ABSTRACT

Kester, Philip M. Ph.D., Purdue University, May 2020. Hydrothermal synthesis methods to influence active site and crystallite properties of zeolites and consequences for catalytic alkane activation. Major Professor: Rajamani Gounder.

Zeolites are crystalline microporous solid acids composed of silica-rich frameworks with aliovalent Al heteroatoms substituted in crystallographically-distinct locations and arrangements, which generate anionic lattice charges that can be compensated by protons and extraframework metal cations or complexes that behave as catalytic active sites. Protons that charge-compensate Al are similar in Brønsted acid strength, yet differ in reactivity because their bound intermediates and transition states are stabilized by van der Waals interactions with confining microporous cavities, and by electrostatic interactions with proximal heteroatoms and adjacent protons. A diverse array of framework Al and extraframework H^+ site ensembles are ubiquitous in low-silica and low-symmetry zeolite frameworks (e.g., MFI, MOR), which cause measured turnover rates to reflect the reactivity-weighted average of contributions from each distinct site ensemble. The reactivity of distinct sites can be further masked by diffusion barriers often imparted by microporous domains and secondary reactions of primary products, which become increasingly prevalent as products encounter higher numbers of active sites during diffusion prior to egress from zeolite crystallites. Consequently, catalytic behavior often depends on zeolite material properties at orders-of-magnitude different length scales, which depend on the specific protocols used in their synthesis and crystallization.

In this work, CHA zeolites that contain only one symmetrically-distinct lattice site for Al substitution are used as model materials to decouple the effects of proton location and proximity in vibrational spectra and turnover rates for acid catalysis.

Interactions between proximal protons influence their equilibrium distribution among anionic lattice O atoms in $AlO_{4/2}^{-}$ tetrahedra, and result in temperature-dependent changes to vibrational frequencies and intensities of the asymmetric OH stretching region in infrared spectra measured experimentally and computed by density functional theory (DFT). Protolytic propane cracking and dehydrogenation, a catalytic probe reaction of the intrinsic reactivity of Brønsted acid protons, occur with turnover rates (748 K, per H^+) that are an order-of-magnitude higher on paired protons than isolated protons, resulting from entropic benefits provided to late carbonium ion-pair transition states by proximal protons. These results indicate that cationic transition states can be stabilized entropically through multi-ion interactions with lattice anion and cation sites. Precise interpretation and quantification of the reactivity of different types and ensembles of Brønsted acid protons in zeolites requires that protolytic chemistry prevails in the absence of secondary active sites or other kinetically-relevant processes, a requirement generally met for alkane cracking but not dehydrogenation on H-form zeolites. Propane dehydrogenation activation energies vary widely (by $>$100 kJ mol^{-1}) among H-form zeolites of different structure (MFI, MOR, CHA) and composition (Si/Al $= 10 - 140$) because reactant-derived carbonaceous deposits form in situ and catalyze alkane dehydrogenation under non-oxidative conditions through hydride transfer pathways. Contributions of reactant-derived active sites to propane dehydrogenation rates are quantified through a series of transient and steady-state kinetic experiments with co-fed alkene and dihydrogen products, and are found to depend on gradients in product pressures that are present in integral reactors under non-ideal plug-flow hydrodynamics. Propane dehydrogenation rates collected at initial time-on-stream and in the presence of co-fed H_2 solely reflect protolytic reaction events and can be used to interpret differences in the reactivity of distinct proton sites and ensembles for alkane activation catalysis. The reaction conditions identified here can be used to remove or suppress thee reactivity of carbonaceous active sites during catalysis, or to engineer the formation of organocatalysts on zeolite surfaces for selective dehydrogenation or hydride transfer reactions.

Synthetic strategies to decouple bulk and active site properties at disparate length scales, which are typically correlated in MFI zeolites crystallized hydrothermally, are developed by adding a second heteroatom and organic structure directing agent (SDA) to synthesis media. Crystallite size and morphology are independently varied from Al content by incorporating B heteroatoms into zeolitic frameworks, which generate protons that are catalytically irrelevant compared to those compensating Al, and NH_3 temperature-programmed desorption methods are developed to differentiate between these two types of proton sites. The siting of Al heteroatoms in distinct locations and ensembles is influenced by the decrease in cationic charge density among occluded SDAs, in cases where ethylenediamine is co-occluded with tetra-*n*-propylammonium cations. The co-occlusion of organic SDAs enables crystallizing MFI zeolites with different bulk properties but similar Al distributions, or with similar bulk properties and different Al distributions. MFI zeolites crystallized with these methods provide model materials that can be interrogated to decouple the effects of bulk and atomic-scale properties on acid catalysis, and open opportunities to exploit these material properties by designing active site ensembles and crystallite diffusion properties for catalytic chemistries that depend on coupled reaction-transport phenomena.