

Morphology Dependent MFI-type Zeolite Intergrowth Structures Leading to Distinct Internal and Outer Surface Molecular Diffusion Barriers

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Materials and Methods

Synthesis of MFI-type zeolite crystals: The crystals under study were synthesized following a procedure elaborated for growing large crystals having a MFI-type structure (for details see the original recipe in [1]). The standard composition of the reaction gel (as the formal molar oxides ratio) was 90 SiO₂ : 1 Al₂O₃ : 12 Na₂O : 2100 H₂O : 9 TPABr, where TPABr denotes tetrapropylammonium bromide, used as the structure directing agent (template). Sample **XVIII** (Supplementary Figure S1, Supplementary Table 1) was prepared with tetrapropylammonium hydroxide in the same amount. The silicalite-1 samples **III** and **IV** were synthesized without Al compound, while the gel for sample **IV** contained only 1000 H₂O. The SiO₂ source was Ludox AS40 and Al₂O₃ was taken as hydrargillite. The sodium salt was mostly NaHCO₃, except Na₂HPO₄ for samples **VI** and **VIII**, Na₃PO₄ for **XIII**, Na₂SO₄ for **XII**, and Na₂SO₃ for **XIV**. Samples **III**, **VIII**, and **XVIII** were synthesized with

addition of methanol to the reaction gel (9, 9, and 20 moles, respectively). The hydrothermal treatment of the reaction gels was performed without stirring at 456 K in stainless steel autoclaves with Teflon inlays for 5 to 12 days. The products were recovered by standard filtration, washing, and drying at approximately 400 K overnight.

Si/Al ratio of the samples was determined by the energy-dispersive X-ray (EDX) analysis in combination with Scanning Electron Microscopy (SEM). The morphology of the MFI-type crystals under study (SEM and confocal fluorescence images are shown in Fig. S1) as well as their dimensions, length/width (L/W) aspect ratio and internal structure vary in a regular order (from the most elongated to cubical). Details on the materials are given in Table 1S.

Confocal fluorescence measurements during template removal: As-prepared samples were placed in a Linkam FTIR 600 cell mounted to the fluorescence microscope stage and heated in-situ under a N₂ stream (20 ml/min) first to 500 K with a ramp of 10 K/min and then to 780 K (5 K/min ramp). Next, the samples were immediately cooled to room temperature. A Nikon Eclipse LV150 microscope with a 50×0.55 NA dry objective was used for the fluorescence investigations. Confocal images were acquired with a Nikon D-Eclipse C1 head equipped with three lasers (405 nm, 488 nm and 561 nm). The emission was detected with three photomultiplier tubes in the range 425-475, 510-550 and 575-635 nm for the three lasers, respectively (in order to avoid channel overlap). Full stacks of the confocal slices were used to reconstruct the three-dimensional spatial distribution of the fluorescent species in the zeolitic material.

Table S1. Overview of the investigated MFI-type crystals, listed in the order of decreasing aspect ratio. The four crystals used as showcase are listed as (A-D). Small case letters indicate to which parent intergrowth group (A-D) they belong.

Sample		Aspect ratio (L/W)	Crystal dimensions, L×W×T [μm]	Si/Al ratio (from EDX)
Type	Number			
A	I	4.80	95×20×20	28
B	II	4.60	50×11×11	over 2000
c	III	3.50	195×55×55	over 2000
c	IV	2.80	205×75×75	over 2000
c	V	2.40	260×110×110	42
c	VI	2.20	280×130×130	24
c	VII	2.15	200×90×90	42
c	VIII	1.90	80×40×40	10
c	IX	1.90	125×60×60	45
c	X	1.85	90×50×50	12
c	XI	1.85	130×70×70	45
c	XII	1.75	210×120×120	24
c	XIII	1.65	60×35×35	36
d	XIV	1.60	145×90×90	18
c	XV	1.60	125×75×75	50
D	XVI	1.60	115×70×70	40
c	XVII	1.20	12×10×10	over 2000
C	XVIII	1.15	70×60×60	24

Electron Backscatter Diffraction (EBSD) and Focused Ion Beam (FIB) milling: Measurements were performed on the Dualbeam (Nova Nanolab600, FEI); a combination of a SEM and a gallium ion beam. In order to record EBSD patterns from a milled zeolite surface, amorphization of a milled surface has to be prevented. For that, FIB experiments were performed using low beam energies (typically 5 kV) and ion currents of 8.4 nA and 1 nA for rough milling and polishing of the surface, respectively. Furthermore, milling was performed parallel to the surface of interest, as conventional top-down resulted in complete amorphization. The electron beam conditions used to obtain the diffraction patterns were acceleration voltage: 30 kV and current: 0.63 nA. Indexing of the recorded diffraction patterns has been performed manually, using an orthorhombic ZSM-5 structure. Unambiguous indexing is feasible if for example the {133}-, {804}-, or {151}-type bands can be recognized.

