Title: Consequences of Proximal Acid Sites and Extra-framework Aluminum Moieties for Zeolite Acid Catalysis

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Abstract

Acid zeolites are heterogeneous catalysts with a microporous structure constructed from a crystalline framework of silicon oxide tetrahedra, in which the substitution of lattice Si^{4+} centers by trivalent heteroatoms such as Al^{3+} creates an anionic framework charge that is compensated by an H^+ (active) site. Zeolitic H^+ sites are confined within voids of molecular dimension (0.4–1.3 nm) that stabilize reactive intermediates and transition states mediating acid-catalyzed reactions. The reactivity of zeolites is governed by the strength of their primary binding (H^+) sites and the size of their confining pore environments, both of which are properties that could be influenced by chemical moieties that are co-occluded within void spaces containing active sites. These species can be other proximal H^+ sites, which can cooperatively stabilize adsorbates at the primary binding sites, or extra-framework aluminum (Al_{ex}) moieties, which may interact with species bound at the primary acid site via electrostatic interactions or occupy void space in ways that alter the effective spatial constraints surrounding the H^+ site. Efforts to tailor the secondary environment of zeolitic H^+ sites for targeted catalytic applications typically rely on heuristic descriptions of confinement on reactivity, often leading to contradicting mechanistic proposals. In this work, we develop a molecular-level understanding of how H^+ sites and Al_{ex} moieties proximal to the primary H^+ active site influence zeolite acid catalysis.

The placement of Al_{ex} moieties in zeolitic voids, either intentionally via hydrothermal treatments that remove framework Al sites (Al_f) or adventitiously during synthesis and subsequent treatments, has been documented to influence the catalytic and adsorptive properties of zeolitic H^+ sites. One school of thought attributes these changes to Lewis acidic Al_{ex} species stabilizing anionic lattice oxygens (i.e., conjugate Brønsted bases) and leading to the formation of stronger H^+ sites, based on analogies to observations in aqueous-phase “super-acidic” mixtures of Lewis and Brønsted mineral acids. Such proposals of stronger H^+ sites, however, are unlikely to rationalize the stronger stabilization of neutral adsorbates (e.g., alkanes) that interact weakly with acidic sites. Herein, we present experimental evidence demonstrating that the preeminent role of

Al_{ex} species is to decrease the effective void spaces in zeolitic micropores, thereby strengthening dispersive stabilization of both adsorbed neutral intermediates and their cationic transition states. We combine site-specific spectroscopic, kinetic, and adsorption studies to quantify entropy-enthalpy tradeoffs for adsorbed charge-neutral alkanes and their carbocationic transition states, which mediate protolytic cracking and dehydrogenation, in model chabazite (CHA) zeolite materials containing isolated H^+ sites. Entropy-enthalpy tradeoffs with increasing Al_{ex} content are quantitatively identical to those describing changes in the size of confining micropore environments among zeolite topologies, a behavior characteristic of changes in the strength of dispersion forces. These findings enable catalyst design strategies that preferentially position extra-framework oxide moieties within confining voids containing H^+ sites to alter dispersive interactions and influence catalytic reactivity, complementing strategies based on varying framework topology or the location of active sites among distinct voids of a given topology.

Acid zeolites provide an ideal platform for studying the effects of active site proximity in catalysis, as they contain spatially isolated active (H^+) sites that allow for the precise control and quantification of proximal site arrangements. The typical approach for controlling active site proximity involves varying the bulk Al (i.e., H^+ site) content, which, on statistical average, leads to varying inter-site distances. Prior studies have varied H^+ site content (i.e., bulk Si/Al ratios) in MFI zeolites and observed concomitant changes in catalytic reactivity for various acid-catalyzed reactions (e.g., alcohol dehydration, alkene oligomerization, alkane activation); however, unambiguous mechanistic explanations are precluded by the complexity of the MFI framework (i.e., 12 distinct T-sites), which presents numerous possible Al-Al pair configurations and H^+ sites in distinct void environments (i.e., ~0.5 nm straight and sinusoidal 10-MR channels and their ~0.7 nm intersections) that complicate the interpretation of kinetic data. Such complications can be circumvented by using high-symmetry CHA zeolites (i.e., one unique T-site), which limit the number of possible Al-Al pair configurations and contain active sites that have equivalent access to the available void space. In addition, for CHA, the fraction of H^+ sites compensating proximal Al-Al can be synthetically controlled at fixed Al density by co-occluding inorganic (e.g., Na^+) and organic (e.g., N,N,N -trimethyl-1-admantylammonium) structure-directing agents, which together compensate proximal anionic oxygens associated with framework Al. Increasing the fraction of proximal H^+ sites in model CHA samples leads to an increase in rate constants for high-temperature (>700 K) protolytic alkane cracking and dehydrogenation. These rate increases occur due to multi-

