

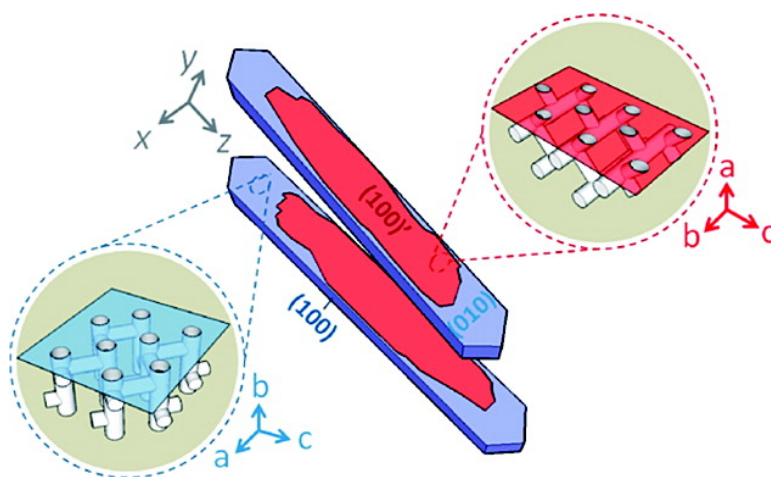
Communication

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Relating Pore Structure to Activity at the Subcrystal Level for ZSM-5: An Electron Backscattering Diffraction and Fluorescence Microscopy Study

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As heterogeneous catalysis is a cornerstone of sustainable chemical technology, it is essential to directly relate the catalytic activity of an interface to its physicochemical characteristics.¹ For metals and oxides, such studies are generally performed on idealized, nonporous surfaces of single crystals. However, in microporous zeolites, catalyst performance is determined not only by the active sites' molecular architecture, but also by the organization of the surrounding pores with varying diameter, shape, and directionality. These pores control transport of reagents and products and induce shape selectivity.² Rather than being ideal single crystals, zeolites often have complex 3-dimensional morphologies, comprising intergrowths and various defect types.

For many years ZSM-5 has been one of the most important shape selective catalysts, making it a prime candidate material for our microscopic structure–activity relationship study. The crystallographic structure of ZSM-5 has been solved previously; it contains two intersecting 10-membered-ring channel types with comparable, but not identical cross sections. The sinusoidal pores ($5.5 \times 5.1 \text{ \AA}^2$) run parallel to the crystallographic *a*-axis, while the slightly larger straight pores ($5.6 \times 5.3 \text{ \AA}^2$) parallel the *b*-axis. In a perfect crystal, one would thus expect the sinusoidal channels to surface at the (100) crystal face and the straight ones at the (010) face. However, when considering the various morphologies encountered for ZSM-5 crystals, it is not always straightforward to relate macroscopic crystal faces and features with the underlying crystallographic pore orientation. Indeed, there is currently a lively debate on the possible orientations of the various pore types within ZSM-5 crystallites.^{3–6}

To understand catalysis in the pore structure of an individual ZSM-5 crystallite, we here combine *in situ* fluorescence microscopic reactivity imaging (FMI)⁷ with highly spatially resolved structure determination by electron backscatter diffraction (EBSD).⁸ The overlay of the reactivity and structural information provides the unequivocal assignment of product formation to the various pore types within a zeolite crystallite.

We used the liquid phase acid-catalyzed self-condensation of furfuryl alcohol (FA) in dioxane (for experimental details see Supporting Information) as a reporter reaction for imaging the initial catalytic activity of individual coffin-shaped H-ZSM-5 crystals (Scheme 1). Confocal fluorescence microscopy was used to locate the emissive oligomeric reaction products inside the zeolite crystals (Figures 1 and Supporting Information, S1). The reactivity maps of the hexagonal top and bottom faces of the crystal recorded with circular polarized

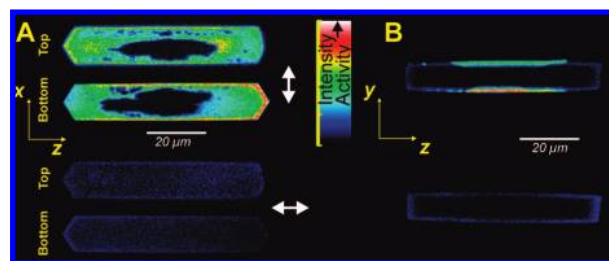
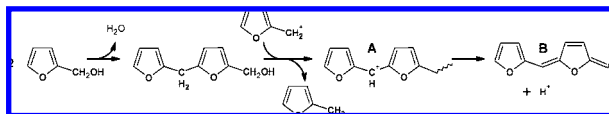


Figure 1. Initial fluorescence reactivity maps for the H-ZSM-5-catalyzed self-condensation of furfuryl alcohol recorded using linear polarized light: (A) (010)-projection reactivity map of the top and bottom hexagonal faces and (B) (100)-projection reactivity map of the crystal's cross section. White arrows indicate the fluorescence polarization with respect to the crystal orientation (see also Figure S1).

Scheme 1



excitation light (see Figure S1,A) clearly show a nonuniform fluorescence: in contrast to the active peripheral part of the hexagonal facet, the central domain seems much less reactive toward FA. The observation of nonuniform catalytic activity on the well-developed crystal facet is somewhat unexpected, as the crystal face, with the exception of a very small ramp, looks smooth and regular under the optical microscope (Figure S1,C).

