CONSEQUENCES OF CONFINEMENT AND ACID STRENGTH WITHIN AND ACROSS ZEOLITE FRAMEWORKS FOR ARENE METHYLATION CATALYSIS

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Abstract

Brønsted acid zeolites are catalysts comprised of micropores of molecular dimensions (< 2 nm) that confine and stabilize guest species via non-specific van der Waals interactions, which can lead to order-of-magnitude differences in rate constants across materials of different topology. Brønsted acid sites are generated upon the aliovalent substitution of a trivalent heteroatom (e.g., Al3+, Fe3+, Ga3+, B3+) for a tetravalent silicon covalently bound in tetrahedral arrangements to four corner-sharing oxygen atoms. Brønsted acid strength depends on the identity of the trivalent heteroatom and is rigorously described by the deprotonation energy (DPE), which dictates the strength of electrostatic interactions between framework anionic charges and guest cationic species, such as active H+ sites or carbocationic transition states. Secondary confining environments also stabilize guest species, with analogies to enzyme binding pocket-substrate stabilization, as both the host (inorganic pore) and guests (reactive intermediates and transition states) influence reactivity, wherein rate constants are often observed to increase as the size and shape of the guest species approach that of the confining host. The diameter of the confining microporous void (Dvoid) is dictated both by the identity of the zeolite framework as well as the location of the trivalent heteroatom substituted amongst unique tetrahedral sites (T-sites) within a given zeolite framework, which causes acid sites to become positioned within distinct void environments of a given framework. In this work, we elucidate the independent contributions of electrostatic and van der Waals contributions to the stability of reactive intermediates and transition states through kinetic assessments of low-temperature (403 K) arene methylation by dimethylether (DME) to form polymethylbenzenes of varied size and shape.

Synthetic methods have been proposed to bias active site distributions within MFI zeolites, which have 12 crystallographically distinct T-sites that form a network of sinusoidal and straight channels (Dvoid ~0.55 nm) that intersect to form larger voids (Dvoid ~0.70 nm). Density functional theory (DFT) barriers calculated at each of the 12 T-sites predict that ortho-xylene

(Dcritical ~0.66 nm) will be preferentially formed on acid sites confined within intersections, while the smaller para-xylene regio-isomer as quantified by the product critical diameter (Dcritical ~0.55 nm) will be selectively formed at acid sites within the smaller channels. Prior studies have found that MFI zeolite samples synthesized using the conventional organic structure-directing agent (OSDA), tetrapropylammonium (TPA+), display low p-xylene selectivity (<30%), indicative of Al incorporation biased towards intersections near the central quarternary ammonium center in TPA+. Conversely, MFI synthesized with OSDA systems that involve cooperation between ethylenediamine (EDA) and TPA+ or 1,4-diazabicyclo[2.2.2]octane (DABCO) and methylamine (MA) exhibit biased product selectivity towards the smaller p-xylene product (>70%), consistent with a channel-biased active site distribution. The intermolecular interactions governing this channel-biased siting are hypothesized to be driven by hydrogen-bonding interactions between terminal hydroxyl groups and framework-incorporated Al3+ anionic centers. However, these interpretations are complicated by the effects of multiple organic species and inorganic cations present during crystallization, and because alternative hypotheses have proposed that these molecules merely act as space-filling species within intersections. We distinguish these proposals by considering the OSDA pentaerythritol (PET), which possesses terminal hydrogen-bonding groups and occupies only 50% of available MFI intersections, in the presence of Na+ ions incorporated at substoichiometric amounts relative to Al. MFI samples synthesized with PET exhibit >70% p-xylene selectivity, indicative of channel-biased distributions as predicted by DFT-derived barriers. We thus conclude that hydrogen-bonding groups play a dominant role in biasing heteroatoms towards T-sites that access the channels via co-adsorbed or derivatized solvent molecules, which form because the local pH within microporous regions differs from the pH in the bulk synthesis gel.

This framework for interpreting OSDA-Al3+ interactions in MFI zeolites was extended to trivalent atoms of different identity (Al3+, Fe3+, Ga3+, B3+), prepared using either TPA+ or TPA+ and EDA as co-SDAs that are representative of conventional and non-conventional OSDAs. Toluene methylation rate constants show a semi-logarithmic dependence on DPE for both families of MFI materials, consistent with prior studies across various hydrocarbon and oxygenate reactions, because the electrostatic interactions that stabilize carbocationic transition states become less effective as acid sites become weaker. Furthermore, DFT-derived methylation barriers across all T-sites (normalized to the respective barrier on Al3+-substituted MFI) quantitatively follow a similar dependence on acid strength (DPE) as experimentally measured barriers. Individual rate constant ratios, and thus xylene product isomer selectivity, are independent of acid strength (DPE) and depend solely on the OSDAs used to crystallize T-MFI samples, consistent with DFT calculations, providing evidence that generalizes how Coulombic and hydrogen-bonding forces that are influential in determining SDA-framework interactions apply generally to any lattice-incorporated trivalent heteroatom.