TEM lamella preparation: Preparation of the TEM lamella of crystal D has been done using the Dualbeam. After milling off parts of the zeolite, the remainder was attached to an Omniprobe using Pt deposition. The lamella was then mounted on a TEM grid and secured using Pt deposition. Finally, parts of the lamella were milled off to obtain regions of 100 nm thickness with 5 kV, 70 pA. The preparation is shown in Fig. S2.

Transmission Electron Microscopy (TEM): Measurements were conducted in a FEI 200kV FEG microscope, using a double tilt holder, with bright field diffraction contrast imaging and selected area diffraction patterns (SADP) collected from areas a few microns in diameter. All images and diffraction patterns were recorded digitally with a CCD camera.

Confocal fluorescence measurements after stilbene dye inclusion: After calcination of crystal D (823K for 24 h) a 2mM solution of stilbene-butanol solution was added to the crystals in a

similar manner as outlined in ref. [2]. Typically, 60 min after addition the crystals were placed under the fluorescent microscope. A Nikon Eclipse LV150 microscope with a 50×0.55 NA dry objective was used for the fluorescence investigations. Confocal images were acquired with a Nikon D-Eclipse C1 head. The excitation was set at 561 nm, the emission was detected in the range 575–635 nm.

Atomic Force Microscopy (AFM): Measurements were performed on a Nanowizard II AFM from JPK Instruments. All images were recorded in intermittent contact mode using high aspect ratio silicon tips (Veeco probes) with a nominal tip radius < 10 nm. In order to prevent the crystals from moving, they have been mounted in a polymeric Crystalbond 509 resin on a glass slit and placed under a Xiovert 200, Zeiss inverted microscope. The entire crystal surface was measured in several steps, varying the scanned area from $15 \times 15 \mu\text{m}$ to $0.5 \times 0.5 \mu\text{m}$. The individual images have been reconstructed into one image using JPK processing software.

X-ray Photoelectron Spectroscopy (XPS): Data were collected using monochromatic AlK α radiation (1486.6 eV) using a Physical Electronics Quantum2000 scanning XPS spectrometer. A pass-energy of 58 eV was used for the individual region scans. Individual zeolite MFI-type crystals were deposited onto a vitreous carbon substrate to ensure dispersion. A nominal 5 μm or 10 μm X-ray beam have been used for the surface analysis of single points on a zeolite crystal. Bulk averaged signal was obtained by grinding the zeolite crystals prior to XPS analysis. For this, the XPS was performed using a 100 μm beam, rastered over an area of $1400 \times 300 \mu\text{m}$. The depth calibration for the sputter depth profiling was determined from the time required to sputter through a known thickness of SiO₂ on a silicon wafer using the same ion gun settings. The depths on the zeolites are thus approximate.

Table S2. Overview of the surface and bulk Si/Al ratio for the six MFI-type crystals analyzed with XPS. The crystals are listed in the order of decreasing aspect ratio. The Si/Al ratios are averaged values over three XPS scans guaranteeing the reproducibility of the results.

Sample		Si/Al ratio (surface)	Si/Al ratio (bulk)
Type	Number		
A	I	163.2	17.0
C	X	13.1	11.8
C	XIII	43.6	16.6
C	XIV	10.4	9.3
D	XVI	∞	15.8
C	XVIII	16.6	7.9

