

Chemical & Biomolecular Seminar Series



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Davidson School of
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10:00—11:00 a.m.

102 Colburn Lab

Raj Gounder is the Larry and Virginia Faith Assistant Professor of Chemical Engineering at Purdue University. He received his B.S. in Chemical Engineering and Chemistry at Wisconsin, his Ph.D. in Chemical Engineering from UC-Berkeley, and a Postdoctoral Fellowship at Caltech. His group researches the science and applications of catalysis for energy and the environment, focusing on carbon feedstock conversion to fuels and chemicals, automotive pollution abatement, the kinetic and mechanistic details of catalytic reactions, the synthesis of zeolites with tailored site and structural properties, and the spectroscopic characterization and titration of active sites in catalytic surfaces. He received the NSF CAREER Award, the Shreve Award for Outstanding Teaching in Chemical Engineering, and the inaugural Outstanding Mentor of Engineering Graduate Students Award.

Beyond Single-Site Heterogeneous Catalyst Design: Controlling the Spatial Proximity and Mobility of Active Sites

Single-site heterogeneous catalysts contain active sites that behave uniformly because of their functional isolation and well-defined structure. They are discernable using quantitative measurements of catalytic behavior in the form of turnover rates, normalized per active site, that are independent of the spatial density or proximity of such sites. We explore this concept using chabazite (CHA) zeolites, which are nominally single-site materials given that their crystalline silica frameworks are comprised of symmetry-equivalent tetrahedral lattice sites. Substitution of a lattice silicon atom with aluminum generates an anionic charge, which is compensated by an extra-lattice proton or metal cation that behave as active sites. We have developed synthetic routes to systematically control the proximity of active sites in CHA zeolites, and use these materials to show that the spatial arrangement of active sites influences catalysis, given a mechanism for sites and reactive intermediates to communicate. Consequences for Brønsted acid catalysis are probed using methanol conversion on H-form CHA zeolites, which is also practiced industrially to produce chemical precursors (alkenes, aromatics) and transportation fuels (gasoline). Turnover rates for methanol dehydration to dimethyl ether (per H^+ , 415 K) are an order-of-magnitude higher at paired than at isolated acid sites. Here, catalytic communication occurs through sites positioned at sub-nanometer (<0.4 nm) distances, which catalyze lower free energy methanol dehydration pathways than isolated sites. Consequences for redox catalysis are probed using the selective catalytic reduction (SCR) of nitrogen oxides with ammonia on Cu-exchanged CHA zeolites, which is a commercial pollution abatement technology in diesel emissions control. At low temperatures (<623 K), the SCR reaction involves a one-electron $\text{Cu}^{2+}/\text{Cu}^+$ redox cycle, yet uses a four-electron (O_2) oxidant that requires activation by two copper sites separated over distances greater than one nanometer. In this case, homogeneous-like copper complexes are formed upon solvation by ammonia, and communication occurs because ionic tethers to anionic framework Al centers enables localized diffusion of copper ions, which occupy nanometer-scale volumetric footprints (~ 1 nm radius sphere). This mechanism enables dynamic, reversible formation of multinuclear sites from mobilized single atoms, a distinct phenomenon that blurs conventional boundaries of heterogeneous and homogeneous catalysis.