

# Catalytic implications of confined solvent ensembles within Lewis acid zeolites

by  
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## Abstract

Lewis acidic zeolites are microporous crystalline materials that offer promise as catalysts for the activation and conversion of biomass-derived precursors in the liquid-phase due to their unique water-tolerance and synthetic versatility. The active site environment in zeolite catalysts is multifaceted in nature and is composed of a primary catalytic binding site, the secondary pore structure that confines such binding sites, and occluded solvent and reactant molecules that interact with adsorbed species. Moreover, Lewis acidic heteroatoms can adopt structurally diverse coordination that selectively catalyze different classes of chemical transformations and can be difficult to control synthetically or characterize spectroscopically. In this thesis, precise mechanistic interpretation of liquid-phase zeolite catalysis was realized through the development of synthetic, spectroscopic, and kinetic methods that decouple complex active site structures and probe the interactions that occur between confined active sites, solvent and reactant molecules, and adsorbed intermediates and transition states.

First, we show how hydrophobic Beta zeolites containing framework Sn atoms catalyze transfer hydrogenation reactions of cyclohexanone in a 2-butanol solvent 10x faster than their hydrophilic analogues. This rate enhancement stems from the ability of hydrophobic Sn-Beta to inhibit the formation of extended liquid-like 2-butanol oligomers and promote dimeric H-bonded 2-butanol networks. The ordered H-bonding solvent network present in hydrophobic Sn-Beta stabilizes transfer hydrogenation transition states to a greater extent than the liquid-like 2-butanol solvent present in hydrophilic Sn-Beta, giving rise to higher turnover rates on hydrophobic Sn-Beta. Additionally, reactant adsorption within hydrophobic Sn-Beta is entropically-driven by the breakup of intraporous solvent-solvent interactions, resulting in positive enthalpies of adsorption that are partially compensated by an increase in the solvent reorganization entropy. These results emphasize the ability of the zeolite pore to regulate the structure of confined non-aqueous H-bonding solvent networks, which offers an additional dimension to modulate adsorption and reactivity.

Next, we extend our studies to understand how different intraporous alcohol networks reorganize in response to adsorbate sterics and the presence of non-H-bonding co-solvents. Here, we find that first-order rates for methyl-cyclohexanone transfer hydrogenation are ~2-5x higher than for tert-butyl-cyclohexanone, but converge in the zero-order regime across all temperatures (333-393 K) in a bulk 2-butanol solvent. These results show that, while intrinsic bond-activation steps at the active site are largely independent of molecular functionalization of the ketone reactant, adsorption within

hydrophobic Sn-Beta is still driven by the breakup of intraporous solvent-solvent interactions. Furthermore, comparisons between bulk toluene or acetonitrile solvents, with 1 M 2-butanol as a reactant, show the significance of intraporous solvent for stabilizing kinetically-relevant species and the complex interdependencies between solvent and catalyst hydrophilicity. Apparent zero-order activation enthalpies and entropies increase with decreasing solvent polarity over hydrophobic zeolites indicating that the transition state is more tightly bound to the open Sn site when first-shell solvent molecules become more polarizing. Conversely, adsorption and activation entropies and enthalpies measured on hydrophilic zeolite in toluene and acetonitrile solvents are nearly identical to those measured in a bulk 2-butanol solvent, suggesting that the intraporous solvating environment in bulk, non-H-bonding co-solvents is similar to that observed when bulk 2-butanol is the solvent.

Finally, we exploit the ability of carbonyl groups to measure electric field differences arising from the different intraporous solvent structures through the vibrational Stark effect. By measuring infrared absorption spectra of Ti-bound acetone in Beta zeolites of varying framework hydrophobicity across a range of non-coordinating solvents, we find unique electric field differences arising from distinct solvation under nanoconfinement. Moreover, in the absence of intraporous solvent, we find a  $\sim 7 \text{ cm}^{-1}$  shift in the Ti-bound carbonyl stretching frequency. These results suggest that local differences in the Lewis acid site environment, which influence observed kinetics across reaction classes, arise from the synthetic protocol used to produce each material.

Taken together, the results of this thesis reveal how different solvent-mediated, non-covalent interactions control liquid-phase reactivity within porous, Lewis acid zeolite catalysts. It is our hope that the kinetic and spectroscopic approaches advanced here will provide a useful roadmap for further experimental investigations into the catalytic implications of confined solvent.

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