Supplementary Figures

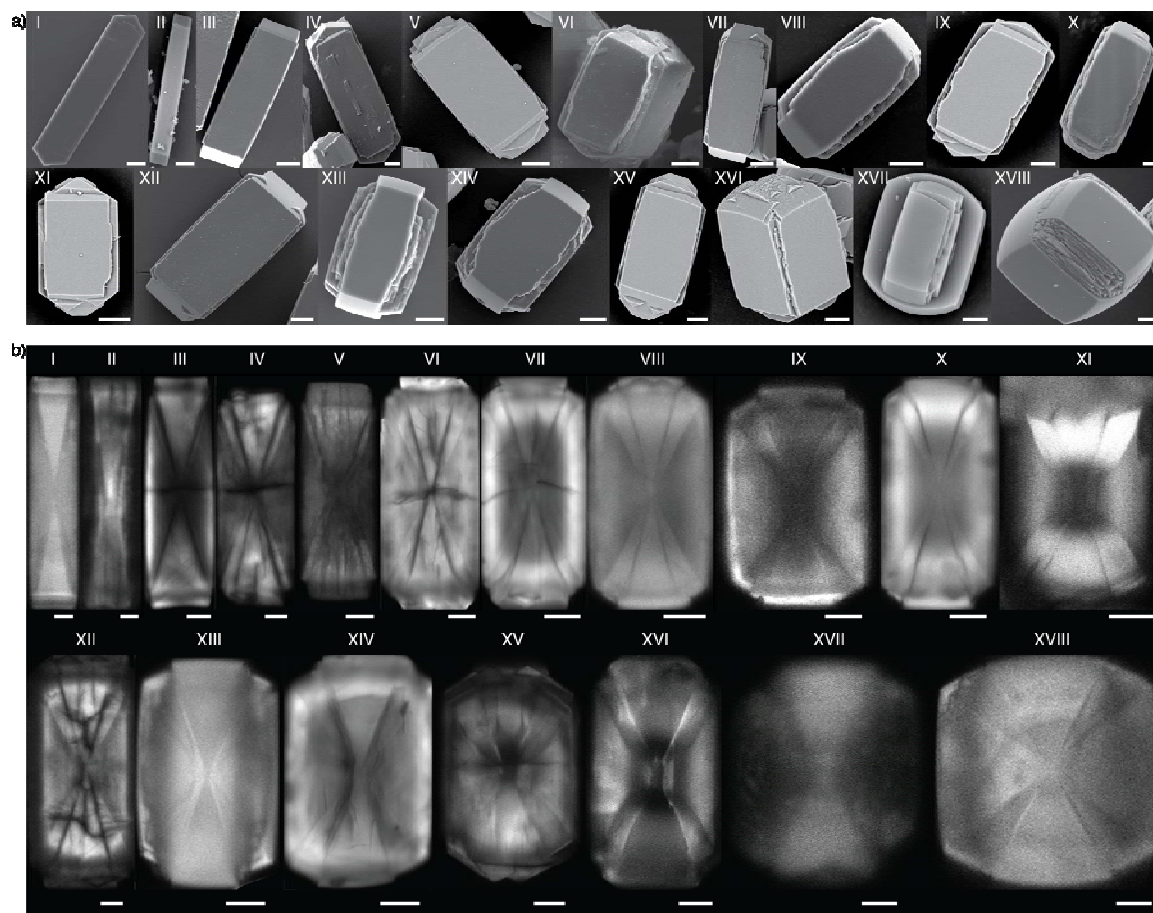


Figure S1. a, SEM microphotographs of the MFI-type crystals under study, listed according to a decreasing aspect ratio. Scale bar represents: 10 μm for crystal I, 5 μm for crystal II, 25 μm for crystals III and IV, 40 μm for crystal V, 50 μm for crystal VI, 40 μm for crystal VII, 20 μm for crystal VIII, 20 μm for crystal IX, 10 μm for crystal X, 30 μm for crystals XI and XII, 15 μm for crystal XIII, 30 μm for crystal XIV, 25 μm for crystals XV and XVI, 2 μm for crystal XVII and 10 μm for crystal XVIII (see Table 1 for the exact dimensions). **b**, Confocal fluorescence images of all zeolites presented in (a) recorded halfway through the crystal. Scale bars lengths are as in (a). The images are presented in grayscale; the brighter the image, the higher the fluorescent intensity.

