ABSTRACT

Ezenwa, Sopuruchukwu A., Ph.D. Candidate, May 2024. Catalytic Consequences of Active Site Environments in Brønsted Acid Aluminosilicates on Toluene Methylation.
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Zeolites are microporous crystalline aluminosilicates that are widely used as catalysts for upgrading hydrocarbons and oxygenates to higher value chemicals and fuels. The substitution of tetrahedral Si^{4+} with Al^{3+} in a charge-neutral silica framework ($[SiO_{4/2}]$) generates anionic centers ($[AlO_{4/2}]^-$), which charge-compensate Brønsted acid protons (H^+) that serve as active sites for catalysis. Brønsted acid sites in aluminosilicates of diverse topologies have similar acid strength, but can be located within varying intracrystalline microporous environments (0.4–2 nm diameter) or at extracrystalline surfaces and mesoporous environments (>2 nm diameter); yet, catalytic diversity exists, *even* for a fixed zeolite framework topology, because micropores impose constraints on molecular access to and from intracrystalline active sites and provide van der Waals contacts that influence the stabilities of reactive intermediates and transition states. Tailoring the material properties of a given zeolite framework for targeted catalytic applications requires strategies to design both the bulk crystallite properties (e.g., morphology, active site density) that influence intracrystalline diffusion and the secondary environments that surround active sites and influence intrinsic kinetics, and further necessitates molecular-level insights to elucidate the influences of bulk and active site properties on catalysis. In this work, we provide synthetic and post-synthetic strategies to respectively tune active site environments within varying micropore voids and at external surfaces of zeolites, and develop gas-phase toluene methylation and liquid-phase mesitylene benzylation as probe reactions to quantify the catalytic consequences of active site environments on aromatic alkylation catalysis.

The MFI framework (orthorhombic phase) consists of 12 crystallographic distinct tetrahedral-sites and 26 unique framework oxygen atoms located around channels (~0.55 nm diameter) or channel intersections (~0.70 nm diameter). The synthesis of MFI zeolites using the conventional tetra-*n*-propylammonium (TPA^+) organic structure directing agent (OSDA) is known to place framework Al and their attendant H^+ sites within the larger intersection environments, because electrostatic interactions are favorable between such locations of $[AlO_{4/2}]^-$ and the

quaternary N^+ center in TPA^+ that becomes positioned rigidly within channel intersections during crystallization. The methylation of toluene by dimethyl ether (DME; 403 K) on MFI-TPA zeolites of fixed active site densities (~2 Al per unit cell) result in *ortho*-xylene (*o*-X; ~65%) as the major product over *para*-xylene (*p*-X; ~27%) and *meta*-xylene (*m*-X; ~8%). In contrast, toluene methylation on MFI zeolites (~2 Al per unit cell) synthesized using non-conventional OSDAs, such as ethylenediamine (EDA) or 1,4-diazabicyclo[2.2.2]octane (DABCO), predominantly forms *p*-X (~75%) over *o*-X (~23%) and *m*-X (~2%). Within the subsets of MFI-TPA and MFI-EDA/DABCO zeolites, measured xylene formation rates and isomer selectivities are independent of crystallite sizes (0.1–13 μm), toluene conversions (0.02–2.0%) and external H^+ content (up to 9% external H^+ per total Al), indicating negligible effects of diffusion-enhanced secondary xylene isomerization reactions at intracrystalline or extracrystalline domains. The invariance of xylene isomer selectivity with reactant pressures (0.2–9 kPa toluene, 25–66 kPa DME) or methylating agent (1–4 kPa methanol) indicate that differences in reactivity of toluene to form each xylene isomer reflects differences in the stabilities of their respective kinetically relevant transition states that share the same reactive intermediate. Measured xylene isomer formation rate constants and rate constant ratios, obtained from mechanism-derived rate expressions and interpreted using transition state theory formalisms, are used alongside density functional theory (DFT) calculations to reveal that intersection void environments (~0.70 nm diameter) similarly stabilize all three xylene transition states over unconfined surfaces (>2 nm diameter) without altering the established aromatic substitution patterns, while channel void environments (~0.55 nm diameter) preferentially destabilize bulkier *o*-X and *m*-X transition states thereby resulting in high intrinsic *p*-X selectivity. DFT calculations reveal that the ability of protonated DABCO complexes to reorient within MFI intersections and participate in additional hydrogen-bonding interactions with anionic Al centers during synthesis, facilitates the placement of Al in smaller channel environments that are less favored by TPA^+. These molecular-level details, enabled by combining synthesis, characterization, kinetics and DFT, establish a mechanistic link between OSDA structure, active site placement and transition state stability, and provide active site design strategies orthogonal to crystallite design approaches that rely on complex reaction-diffusion phenomena.

For various reactions including toluene methylation at higher reaction temperatures (573–773 K) and toluene conversions (>10%), extracrystalline H^+ sites in MFI zeolites are reported to

influence reactivity, selectivity, and deactivation behavior during catalysis in undesired ways. Post-synthetic chemical treatments to passivate external H^+ sites on MFI zeolites result in unintended (but not always undesirable) changes to bulk structural properties and Al and H^+ contents. The number of extracrystalline H^+ sites is difficult to quantify using conventional spectroscopic or titrimetric methods, especially when present in dilute amounts on samples whose surfaces have been passivated. The systematic treatment of MFI zeolites (2.4, 5.7 and 7.1 Al per unit cell) using ammonium hexafluorosilicate (AHFS) at varying treatment duration times, AHFS concentrations and number of successive treatments resulted in MFI zeolites that retain their bulk structural properties and total Al and H^+ contents, except for one parent MFI sample containing a significant amount of non-framework Al species. The benzylation of mesitylene by dibenzyl ether (363 K) occurs exclusively at external H^+ sites because the bulky 1,3,5-trimethyl-2-benzylbenzene product is sterically prevented from forming at intracrystalline H^+ sites. The intrinsic zero-order rate constant (per external H^+) for mesitylene benzylation is extracted from rate measurements (per total Al) on a suite of untreated MFI samples with known amounts of external H^+ sites (1–15% external H^+ per total Al) quantified using bulky 2,6-di-*tert*-butylpyridine base titrants. Measured zero-order rate constants on AHFS-treated MFI zeolites are used to quantify the extent to which AHFS treatments passivate external H^+ sites, revealing efficacies that depend on the specific treatment conditions and the parent sample used. The developed kinetic methods demonstrate the utility of catalytic probes, when compared to stoichiometric probes based on spectroscopic or titration methods, in amplifying and quantifying dilute concentrations of external H^+ sites on zeolites. The methods enable comparisons of the efficacy of various post-synthetic passivation strategies and permit rigorous assessments of the influence of external H^+ during acid catalysis.

Overall, this work provides (post-)synthetic strategies to tune active site environments within intracrystalline micropores or at extracrystalline surfaces and develops quantitative kinetic probes that enable a molecular-level understanding of catalytic consequences of active site environments on aromatic alkylation reactions. Taken together, the methodology and findings of this study have broader implications in zeolite catalyst design for selectively upgrading traditional fossil feedstocks (crude oil and shale gas) and emerging feedstocks (biomass and waste plastics).