ABSTRACT

Zeolites contain distinct Brønsted acid site (H^+) ensembles that arise from differences in the arrangement of framework Al atoms (Al−O(−Si−O)x−Al) between isolated (x ≥3) and paired (x=1,2) configurations, the latter defined by their ability to exchange certain divalent cations (e.g., Cu^{2+}, Co^{2+}). Manipulation of the synthesis conditions used to prepare MFI zeolites has been proposed to influence the proximity of framework Al atoms, but in a manner that is neither determined randomly nor by any simple predictive rules. Moreover, the effects of proton proximity have been studied for hydrocarbon catalysis in MFI zeolites, but interpretations of catalytic phenomena are convoluted by effects of the distribution of framework Al atoms among different crystallographic tetrahedral sites (T-sites) and diverse pore environments (i.e., confining environments) present in MFI. This work instead focuses on the chabazite (CHA) framework, which contains a single crystallographically-distinct lattice tetrahedral site (T-site) that allows clarifying how synthesis conditions influence Al proximity, and in turn, how H^+ site proximity influences catalysis independent of T-site location.

Selective quantification of the number and type of H^+ site ensembles present in a given zeolite allows for more rigorous normalization of reaction rates by the number of active sites, but also for probing the number and identity of active sites on bifunctional catalysts that contain mixtures of Brønsted and Lewis acid sites. Gaseous NH_3 titrations can be used to count the total number of protons on small-pore CHA zeolites, which are inaccessible to larger amine titrants (e.g., pyridine, alkylamines), and can be used to quantify the exchange stoichiometry of extraframework metal cations (e.g., Cu^{2+}, $[CuOH]^+$) that are stabilized at different framework Al arrangements. Additionally, paired Al sites in CHA zeolites can be titrated selectively by divalent Co^{2+} cations, whose sole presence is validated by measuring UV-Visible spectra, counting residual protons after Co^{2+} exchange, and titration of paired Al with other divalent cations (e.g., Cu^{2+}). These different titration procedures enabled reliable and reproducible quantification of different Al arrangements, and recognition of the effects of different synthetic methods on the resulting arrangement of framework Al atoms in CHA zeolites.

Upon the advent of this suite of characterization and titration tools, different synthetic methods were developed to crystallize CHA zeolites at constant composition (e.g., Si/Al = 15) but with systematic variation in their paired Al content. The substitution of N,N,N-trimethyl-1-

adamantylammonium ($TMAda^+$) cations for Na^+ in the synthesis media ($Na^+/TMAda^+<2$), while holding all other synthetic variables constant, resulted in CHA zeolites of similar composition (Si/Al = 15) and organic content (ca. 1 $TMAda^+$ per cage), but with percentages of paired Al (0-44%) that increased with the total amount of sodium retained on the zeolite product. This result suggests that sodium atoms are occluded near the ammonium group of $TMAda^+$ leading to the formation of a paired Al site. Replacement of Na^+ by other alkali cations in the synthesis media allowed for the crystallization of CHA (Si/Al = 15) at higher ratios of alkali to $TMAda^+$ than accessible by Na^+, likely due to the ability of different alkali cations to favor (or inhibit) crystallization of other zeolite phases. Incorporation of different alkali cations during CHA crystallization influences the formation of paired Al sites in different ways, likely reflecting the nature of different alkali to preferentially occupy different positions within the CHA framework. *Ab initio* molecular dynamics simulations were used to assess the stability of various Al-Al arrangements in the presence of combinations of alkali and $TMAda^+$ cations, and provide thermodynamic insight into electrostatic interactions between cationic structure-directing agents that stabilize paired Al sites in CHA.

Using these synthetic procedures to prepare CHA zeolites of similar composition, but with varied arrangements of framework Al, the catalytic consequences of framework Al arrangement were investigated using acid and redox catalysis. The low-temperature (473 K) selective catalytic reduction of NOx with NH_3 (NH_3-SCR) was investigated over Cu-exchanged CHA zeolites containing various Al arrangements. Cu cations exchange as both divalent Cu^{2+} and monovalent $[CuOH]^+$ complexes, which exchange at paired and isolated Al sites, respectively, and turnover with similar SCR rates (473 K). *In situ* and *operando* X-ray absorption spectroscopy (XAS) were used to monitor the oxidation state and coordination environment of Cu as a function of time and environmental conditions. Rationalization of these experimental observations by first-principles thermodynamics and *ab initio* molecular dynamics simulations revealed that both Cu^{2+} and $[CuOH]^+$ complexes are solvated by NH_3 and undergo reduction to Cu^+ upon oxidation of NO with NH_3. Cu^+ cations become mobilized by coordination with NH_3 under reaction conditions (473 K, equimolar NO and NH_3 feed), and activate O_2 through a dicopper complex formed dynamically during reaction. These results implicate the spatial density of nominally site-isolated Cu cations and, in turn, the arrangement of anionic framework Al atoms that anchor such cationic Cu complexes, influence the kinetics of O_2 activation in selective oxidation reactions, manifested as

SCR rates (per 1000 A^3) that depend quadratically on Cu density (per 1000 A^3) and become rate-limiting processes in practice at low temperatures.

Furthermore, first-order and zero-order rate constants (415 K, per H^+) of methanol dehydration, a probe reaction of acid strength and confinement effects in solid Brønsted acids, are nearly one order of magnitude larger on paired than on isolated protons in CHA zeolites, reflecting differences in prevalent mechanisms and apparent enthalpic and entropic barriers at these different active site ensembles. Yet, these differences in rate constants and activation parameters at isolated and paired protons do not persist within larger pore zeolites (e.g., MFI). *In situ* IR spectra measured during steady-state methanol dehydration catalysis (415 K, 0.05-22 kPa CH_3OH) reveal that surface methoxy species are present in CHA zeolites containing paired protons, but not in CHA zeolites containing only isolated protons or MFI zeolites, providing evidence that sequential dehydration pathways via methoxy intermediates become accessible on paired protons in CHA. Density functional theory is used to provide atomistic detail of confined intermediates and transition states at isolated and paired protons in CHA and MFI zeolites, indicating that paired protons in CHA preferentially stabilize dehydration transition states that are partially-confined within the 8-membered ring (8-MR) of CHA. These findings provide evidence that catalytic diversity for the same stoichiometric reaction among zeolites of fixed structure and composition, even for frameworks containing a single T-site, can be introduced deliberately through synthetic control of the atomic arrangement of matter.