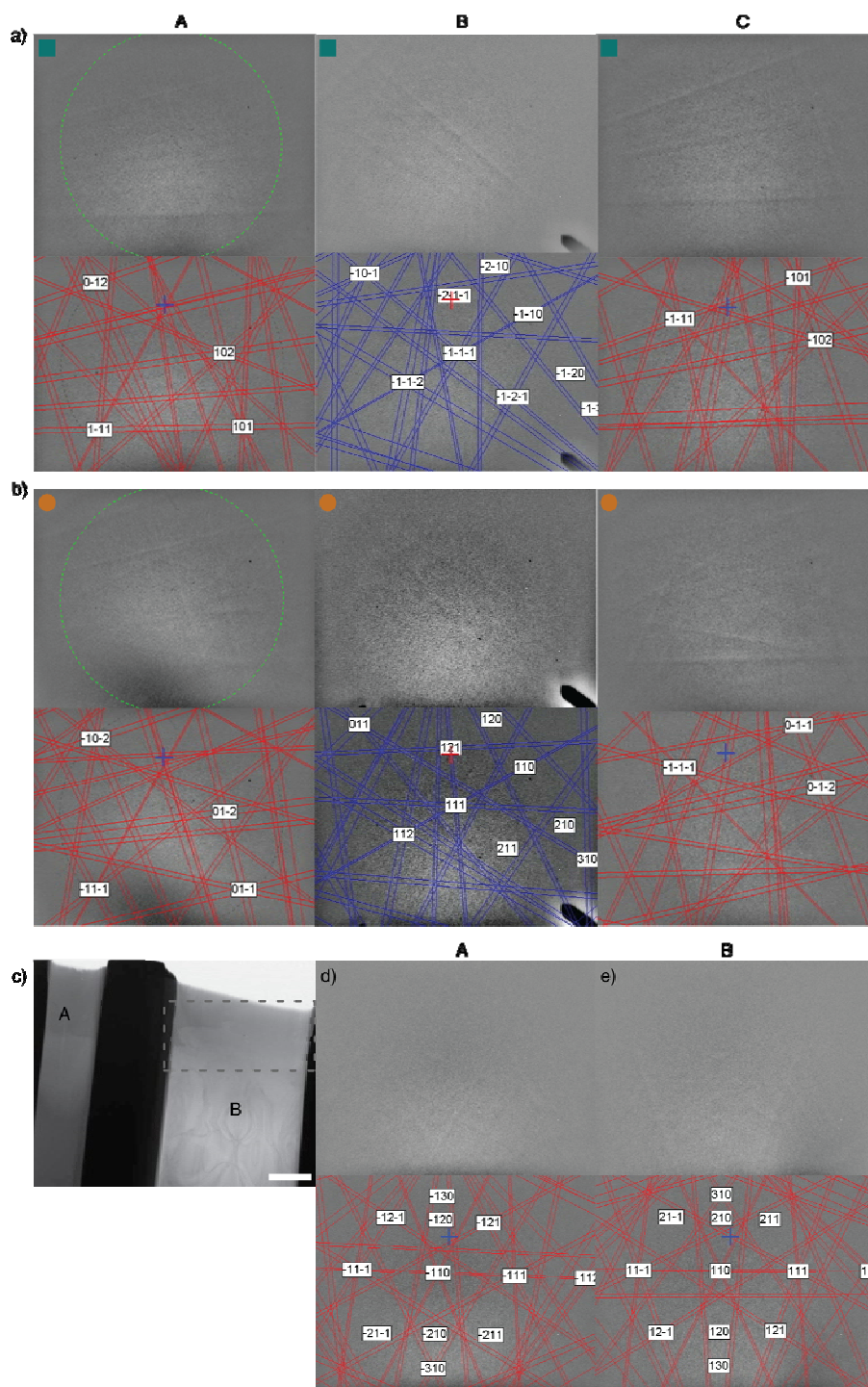


Figure S2. a, (top)

Electron backscatter diffraction patterns recorded from different regions on the crystals A - C, marked blue in Fig 1b.

(bottom) Corresponding manually indexed patterns. **b**, Same as **(a)** but for region on the

crystals that are marked orange in Fig. 1b. **c**, High resolution TEM image of the lamella. Bright regions correspond to a lamella thickness of approximately 100 nm; the gray dashed rectangle indicates the area from where TEM diffraction

patterns were recorded. **d**, **(top)** EBSD diffraction patterns recorded from the lamella region marked as A in **(c)** **(bottom)**

Corresponding manually indexed patterns. **e**, Same as **(d)** but for region of the lamella region marked as B in **(c)**.

