

Inhomogeneous Distribution of Water Adsorbed under Low Pressure in CrAPO-5 and SAPO-5: An Interference Microscopy Study

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Intracrystalline concentration profiles of water, adsorbed in large crystals of CrAPO-5 and SAPO-5 under equilibrium with water vapor at 1 and 20 mbar, were determined with use of interference microscopy. At lower pressure, the profiles reveal highly inhomogeneous distributions of intracrystalline water in both crystal types. This effect is attributed to structural heterogeneity of the crystals. Its possible relation to the progress of the crystal growth process is considered. Under the vapor pressure of 20 mbar, the water molecules are homogeneously distributed over the crystals. In this case, the pore volume is saturated with liquid-like water. The structural heterogeneity has been found to have a low or no influence on the final uptake level of the crystals.

The dynamics of water adsorption in microporous materials is of crucial importance for industrial applications such as catalysis and mass separation. For example, an understanding of this process is essential for fluid catalyst cracking (FCC) because such catalysts are routinely regenerated by high-temperature steaming. In the case of mass separation, adsorption of water is important since many industrial feeds contain moisture.

It is usually assumed that water molecules, adsorbed under equilibrium with the gas phase, are homogeneously distributed over the crystals because of a well-defined, regular structure of the latter. Our intracrystalline concentration profiles show a surprising behavior of water adsorbed in the SAPO-5 and CrAPO-5 crystals at room temperature under the low water vapor pressure of 1 mbar ($p/p_s \approx 0.043$, where p_s is the pressure of saturated water vapor). The profiles have been recorded by the interference microscopy technique, which was recently adopted for the studies of adsorption in zeolites.^{1–4} In contrast to the IR microscopy method,^{4,5} this new technique offers a high spatial resolution ($0.45 \mu\text{m} \times 0.45 \mu\text{m}$) and extremely precise concentration profiles. The details of the technique are described elsewhere.^{1–3} Briefly, the method is based on the changes of optical density of porous crystals following adsorption or desorption of guest molecules. Assuming proportionality between the local adsorbate concentration and the change of the local refractive index, the experimental data allow us to determine a value proportional to the integral of the local concentration in the direction of light propagation.

SAPO-5 and CrAPO-5 belong to the AFI-type molecular sieves.⁶ The ideal pore structure of these crystals is a hexagonal

array of parallel tubes which can be filled with adsorbate molecules.^{7,8}

The samples of SAPO-5 and CrAPO-5 were prepared and calcined as described in refs 7–10. Chromium content of CrAPO-5 was 0.25 Cr per u.c. Prior to the measurements, the samples were placed in the special optical cell and activated at 150 °C under high vacuum for over 12 h. Then, the samples were cooled to room temperature under high vacuum, and the following three consecutive steps were performed: (i) rapid increase of the water vapor pressure in the cell from 0 to 1 mbar; (ii) rapid increase of the water vapor pressure from 1 to 20 mbar; (iii) rapid decrease of the water vapor pressure back from 20 to 1 mbar. After each step the resulting water pressure in the cell, i.e., 1 or 20 mbar, was maintained for 24 h before the next step was started or, in case of step (iii), before the measurements were completed. The concentration profiles of water in the crystals were monitored after each step and additional waiting time of 6 and then 18 h. Figure 1 shows the results of the measurements after the initial waiting time of 6 h. During the following 18 h, no changes in the profiles were observed, which suggests that the profiles in Figure 1 reflect the intracrystalline water distribution under equilibrium with the gas phase. The equilibrium nature of the profiles corresponding to the pressure of 1 mbar is confirmed by the fact that these profiles are essentially independent of the sample history (compare the profiles in Figure 1 a1, b1 and a3, b3), i.e., of the way of getting to the pressure of 1 mbar (water adsorption or desorption).

The values of 1 and 20 mbar correspond to p/p_s of ca. 0.043 and 0.855, respectively. The profiles obtained under 1 mbar revealed highly inhomogeneous patterns, which were reproducible. Noteworthy is that the profile in CrAPO-5 (Figure 1 a1, a3) resembles, to some extent, the methanol profile observed previously⁴ for these crystals under equilibrium with methanol vapor at 1 mbar. The inhomogeneous distribution of methanol has been related to the intergrowth phenomena in CrAPO-5.