However, when the same crystal is rotated over 90°, a reverse picture is obtained: the cross section through the middle of the crystal (Figure S1D) 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 the observations on the viewing direction, one should consider that the linear oligomeric products (Scheme 1) have transition dipole moments of absorption and emission parallel to the long molecular axis. As a consequence of the anisotropy, the efficiency of excitation and emission is strongly orientation-dependent. Our observations thus suggest that the emissive product molecules are differently oriented in the various zones of the crystal.

A more profound insight in the products' orientation can be obtained by employing linear instead of circular polarized light. Thus, the crystal of Figure S1A–C was reinvestigated after inserting a linear polarizer in the beam path; Figure 1 panels A and B show activity maps for two viewing directions and with the polarization parallel to the crystal's main *x*- or *z*-axes. The bright fluorescence in the upper images of Figure

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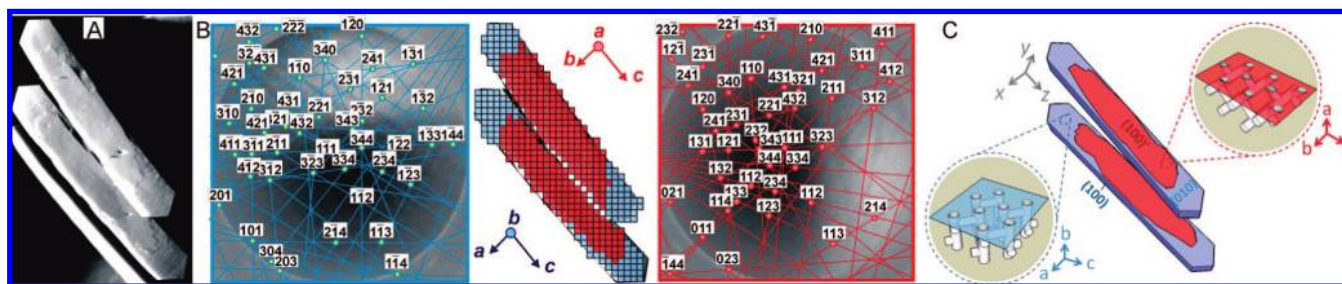


Figure 2. EBSD image of a single ZSM-5 crystal ($1 \times 1 \mu\text{m}^2$ resolution): (A) electron microscopic image of the analyzed crystals; (B) indexing of the two types of EBS diffractograms measured for the hexagonal faces (red and blue) along the construction of spatially resolved structure maps; (C) scheme of the relationship between the crystallographic *abc*-axes and the morphological *xyz*-axes for typical crystals of the employed batch.

1A suggests that the product molecules in the peripheral parts of the hexagonal facet are mainly oriented according to the *x*-axis; however, in the central section of the hexagonal facet, an orientation along the *y*-axis seems to prevail (Figure 1B). Summarizing, the fluorescence measurements indicate that both 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 of the crystal.

Knowing the relative orientation of the product molecules with respect to the crystals' main body, we attempted a straightforward correlation with the pore structure of the crystal by using electron backscatter diffraction (EBSD). This scanning electron microscopic tool records the characteristic electron diffraction patterns of surfaces in the upper 50 nm of the beam-specimen interaction volume. EBSD measurements on zeolites are nevertheless extremely difficult; because of the low density of zeolites, long accumulation is required during which surface structure degradation will unavoidably occur.^{8b} Taking advantage of the recent instrumental advances in detector sensitivity, we carefully recorded spatio-resolved electron backscatter patterns (resolution up to $0.5 \times 0.5 \mu\text{m}^2$) on individual zeolite crystals (Figure 2). A complete crystallographic orientation map of the surfaces of both hexagonal facets is illustrated in 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). These findings are supported by multiple measurements on different ZSM-5 crystals of which one is elaborated in the Supporting Information (see Figures S2–S4). A similar structural picture has been recently proposed from structure-sensitive adsorption experiments with fluorogenic probes.^{3b}

The reactivity for FA and the orientation of the oligomers can now be related with the structural knowledge from EBSD. Irrespective of the presence of the 90° intergrowths in the hexagonal (010) facet, the whole surface shows a comparable initial oligomerization activity. In the peripheral part of this facet, which retained the expected crystallographic orientation, the oligomers are in the *x*-direction, that is, in the sinusoidal pores. As there is no gradient of fluorescence within the stained sections of Figure 1A, it seems that substrate supply to the sinusoidal pores takes place by diffusion via the straight pores, which surface at the hexagonal face. The situation is different in the central part. Here, the oligomers are aligned along the *y*-direction of the mother crystal, which again coincides with the sinusoidal pores, but of the 90° intergrowths. These observations are in line with the structural model proposed in previous work in which a three-component structure with 90° intergrowths on the hexagonal facets was reported.^{3b,6b}

In summary, we have shown how a combination of fluorescence microscopy and EBSD can be used to acquire new insights in the catalytic activity of a working microporous crystalline material. As

we have demonstrated here on ZSM-5 zeolites, unexpected details of pore organization and product location are revealed when tools with high spatial resolution are employed. We believe that 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 providing essential feedback in the design of high performance porous materials.

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Supporting Information Available: Experimental procedures, further experimental results, and more extensive figures. This material is available free of charge via the Internet at <http://pubs.acs.org>.

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