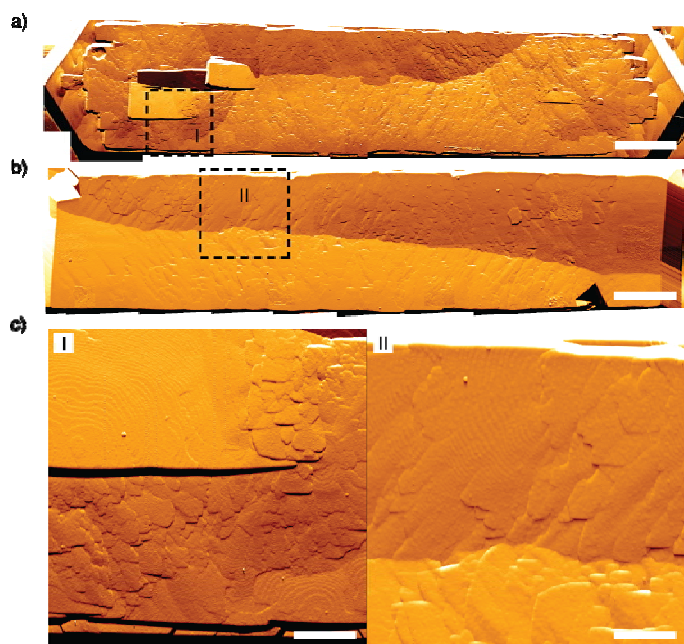
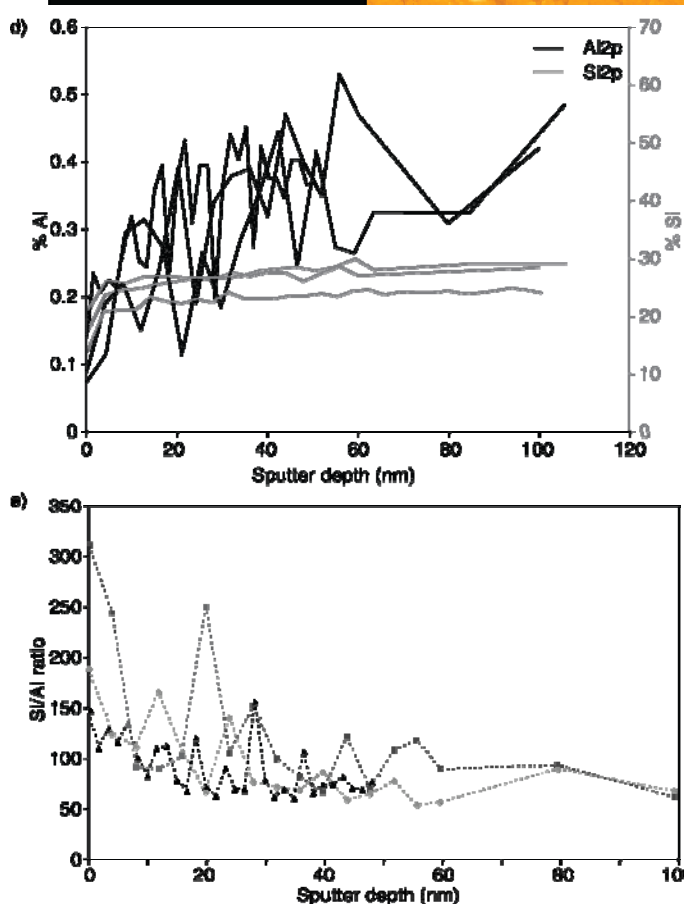


Figure S3. **a**, AFM image of the (010) face of the crystal A. Scale bar represents 10 μm . **b**, Same as **(a)** but for the (100) face. **c**, Enlarged AFM images from different regions; region I - crystal face (010) and region II – crystal face (100). Scale bar represents 2 and 3 μm respectively, for region I and II. **d**, XPS sputter depth profile plot, showing the Si and Al atomic wt. % as a function of sputter depth for three examined crystals A. Here, it can be observed that the $\sim 10\text{--}20$ nm surface region is depleted in Al, however, some traces could be detected (0.1 atomic wt.%). The Si content remains equal over the measured crystal volume. **e**,



Corresponding Si/Al ratio plot as function of sputter depth for the three crystals A.

References

- [1] Kornatowski, J. *Zeolites* **8**, 77 (1988).
- [2] Seebacher, C. et al. *Adv. Mater.* **13**, 1374 (2001).