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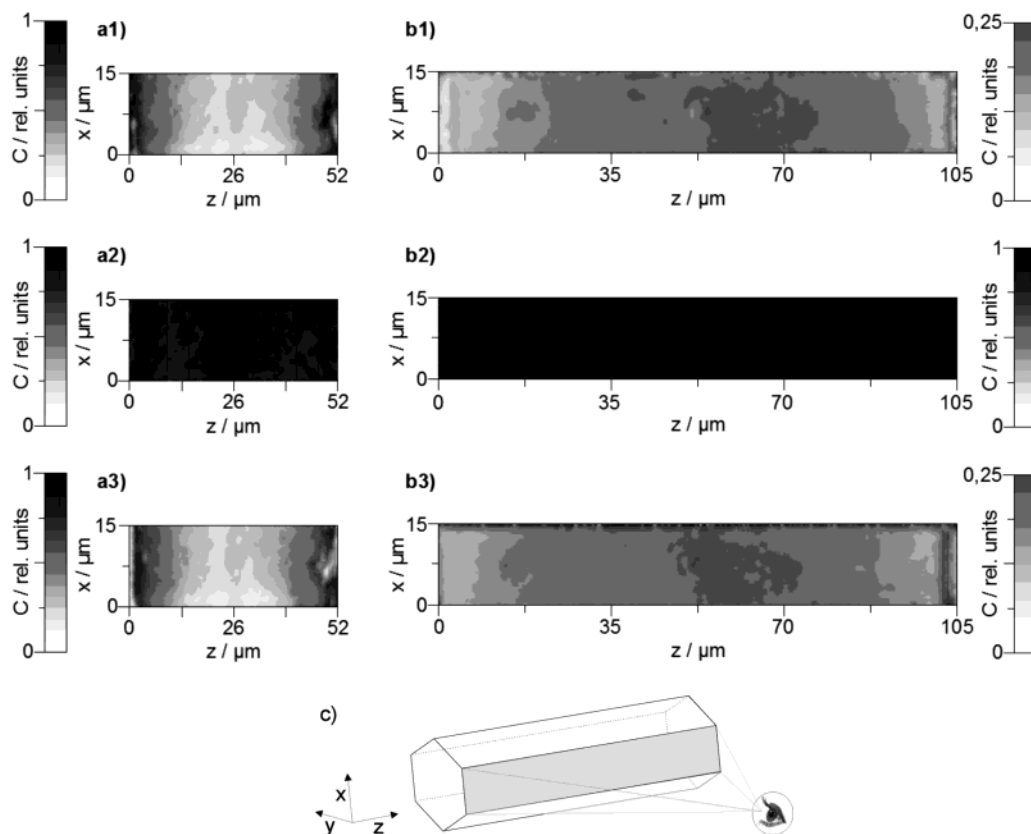


Figure 1. Intracrystalline concentration profiles of water in the CrAPO-5 (a1, a2, a3) and SAPO-5 (b1, b2, b3) crystals integrated along the y direction under equilibrium with water vapor at 1 mbar (a1, b1, a3, b3) and 20 mbar (a2, b2). The profiles under the pressure of 1 mbar were recorded after the change of the water pressure from 0 to 1 mbar (a1, b1) and from 20 to 1 mbar (a3, b3). The profiles are shown only for the crystal surface marked on the image (c). The channels run along the z axis. Darker regions correspond to higher concentration integrals.

The profiles were qualitatively explained by assuming that, under the measurement conditions, the central constituent of the crystal intergrowth, exhibiting the dumbbell form, was filled by the adsorbate molecules to a much higher extent than the other constituents. Apparently, this explanation might also be applied to water.

The origin of the intergrowth effects may be derived from the progress of the crystal growth process. As has been shown in refs 11,12, the dumbbell shape is characteristic of some AFI-type crystals in the intermediate stage of growth. Further growth leads to the filling of the gap in the central part of the crystals. As a result, the crystals of a perfect hexagonal shape can be formed (Figure 1c).

