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Regular Intergrowth in the AFI-Type Crystals: Influence on the Intracrystalline Adsorbate Distribution As Observed by Interference and FTIR-Microscopy

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Abstract: Interference microscopy and FTIR microscopy are applied to study intracrystalline concentration profiles of methanol in CrAPO-5 zeolite crystals. By using both techniques, the high spatial resolution of interference microscopy is complemented by the ability of FTIR spectroscopy to pinpoint adsorbates by their characteristic IR bands. For the first time two-dimensional concentration profiles of an unprecedented quality are reported which show a nonhomogeneous distribution of adsorbate in zeolite crystal under equilibrium with the adsorbate vapor. These nonhomogeneous profiles are attributed to regular intergrowth effects in CrAPO-5. A possible internal structure of CrAPO-5 crystals is suggested.

Introduction

Due to their regular structure and a well-defined morphology zeolites are broadly used as catalysts and molecular sieves in different fields of applied chemistry and technology. While the ideal structure of zeolites is routinely used to elucidate their adsorption and transport properties it was only recently appreciated that these properties can be influenced to a great extent by building defects of the crystals. Investigation of intergrowth effects in zeolites is particularly important since these phenomena may strongly influence molecular uptake and intracrystalline diffusion.[1−5]

Interference microscopy has proved to be a powerful technique for studying the influence of internal crystal structure on molecular uptake. It was recently used to study the role of regular intergrowth effects on molecular uptake in large silicalite-1 crystals.[5] In the present work this technique, together with FTIR microscopy, is applied to investigate intracrystalline equilibrium concentration profiles of methanol in large CrAPO-5 crystals. The channel system of CrAPO-5 is composed of parallel one-dimensional tubes.[6,7] Intergrowth in the structure may cause a partial inaccessibility of the channels to the guest molecules and/or their inhomogeneous intracrystalline distribution. Here, we report the first direct observation of such inhomogeneous intracrystalline concentration profiles in CrAPO-5 crystals under equilibrium with the methanol vapor in the surrounding gas phase.

Experimental Section

The detailed description of the experimental setup used to monitor intracrystalline concentration profiles by the interference microscopy method may be found in refs 5, 8, and 9. The setup consists of the interference microscope Jenamap p dyn (Carl Zeiss GmbH) controlled by a personal computer, a CCD camera (XC-77CE, Sony), and a vacuum system. The measurements were always performed with a selected individual zeolite crystal. Using the shearing mechanism of the interferometer, the images of the crystal and of the surrounding gas phase were superimposed in the ocular plane of the microscope. The interference pattern produced by the superposition reflects the difference in the optical path length through the crystal and the gas phase. Molecular adsorption leads to changes of the refractive index $n(x,y,z,t)$ of the crystal and thus also to changes of the optical path

$$\Delta s(y,z,t) = \int_0^L \Delta n(x,y,z,t)\, \mathrm{d}x \qquad (1)$$

length $s(y,z,t)$ of the light passing through the crystal, where x, y, z, and t denote the three spatial coordinates and time, respectively. The x-axis was assumed to coincide with the direction of light propagation. L in (1) stands for the crystal extension in the x direction. Assuming proportionality between the local concentration $c(x,y,z,t)$ of adsorbate molecules in a zeolite crystal and the change of the local refractive

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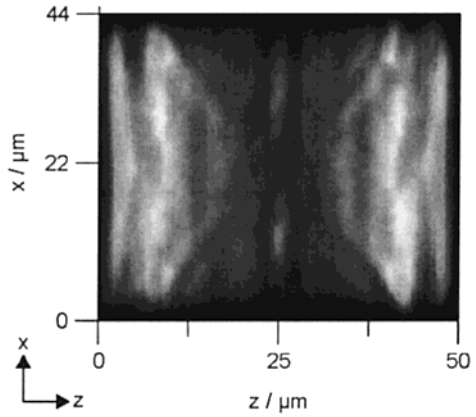

Figure 1. Typical image of an activated CrAPO-5 crystal under application of crossed Nicols. *x* and *z* denote crystallographic directions.

index, via (1), the experimental data allow the calculation of a quantity proportional to the integral of the local concentration in the direction of light propagation. The calculations were performed by using the method described in refs 8 and 9. The spatial resolution of the measurements was $0.45 \times 0.45\ \mu m^2$.

