ABSTRACT

The catalytic conversion of ethene, which can be derived from biogenic sources (e.g., via ethanol dehydration) or shale gas (e.g., via ethane dehydrogenation), through oligomerization routes on Brønsted acid zeolites enables the conversion of chemical feedstocks with smaller carbon footprints into larger alkenes that are useful as chemical precursors and transportation fuels. Rates of ethene oligomerization reactions and of side reactions that determine product selectivity and influence deactivation rates depend not only on the size and shape of zeolite voids, which influence rate constants, but also on intracrystalline diffusional hurdles that lead to concentration gradients of alkene oligomers. This study describes methods of characterization and analysis to assess intracrystalline diffusional constraints within MFI zeolite crystallites with a range of proton site density (0.14–0.75 H^+ per MFI intersection), crystallite size, and the extent to which active protons are replaced with inert Ca^{2+} cations (0.12–0.30 Ca^{2+}/Al) present as $Ca(OH)^+$ species. In doing so, this work provides a unified mechanistic framework for understanding how site reactivity and void structure combine to determine ethene reaction rates, selectivities, and deactivation tendencies.

The severity and kinetic consequences of concentration gradients within a zeolite crystallite are uniquely determined by a Thiele modulus, the dimensionless parameter that gives the ratio of characteristic rates of reaction to diffusion processes. Reaction rates are proportional to the density of active H^+-sites ($[H^+]$) and the kinetic rate constant, while diffusion rates are proportional to the effective molecular diffusivity (D_e) and inversely proportional to the square of the characteristic diffusion pathlength (the radius, R, for spherical crystallites), which combine to give the characteristic diffusion time (R^2/D_e). Under the conditions of practical ethene reactions, bound ethoxide intermediates are present at saturation coverages; they occupy some of the voids, thus interfering with diffusion and causing longer characteristic diffusion times than for voids without bound ethoxides. These characteristic diffusion times among zeolite samples of a given framework structure can be compared from transient uptakes of an unreactive probe molecule (2,2-dimethylbutane (22DMB)) to determine a structural Thiele parameter, $([H^+]\times R^2/D_e)^{1/2}$, that solely reflects the structural properties of each catalyst.

Transient uptake data at different extents of void occupancy by 22DMB (0.02–0.4 per MFI intersection) were used to determine effective diffusivities relative to those at zero occupancy ($D_e/D_{e,0}$). These ratios decreased with increasing occupancy as a result of interference by adsorbed

species with trends accurately described by percolation theory concepts for Bethe lattice models with nodes of four-fold coordination characteristic of MFI intersections (the lattice nodes). The translation of these R^2/D_e values to reaction conditions at saturated ethoxide coverages assumed that such intermediates obstruct transport in a manner similar to the 22DMB molecules adsorbed during transient uptakes. These characteristic diffusion times were estimated, through interpolation or extrapolation, of $D_e/D_{e,0}$ values measured at 22DMB occupancies equivalent to those for ethoxides at all intersections that contain a H^+ site for each MFI catalyst. The replacement of some of the H^+ sites by $Ca(OH)^+$ cations also introduces obstacles to transport. Indeed, the $D_e/D_{e,0}$ values measured for a given Ca-MFI and its parent H-MFI sample were similarly affected by the presence of a given number of adsorbed 22DMB or $Ca(OH)^+$, consistent with their similar effectiveness in blocking the diffusion of molecules through an occupied MFI intersection. $D_e/D_{e,0}$ values and H^+ densities, measured by selective NH_3 titration of H^+ sites in H-MFI and Ca-MFI, were combined to give structural Thiele parameters for all samples and to compare the severity and kinetic consequences of intracrystalline oligomer concentration gradients among these MFI catalysts.

The differences in the structural Thiele parameters for these samples were able to account for their different ethene conversion turnover rates (per H^+), the relative amounts of products formed by primary and secondary reactions, and their respective deactivation rate constants for all H-MFI and Ca-MFI samples; the elucidation of these previously misinterpreted observations required, however, the elimination of bed-scale temperature gradients that are ubiquitous artifacts in rate and selectivity data for exothermic reactions. The intracrystalline concentrations of larger alkenes increased with increasing magnitude of the structural Thiele parameters; this led, in turn, to diffusion-enhanced β-scission rates and to products with the binomial distribution of chain lengths expected from extensive oligomerization and β-scission events. These oligomer concentration gradients also favored hydrogen transfer reactions among oligomers, as evident from higher ratios of alkanes to alkenes in products and to a greater tendency to form dienes and arenes that act as precursors to unreactive organic residues. As a result, deactivation rate constants were higher on samples with larger structural Thiele parameters. Samples with larger structural Thiele parameters also gave higher ethene conversion turnover rates (per H^+), a trend seemingly contrary to the usual decrease in rates for larger Thiele parameters for reactions where the prevalent intracrystalline gradients are those of reactants. In this instance, oligomer (instead of reactant) gradients lead to a preference for ethene reactions with larger alkenes instead of its reaction with another ethene reactant. C-C coupling in ethene-oligomer steps involves larger and more stable carbenium-ion transition states than for ethene-ethene reactions, because of the greater proton affinity and more effective van der Waals contacts with confining voids for the larger transition states. As a result, ethene is converted via faster reactions as oligomer concentrations increase within MFI crystallites, leading to higher ethene conversion turnover rates (per H^+) for catalysts with larger structural Thiele parameters.

These observations and mechanism-based analyses of the inextricable coupling between chemical reactions and transport processes within microporous solids demonstrate how ethene conversion turnover rates, oligomer and hydrogen transfer selectivities, and deactivation rates on MFI catalysts depend on intracrystalline product concentrations and the diffusional enhancement of their secondary reactions. Such a unifying assessment of seemingly disparate features of these reactions replaces the seemingly ad hoc separate proposals for each of these effects in terms of the prevalence and involvement of H^+ sites with distinct reactive properties or of extraneous sites introduced by extraframework Al structures or $(CaOH)^+$ moieties and their ability to mediate or suppress certain reactions. The conclusions and methods are shown here for ethene reactions on MFI frameworks, but they apply generally to coupled reaction-diffusion processes in zeolite frameworks.