



DEPARTMENT OF CHEMISTRY BK21-MSRI SPECIAL SEMINAR

Single-Site Catalysts by Metal-Ligand Complexation at Surfaces: From Model Systems in Vacuum to High-Pressure Catalysis on Oxide Supports

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A grand challenge in heterogeneous catalysis is to achieve high levels of selectivity by controlling the chemical uniformity of metal catalyst sites at surfaces. Our group is working to apply principles of on-surface metal-organic redox assembly to develop a new approach to this problem. Metal-organic coordination networks at surfaces hold promise for selective chemical function, but there is a limited understanding of the chemical reactivity of these systems. We tested chemical activity of vanadium single-site complexes that are stabilized by tetrazine-based ligands. We demonstrate activity toward dioxygen activation and a high degree of selectivity compared to vanadium nanoparticles. Reaction with dioxygen causes an increase in V oxidation state from V(II) to V(IV), resulting in a single strongly bonded V-oxo product and spillover of O to the Au surface. The metal centers are stabilized in extended, ordered metal-organic complexes that self-assemble through an on-surface redox process on the Au(100) surface and are characterized by X-ray photoelectron spectroscopy, scanning tunneling microscopy, high-resolution electron energy loss spectroscopy, and density functional theory. New results extend these chemical studies to more complex systems that include bimetallic sites and redox isomer systems, which will also be highlighted in this presentation.

We have also developed synthesis schemes to assemble quasi-square planar metal-organic complexes on high surface area powdered oxides through a modified wet-impregnation-style method. X-ray photoelectron spectroscopy measurements demonstrate loading of metal and ligand on the surface and synchrotron-based X-ray absorption spectroscopy measurements of the coordination shell of the metal centers demonstrates single site formation rather than nanoparticle assembly. These systems are shown to be active for the catalysis of hydrosilylation reactions at a level that is competitive with current homogeneous catalysts.



Time: 3:30 PM, June 3 (Mon) 2019
Place: Bldg 25-1 (Int'l Conference Rm)

Hosted by Professor Dongwhan Lee