The FTIR microscopy setup is comprised of an IR-Microscope UMA 500 (Bio-Rad) equipped with a FTIR FTS 6000 spectrometer and a vacuum system. The measurements by FTIR microscopy were performed as follows. First, the microscope was switched to the optical mode, which allows the choice of a particular zeolite crystal for the measurements and the masking of a part of it by a rectangular aperture ($20 \times 20\ \mu m^2$) in the plane of the crystal image. Then, the microscope is switched to the IR mode. In this mode the intracrystalline FTIR absorbance spectra of the masked part of the crystal are recorded. To scan the whole crystal the position of the rectangular aperture was changed along the chosen direction with $\sim$10 μm steps and FTIR absorbance spectra are recorded after each step. The spectra were recorded before and after loading of the crystal from the gas phase with methanol. By dividing the absorbance spectra obtained before and after loading the crystal the absorption spectra are obtained. The integrals under characteristic absorption bands of the guest molecules in these spectra were assumed to be proportional to the integrals of the local concentration in the direction of the IR beam. For the measurements, the C−H stretching-vibration band of methanol at around 2960 cm^{-1} was chosen. All spectra were measured with a spectral resolution of 16 cm^{-1}. The spatial resolution of the measurements was limited by the aperture size ($20 \times 20\ \mu m^2$).

The samples of CrAPO-5 were prepared and calcined as described elsewhere.[6,7] The chromium content was 0.25 Cr per u.c.

For the measurements and the zeolite activation the zeolite sample was introduced into the specially made optical or IR cell connected to the vacuum system. Prior to the measurements, the sample was activated by keeping it under high vacuum at 200 °C for over 12 h. Upon activation it was loaded with methanol from the gas phase at room temperature.

The measurements of the concentration profiles in all cases were carried out with at least 6 different crystals to make sure that the results are reproducible.

Results and Discussion

The image of a typical CrAPO-5 crystal, recorded directly after activation under crossed Nicols (Figure 1), reveals the vague intracrystalline features which are usually indicative of intergrowth effects.[10]

Figure 2 shows the concentration profiles recorded by interference microscopy after 12 h upon exposure of the zeolite sample to methanol vapor at a pressure of 1 mbar. These profiles

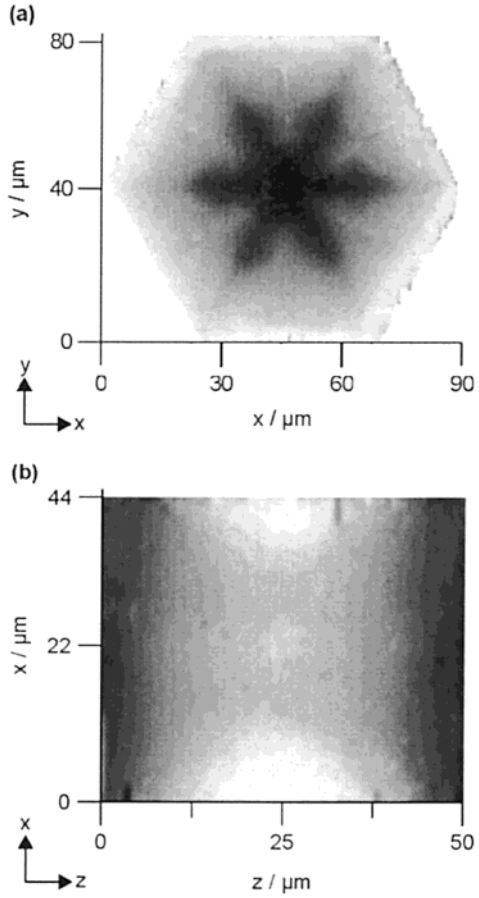

Figure 2. Equilibrium intracrystalline concentration profile of methanol in a CrAPO-5 crystal. The color intensity is proportional to the integrals of local concentration in the *z* direction (a) and in the *y* direction (b). Darker regions correspond to larger concentration integrals. *x*, *y*, and *z* are the crystallographic directions (the channel direction is *z*).

remained unchanged after additional 48 h of exposure of the zeolite to the methanol vapor. Hence, we conclude that under our experimental conditions the profiles in Figure 2 represent the equilibrium concentration profiles.

