Exploring Crystal Morphology of Nanoporous Hosts from Transient Guest Profiles

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We performed measurements with three different specimens, namely with a representative crystal of the starting material (186 μm × 33 μm × 33 μm; Fig. S1a), with another crystal additionally subjected to an etching treatment by HF (193 μm × 30 μm × 30 μm; Fig. S1b)

With the etching process (treatment of the crystallites with 2% hydrogen fluoride solution for 30 seconds, followed by intense washing with de-ionized water), we essentially followed the procedure by which Wloch succeeded in reducing the intensity of the surface barriers generated during the synthesis of the MFI-type zeolites considered in his studies. This was most likely achieved due to the removal of oxidic layers which are created on the external crystal surface during crystal formation. By the application of interference microscopy it could be directly shown, however, that even after this treatment there was still a substantial surface resistance.

The fragments were obtained by a combination of chemical (heating in alkaline hydrogen peroxide solution under microwave irradiation at 120 °C) and physical (ultrasound treatment in de-ionized water) treatment which led to a disintegration of the crystal to its intergrowth fragments. Further details of the procedure may be found in ref. 2. A closer look to Figs. S1c-e reveal that the actual shape of the segments obtained through the described treatment deviate from the shape suggested by Fig. 1b. This finding has to be associated with the fact that channel directions in segments 1 and 2 coincide with those in segments 4 and 6, while they are perpendicular to those in segments 3 and 5. It is not unexpected, therefore, that, during the disintegration process, the remaining particles (as shown in Figs. S1c-e) are intergrowths between segment 1(or 2) with the adjacent parts of segments 4 and 6. The black (non-transparent) regions along the Z - axis of the segment (Fig. S1c) are schematically represented in Figs. S1d and e, respectively. It is indicated (Fig. S1d) that only a thin layer of irregular shape from segments 3 and 5 is still attached to the segment 1 (or 2) after the disintegration. On the other hand, as explained above, the units of segments 4 and 6 remain attached to the segment 1(or 2), due to the conformity of the crystallographic axes, forming, therefore, the particle under study.

All three types of systems considered in our experiments originate from the same batch of synthesis.

In previous studies zeolite etching with HF has been found to accelerate molecular uptake and release by the thus treated nanoporous material. This could be easily referred to the removal of the surface barriers present in these samples. In the focus of our present study is a material which we have characterized to be free of any perceptible surface resistances. Hence, any etching with HF is anticipated to be of no effect on the transient sorption properties of this material. This expectance is confirmed by the transient desorption profiles shown in Fig. S2, which are found to be essentially identical for the starting material and the material additionally subjected to the etching procedure.

In contrast to the measurements with the starting material (Fig. S1a), where the transient sorption phenomena under study were found to proceed essentially at the same rate for different (X-Y) cross-sections (Figs. 2c and d), for the wedge-like segments (Figs. S1c-e) a different behaviour has to be expected. This is confirmed by the transient concentration profiles during molecular desorption from different cross-sections shown in Fig. S3. It is clearly seen that the desorption proceeds the faster (i.e., at a given time, here 10 s, the percentage of molecules still to leave the crystal is the smaller), the smaller the segment width is. The peculiar shape of the segments – reflected by both the images shown by Figs. S1c-e and the irregular shape of the concentration profiles in Fig. S3 - prevents, however, a more detailed quantitative analysis.

References

**Figure S1:** An overview of the crystal specimens used in these studies. a. crystal as starting material. b. etched crystal. c. crystal of fragment. d, e. Schematic representations of the actual segment for both orientations (d refers to Fig. S1c (left) and e to Fig. S1c (right)).

**Figure S2:** Intracrystalline concentration profiles of 2-methyl-propane. Comparison of transient guest profiles along the $X$-axis at $Z=10\mu m$ during the release of 2-methyl-propane from the etched crystal (open symbols) and from the starting material (filled symbols).
Figure S3: Guest profiles in case of silicalite-1 crystal fragment. Transient guest profiles (2-methyl-propane) along the X-axis, 10 seconds after the onset of release, from a silicalite-1 crystal fragment recorded for different cross sections (see inset).