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Controlling Catalysis in Calixarene-Bound Metal Clusters: Surface Accessibility and Microenvironment

Metalloproteins are known to tune redox potential of metal clusters via control of microenvironment over an extraordinarily broad range (0.5 eV), while providing accessibility, often in the form of coordinative unsaturation, to the metal cluster active site. An open question is: what degree of complexity needs to be incorporated into synthetic systems in order to be able to accomplish these feats?

Our research turns to organically-modified metal clusters because the organic portion of these materials makes the electronic structure of the metal near the surface easily tunable via synthesis, and useful as building block for heterogeneous catalysis. When using calixarenes as surface ligands for metal clusters, we demonstrate that this passivation decreases the ubiquitous tendency of metal colloids to aggregate, even during high temperature treatment resulting in calixarene removal via combustion, and enables programming of the electronic and steric environment on the metal surface, akin to using residues in a metalloprotein. We demonstrate programming of the environment on the metal surface with chiral calixarene ligands using circular dichroism CD spectroscopy. Adsorption of a chiral ligand in this case renders an achiral gold nanoparticle to have a chiral surface plasmon band in the CD spectrum. Additional corroborative data for programming the electronic environment on the metal surface via choice of ligand is provided by X-ray photoelectron spectroscopy (XPS) and single-crystal X-ray diffraction in comparative studies of Ir₄ clusters and gold colloids bound with calixarene phosphine ligands. These data clearly demonstrate the effect of the calixarene in creating a more electron-rich metal center.

A heretofore unrealized lofty goal for such a passivating layer is to facilitate two at first-appearance mutually incompatible functions: (i) bind an organic ligand to the surface of a metal colloid, and (ii) offer access to the metal surface for ease of binding and conjugation to other molecules. We investigate in detail the mechanism of synthesizing accessibility in 4 nm gold nanoparticles using various-sized calixarenes ranging in macrocycle ring sizes from four to eight arene repeat units. We also investigate how surface accessibility changes systematically as the size of the gold core in calixarene-bound gold colloids decreases, using a new family of gold colloids that are unique when compared with similarly-sized, subnanometer, phosphine-stabilized Au₁₁ clusters as well as much larger 4 nm gold nanoparticles. These results highlight a new general mechanism for synthesizing accessibility in organically-functionalized metal colloids. This mechanism also has broad repercussions on how site accessibility may be created in other systems, such as in metalloproteins.

Finally, we demonstrate control of heterogeneous reduction catalysis by virtue of controlling metal electronic environment, using calixarene-bound gold clusters. These results unequivocally demonstrate the benefit of an electron-rich gold surface for reduction catalysis. We also demonstrate control of decarbonylation and role of calixarene in Ir₄-based clusters, using temperature programmed reduction experiments.



Alexander Katz was born in Minsk, Belarus and immigrated to the United States at age four with his family. Alex and his parents moved to Minnesota, where he grew up in and attended public schools. Alex graduated University of Minnesota with highest honors as a Bachelor of Chemical Engineering in 1992 and a research M.S. in Chemical Engineering with Prof. Michael D. Ward as advisor. It is at that time that he first became inspired by chemical engineering on the molecular level and controlling properties of functional materials via synthesis. He was awarded a Fannie and John Hertz Foundation Fellowship for doctoral studies in catalyst synthesis with Prof. Mark Davis at California Institute of Technology in 1994, and later, in 1998, undertook postdoctoral studies in supramolecular chemistry at Institut Le Bel in Strasbourg, France, with Prof. Wais Hosseini, as a NSF International Awards Postdoctoral Fellow. It is there that Alex learned about calixarene macrocycles and their synthesis. Alex began a multidisciplinary research program as Assistant Professor of Chemical Engineering at UC Berkeley in 2000, and has been promoted to Associate Professor. He was a Technion-Fulbright Fellow visiting professor at the Wolfson Department of Chemical Engineering in Haifa, Israel in 2008-2009. His current research interests are focused on understanding catalysis by using comparative structure-function relations and synthesis as a tool. Much of his efforts are geared at defining new paradigms of synthesizing hybrid organic-inorganic interfaces, and applying them to gain new insight into binding and catalysis involving surfaces. He is on the editorial board of *Chemistry of Materials*, and received a Young Scientist Prize from IACS in 2004 for his contribution of grafted calixarenes as hybrid organic-inorganic scaffolds for catalytic structures.