CONSEQUENCES OF ZEOLITE ACTIVE SITE HETEROGENEITY FOR PROPENE OLIGOMERIZATION AND PARTIAL METHANE OXIDATION CATALYSIS

Lauren Elizabeth Kilburn

Aluminosilicate zeolites are a diverse family of catalysts composed of covalently linked SiO_4 tetrahedra intermittently substituted with Al to form a negatively charged AlO_4^- tetrahedral site (T-site) that hosts a charge compensating active site, either H^+ in the case of Brønsted acid zeolites or M^{X+} (metal ion) in metal-exchanged zeolites. These active sites are often heterogeneous in structure and function, derived from diversity in coordination environment and location within the zeolite framework, with consequences for catalytic reactivity. For example, the low-symmetry MFI framework has multiple distinct void environments and 12 crystallographically unique T-sites that dictate adsorbate access to the 10-membered ring (10-MR) straight and sinusoidal channels (~5.5 Å diam.) and their larger intersections (~7 Å diam.). Confining void environments influence adsorbate stability through non-specific van der Waals interactions, the extent of which depends on the relative sizes of the adsorbate and the confining void. Recent synthetic methods to control T-site biasing during MFI crystallization provide access to samples to enable interrogating effects of H^+ site location within MFI. Propene oligomerization is often catalyzed by H-MFI for applications that produce liquid transportation fuels, but strong transport limitations in 10-MR zeolites cause kinetic and diffusion influences to be inextricably coupled in experimentally measured rates. Density functional theory (DFT) calculations predict greater steric penalties for adsorbates confined within the smaller channels of MFI that outweigh the benefits conferred by more effective dispersive stabilization, leading to lower propene dimerization rate constants compared to the larger intersections. The discrepancy between DFT predictions and higher propene dimerization rates measured experimentally on MFI samples synthesized to bias T-sites towards channel environments indicates that H^+ location must simultaneously alleviate diffusion limitations to an even greater extent to offset the predicted decrease in intrinsic rate constants.

Another class of reactions, reduction-oxidation (redox) reactions such as selective catalytic reduction of nitrogen oxides (NO_x SCR) and partial methane oxidation (PMO), are catalyzed by metal-exchanged zeolites including Cu-CHA. Although nominally a high symmetry framework with only one unique T-site, CHA zeolites can host a diverse array of Cu active site types that vary with framework Al arrangement, Cu density, and reaction conditions. In stoichiometric PMO cycles, where each reactant (O_2, CH_4, H_2O) is introduced separately in a stepwise manner in an attempt to increase selectivity to the partial oxidation product (CH_3OH), a manifold of Cu^{2+} active sites are formed from mononuclear precursors (ZCuOH, Z denotes an AlO_4^- T-site) during a high temperature O_2 activation. Site balances from selective reduction treatments (e.g., inert, CO, CH_4) coupled with H_2 temperature programmed reduction (TPR) quantification reveal a mixture of ZCuOH and binuclear O_x-bridged ($Z_2Cu_2O_x$, x=1,2) Cu sites, all of which are capable of oxidizing CH_4 to CH_3OH, albeit with varying barriers and rates. Overoxidation of CH_3OH to CO and CO_2 was shown to occur at unreacted Cu^{2+} sites that remain in their oxidized state after the CH_4 activation step, demonstrating that selectivity to CH_3OH depends largely on the reducibility of various Cu^{2+} sites in the presence of CH_4, rather than any intrinsic selectivity differences inherent to Cu sites of different structure. H_2 TPR characterization also reveals the lower temperatures and higher H_2O pressures (543 K, 3 kPa H_2O) representative of continuous PMO, where all reactants are contacted simultaneously, leads to a homogeneous distribution of lattice-bound ZCuOH sites.

PMO rates measured as a function of Cu density demonstrate a single-site Cu^{2+} reduction process and a dual-site Cu^{1+} oxidation process that is facilitated by a H_2O- or CH_3OH-derived molecular oxygen shuttle.

Altogether, this thesis establishes a framework to interrogate non-uniform active site distributions in catalytic solids, illustrated here for crystalline zeolites for which representative structural models can be constructed and interrogated by DFT calculations and combined with incisive experimental methods to quantify the number and reactivity of distinct active site types. This work underscores the importance of considering the consequences of site-contact time on series reaction networks and measuring reaction rates in kinetic regimes limited by a single elementary step or redox half-reaction prior to ascribing observed differences in rate or selectivity across reaction conditions and samples of varying composition to inherent differences in distinct active sites. Moreover, for reactions that cannot readily be performed in a solely kinetically limited regime, this work illustrates how complementary DFT studies can be used to evaluate and isolate intrinsic kinetic effects from experimental measurements that convolute kinetic and transport phenomena. The systematic approach for reducing the complexity in heterogeneous site distributions present in catalytic solids illustrated in this work allows developing more accurate site-structure function relationships that provide predictive guidance for tailored catalyst design.