

The relation between a non-uniform catalytic behavior of ZSM-5 crystals and their crystal morphology as revealed by a combination of micro-spectroscopy and FIB/EBSD

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Introduction

Zeolites find widespread use in chemical industry due to a unique combination of well-defined framework and acid properties. Many studies have been performed to address the molecular processes taking place in the pores of the zeolite crystals to obtain a thorough understanding of the structure-function relationships. However, the complex structure of zeolite crystals, often comprised of different subunits, imposes difficulties in the interpretation of experimental results, as the interfaces of these subunits may constitute diffusion boundaries and making certain regions of the crystals inaccessible. Over the past years, several methods have been proposed to unravel the intergrowth structure of zeolite crystals, including optical and interference microscopy. In this work, the space- and time-resolved catalytic activity of large zeolite ZSM-5 crystals is related to its complex crystal structure and pore morphology. Using optical and fluorescence micro-spectroscopy during the oligomerization of various styrene derivatives, a non-uniform catalytic behavior is observed, showing differences in product formation, distribution and reactivity in distinct regions within one zeolite crystal. Concurrent Focused Ion Beam (FIB) milling experiments in combination with Electron Backscatter Diffraction (EBSD) allow determination of the crystallographic axis in distinct regions of the crystals, i.e. the orientation of the zeolite pore network.

Materials and Methods

The ZSM-5 crystals (100x20x20 μm) used for this study consist of 6 different building blocks. A Si/Al ratio of 17 was determined by X-ray fluorescence spectroscopy. The acid form of the zeolite was obtained by triple ion-exchange using 10 wt% ammonium nitrate and subsequent calcination at 723 K. Styrene derivatives were used as received (Acros Organics and Aldrich). More information on the micro-spectroscopic techniques can be found elsewhere [1,2]. EBSD measurements were carried out using a Scanning Electron Microscope FEI Nova Nanolab600 equipped with an EBSD detector (OXFORD-HKL Norlys II) and ion source. Furthermore, ion milling was performed with the beam parallel to the surface of interest. OXFORD-HKL Channel 5 EBSD software was used for indexing.

Results and Discussion

After exposure of the zeolite crystals to styrene derivatives at elevated temperature (373 K), a non-uniform coloration behavior is observed (Figure 1). Furthermore, as revealed by optical micro-spectroscopy, the edge and main body of the crystals show a distinct product distribution, i.e. mainly dimeric carbocations are present in the edges of the crystals whereas

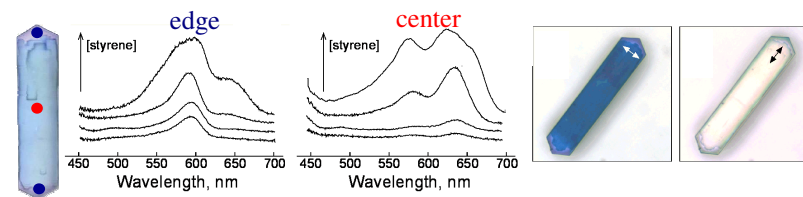


Figure 1. Optical microphotograph of the zeolite crystal after oligomerization with 4-methoxystyrene at 373K and corresponding optical absorption spectra of the edge and main body of the crystal at different styrene concentrations. Optical images of the crystals taken with polarized light (indicated by the arrows) are shown on the right-hand side.

dimeric and trimeric carbocations, with absorptions around 585 and 635nm respectively, are the predominant species in the main body of the crystal. Optical absorption measurements using polarised light reveal that the product molecules have a specific orientation within the zeolite crystal as the coloration vanished completely when the light is polarised parallel to the crystals long axis [1,2]. From EBSD measurements it is evident that this molecular alignment occurs within the straight pores of the zeolite, as indexing of diffraction patterns measured at different positions on the crystal reveals the orientation of the crystallographic b-axis, coinciding with the straight pore orientation [3]. This is shown in Figure 2, where the patterns and pore orientation in different regions of the crystals are presented.

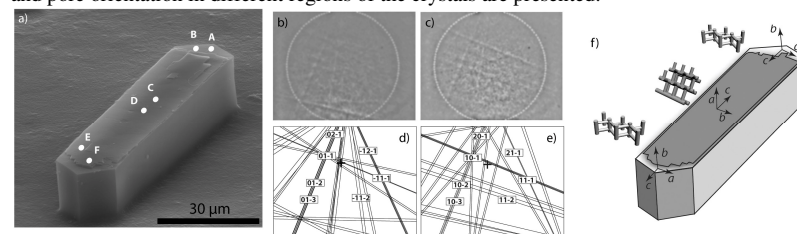


Figure 2. SEM image of the ZSM-5 crystal (EBSD spots are marked) and the diffraction patterns from spot A(edge) and D(center) on the crystal together with the indexed patterns. The crystal orientation and pore orientation obtained after indexing is shown on the right-hand side.

Significance

ZSM-5 is one of the most widely used zeolite catalysts in industry. Therefore, it is very important to get a fundamental understanding on how its structural features renders into catalytic function, down to the molecular level, in a space- and time-resolved manner.

References

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