ABSTRACT

Bates, Jason S. Ph.D., Purdue University, December 2019. Structure and Solvation of Confined Water and Alkanols in Zeolite Acid Catalysis. Major Professor: Rajamani Gounder.

Brønsted and Lewis acid sites located within microporous solids catalyze a variety of chemical transformations of oxygenates and hydrocarbons. Such reactions occur in condensed phases in envisioned biomass and shale gas upgrading routes, motivating deeper fundamental understanding of the reactivity-determining interactions among active sites, reactants, and solvents. The crystalline structures of zeolites, which consist of SiO_4 tetrahedra with isomorphously-substituted M^{4+} (e.g., Sn^{4+}, Ti^{4+}) as Lewis acid sites, or Al^{3+} with charge-compensating extraframework H^+ as Brønsted acid sites, provide a reasonably well-defined platform to study these interactions within confining voids of molecular dimension. In this work, gas-phase probe reactions that afford independent control of solvent coverages are developed and used to interpret measured rate data in terms of rate and equilibrium constants for elementary steps, which reflect the structure and stability of kinetically relevant transition states and reactive intermediates. The foundational role of quantitative kinetic information enables building molecular insights into the mechanistic and active site requirements of catalytic reactions, when combined with complementary tools including synthetic approaches to prepare active sites and surrounding environments of diverse and intended structure, quantitative methods to characterize and titrate active sites and functional groups in confining environments, and theoretical modeling of putative active site structures and plausible reaction coordinates.

Bimolecular ethanol dehydration to diethyl ether was developed as a gas-phase catalytic probe reaction for Lewis acid zeolites. A detailed mechanistic understanding of

the identities of reactive intermediates and transition states on Sn-Beta zeolites was constructed by combining experimental kinetic measurements with density functional theory treatments. Microkinetic modeling demonstrated that Sn active site configurations undergo equilibrated interconversion during catalysis (404 K, 0.5–35 kPa C_2H_5OH, 0.1–50 kPa H_2O) from hydrolyzed-open configurations ((HO)-Sn-(OSi≡)$_3$---HO-Si) to predominantly closed configurations (Sn-(OSi≡)$_4$), and identified the most abundant productive (ethanol-ethanol dimer) and inhibitory (ethanol-water dimer) reactive intermediates and kinetically relevant transition state (S_N2 at closed sites). Mechanism-based interpretations of bimolecular ethanol dehydration turnover rates (per Lewis acidic Sn, quantified by CD_3CN IR) enabled measuring chemically significant differences between samples synthesized to contain high or low densities of residual Si-OH defects (quantified by CD_3CN IR) within microporous environments that confine Sn active sites. Hydrogen-bonding interactions with Si-OH groups located in the vicinity of Sn active sites in high-defect Sn-Beta zeolites stabilize both reactive and inhibitory intermediates, leading to differences in reactivity within polar and non-polar micropores that reflect solely the different coverages of intermediates at active sites. The ability of confining microporous voids to discriminate among reactive intermediates and transition states on the basis of polarity thus provides a strategy to mitigate inhibition by water and to influence turnover rates by designing secondary environments of different polarity via synthetic and post-synthetic techniques.

