Title: Synthesis of Medium-Pore Brønsted Acid Zeolites with Tailored Active Site and Crystallite Properties and Their Application for Propene Oligomerization Catalysis

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Abstract

Brønsted acid zeolites can be synthesized in a wide range of topologies, each characterized by diverse void sizes, shapes, and micropore connectivity. The location of Brønsted acid sites (H^+-sites) within microporous voids of different size and shape, and the relative proximity of H^+-sites influences their reactivity. Additionally, the diffusion of reactant and product molecules through a given zeolite topology depends on micropore size, tortuosity, and connectivity. The coupled influences of reaction kinetics and intrazeolite reactant and product diffusion govern rates and selectivity for a plethora of zeolite-catalyzed reactions and underlie the well-established effects of "shape-selectivity". The independent effects of reaction and diffusion on rates and selectivity for a given reaction are often obfuscated by concomitant changes in the zeolite properties governing diffusion (e.g., crystallite size) and reactivity (e.g., H^+-site density or proximity) in zeolite materials synthesized with conventional methods. Herein, we develop synthetic methods to decouple H^+-site density, proximity and crystallite size in medium-pore, 10-membered ring (10-MR) zeolites, and evaluate the independent effects of these material properties on the kinetic and transport phenomena that govern propene oligomerization catalysis.

Among synthetic methods to influence H^+-site proximity in zeolites, varying the charge-density and ratio of structure directing agent (SDA) cations that compensate anionic charges in frameworks at Al centers has been reported to influence H^+-site proximity in MFI and CHA zeolites of fixed H^+-site density. Changes in H^+-site proximity can be evaluated using Co^{2+} cations to selectively titrate and quantify subsets of proximal H^+-sites (H^+-site pairs); conditions to perform such titrations were identified for MEL zeolites. The fraction of paired H^+-sites changed concurrently with changes in framework Al content in MEL zeolites synthesized using a single organic SDA (OSDA), tetrabutylammonium hydroxide (TBA^+). Synthesis of MEL with mixtures of TBA^+ and Na^+ as an inorganic SDA (ISDA), at fixed total SDA and Al content, allowed the fraction of paired H^+-sites to be systematically varied in MEL zeolites of fixed H^+-site density,

reflecting changes in the location and quantity of charge-balancing SDAs with Na^+/TBA^+ ratio. The energetic favorability of SDA occlusion in MEL was also evaluated with density functional theory (DFT). In contrast to MEL, occluded SDA content in TON zeolites crystallized with varied OSDA (1,6-diaminohexane, or 1,8-diamooctane) and K^+ content, at fixed total SDA content, was invariant with K^+/OSDA ratio, reflecting a different mechanism of SDA occlusion in TON. These findings provide an approach to influence H^+-site pairs in 10-MR zeolites of fixed H^+-site density and demonstrate the dependence of SDA occlusion on zeolite topology.

The independent influences of H^+-site and crystallite properties on rates and selectivity of propene oligomerization to heavier alkenes in a representative medium-pore zeolite topology (MFI) were explored by interrogating suites of samples crystallized with independently varied H^+-site density (0.3–5.7 H^+/u.c.), proximity, and crystallite size (0.03–2.65 μm) over a wide range of reaction conditions (483–523 K, 7–615 kPa C_3H_6). Dimerization rates (per H^+) decreased with increasing crystallite size among MFI materials synthesized with fixed H^+-site density (0.3 or 1.3 H^+/u.c.), revealing the strong and ubiquitous influence of intrazeolite diffusion limitations on measured dimerization rates. Weisz-Prater criterion analyses, in conjunction with dimerization rate transients upon step-changes in reaction conditions, indicate that these intrazeolite diffusion limitations arise from a product-derived organic phase occluded within zeolitic micropores during propene oligomerization catalysis, which restricts intrazeolite diffusion by lowering the effective diffusivities of propene and product alkenes. This occluded organic phase becomes heavier in composition at higher propene pressures and lower reaction temperatures, which favor chain growth over β-scission, resulting in more severe intrazeolite diffusional constraints. The composition of the occluded organic phase was also found to depend on H^+-site density in MFI zeolites. Rate constants (per H^+) of dimerization and trimerization were higher on MFI samples of dilute H^+-site density, resulting in faster growth of heavier oligomer products and consequently lower effective diffusivities compared to MFI samples of higher H^+-site density. The convoluted influences of reaction and diffusion on measured propene oligomerization rates result in apparent reaction orders that deviate from the first-order dependence of rates on propene pressure expected in the limit of strict kinetic control. Accounting for the coupled influences of reaction and diffusion on propene oligomerization rates and the influence of H^+-site density on intrazeolite diffusion, rationalizes contradictory conclusions among prior reports about the dependence of oligomerization rates on H^+-site density, proximity, and crystallite size, which did not identify or consider the influences of intrazeolite diffusion in their interpretations of rate data.

Finally, we explore the consequences of zeolite pore size and connectivity for reactivity and intrazeolite diffusion during propene oligomerization by interrogating H-zeolites of different topologies. Intrazeolite diffusional constraints are imposed by an occluded organic phase and influence dimerization rates among medium-pore zeolite topologies (MFI, MEL, TON), but such constraints are alleviated on large-pore zeolite topologies (FAU, MOR, *BEA), reflecting the slower growth and faster diffusion of heavy oligomer products in large-pore zeolites. Among medium-pore zeolites, the composition of the occluded organic phase, and consequently the effective diffusivities of propene and product alkenes, is influenced by void size. Analysis of product selectivity on zeolites of different pore size and connectivity (TON, MOR, MFI) reveals that TON restricts the growth of heavier oligomer products, resulting in effective diffusivities that are higher on TON compared to MFI, and are relatively invariant with propene pressure and H^+-site density. Together, the findings herein demonstrate the ability of slow-diffusing products to impose intrazeolite diffusional constraints on other products during alkene oligomerization catalysis, and reveal the critical influence of reaction conditions, H^+-site density, and micropore size on the composition of this occluded organic phase, and consequently intrazeolite diffusional constraints. Ultimately, this work demonstrates how kinetic studies performed on well-defined zeolite materials can reveal important changes in reaction and diffusion phenomena, which are otherwise inextricably convoluted, and provides a framework through which such effects can be assessed for other zeolite-catalyzed molecular chain-growth reactions.