The highly inhomogeneous profiles in Figure 2 exhibit the reproducible regular pattern characteristic for regular intergrowth effects. An occurrence of such effects in the crystals under investigation is not unexpected in view of the results of Figure 1. Hence, we ascribe the nonhomogeneous pattern of the profiles in Figure 2 to the influence of regular intergrowth effects rendering part of the channel system to be inaccessible for methanol molecules. The results of Figures 1 and 2 suggest that the internal structure of the crystal possesses a reflection symmetry with respect to the center of symmetry of the crystal. Using this consideration as well as the concentration profiles presented in Figure 2 we propose the internal structure schematically shown in Figure 3 for the lower part of the crystal. The semi-pyramid in Figure 3 marks the section accessible for adsorbate molecules. The channel direction in this section coincides with the *z* direction.

To confirm the results obtained by interference microscopy the equilibrium intracrystalline concentration profiles of methanol in CrAPO-5 crystals were recorded under the same measurement conditions by FTIR microscopy. Due to much

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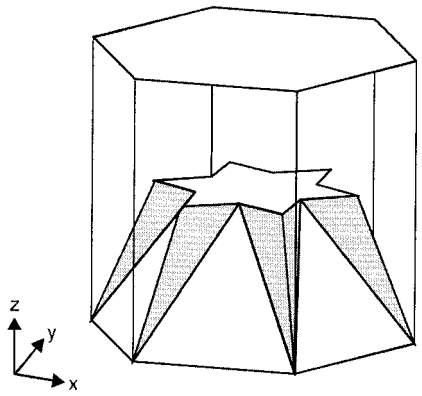

Figure 3. Suggested internal structure of CrAPO-5 crystals (shown only for the lower part of the crystal). *x*, *y*, and *z* are the crystallographic directions.

lower spatial resolution of FTIR microscopy ($20 \times 20\ \mu m^2$) a direct comparison of two-dimensional concentration profiles obtained by these two techniques is not feasible. Instead, the one-dimensional profiles along the *y* and the *z* directions were compared (Figure 4).

The results in Figure 4 represent the mean concentration integrals obtained by both techniques for *x* values between 35 and 55 μm (Figure 4a) and for *x* values between 12 and 32 μm (Figure 4b). The direction of integration (i.e. the direction of visible and IR radiation propagation) was *z* for the results in Figure 4a and y for the results in Figure 4b. Figure 4 demonstrates good agreement between the results obtained by both techniques.

Conclusion

The equilibrium intracrystalline concentration profiles of methanol were recorded in CrAPO-5 crystals by interference and FTIR microscopy. The detailed two-dimensional concentration profiles recorded by interference microscopy are unique. These profiles represent fully the great potentials of this new technique recently introduced in our laboratory. The recorded profiles revealed a highly inhomogeneous intracrystalline distribution of the adsorbate molecules. The observed inhomogeneities in the intracrystalline concentration were ascribed to the regular intergrowth effects in CrAPO-5 crystals. On the basis of the measured intracrystalline concentration profiles, a model

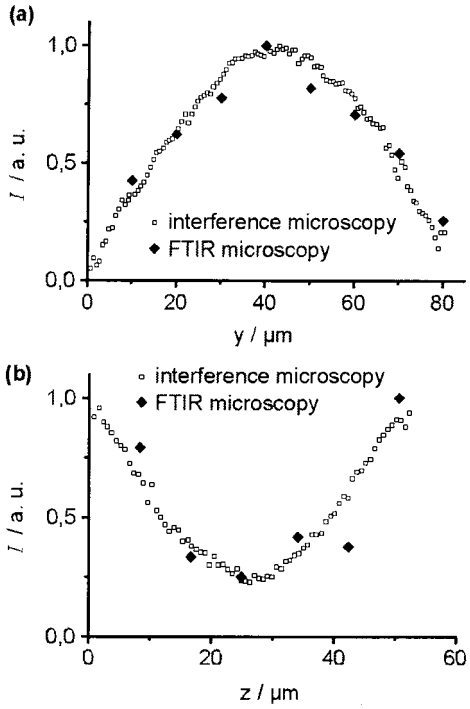

Figure 4. The mean concentration integrals *I* recorded by FTIR and interference microscopy: (a) along the *y* direction for *x* values between 35 and 55 μm and (b) along the *z* direction for *x* values between 12 and 32 μm. *x*, *y*, and *z* are the crystallographic directions.

for the internal structure of the crystals has been proposed. Our ongoing studies address an application of both techniques for the investigation of the evolution of the intracrystalline concentration profiles during adsorption/desorption of guest molecules in CrAPO-5 crystals.

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