Zeolite Catalysis

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Morphology of and Catalysis in Single Crystals of Zeolites

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A major goal of research in catalysis is 1) to identify the active site, 2) to establish the catalytic cycle, 3) to construct structure–activity relationships, and 4) with the knowledge of (1)–(3), to design catalysts appropriate for a specific reaction or a specific set of reactions with optimal activity, selectivity, and stability. This is an enormous, multidisciplinary task, but success can be extremely rewarding. Such was the case for the elucidation of all reaction steps in the synthesis of ammonia over supported iron catalysts.[1] The development of an appropriate set of techniques is essential for the study of the catalytic surface and the catalytic events in conditions as close as possible to the "real" catalytic conditions.[2]

In the case of zeolites, the active sites are situated in pores and channels of different dimensions and on the external surface of the microcrystals in the catalytic bed. Active sites might be hidden and unavailable for the reactants. In space- and time-averaged measurements, many details of sorption, diffusion, and catalysis are then either lost or very difficult to obtain. For example, for catalysis on the external surface of the microcrystals versus catalysis in the micropores, and crystal-face-dependent catalysis, in which channels and cages is the catalysis really observed? For defects and impurities as active sites, with shape selectivity in single crystals versus shape selectivity averaged over a multitude of crystals randomly oriented in a catalyst bed?

The answer to these questions has now come within reach by the development of a range of techniques that combine spectroscopy and microscopy. Spectroscopy is typically performed on a single crystal under the microscope using the following techniques: interference microscopy (IM), optical microscopy (OM), fluorescence microscopy (FM), single molecule fluorescence microscopy (SMFM), and infrared microscopy (IRM). Figure 1 gives schematic representations of the so-called inverted confocal and wide-field FM set-ups with the corresponding in-situ cell.[3] Figure 2 shows FM and OM procedures with the single crystal in an in-situ cell at the bottom of the instrument.[4] This in-situ cell allows studies of single crystals in gas and liquid environments and over the temperature range 298–1273 K. It can also be used for IRM.

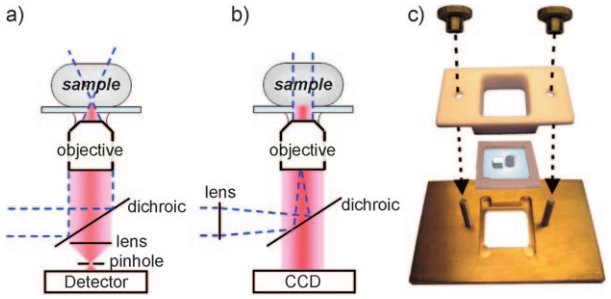

Figure 1. Representations of the a) inverted confocal and b) wide-field fluorescence microscopes, and c) of the reaction cell. CCD = charge-coupled device.

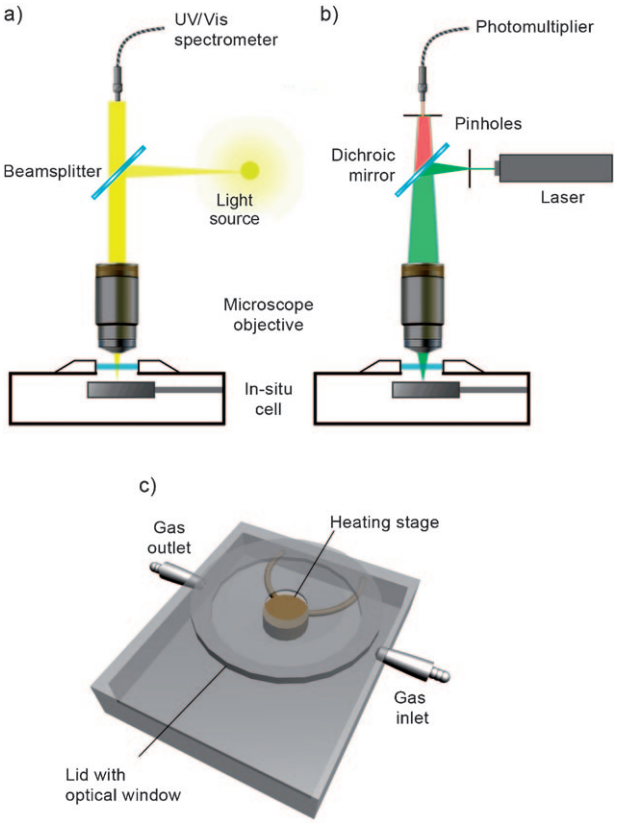

Figure 2. Representations of the a) upright optical and b) fluorescence microscopes, and c) of the reaction cell.