As a probe reaction, toluene methylation is conducted under conditions of strict kinetic control with differential conditions (403 K, <2% conversion), distinct from conventionally studied conditions of industrial relevance wherein diffusion-controlled product-sieving occurs at higher temperatures (573–773 K) and conversions (>10%). The reactive intermediates governing toluene methylation rates across MFI voids of differing size were incompletely understood, as demonstrated by discrepancies between computational and experimental adsorption equilibrium and rate constants. We thus embarked on a mechanistic study of toluene methylation on two Al-MFI materials with intersection-dominant and channel-dominant acid site distributions to distinguish between computational proposals that suggest several pathways: (i) methylation by trimethyloxonium, (ii) concerted methylation with DME, (iii) stepwise methylation via surface methoxy groups, or (iv) the kinetically relevant formation of methoxy species. Active sites were found to be covered by species containing two carbon atoms, restricting the dominant pathways to concerted methylation or the kinetically relevant formation of surface methoxy species. The barriers for these pathways are computationally indistinguishable, but the DFT-predicted relative barriers (or selectivity) for forming o-xylene and p-xylene on these two samples differ significantly among mechanisms. Experimentally measured product selectivities were inconsistent with the concerted mechanism, in which transition states are situated farther from anionic centers localized within channels and occupy intersection voids regardless of T-site distributions, thereby attenuating influences of shape selectivity. Thus, surface methoxy formation must be kinetically relevant, and the methylation of arene rings by methoxy surface species governs observed product selectivity. Toluene adsorption from the gas phase reflects a net reaction step that displaces physisorbed DME molecules, evidenced by kinetic assessments of toluene adsorption equilibrium constants, ex-situ DME and toluene adsorption isotherms, and DFT-derived free energies for the displacement of DME by toluene. These physisorbed species form an intrapore solvent network that suppresses rates and sterically crowds transition states, leading to higher selectivity towards the smaller p-xylene isomer. We extended these conclusions by demonstrating that the observed effects are agnostic to the identity of the pore-occupying species that crowd transition states, as both physisorbed reactants present in excess (i.e., DME) and spectator molecules co-fed deliberately (i.e., n-pentane) alter reactivity and selectivity equivalently.

Following this mechanistic interpretation, a series of arene methylation reactions on porous materials of varying void size (TON, BEA, AFI, FAU, MCM-41) were performed to elucidate the tradeoffs between attractive and repulsive van der Waals forces and framework distortion penalties across a wide range of confining environments (0.55–3.0 nm). Methylation of different arenes forms transition states of varying size and structure (i.e., those forming toluene, xylenes (meta-, ortho-, para-), and 1,2,4-trimethylbenzene), resulting in finer variations in guest-host "fits" than can be accessed by studying a single reaction across different zeolite frameworks. Rate constants on zeolites are normalized by those on MCM-41 (a prototypical unconfined solid acid) to account for differences in the inductive electronic stabilization of transition states with varying numbers and positions of methyl substituents. By deriving an empirical parameter for the average difference in the host void diameter and guest critical diameter, we establish a single correlation between the "fit" of a guest-host complex, (Dvoid – Dcritical)/2, and the rate constant ratios that vary by nearly four decades due solely to confining void interactions. These considerations of electronic stability and the confining void shape and size permit fitting a single-valued function across all five distinct transition states and five aluminosilicates, according to the functional form predicted by a 12-6 Lennard-Jones potential. Through this work, we unify active site interactions governing van der Waals stabilization, entropic effects, and distortion of the inorganic framework into a tractable 1-dimensional potential that quantitatively describes the influence of confinement on reactivity. The reactivity of zeolite frameworks that possess multiple void environments (e.g., MFI, STF) are interpreted using this trend, developed for materials with a single characteristic Dvoid, enabling arene methylation kinetics to probe the distribution of active sites among distinct confining environments. This correlation provides predictive guidance for the selection of a zeolite framework with desired reactivity and selectivity by preferentially stabilizing transition states of varying sizes.

The research conducted in this dissertation has assessed synthetic strategies to place active sites within distinct local environments of zeolites to tailor desired reactivity and selectivity through orthogonal control of acid strength and the confining void environment. Arene methylation provides yet another reminder that selectivity among similarly sized and charged regioisomers is independent of acid strength, although rates depend semi-logarithmically on acid strength. Shape-selectivity conferred to differently sized methylated arenes is governed by the confining environment, whether across different zeolite framework topologies or within a given framework with biased active site distributions among different void environments. Solvent crowding of transition states provides an orthogonal strategy in which to alter catalytic reactivity while preferentially enhancing selectivity towards smaller products. This dissertation also illustrates how a comprehensive approach to synthetically vary active site compositions and distributions and measure kinetic rate constants across a family of zeolite materials permits coherent integration with computational simulations to characterize the structure and function of active sites within zeolites incisively, particularly for complex materials where direct structural characterization methods of active site distributions remain elusive.