Understanding and controlling the complexity of catalytic active sites

Abstract
Heterogeneous catalysis is of central importance to the global economy today, facilitating the conversion of raw materials into valuable fuels and chemicals, and the abatement of chemical pollutants in an efficient way. As environmental concerns associated with the use of fossil fuels and increased viability of alternative technologies motivate a transition away from traditional chemical processes, continued development and understanding of catalytic reactions will be of vital importance. At the atomic level, catalytic reactions involve the making and breaking of chemical bonds between reacting molecules and active sites. As our understanding of catalytic reactions advances, it has become apparent that the environment in which active sites operate can significantly impact reactivity, both by influencing the structure of these active sites, and by directly affecting reaction energetics. Appreciation of the dynamic behavior of active sites and the influence of the reaction environment on catalysis is therefore required for a full description of a catalytic process, and once understood, can provide additional tools for designing catalysts. Control over both the binding site and the non-reactive components in its vicinity can lead to optimal activity, as elegantly demonstrated by nature’s catalysts, enzymes. In this talk, two illustrative examples are provide that demonstrate the consequences of the reaction environment surrounding an active site on catalyst structure and reactivity.

In the first, it is demonstrated that the coordination of atomically dispersed Platinum (Pt) catalysts to oxide supports influences activity for the oxidation of carbon monoxide (CO). Through a combination of state-of-the-art in-situ atomic resolution microscopy and spectroscopy based characterization supported by first principles calculations it was demonstrated that isolated Pt species can adopt a range of local coordination environments and oxidation states, which evolve in response to varied environmental conditions. The variation in local coordination showed strong influence on chemical reactivity and could be exploited to control catalytic performance.

In a second example, the effects of ions present in the electrolyte solution on the activity and selectivity of metal catalysts for the electrochemical reduction of carbon dioxide (CO2) are elucidated. Kinetic studies, supported by density functional theory calculations, demonstrated that solvated cations interact electrostatically with adsorbed species, having a preferential effect on intermediates with high polarity. Thus cations in solution act as a built in promoter with a function analogous to alkali metal promoters for gas phase reactions.

Biosketch
Joaquin Resasco completed his B.S in Chemical Engineering at the University of Oklahoma, and his Ph.D. in Chemical Engineering at the University of California, Berkeley under the guidance of Professor Alexis Bell. His doctoral research elucidated the effects of electrolyte ions on the kinetics of electrochemical CO2 reduction. Joaquin was the recipient of the UC Berkeley Chancellor’s Fellowship and NSF GRFP. Joaquin is currently a postdoctoral scholar in the Department of Chemical Engineering at the University of California, Santa Barbara working with Professor Phillip Christopher. His postdoctoral work focuses on developing relationships between the dynamically evolving structure of atomically dispersed catalysts and their reactivity.