ABSTRACT

Nimlos, Claire T. Ph.D., Purdue University, October 2020. Influence of Organic and Inorganic Cations on Directing Aluminum Distributions in Zeolite Frameworks and Effects on Brønsted Acid Catalysis. Major Professor: Rajamani Gounder.

Zeolites are microporous crystalline solids with tetrahedrally bonded Si^{4+} atoms linked together with bridging oxygens, interconnected in various geometries and arrangements to generate a diversity of microporous topologies. The substitution of Al^{3+} into framework tetrahedral sites (T-sites) generates anionic lattice charges that can be counterbalanced by protons (Brønsted acid sites) or extraframework metal cations and complexes that can act as catalytic active sites. The local arrangement of Al ensembles can be categorized by the size of the (alumino)silicate rings and the number and order of the Al atoms they contain, which are critical structural features that influence their ability to serve as binding sites for extraframework cations of different size and oxidation state. The ability to exercise control over the isomorphic substitution of Al^{3+} into the zeolite framework during hydrothermal crystallization has long been envisioned, but recognized to depend on complex and kinetically-controlled nucleation and crystal growth events that challenge the development of reproducible synthesis routes and predictive synthesis-structure relations. Here, we present the results of extensive experimental and theoretical investigation of the chabazite (CHA) zeolite topology, which contains a single crystallographically distinct T-site that enables studying effects of Al arrangement independent of T-site location. We then extend these findings and methodologies to investigate more complex zeolite topologies with larger numbers of distinct T-sites, including other small-pore (AEI, LEV) and medium-pore zeolites (MFI, MEL), with a specific focus on MFI zeolites because of their versatility in commercial applications.

Cationic species are often present during hydrothermal zeolite crystallization, in the form of inorganic and organic structure directing agents (SDAs), to help guide formation of the intended zeolite topology and to compensate charge when Al is incorporated into the lattice. Variations in the type and amount of cationic SDAs have been shown to influence both the Al siting within different void locations of a given zeolite and the local Al arrangement. In order to make quantitative assessments of the

number of Al-Al site pairs formed in a given zeolite, experimental protocols to titrate the specific Al-Al site ensembles are required. We specifically explore the use of Co^{2+} titrants at saturation uptakes, verifying the sole presence of Co^{2+} cations via spectroscopic identification and a cation site balance that is closed by quantifying residual Brønsted acid sites by NH_3 titration. We then investigate the role of the cationic SDA content in the synthesis mixture on the Al arrangement in MFI zeolites. Depending on the specific mixture of the organic cation tetrapropylammonium (TPA^+) or various neutral organic molecules when used together with smaller Na^+ cations, MFI zeolites can be crystallized over a range of Al content. Moreover, the fraction of Co^{2+}-titratable Al-Al pairs correlates with the amount of occluded Na^+ cations when the total Al content is held approximately constant (Si/Al ~ 50). These results are consistent with our prior reports of CHA zeolites, wherein the occlusion of smaller Na^+ cations correlates positively with the formation of Al-Al pairs in six-membered ring (6-MR) locations. Unlike the N,N,N-trimethyl-1-adamantylammonium ($TMAda^+$) cation used to crystallize CHA, which alone does not form Co^{2+}-titratable Al-Al site pairs, the organic TPA^+ alone can form Al-Al site pairs in MFI. DFT calculations of Al siting energies, using a 96 T-site MFI unit cell containing either one or two Al charge-balanced by one or two occluded TPA^+ respectively, reveal the dominant influence of electrostatic interactions between the cationic N of TPA^+ and the anionic lattice charge. DFT calculations of probable Co^{2+} exchange sites are used to identify a subset of Al-Al site pairs with favorable energies when compensated either by Co^{2+} or by two TPA^+ molecules in adjacent MFI channel intersections. MFI crystallized with one cationic species (TPA^+ or Na^+) with a neutral organic species (ethylenediamine, pentaerythritol, or a mixture of methylamine and 1,4-diazabicyclo[2.2.2]octane) contain significantly lower fractions of Co^{2+}-titratable Al-Al pairs at similar bulk Al content (Si/Al = 43–58), demonstrating the role of neutral organic species to occupy void spaces without providing the capacity to compensate charge, thus serving to increase the average spatial separation of framework Al sites.

The kinetics of methanol dehydration to dimethyl ether can be quantified by first-order and zero-order rate constants (415 K, per H^+) to probe acid strength and confinement effects in solid Brønsted acids. Here, we use this quantitative probe reaction to investigate how Al arrangements in MFI and CHA affect the mechanism and kinetics of this reaction, in order to connect synthetic protocols to structure and to catalytic function. This effort first involved measurement of methanol dehydration kinetics on a suite of commercially sourced MFI samples to benchmark results obtained on our kinetic instruments to prior literature reports. CHA zeolites with 6-MR isolated protons show zero-order rate constants similar to those for commercial MFI zeolites and other topologies previously studied in the literature, reflecting the invariance in Brønsted acid strength with zeolite topology. First-order rate constants on isolated acid sites in CHA are an order of magnitude higher than acid sites in MFI, reflecting the smaller confining environments present in CHA than in the medium-pore zeolite MFI. In contrast, both first-order and zero-order rate constants among CHA samples increase systematically with the fraction of 6-MR Al pairs, even for samples of nominally similar composition (Si/Al ~ 15). DFT provides evidence for lower activation barriers at protons of 6-MR paired Al sites in CHA, which stabilize transition states via H-bonding interactions through co-adsorbed methanol bound at the proximal acid site, in a manner dependent on the specific Al arrangement and ring size and structure. Such favorable configurations are identified for 6-MR paired Al sites in CHA, but were not identified within MFI zeolite, which shows first-order and zero-order rate constants that are invariant with varying Al-Al site pair content. These findings and conclusions demonstrate how quantitative experimental characterization and kinetic data, augmented by theory insights, can aid in the development of more predictive synthesis-structure-function relations for zeolite materials and help transform empirical efforts in active site design and engineering into a more predictive science.