MITIGATING THE EFFECTS OF DIFFUSION LIMITATIONS IN ZEOLITE CATALYSIS

Jeffrey D. Rimer*, Yufeng Shen, Thuy T. Le
University of Houston
Houston, TX 77204

Abstract

Micropore topology and crystal size are two independently adjustable properties that govern the internal mass transport limitations of zeolite catalysts. Deciphering the relative impact of each factor on catalyst performance is often nontrivial owing to the inability to synthesize zeolites with predetermined physicochemical properties. In this talk, comparisons will be made among zeolites MFI (ZSM-5), MEL (ZSM-11), and CHA (SSZ-13 and SAPO-34) over a range of physicochemical properties. Zeolites were prepared with well-defined crystal sizes to elucidate the effects of diffusion path length versus topology on catalyst lifetime and selectivity. For these studies, we selected the methanol to hydrocarbons (MTH) reaction to assess the impact of design variables on the hydrocarbon pool (HCP) mechanism. Our findings reveal that variations in framework topology lead to marked differences in the evolutionary behavior of HCP species within the zeolite pores. We will discuss how diffusion limitations imposed by tortuous channels and/or long diffusion path lengths can have significant effects on MTH selectivity and HCP speciation. Moreover, we will discuss synthesis strategies to mitigate intracrystalline diffusion limitations using commercially viable pathways to tailor zeolite properties for improved catalytic performance.

Keywords

zeolite, ZSM-11, ZSM-5, SAPO-34, SSZ-13, methanol to hydrocarbons, heterogeneous catalysis

Introduction

Methanol to hydrocarbons (MTH) is an increasingly utilized industrial process as the world economy gradually trends away from crude oil dependency with concomitant increases in the demand for gasoline and petroleum derived products.[1, 2] MTH is a central step in many fuel and olefin production processes that utilize alternative carbon sources, such as natural gas, biomass, and coal.[3] Subsets of the general MTH process include methanol to gasoline (MTG), methanol to olefins (MTO), and other variations of the aforementioned reactions.[4] Zeolite catalysts play an important role in directing and improving these industrial processes, yet only zeotype SAPO-34 (CHA) and zeolite ZSM-5 (MFI) are reported to be used commercially.[5-7] A ubiquitous problem of these and other catalysts in hydrocarbon processing reactions is deactivation due to coking.[8] To this end, numerous studies have focused on elucidating structure-deactivation relationships for zeolite catalysts in MTH reactions.[9-14] The judicious selection of framework topology can minimize catalyst deactivation, while also impacting MTH reaction selectivity and catalyst activity.[15-17] Prior studies often compare zeolite frameworks with significant differences in pore size, cage/intersection size, and/or pore dimensionality and connectivity between samples; however, direct comparison between two very similar zeolite frameworks can be challenging given the difficulty of controlling additional physicochemical properties that influence catalyst performance, such as crystal size and morphology as well as acid site density and distribution. As such, when comparing two or more different zeolite frameworks, it is imperative to synthesize

* To whom all correspondence should be addressed: jrimer@central.uh.edu

catalysts with fixed properties while allowing for only a single variable to be systematically altered.

The effect of zeolite crystal size in MTH reactions has been studied for MFI[18, 19] and CHA[20-22], while similar investigations of MEL[23] are relatively scarce. The general conclusion in these studies is that smaller crystal size enhances the time-on-stream (TOS) lifetime of catalysts, consistent with a concomitant reduction in the internal mass transport limitations.[24] Ryoo and coworkers successfully synthesized 2-dimensional MFI nanosheets with [010] dimensions of ca. 2 nm (*i.e.*, on the order of a unit cell), and showed by comparison with a conventional ZSM-5 catalyst that the former dramatically extended the catalyst lifetime.[25] Bleken et al.[15] compared the lifetime of ZSM-5 and ZSM-11 catalysts in MTH reactions, showing an approximate 3-fold increase in lifetime for ZSM-11; however, catalyst samples used in their study exhibited disparate crystal sizes, rendering the direct comparison of diffusion path length complex. Bhan and coworkers[18] provided a systematic study of ZSM-5 crystal size effects in MTH reactions, showing that the selectivity towards light olefins (notably ethene) decreases with decreasing catalyst size, leading to an associated increase in the selectivity towards heavier aliphatic and aromatic products. In their study, Bhan attributed the effect of crystal size to differences in the length of pores across the zeolite particle, which impacts the internal diffusion of product molecules and the concentration of the HCP species. One of the challenges encountered during the preparation of catalysts with large variations in crystal size is the unintended alteration of other properties, such as the Si/Al ratio, which can have a notable impact on catalyst performance.[26] Indeed, it can be challenging to simultaneously tailor a single physicochemical property of the catalyst during synthesis, while holding all other properties constant, in order to properly evaluate structure-performance relationships.

Results and Discussion

The material to be presented in this talk will be drawn primarily from three publications [27-29]. Our work, in collaboration with the Bhan Group (U. Minnesota) and the Weckhuysen Group (U. Utrecht), has led to advancements in our understanding of structure-property-performance relationships in MTH catalysis. The preparation of zeolites with varying crystal size and acid site density has allowed for the determination of appropriate descriptors for evaluating catalyst performance with respect to lifetime and selectivity. For example, the determination of internal diffusion through the measurement of D/R^2 values, as shown in Figure 1, where D is the diffusivity and R is the average dimension of zeolite crystals. We observe distinct trends of increasing catalyst lifetime with increasing D/R^2, which highlights the importance of synthesizing materials with reduced crystal size. Moreover, in this talk we will discuss contributions to the internal diffusion, D, that can be attributed to defects in zeolites, which is often overlooked when reporting structure-performance relationships. In this talk, catalytic studies will be presented along with descriptions of the syntheses and high resolution characterization techniques that were performed in order to gain insight into MTH reactions and methods of tailoring catalyst performance.

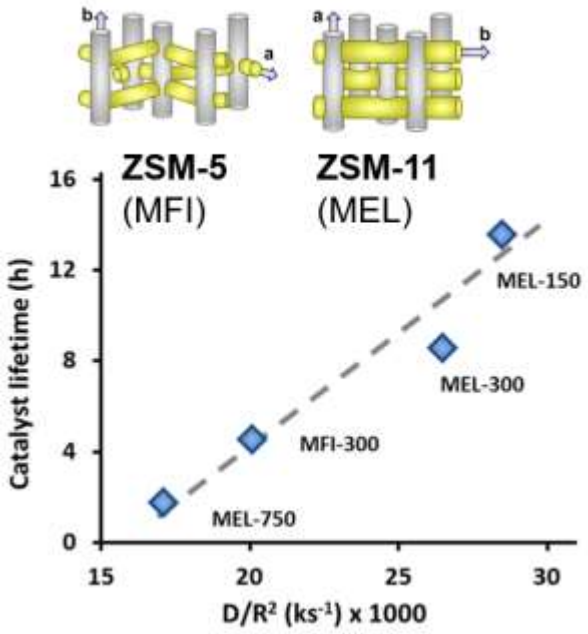

Figure 1. Time-on-stream lifetime of ZSM-11 (MEL) and ZSM-5 (MFI) catalysts of various crystal sizes (150, 300, 750 nm) in MTH reactions at 350 °C and WHSV = 9 h^{-1}, plotted as a function of characteristic diffusion rates.

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