Zeolite Nanoslabs

Reply**

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Stichwörter:
nanoblocks · nanoslabs · silicates · zeolites

In earlier work some of us claimed the existence of nanoslabs at an early stage in the synthesis of silicalite-1 (siliceous ZSM-5) from tetraethylorthosilicate (TEOS), tetrapropylammonium hydroxide (TPAOH), and water.[1] These nanoslabs have discrete sizes, for example, 1.3 × 4.0 × 4.0 nm. The framework connectivity is as in the final zeolite.[1] Nanoslabs can be extracted from suspension and obtained as a powder by neutralization with strong acid, adding hydrogen-bonding organic solvent, salting out by addition of NaCl, and finally evaporation of the organic solvent.[1b,2,3] In recent work by Kragten et al.,[4] an attempt was reported to reproduce the preparation of nanoslab extract. Using those samples, in the preceding correspondence by Ramanan et al.,[5] the observation of the zeosil nanoslabs by transmission electron microscopy (TEM) and atomic force microscopy (AFM) was doubted. We experienced that whereas the preparation of nanoslabs itself is easy, the extraction is much more difficult to achieve. Herein we elaborate the arguments in favor of the observation of nanoslabs with TEM and discuss extraction procedures.

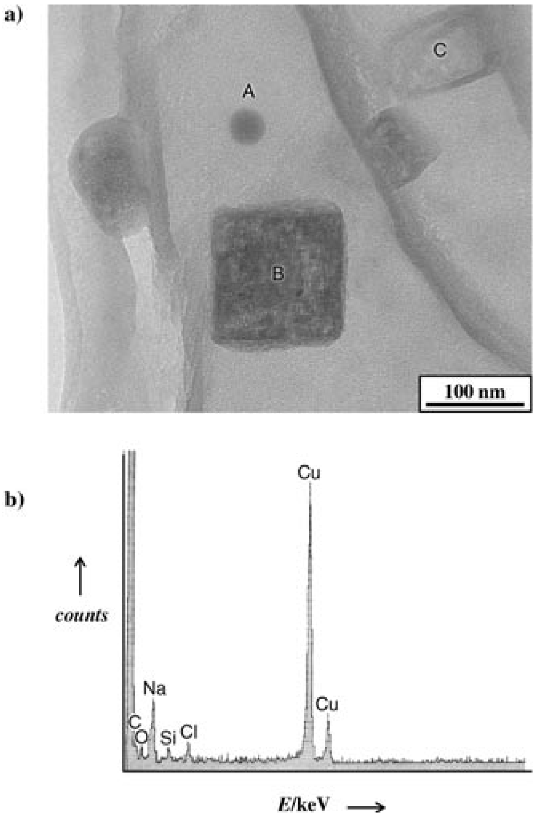

Figure 1. a) TEM image of extracted nanoslab sample prepared according to procedure 1 of Table 1; composition has been measured on the NaCl crystal (region B) and away from it (region A); in region C a NaCl crystal has probably dropped out and only the rim is remaining; b) EDX pattern of region B. Region C is Si/O rich; region A is an EDX contamination spot measured for reference.

Nanoslab suspension (clear solution) is expected to contain very little NaCl. It is possibly present as an impurity in the TPAOH reagent. Extracted material inevitably contains NaCl. We prepared a new sample of extracted nanoslab (procedure 1 of Table 1) and investigated it with TEM (Figure 1 and Figure 2). The sample contains NaCl cubes, as confirmed by energy dispersive X-ray analysis (EDX; Figure 1b), they appear as single crystalline cubes with dimensions of 50–100 nm (Figure 1 and Figure 2). The NaCl particles exhibit small square domains of lighter contrast. One possible explanation for the presence of these domains is the formation of etch pits in the NaCl introduced by the electron beam. An alternative explanation is that these domains are nanoslabs on top of the NaCl and are stabilized because of the epitaxial relationship with the cubic NaCl. There are several arguments in favor of this latter explanation. Under the electron beam NaCl crystals are damaged and that NaCl is evaporated. We prepared a sample of NaCl using the same procedure as for nanoslab preparation and extraction but omitted the TEOS from the reaction mixture. TEM experiments on these NaCl particles (Figure 3) indeed show severe electron-beam dama-

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[**] J.A.M. and G.V.T. acknowledge the Flemish FWO for a research grant. C.E.A.K acknowledges the Flemish FWO for a postdoctoral fellowship. J.A.M. and P.A.J. acknowledge the Belgian government for financial support in the frame of the IAP-PAI program.

