

A Mechanistic Basis for the Effects of Crystallite Size on Light Olefin Selectivity in Methanol to Hydrocarbon Conversion on MFI

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Introduction

Methanol to hydrocarbons (MTH) conversion is the final processing step in converting alternative carbon-based feedstock such as coal, natural gas, and biomass, to energy carriers and petrochemicals, such as light olefins, which are widely used in chemical industry as raw materials. Catalytic conversion of methanol (or dimethyl ether (DME), its dehydration product) on zeolites proceeds via an indirect “hydrocarbon-pool” mechanism in which unsaturated hydrocarbon species act as scaffolds for C-C bond formation. [1,2] Isotopic, chemical transient, and DFT studies suggest that olefins and aromatics comprise this “hydrocarbon-pool” and form two distinct methylation/cracking cycles. Product distribution in MTH can be rationalized as an effect of relative propagation of the olefins-based and the aromatics-based catalytic cycles. [3] In this work, we show that the selectivity of MTH towards ethene and total light olefins increases with increasing crystallite size of MFI because intra-crystalline residence time of MBs increases as a consequence of increased transport restrictions, which enables these MBs to undergo multiple methylation/dealkylation reactions before exiting the crystal.

Materials and Methods

Five MFI samples with varying crystallite sizes were investigated in this study: 2nm-MFI, 40nm-MFI, 500nm-MFI, 2 μ m-MFI, and 17 μ m-MFI. The 500nm-MFI sample was silylated 1 – 3 times with tetraethyl orthosilicate (TEOS) to obtain three silylated MFI samples: Si-MFI-1x, Si-MFI-2x, and Si-MFI-3x. All catalytic reactions were carried out in a packed-bed reactor at 623 K and 60 kPa DME pressure. DME space velocity was varied to achieve the desired DME conversion. Reaction effluents were analyzed using an online GC-MS equipped with a flame ionization detector. Transport restrictions in the silylated samples were described using 2,2-dimethylbutane (DMB) adsorption uptake measurements at 298 K and 20 kPa DMB pressure, and an ‘effective’ crystallite size was calculated.

Table 1. Zeolite samples used in this study

| Catalyst | Si/Al ^a | SiO ₂ deposited ^b (wt%) | Crystallite size (nm) |
|----------------|--------------------|--|--------------------------|
| 2nm-MFI | 87.5 | - | 2 ^c |
| 40nm-MFI | 72.0 | - | 40 ^c |
| 500nm-MFI | 42.6 | - | 500 ^d |
| Si-MFI-1x | 45.8 | 7 | 1250 ^f |
| 2 μ m-MFI | 60.0 | - | 1750 ^d |
| Si-MFI-2x | 47.6 | 12 | 5200 ^f |
| 17 μ m-MFI | 38.0 | - | 17000 ^c |
| Si-MFI-3x | 49.5 | 16 | 17600 ^f |

^a from ICP-OES elemental analysis

^b assuming SiO₂ is the only Si species deposited

^c from reference [5]

^d from SEM analysis

^f from DMB adsorption uptake measurements

Results and Discussion

Table 1 shows the silicon to aluminum ratio (Si/Al) and the ‘effective’ crystallite size of all the zeolite samples

used in this study. Light olefin selectivity, for the reaction of DME at 623 K and 46 – 59 % DME conversion, increased monotonically from 22.0 % in 2nm-MFI (~ 2 nm crystallite size) to 46.5 % in 17 μ m-MFI (~ 17 μ m crystallite size). The ‘effective’ crystallite size of silylated MFI samples, relative to the parent zeolite (500nm-MFI with ~ 500 nm crystallites), was calculated from DMB adsorption uptake curves at short contact times assuming spherical particles and a simple Fickian diffusion model. Light olefin selectivity, for the reaction of DME at 623 K and at 46 – 59 % net DME conversion, increased from 33.2 % in the parent zeolite to 49.2 % in a sample that had undergone three silylation treatments and showed the slowest uptake of DMB.

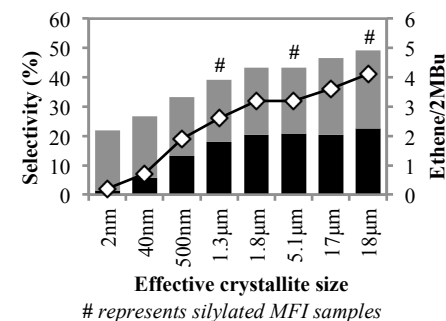


Figure 1. Ethene selectivity (■), propene selectivity (▒), and Ethene/2MBu (◇), as a function of ‘effective’ crystallite size.

Figure 1 shows that ethene and total light olefin selectivity increases monotonically with an increase in the ‘effective’ crystallite size for all zeolite samples used in this study, irrespective of their provenance. We postulate that this increase is due to an increase in (i) the concentration of MBs inside the zeolite pores, and/or (ii) the intra-crystallite residence time of MBs. Both these effects enhance the propagation of aromatics-based catalytic cycle, which enables the MBs present inside the zeolite pores to interact with multiple Brønsted acid sites and undergo multiple aromatic methylation/dealkylation reactions whilst producing a light olefin during each catalytic cycle. Enhanced propagation of the aromatics-based catalytic cycle is substantiated by a monotonic increase in Ethene/2MBu (ratio of synthesis rates of ethene and 2-methylbutane + 2-methyl-2-butene), a descriptor of the relative extent of propagation of the aromatics-based and the olefins-based catalytic cycles [4], with the ‘effective’ crystallite size as depicted in Figure 1. Aluminum content of the zeolite samples also has a similar effect on the light olefin selectivity as the crystallite size.

Significance

Ethene selectivity is enhanced in zeolite samples with larger diffusion limitations. Macroscopic variables such as the crystallite size and aluminum content change the selectivity of MTH conversion on zeolites and we provide a mechanistic basis for these effects.

References

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