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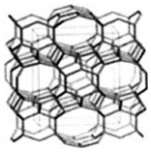
Spatial resolution has the theoretical limit given by Bragg's diffraction law. In practice, the resolution is also determined by the absorption and fluorescence intensities. Indeed, light absorption and fluorescence intensity must exceed the background and noise levels to give a measurable signal. Thus either strongly absorbing or strongly fluorescent molecules have to be used or, if this is not the case, a large area must be scanned to accumulate sufficient intensity. Three-dimensional images can be obtained by moving the focal plane through the crystal at submicrometer resolution.

The data published to date concern 1) the determination of transport diffusivities, 2) intergrowth structures and accessibility of single crystals, and 3) reaction kinetics.

Table 1: Transport diffusivities in zeolites and microporous materials.

Zeolite	Molecule	Transport diffusivity [$m^2 s^{-1}$]	Pore openings[b] [nm]	
NaCa-A	methanol	$(0.8–1.2)\times10^{-13}$	0.41	
Ferrierite	methanol	$10^{-13}–10^{-11}$	10MR: 0.42×0.54 8MR: 0.35×0.48	
Silicalite-1	isobutane	1×10^{-12}	straight: 0.53×0.56 zigzag: 0.51×0.55	
Silicalite-1[a]	isobutene 2-methylbutane	$(1.05–1.7)\times10^{-12}$ $(0.9–5)\times10^{-13}$	straight: 0.53×0.56 zigzag: 0.51×0.55	

[a] Silicalite carefully cleaned with NaOH. [b] 10MR = ten-membered, 8MR = eight-membered ring of oxygen atoms, straight = ten-membered ring of oxygen atoms forming the straight channels, zigzag = ten-membered ring of oxygen atoms forming zigzag channels.

1. Diffusion

With IM, a light beam propagates in the crystal along a chosen crystallographic direction and one measures the refractive index of the zeolite crystal at a given wavelength with respect to the refractive index of the gas phase, which is supposed to be constant. The diffusion of the adsorbate in the zeolite crystal is followed by measuring the change of refractive index as a function of time. Measurements in the different crystallographic directions give information about the anisotropy of the diffusion of the gas molecules in the zeolite crystals. Table 1 gives a survey of the transport diffusivities of methanol, isobutane and 2-methylbutane obtained to date in various zeolites.

In zeolite A, with its three-dimensional system of eight-ring openings to the supercages, the diffusivity of methanol is almost independent of concentration, whereas it is strongly concentration-dependent in ferrierite.[5,6] The ten-membered rings (10MR) of ferrierite were found to be blocked in the main crystal body. Access of methanol in the interior of the crystal was made possible through the eight-membered rings (8MR) in the crystal body and through the 10MR and 8MR in the roof of the crystal. The diffusivity of isobutane in a silicalite-1 crystal and in a carefully cleaned silicalite-1 crystal are almost identical, showing that barriers for diffusion on the external surface and at the interfaces of the different intergrowth structures, making up the silicalite crystals, are absent or weak in any case.[7,8] 2-methyl butane is bulkier than isobutane, and this is reflected well in the smaller diffusivities (Table 1).

2. Intergrowth Structures

Crystal morphology, defects, impurities, and intergrowth structures are all important parameters that determine the accessibility of the interior of the ZSM-5 catalysts and the ability of the reagents to reach the active sites. The intergrowth structure in particular has been the subject of investigation and debate in the literature. A two-component and a three-component model have been proposed with different accessibility of the coffin-shaped ZSM-5 crystal (Figure 3). In the two-component model the sinusoidal

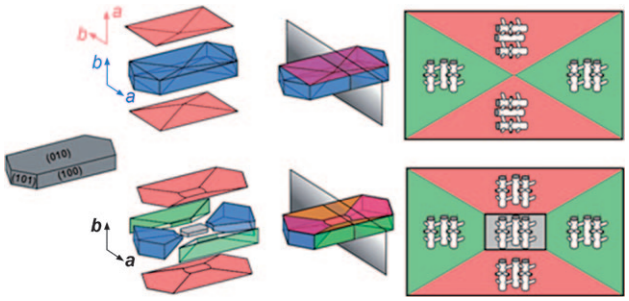


Figure 3. Representation of a coffin-shaped ZSM-5 crystal according to the two-component (top) and three-component (bottom) models.

