Title: Kinetic and Mechanistic Descriptions of Zeolite Framework Dealumination during Hydrothermal Aging
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ABSTRACT

Aluminosilicate zeolites are widely used as catalysts to convert carbon-based feedstocks into chemicals and energy carriers and to abate nitrogen oxide (NO_x) emissions in diesel engine exhaust via selective catalytic reduction (SCR) with ammonia (NH_3). Throughout their lifetime, zeolites are exposed to water-containing environments at high temperatures (>873 K), commonly known as hydrothermal aging (or “steaming”), via regeneration protocols or post-synthetic modification procedures that cause removal of framework aluminum atoms from lattice positions. Despite their ubiquity in commercial practice, current understanding of zeolite hydrothermal stability and its dependence on material properties relies largely on heuristic insights, in part, due to the paucity of kinetic and mechanistic details governing framework dealumination processes. Herein, we develop a kinetic and mechanistic framework to model and predict zeolite dealumination by combining *in situ* methods to titrate and quantify H^+ sites, which serve as structural proxies for framework Al centers, on zeolite samples subjected to hydrothermal aging treatments of increasing severity. This methodology was applied to zeolite materials with varying framework Al densities, amounts of proximal or isolated framework Al sites, concentrations of framework vacancy defects, and zeolite crystal topologies to provide mechanistic insights on how these material properties influence dealumination kinetics.

Chabazite (CHA) zeolites were selected as model materials to develop methods to measure dealumination rates in zeolites since their high-symmetry framework allows studying the loss of framework Al (Al_f) from nominally identical lattice positions, and because they are empirically observed to be among the most resistant topologies to framework dealumination under high-temperature hydrothermal aging conditions. CHA samples of varying framework Al density (0.6–1.1 Al_f per unit cell) were synthesized and hydrothermally aged to remove varying amounts of Al_f sites as a function of treatment time (0–64 h), while preserving their bulk crystalline structure.

Dealumination rates were quantified as a function of H_2O pressure (3–30 kPa H_2O), hydrothermal aging temperature (823–973 K), and framework Al site density (0.04–1.1 Al_f per unit cell). Measured apparent reaction orders in framework Al revealed a slightly greater than second-order dependence (2.1–2.3) at high H_2O pressures (>10 kPa H_2O) and temperatures (>923 K), for a range of initial framework Al density (0.6–1.1 Al_f per unit cell), in contrast with the first-order dependence on framework Al expected for rates limited by H_2O-assisted hydrolysis of Al–O bonds. Instead, the second-order dependence was consistent with mechanism-derived rate expressions that assume kinetically relevant agglomeration of monomeric extra-framework Al (Al_{ex}) species. Apparent second-order (in Al_f) rate constants ($k_{app,2}$) increased with Al_f density and concomitantly decreasing Al inter-site distance; such deviations from second-order mean-field kinetics are consistent with dealumination rates influenced by the diffusion and agglomeration of Al_{ex} species. These findings provide new mechanistic insights into processes that determine rates of zeolite framework dealumination and rationalize empirical observations that hydrothermal stability increases with decreasing Al content.

This kinetic and mechanistic framework was extended to a suite of CHA samples synthesized to contain predominantly isolated framework Al sites at varying Al_f density (0.6–1.7 Al_f per unit cell), and fixed Al_f density with varying amounts of paired Al_f (0–36%) in six-membered rings (6-MR). The amounts of paired Al_f in 6-MR were titrated with Co^{2+} via aqueous-phase ion-exchange conditions that result in preferential exchange at two Al_f sites contained in 6-MR over other ring structures (e.g., 4-MR, 8-MR) in CHA. Evidence from density functional theory (DFT), statistical calculations, experimental titrations, and solid-state NMR indicated that Ba^{2+} cations titrate paired Al sites in both 6-MR and 8-MR of CHA, demonstrating that Ba^{2+} complements Co^{2+} as a reporter of paired Al_f sites separated by different inter-site distances in CHA frameworks. Dealumination rates (923 K, 10–30 kPa H_2O) measured on CHA samples with varying amounts of isolated Al_f sites and 6-MR paired Al_f sites followed a pseudo-second-order dependence on framework Al_f, with $k_{app,2}$ values that systematically increased with Al_f density, consistent with rates limited by Al_{ex} diffusion and agglomeration. At fixed Al_f density, $k_{app,2}$ values measured on samples with predominantly isolated Al_f increase with initial Al_f content, and those measured on samples with different amounts of 6-MR paired Al_f increase with the fraction of isolated Al_f. These results suggest that increasing Al_f density and extent of isolation decreases initial Al inter-site distances, leading to higher Al_{ex} diffusion and agglomeration rates. CHA samples with varying amounts of initial framework vacancies showed dealumination rates (923 K, 3–10 kPa H_2O) that increase with framework vacancy concentration at fixed Al_f density, suggesting that framework vacancies increase effective 8-MR window sizes to facilitate the migration of Al_{ex} species.

The methods developed herein on CHA zeolites were used to measure dealumination kinetics on other zeolite topologies with varying framework dimensionality (e.g., 3D, 1D), void size (e.g., 8-MR, 10-MR), and void environment around framework Al (e.g., channels, intersections). Dealumination rates were measured on TON (Si/Al = 45) and MFI (Si/Al = 45) zeolites, which are respectively 1D and 3D 10-MR pore topologies, under hydrothermal aging conditions (923 K, 10 kPa H_2O) expected to be limited by Al_{ex} diffusion and agglomeration. Values of $k_{app,2}$ on TON (at similar Al_f density) were systematically higher than for CHA, a 3D 8-MR pore topology, suggesting that larger pores facilitate the diffusion of Al_{ex} species. Dealumination rates (per Al_f density) measured on MFI with low Al_f density (< 0.1 Al_f per g) were similar to those measured on TON, but remain invariant with Al_f on MFI with high Al_f density (> 0.1 Al_f per g), reflecting a transition from mixed kinetic regime to first-order in framework Al as Al_f density increases; a first-order dependence in Al_f is consistent with dealumination rates limited by H_2O-assisted hydrolysis of Al–O bonds. First-order dealumination rates measured on MFI zeolites (Si/Al = 45) were higher (4×) for Al_f sites associated with intersection than channel voids, where Al_f location was characterized by differences in toluene methylation rates and *para*-xylene selectivity. Taken together, these results highlight the influence of zeolite framework material properties on regulating the relative rates of Al–O hydrolysis and Al_{ex} diffusion and agglomeration.

This work provides a kinetic and mechanistic framework to quantitatively measure zeolite dealumination and hydrothermal stability under conditions wherein the bulk framework remains intact, but local structural changes can be monitored via *in situ* titration of H^+ sites that are proxies for framework Al. Quantitative kinetic descriptions of dealumination processes can be compared among zeolites to establish a link between different site and topological properties and observed hydrothermal stability. Ultimately, this thesis develops an approach to replace heuristic insights and empirical guidance with mechanistic understanding and kinetic descriptions, thereby providing more incisive criteria for catalyst design with predictable hydrothermal stability and dealumination behavior.