Title: Synthetic Methods to Manipulate Spatial Distributions of Aluminum in Zeolite Crystallites and Consequences for Alkene Oligomerization Catalysis.

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ABSTRACT

Zeolites are microporous, crystalline aluminosilicates widely used in catalysis and separation. The substitution of Si^{4+} with Al^{3+} ($[AlO_{4/2}]^-$) creates a charge imbalance that can be compensated by a metal cation or complex (M^{n+}) or a Brønsted acid proton (H^+) within microporous voids and at external surfaces. Brønsted acid sites in aluminosilicates of diverse topologies have similar acid strength, but the diffusion of reactants and products can vary depending on the micropore size, tortuosity, and connectivity. The coupled effects of H^+-site reactivity and diffusional constraints imposed by the inorganic zeolitic framework can be assessed by the diffusion parameter, which depends on the bulk proton density ($[H^+]$) and the diffusion pathlength (L), derived from the Thiele modulus expression that relates reaction and diffusion rates within porous catalysts. This motivates synthetic approaches to control zeolite properties that influence diffusion and reactivity such as crystallite size and proton density. Prior synthetic methods have tried to minimize the diffusional constraints by decreasing the diffusion pathlength (L) by synthesizing zeolite crystallites at the nanometer scale or by increasing the effective diffusivity (D_e) by synthesizing hierarchical materials. However, these synthetic approaches may simultaneously influence multiple zeolite properties, such as the spatial distribution of acid sites throughout crystallites or at extracrystalline surfaces, convoluting the influence of these properties on the rates, selectivity, and deactivation of acid-catalyzed reactions.

Two types of spatial distribution of acid sites could be present within a zeolite. The first is the fraction at unconfined extracrystalline surfaces, and this property is often convoluted with the effect of crystallite size. Assuming acid sites are evenly distributed through the crystallite, as the crystallite size increases, the fraction of external acid sites decreases because the surface area-to-volume decreases. The second type of spatial distribution of acid sites is referred to as "zoning"—a concentration gradient of active sites from the external surface to its core, or vice versa. This

type of spatial distribution of acid sites is challenging to quantify accurately. “Zoning” effects may also occur inadvertently during zeolite synthesize using conventional methods. In this work, we synthesize zeolitic materials (i.e., MFI) with controlled spatial distribution of acid sites independently of crystallite size and H^+-site density to study their effects on propene oligomerization catalysis. A core@shell synthesis approach was used to passivate external MFI zeolite surfaces by an inert shell (Si-MFI) of short thickness relative to the size of the core crystallite. Although other passivation treatments can cause pore blockage or narrowing, transient sorption measurement showed no additional diffusional limitations were introduced by the growth of the Si-MFI shell. Propene dimerization rates (per H^+, 503 K, 16 – 620 kPa C_3H_6) and transient behavior upon pressure step-changes persist reveal the influence of intrazeolite diffusional constraints on the Al-MFI core due to heavier oligomer products that accumulate inside micropores. On the contrary, dimerization rates did not reach a pseudo-steady-state on Al-MFI@Si-MFI and required high temperature caused by the formation of surface carbonaceous deposits in the absence of acid sites that otherwise assist in the cracking and desorption of coke precursor species. Thus, the passivation of the external surface imposes a transport limitation at the surface due to a carbonaceous layer that forms during the reaction, restricting the diffusion of products out of crystallites and shifting the selectivity towards a lighter product composition.

An inverted core@shell (Si-MFI@Al-MFI) material was also synthesized to investigate the effect of the spatial distribution of acid sites on the diffusion parameter, where the acid sites are preferentially located at the external surface and the core is inert (i.e. Si-MFI). The spatial distribution of acid sites was varied by growing an Al-MFI shell on a siliceous core and maintaining a similar bulk crystallite size. Mesitylene benzylation was used to quantify the fraction of external acid sites. Differences in measured propene dimerization rates (per H^+) and product selectivity can be rationalized considering the thickness of the Al-rich shell in the core@shell material to an Al-MFI sample of similar crystallite size, evincing the dominant influence of the diffusion parameter on propene oligomerization catalytic behavior. Overall, this study demonstrated how zeolite synthetic methods can be used to isolate the effects of spatial distributions of Al from crystallite size and H^+-site density and provide guidance for zeolite catalyst design efforts to control structural properties that influence reactions driven by coupled kinetic-transport phenomena.