Morphology Induced Shape Selectivity in Zeolite Catalysis

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Introduction

In this contribution, we outline a new concept within zeolite shape selectivity. The SUZX4 zeolite, which has two interconnected channel systems of distinctly different geometric size, has been studied as catalyst for the conversion of methanol to hydrocarbons. By using bulk X-ray diffraction analysis, selected area electron diffraction (SAED), and simulations of crystal growth, we demonstrate that the shape selectivity of SUZX4 during the reaction is determined by crystal morphology, not by framework topology. Crystal facets terminated exclusively by one of the two channel systems are preferentially exposed, thereby leading to morphology induced shape selectivity.

Materials and Methods

Several batches of SUZX4 catalysts were synthesized according to a published procedure [1]. Briefly, a clear solution of 0.4 g Al wire (Sigma-Alderich), 3.3 g KOH and 50.6 g water was prepared. To the resulting solution, 7.93 g TEAOH (25 wt % in water) and 18.23 g LUDOX AS-40 were successively added under stirring. The resulting gel with a composition 7.92 K2O : Al2O3 : 16.21 SiO2 : 1.83 TEAOH : 500 H2O was transferred into a 40 ml Teflon lined stainless steel autoclaves and crystallized in an oven with an inset that tumbles the autoclaves (37 rpm) for 3 to 7 days at 160 °C. The resulting SUZX4 catalyst was recovered by filtration, washed using distilled water, and dried at 60 °C overnight. The organic template was removed after calcination 3 × 2 hours with 1M NH4NO3 at 70 °C, and calcining in air at 550 °C to desorb ammonia. The obtained materials were characterized using XRD, SEM, TEM, FT-IR, N2 sorption and NH3-TPD. The catalytic performance of SUZX4 in the MTH reaction was investigated using 50 mg of the catalyst in a fixed bed reactor (i.d. 10 mm), at 400 °C and WHSV = 2 g·h⁻¹. Conversion and selectivity were determined using an online GC. Growth of SUZX4 crystal was simulated from the arrangement of atoms in the unit cell using the BHDF theory of the Materials Studio 4.2 software.

Results and Discussion

A characteristic feature of the SUZ-4 crystals is the distinct needle shape morphology. Typical needles are 2-5 µm long and 50-70 nm wide. The SUZ-4 (SZR topology) has a three-dimensional pore system consisting of medium (10-ring, 4.1 × 5.2 Å, viewed along [001]) and small (8-ring, 4.8 × 3.0 Å, viewed along [110] and 4.8 × 3.2 Å, viewed along [010]) pores. The topology of SUZ-4 contains a combination of the structural elements of SAPO-34, ZSM-5, and ZSM-22 and it is therefore relevant to compare the shape selectivity of such catalysts during the MTH reaction (Figure 1, left) [2]. Despite the presence of 10-ring channels in the framework, the shape selectivity of SUZ-4 is very similar to SAPO-34, for which the 8-ring windows control the diffusion of molecules. The catalytic test results thus suggest that the selectivity of SUZ-4 is controlled by the smaller 8-ring windows. This is unexpected, as it is reasonable to assume that the diffusion of product molecules is enhanced through the 10-ring channels, thereby overshadowing the contribution of the 8-rings. A combination of TEM imaging and selected area electron diffraction (SAED) analysis, and crystal growth simulations, reveal unambiguously that the 10-ring channels are oriented along the c direction i.e. along the needles, and the 8-ring channels are perpendicular. Thus, the only access to the 10-rings is via the ends of the needles, whereas the external sides of the needles are covered by 8-ring pores. The shape selectivity of SUZ-4 is therefore induced by the crystal morphology which dictates the topological expression.

Figure 1. Left: Product distribution of the methanol to hydrocarbons reaction over ZSM-5, ZSM-22, SUZ-4 and SAPO-34 catalysts, at full conversion, 400 °C and WHSV = 2 g·h⁻¹. Right: TEM image of a SUZ-4 crystal lying on a gold coated lacy carbon film. The inset shows the selected area electron diffraction pattern of the shown area. The row of diffraction spots parallel with the needle morphology is consistent with the 7.46 Å axis of SUZ-4. The scale bar represents 100 nm.

Significance

Obviously, the concept of morphology induced shape selectivity as presented herein may be extended to different framework topologies and should be added to the conceptual toolbox in zeolite synthesis and shape selective catalysis.

References