(zigzag) channel openings appear at the (100) and the (010) faces. Access to the straight channels is possible at the tips of the crystals. The three-component model implies that the straight pores can be accessed from the (010) faces as well.

The acid-catalyzed oligomerization of furfuryl alcohol and of styrenes have been used to visualize the intergrowth structure. Both molecules produce intermediate carbocations that absorb and fluoresce in the visible-light range. The mapping of the absorbance intensity or the fluorescence intensity over the crystal then reveals the intergrowth structure of the ZSM-5 crystals. Furfurylalcohol enters the ZSM-5 crystal at the (100) and (010) faces, and much less so at the tips of the crystal. This is interpreted in terms of hindered diffusion into the tips of the crystal, the interfaces between the components of the intergrowth structure creating weak

barriers to diffusion. Likewise, after some reaction time the oligomerization products accumulate in the tips because of the hindered diffusion out of the crystal. Thus, the intergrowth structure can be explained by the hindered diffusion into the different crystal elements, not by preferred access of one crystal face over the other.[9]

In the oligomerization of styrene, the inhomogeneous coloration of the crystal is interpreted in terms of the two-component model. Styrene molecules enter the crystal at the main crystal faces (zigzag channels) and at the tips (straight channels). Dimeric cations are formed in the straight channels but block their pore entrances, preventing further oligomerization. In the crystal body, styrene molecules diffuse towards the dimeric carbocation through the sinusoidal channels and react to form the corresponding trimeric carbocations. These carbocations cannot be formed in the sinusoidal channels, because their size exceeds the length of the sinusoidal channel segments. This is a clear example of shape selectivity.[4,10,11]

The intergrowth structure of ZSM-5, SAPO-5, CrAPO-5, and SAPO-34 has also been revealed by FM of the template decomposition reaction, and a similar intergrowth pattern could be presented for the four structures.[12] For ZSM-5 these data support the two-component model. Direct evidence for the two-component model is now also obtained by electron-backscatter diffraction-focused ion-beam experiments.[13] However, ZSM-5 crystals from a different origin do not necessarily belong to the two-component model. Indeed Roeffaers et al,[14] investigating coffin-shaped ZSM-5 crystals from different synthesis batches, concluded in favor of the three-component model. But in defect-rich crystals, 90° rotation sections are present, as proposed in the two-component model. It might well be then that every ZSM-5 crystal is unique and that the discussion in terms of the two-component and three-component models is an oversimplification. The size, shape, and structure of the ZSM-5 crystals are determined by the chemical composition of the synthesis mix, the synthesis conditions, the distribution of lattice aluminum over the crystal, and the presence of defects.

3. Kinetics

In a crystal of ZSM-5, the kinetics of the dimeric carbocation formation has been measured by following the intensity of the characteristic absorption at 585 nm as a function of time.[4] The formation of the monomeric cation is considered to be rate-determining. This means that the formation of the dimeric cation is very fast and the subsequent formation of oligomers negligibly slow. The absorption intensity as a function of time has been fitted with a second order reaction equation and the corresponding rate constants reflect the accessibility of the crystal and the effect of the substituent. Thus, styrenes that are too large are unable to enter the crystal. There is no development of color, and the rate approaches zero. Electron-withdrawing substituents, such as fluorine, slow the reaction down. These results are in line with the shape-selectivity concept and with our knowledge of substituent effects. Thus, the assumptions of the kinetic analysis seem to be correct.

For the analysis of catalytic reactions, reaction pathways, and kinetics, OM, FM, and SMFM have limited applicability. Researchers are indeed restricted to a very small set of molecules that give reaction intermediates that absorb light and/or fluoresce in the visible. In addition, relatively stable reaction intermediates are needed, because of the low time resolution of the techniques.