Despite the expectation from theory that Sn active sites adopt the same closed configurations after high-temperature (823 K) oxidation treatments, distinct Sn sites can be experimentally identified and quantified by the ν(C≡N) infrared peaks of coordinated CD_3CN molecules, and a subset of these sites are correlated with first-order rate constants of aqueous-phase glucose-fructose isomerization (373 K). In contrast, *in situ* titration of active sites by pyridine during gas-phase ethanol dehydration catalysis (404 K) on a suite of Sn-zeolites of different topology (Beta, MFI, BEC) quantified the dominant active site to correspond to a different subset of Sn sites than those dominant in glucose-fructose isomerization. An extensive series of synthetic and post-synthetic routes to prepare Sn-zeolites containing Sn sites hosted within diverse local coordination environments identified a subset of Sn sites located in defective environments such as grain boundaries, which are more pronounced in Beta crystallites comprised of intergrowths of two polymorphs than in zeolite frameworks with un-faulted crystal structures. Sn sites in such environments adopt defect-open configurations ((HO)-Sn-$(OSi\equiv)_3$) with proximal Si-OH groups that do not permit condensation to closed configurations, which resolves debated spectroscopic assignments to hydrolyzed-open site configurations. Defect-open Sn sites are dominant in glucose-fructose isomerization because their proximal Si-OH groups stabilize kinetically relevant hydride shift transition states, while closed framework Sn sites are dominant in alcohol dehydration because they stabilize S_N2 transition states via Sn site opening in the kinetically relevant step and re-closing as part of the catalytic cycle. The structural diversity of real zeolite materials, whose defects distinguish them from idealized crystal structures and allows hosting Lewis acid sites with distinct local configurations, endows them with the ability to effectively catalyze a broad range of oxygenate reactions.

During aqueous-phase catalysis, high extra-crystalline water chemical potentials lead to intra-pore stabilization of H_2O molecules, clusters, and extended hydrogen-bonded networks that interact with adsorbed intermediates and transition states at Lewis acid sites. Glucose-fructose isomerization turnover rates (373 K, per defect-open Sn, quantified by CD_3CN IR) are higher when Sn sites are confined within low-defect, non-polar zeolite frameworks that effectively prevent extended water networks from forming; however, increasing exposure to hot (373 K) liquid water generates Si-OH groups via hydrolysis of siloxane bridges and leads to lower turnover rates commensurate with those of high-defect, polar frameworks. Detailed kinetic, spectroscopic, and theoretical studies of polar and non-polar titanosilicate zeolite analogs indicate that extended water networks entropically destabilize glucose-fructose isomerization transition states relative to their bound precursors, rather than influence the competitive adsorption of water and glucose at active sites. Infrared spectra support the stabilization of extended hydrogen-bonded water networks by Si-OH defects located within Si- and Ti-Beta zeolites, consistent with *ab initio* molecular dynamics simulations that predict formation of distinct thermodynamically stable clustered and extended water phases within Beta zeolites depending on the external water chemical potential and the nature of their chemical functionality (closed vs. hydrolyzed-open Lewis acid site, or silanol nest defect). The structure of water confined within microporous solids is determined by the type and density of intracrystalline polar binding sites, leading to higher reactivity in aqueous media when hydrogen-bonded networks are excluded from hydrophobic micropores.

Aluminosilicate zeolites adsorb water to form $(H_3O^+)(H_2O)_n$ clusters that mediate liquid-phase Brønsted acid catalysis, but their relative contributions to the solvation of reactive intermediates and transition states remain unclear. Bimolecular ethanol dehydration turnover rates (per H^+, quantified by NH_3 temperature-programmed desorption and *in situ* titrations with 2,6-di-*tert*-butylpyridine) and transmission infrared spectra measured on Brønsted acid zeolites under conditions approaching intrapore H_2O condensation (373 K, 0.02–75 kPa H_2O) reveal the formation of clustered, solvated $(C_2H_5OH)(H^+)(H_2O)_n$ intermediates, which are stabilized to greater extents than bimolecular dehydration transition states by extended hydrogen-bonded water networks. Turnover rates deviate sharply below those predicted by kinetic regimes in the absence of extended condensed water networks because non-ideal thermodynamic formalisms are required to account for the different solvation of transition states and MARI. The condensation of liquid-like phases within micropores that stabilize reaction intermediates and transition states to different extents is a general phenomenon for Brønsted acid-catalyzed alcohol dehydration within zeolites of different topology (CHA, AEI, TON, FAU), which governs the initial formation and structure of clustered hydronium-reactant and water-protonated transition state complexes. Systematic control of liquid-phase structures within confined spaces by gas-phase measurements around the point of intrapore condensation enables more detailed mechanistic and structural insights than those afforded by either kinetic measurements in the liquid phase, or structural characterizations of aqueous systems in the absence of reactants.