

# Relating Pore Structure to Activity at the sub-Crystal Level: an Electron Backscatter Diffraction and Fluorescence Microscopy Study

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## Introduction

In microporous zeolites, catalyst performance is determined not only by the active sites' molecular architecture, but also by the organization of the pores with varying diameter, shape and directionality. Rather than being ideal single crystals, zeolites often have complex 3-dimensional morphologies, comprising intergrowths and various defect types. Since decades ZSM-5 has been one of the most important shape selective catalysts, making it a prime candidate material for our microscopic structure-activity exploration. The crystallographic structure of ZSM-5 has been solved; it contains two intersecting 10 membered-ring channel types with comparable, but not identical cross sections. The sinusoidal pores run parallel to the crystallographic a-axis, while the straight pores parallel the b-axis. A perfect single crystal thus has the sinusoidal channels surfacing at the (100) crystal face, and the straight ones at the (010) face. Considering the various morphologies of ZSM-5, it is not straightforward to relate macroscopic crystal faces and features with the underlying crystallographic pore orientation.

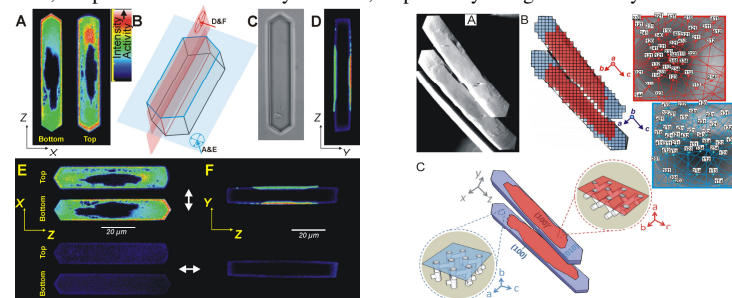
## Materials and Methods

The presented work uses a home-made confocal fluorescence microscope and an EBSD tool. More details will be presented during the presentation.

## Results and Discussion

In order to understand catalysis in the pore structure of an individual ZSM-5 crystallite, we here combine in situ fluorescence microscopic imaging (FMI) with spatially resolved structure determination by electron backscatter diffraction (EBSD). We used the acid-catalyzed self-condensation of furfuryl alcohol (FA) as reporter reaction for imaging the initial catalytic activity of individual coffin-shaped H-ZSM-5 crystals.<sup>1,2</sup> Circularly polarized excitation light was used to locate the emissive oligomeric reaction products along two main crystal axes (Figure 1B) using a confocal fluorescence microscope. The reactivity maps of the hexagonal top and bottom faces of the crystal (Figure 1A) show a non-uniform fluorescence: an active peripheral part, and a much less reactive central part. The observation of non-uniform catalytic activity on the well-developed crystal facet is somewhat unexpected, as the crystal face, looks smooth under the optical microscope (Figure 1C). Rotating the same crystal over 90° shows a reverse picture: the cross section through the middle of the crystal (Figure 1D) reveals the central zones of the hexagonal facet as the most emissive ones, while almost no photoemission is detected in the peripheral part. To explain such dependence of on the viewing direction, one

should consider that linear oligomeric products have transition dipole moments of absorption and emission parallel to the long molecular axis. Due to this anisotropy, the efficiency of excitation and emission is strongly orientation-dependent. The fluorescence measurements thus indicate that the central and peripheral zones on the hexagonal face possess catalytic activity; however, the products are differently oriented, respectively along the x- and y-axis.



Knowing the relative orientation of the product molecules, we attempted a straightforward correlation with the pore structure by using electron backscatter diffraction (EBSD).<sup>3</sup> This scanning electron microscopic tool records the characteristic electron diffraction patterns of surfaces in the upper 50 nm of the beam-specimen interaction volume (Figure 2B). While in the tip regions of the scanned surfaces the expected (010) crystallographic orientation was found, indexing of the diffractograms stemming from the central zone reveals a local rotation of the crystal lattice with 90° with respect to the c-axis. Hence the central zone corresponds to a (100) face on which sinusoidal pores are surfacing (Figure 2C).

The reactivity for FA and the orientation of the oligomers can now be related with the structural knowledge from EBSD. In the peripheral part of the hexagonal facet, which retained the expected crystallographic orientation, the oligomers are in the sinusoidal pores. The situation is different in the central part. The oligomers are aligned along the y-direction of the mother crystal, which again coincides with the sinusoidal pores, but of the 90° intergrowths.

## Significance

FMI and EBSD provide new insights in the catalytic activity of a working microporous crystalline material. As demonstrated on ZSM-5 zeolites, unexpected details of pore organization and product location are revealed when tools with high spatial resolution are employed. We believe the approach has great potential to study a wide range of phenomena associated with shape-selective catalysis and structure-dependent sorption at surfaces. The effect of crystal morphology and defect zones on the effective performance of porous materials in sorption or catalysis can now directly be imaged.

## References

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