To overcome these severe restrictions, Stavitski et al. have developed synchrotron-based IR microscopy.[15] The spatial resolution of IR microscopy is less than that of OM, because of the difference in wavelength (typically $20 \times 20\ \mu m^2$). However, with synchrotron light with brightness 100–1000 times higher than that of a conventional IR light source, the spatial resolution can be brought in the neighborhood of the diffraction limit (typically below $5 \times 5\ \mu m^2$). A second advantage is that in principle every reaction can be studied. If reagents, intermediates, and/or products have a characteristic IR absorption band, the reaction can be monitored in a space- and time-resolved manner. The characteristic IR bands are due to vibrations of the molecules in their ground state and can be calculated theoretically to support the interpretation. Also, the synchrotron light is polarized and the cell developed for OM and FM in Weckhuysen's group (Figure 2) can be used in IRM.

Thus, upon adsorption of 4-fluorostyrene in a ZSM-5 crystal, characteristic absorptions are found at 1510 cm^{-1} that are due to 4-fluorostyrene, and at 1534 cm^{-1} that arise from the dimeric carbocation (Figure 4) This interpretation is

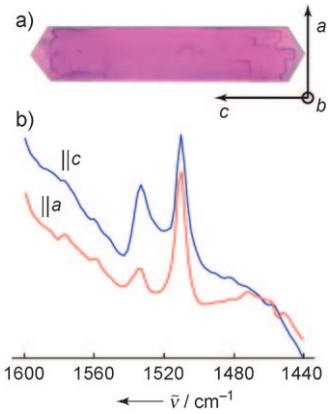


Figure 4. In-situ synchrotron-based IR microscopy of 4-fluorostyrene dimerization in a ZSM-5 crystal. Bands appear at 1510 cm^{-1} for 4-fluorostyrene and at 1534 cm^{-1} for the dimeric carbocation of 4-fluorostyrene.

supported by DFT calculations. The polarized light of the synchrotron source can be used to reveal the orientation of the dimeric cation in the straight channels. The distribution over the crystal as a function of time can be mapped. It is clear that IRM opens the route to fundamental studies of a large number of catalytic reactions in zeolite crystals.

A set of powerful microscopic techniques has been developed to study diffusion and catalysis in relatively large single crystals of zeolites. Relevant information has been obtained about diffusion of molecules, about the intergrowth

structure of ZSM-5, and about accessibility of these crystals and others, such as mordenite.[3,16] Space resolution is limited (500 nm–5 μm), but techniques have been developed to overcome this hurdle.[17] Only acid-catalyzed reactions with formation of stable carbocationic intermediates have been studied to date. With synchrotron IR microscopy the set of reactions will be extended.

The data that has been published will generate activities in various areas of zeolite research. Three research areas are of particular importance:

1) Zeolite synthesis: It is clear now that several intergrowth structures of ZSM-5 can be obtained. Improved synthesis procedures have to be developed aimed at increasing the synthesis selectivity towards a specific intergrowth structure. A quantitative conversion of the synthesis mixture into zeolite crystals without any residual oxidic material that contaminates the external surfaces of the crystals and hinders accessibility, and diffusion is another synthesis route to explore systematically.
2) Theoretical studies: Firstly, they are needed to support the interpretation of the spectroscopic data, as shown by the IRM study of styrene oligomerization,[15] and secondly, adsorption complexes, transition states, and product complexes can be studied computationally with periodic calculations. They can now be measured and a direct comparison of theory and experiment is possible. This will give new insight into shape selectivity and will assist in the development of structure-activity relationships.
3) Chemical engineering: To bridge the gap between single crystal studies and a zeolite catalyst in a typical catalytic laboratory, single crystal studies have to be performed on < 10 μm-sized crystals. To predict the behavior of a catalyst bed, composed of these submicron-sized crystals from data obtained on the single crystal is a challenge for chemical engineering research.

Microspectroscopic techniques are now added to the toolbox of the zeolite researcher. Unique insight into diffusion, intergrowth structure, and catalysis has been obtained. Collected data shed light on the fundamental properties of the zeolite crystal, and are indispensable for the development of our insight into zeolite chemistry and heterogeneous catalysis. With a judicious organization of dye molecules in the channels of zeolite L, crystals can be developed that serve as building blocks for optical, electro-optical, and sensing devices.[17–19] The future of zeolite research is bright.

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