ion-pair interactions that enable carbocationic alkane activation transition states to gain higher entropic stability, which becomes a preeminent factor in lowering their Gibbs free energy of formation at high temperatures. Methanol dehydration rates measured at low temperatures (<450 K) also increase with increasing site proximity. In contrast, these increases are associated with the enthalpic stabilization of carbocationic transition states, which becomes a preeminent factor in lowering Gibbs free energy barriers at low temperatures, via hydrogen bonding interactions from spectator adsorbates bound at a proximal site. These kinetic data and their interpretation provide a mechanistic understanding of how proximal active sites in acid zeolites cooperate during catalysis at both high and low temperatures, building a framework that accounts for condition-dependent inter-site communication in the interpretation of catalytic phenomena.

During zeolite synthesis, Columbic interactions between framework anionic centers, introduced by Al^{3+} substitution into a primarily SiO_2 lattice, and cationic charges in structure directing agents (SDA) strongly influence the thermodynamic preference of Al siting among different tetrahedral-sites (T-sites). For MFI zeolites, quaternary N^+ centers of tetra-n-propylammonium (TPA^+) bias Al in T-sites adjacent to larger channel intersections (~0.7 nm), while co-occlusion of ethylenediamine (EDA) biases Al siting towards smaller (~0.5 nm) channels via H-bonding interactions. Acid sites confined in smaller channels have higher selectivity (>70%, 403 K) to para-xylene (p-X) during toluene methylation by C_1 species because larger transition states that form m-X and o-X isomers are preferentially destabilized in smaller voids. Herein, we show that synthetic strategies to bias active sites in MFI hold generally for other trivalent heteroatoms (Ga^{3+}, Fe^{3+}, B^{3+}), which alter acid strength and, in turn, rates of C–C bond formation and cracking reactions (i.e., toluene methylation, alkane cracking), while preserving confinement-induced regioselectivity. MFI synthesized with EDA and TPA^+ showed marked increases in p-X selectivity (~75%) compared to MFI made with TPA^+ (~30%), and these selectivity trends persist with varying trivalent atoms (Al^{3+}, Ga^{3+}, Fe^{3+}, B^{3+}). MFI synthesized with similar SDAs (TPA^+ only or EDA/TPA^+) showed xylene formation (per H^+, 403 K) and alkane cracking rate constants (per H^+, 748 K) that decreased exponentially with deprotonation energy (i.e., acid strength), reflecting the less effective stabilization of carbocationic transition states by less stable conjugate anions of weaker acids. Our findings reveal that synthesis-structure relationships governing active site biasing in MFI are generalizable for any heteroatoms with H^+ sites of varying strength.

Overall, this work provides a precise mechanistic understanding of how the catalytic reactivity of zeolitic H^+ sites is governed by their strength and the size of their confining voids, which can be tuned by introducing other species in the reaction environment, both in the form of other active (H^+) sites and Al_{ex} moieties. These molecular-level insights were developed using model zeolites, which allow for systematic and independent tuning of active site secondary environments, and quantitative kinetic and adsorptive probes that faithfully report changes in chemical interactions experienced by guest molecules. Taken together, the methodology and findings developed in this work provide an exemplary case of how to probe and design active sites in acidic zeolite catalysts, which are widely used in the upgrading of fossil-based and renewable carbon resources.