Second Sphere Coordination Effects, and the Limits of Uniformity in Heterogeneous Redox Catalysis

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Immobilization of active site moieties on heterogeneous catalyst surfaces, although enabling their use in large-scale industrial applications, almost invariably results in a *distribution* of active site speciation. Metal-organic framework materials (MOFs) - crystalline porous networks formed through the interconnection of inorganic nodes and organic linkers - enable, in principle, the replication of organometallic catalyst coordination environment over the *entirety* of the active site pool of a heterogeneous catalyst surface. In this talk, I will present methods for understanding whether such replication is achievable (with a high degree of fidelity) in practice, and how one can meaningfully test the prevalence of active site uniformity in MOF materials.

Using carbon monoxide oxidation with nitrous oxide as a probe reaction, I will describe how the spectroscopic, adsorptive, and catalytic characterization of MIL-100(Fe) - a prototypical MOF material carrying trinuclear oxo nodes - can be reconciled with a picture of a heterogeneous catalyst exhibiting a high degree of homogeneity in active site speciation. Crucially, these investigations unravel second sphere coordination effects in which ligands peripheral to the primary coordination sphere of an active center alter free energies of catalytically relevant intermediates and transition states. The study advances the limits of definition in redox catalysis over multi-metal oxo clusters, and provides a template for the design of highly selective catalysts for industrially relevant partial oxidation reactions.

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Praveen Bollini obtained his Ph.D. degree from Georgia Tech in 2013 under the advisement of Christopher Jones, and completed a postdoctoral appointment under Aditya Bhan at the University of Minnesota in 2017 following a brief stint conducting heterogeneous catalysis research at The Dow Chemical Company. Since the Fall of 2017 he has been an Assistant Professor in the Department of Chemical and Biomolecular Engineering at The University of Houston, where he leads a research group focused on developing a molecular-level understanding of diffusion, adsorption, and reaction phenomena occurring in nanoporous materials.

His group uses a range of synthetic, spectroscopic, and kinetic tools to develop advanced adsorbent and catalyst materials for the sustainable production of chemical and energy carriers. Current research themes include the development of metal-organic framework materials with biomimetic active sites, elucidation of structure-catalytic property relationships over bulk oxide catalysts, and the development of dynamic approaches and advanced reactor configurations for effecting high temperature catalytic partial oxidation reactions. He is a recipient of the Georgia Tech Chemical Engineering Exceptional Academic Achievement Award, The Air Products Fellowship Award for Outstanding Graduate Research, the ACS PRF Doctoral New Investigator Award, and a Scialog Fellowship.