The increase in water vapor pressure to 20 mbar results in an essentially homogeneous profile in CrAPO-5 (Figure 1 a2). Obviously under these conditions, all the crystal constituents are equally filled with water. The isotherms of water adsorption in CrAPO-5 belong to type IV according to the IUPAC classification.¹³ Such isotherms reflect a relatively slow adsorption with increasing adsorbate pressure, which is followed by a steep increase in the amount adsorbed at a certain “critical” pressure. The initial slow adsorption is usually associated with the adsorption of single molecules on different adsorption centers, e.g., functional groups, or formation of a monolayer of adsorbate on the pore surface. The steep increase of the isotherm at a certain pressure is explained by the volume filling of the micropores and formation of a liquid-like adsorbate phase.¹³ It is reasonable to assume that the internal order of the particular intergrowth constituents of the CrAPO-5 crystals may be slightly different. Imaginable structural factors which can influence the intracrystalline water concentration in CrAPO-5 at low water vapor pressure are the content and the distribution of the Cr

atoms and/or the presence of defect sites. Thus, the differing contents/distributions of Cr or defects in various crystal components might be responsible for the nonhomogeneous intracrystalline concentration profiles observed at the low water vapor pressure. Obviously, an inhomogeneous distribution of any other adsorption sites might lead to a similar result. However, the concentration and the strength of the adsorption sites do not influence the final sorption capacity of CrAPO-5 for water.¹³ This explains the homogeneous profiles observed at the high water vapor pressure, when the total available pore volume is expected to be filled with liquid-like water.

The profiles recorded for the SAPO-5 crystals also show an inhomogeneous water distribution at the lower pressure (Figure 1 b1, b3), which transforms into the homogeneous one upon the pressure increase (Figure 1 b2). The inhomogeneous profile of water in SAPO-5 may result from a structural heterogeneity of the crystals as well. The structural heterogeneity of SAPO-5 has been indicated by electron microprobe analysis,¹⁰ which revealed that the silicon content of the central part of the SAPO-5 crystals was lower by a factor of 2 to three than that at the crystal margin. Studies of the progress of crystal growth have suggested the reasons for the inhomogeneous silicon distribution.¹⁰ It was found that “pencil-like” crystals are formed initially. At later stages of the growth, the tips of the “pencils” flatten out, which results in some cases in the ideally shaped hexagonal crystals. These later stages proceed with much higher consumption of silicon than the initial one. Hence, in agreement with the results of the microprobe analysis, the “pencil-like” core of the crystals may be expected to have depleted silicon content. This finding is related to the in-homogeneous intracrystalline distribution of pyridine species in SAPO-5 at 373 K.¹⁴ The concentration of the species has been found to be lower at

the crystal edges than in the central part of the crystal. This is in qualitative agreement with the intracrystalline water distribution obtained now by the interference microscopy method under equilibrium with water vapor at 1 mbar (Figure 1 b1, b3). It is interesting to note that the intracrystalline distribution of pyridine species in SAPO-5 becomes more homogeneous at elevated temperatures.¹⁴ This shows that in addition to adsorbate pressure, temperature may also significantly influence intracrystalline adsorbate distributions. Thus, it would not be unexpected that water distributions at high temperatures, which are used for some industrial applications (for example during regeneration of FCC catalysts), remain homogeneous also at low water pressures. The investigation of the role of temperature on the intracrystalline guest distributions will be a subject of future research. At present, our experimental setup is suited only for measurements at room temperature.

At the high water vapor pressure, the condensation of water and the volume filling of the pores of SAPO-5 occur, which are primarily determined by the accessible pore volume. This justifies the homogeneous concentration profile observed for SAPO-5 under equilibrium with water vapor at 20 mbar (Figure 1 b2).

In conclusion, the exceptional spatial resolution of the interference microscopy method has enabled us to obtain the precise intracrystalline concentration profiles of water in the large CrAPO-5 and SAPO-5 crystals. The profiles reveal inhomogeneous distributions of water in these crystals under equilibrium with water vapor at 1 mbar. The inhomogeneity is tentatively attributed to the structural heterogeneity of the crystals studied. We plan to explore this further, in particular by applying the IR microscopy method.⁴ A certain correlation seems to exist between the structural inhomogeneity and the inhomogeneity of the water concentration on one hand and the progress of the crystal growth process on the other. On the basis of the present experimental data and the cited literature, it may be speculated that the crystal components which form at the earlier stages of the growth process, i.e., dumbbell core or "pencil-like" core, can adsorb more water than the other crystal

parts under the low water vapor pressure. The differences in the concentration profiles between CrAPO-5 and SAPO-5 require further investigations. At the high water vapor pressure of 20 mbar, the full saturation of the pore volume with liquid-like water occurs and essentially the fully homogeneous distribution of intracrystalline water is observed in the studied CrAPO-5 and SAPO-5 crystals.

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