysaccharide to adsorb in a manner that confines and constrains the polymer strands.

In the second area, we are interested in stabilizing structures consisting of open sites – where open within this context refers to coordinatively unsaturated sites on the metal surface, which can be used for binding and activating reactants for catalysis. Since such open “coordinatively unsaturated” clusters are inherently unstable, to prevent cluster aggregation, we use calixarene macrocycles as the equivalents of bumpers on bumper cars, to allow small-molecule access to the metal surface while disfavoring cluster aggregation via coalescence. Using this approach, we have been able to synthesize the most accessible metal clusters in solution reported to date, consisting of Au₁₁ clusters. These clusters consist of nearly three open sites per cluster (as determined using steady-state fluorescence). We have also used this approach to synthesize open sites on an Ir₄ metal core, and have used the resulting silica-supported open clusters (and closed counterparts as a comparison) for ethylene hydrogenation. Our catalysis results correlate an open site that can bind ethylene with catalytic activity in this system. Furthermore, our results highlight the importance of electronic environment of the open site on its ability to bind ethylene and catalyze its hydrogenation.