DOI: 10.1002/ange.200460541

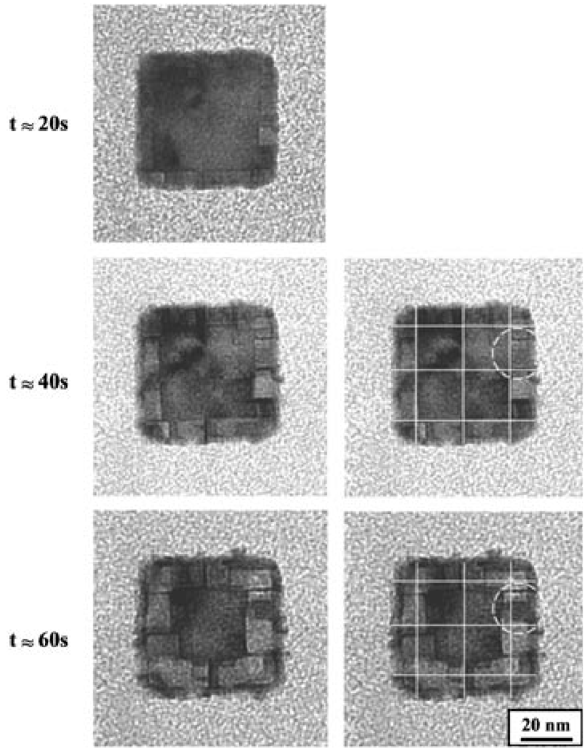

Figure 2. Sequence of TEM images of extracted nanoslab sample prepared according to procedure 1 of Table 1 (the grid superimposed in the right-hand pictures is to aid the eye).

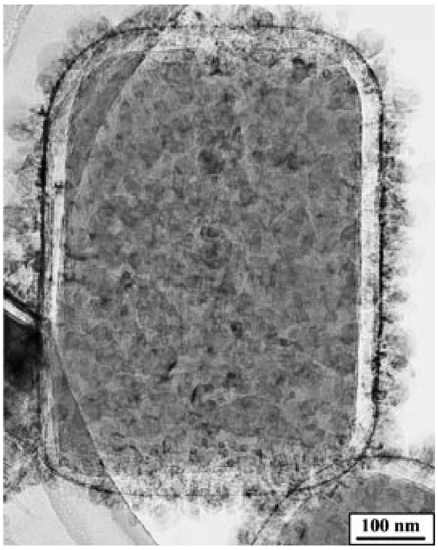

Figure 3. TEM image of a NaCl particle prepared according to procedure 1 of Table 1 in the absence of TEOS from the reaction mixture.

ge, evaporation, and re-deposition of material as evidenced by the observation of flakes on the border of the grain. However, this damage does not follow the crystallographic directions as in Figure 1 and Figure 2. In all the TEM pictures of samples supposed to contain nanoslabs, there is a dark rim around the NaCl particles (see for example, Figure 1 a). The area marked C in Figure 1 a, shows a dark contour, where probably a NaCl crystal has evaporated under the electron beam. This contour, according to EDX, is Si/O. Pure NaCl particles, after irradiation, exhibit a bright rim (Figure 3) owing to material being sputtered away from the surface. This rim grows with increased electron irradiation time.

The square domains on top of the NaCl are subject to changes with time (Figure 2). The encircled area in Figure 2 is particularly bright at the beginning of the observation but turns darker in later images. This observation can not be reconciled with the assignment of the domains to etch pits because a white area corresponding to a thinner sample is unlikely to become a black area corresponding to a thicker sample. We are aware that a contrast change in crystalline samples can also be produced by orientation changes. However, since the NaCl particle is single crystalline, then all contrast should reverse and not just the encircled area. This observation therefore strongly suggests that the changes in contrast are linked with changes of the nanoslabs. We believe to have strong arguments for nanoslabs being stabilized on the NaCl crystals, although TEM alone does not provide direct proof. However, the combination of TEM observations with small-angle X-ray scattering and AFM provides the evidence.

The material prepared by Kragten et al. displayed ^{29}Si magic-angle spinning (MAS) NMR and Fourier transform IR spectra similar to that in the original publication,[1b] but the X-ray diffraction (XRD) pattern was different (Figure 4, curves 1 and 3). In the low-angle region, a diffraction peak at $2\theta \approx 2.7°$ was lacking, while an unexpected diffraction at $2\theta \approx 7°$ was present. Note that the two sharp diffractions at 31.8° and 45.5° are due to NaCl. Redispersion of the extracted material in water[1b] failed with the material prepared by Kragten et al.[4] We revisited the extraction procedures (Table 1) and found the acidification step to be critical. Surface-charge neutralization causes removal of the protective TPA layer from the slabs, rendering them very sensitive towards condensation and degradation reactions. The absence of preferential step heights of 1.2 ± 0.3 nm in the AFM study by Ramanan et al.[5] reflects the poor quality of their extracted material. Our new procedure, involving the use of concentrated HCl (procedure 1 of Table 1) minimizes the damage of the nanoslabs.

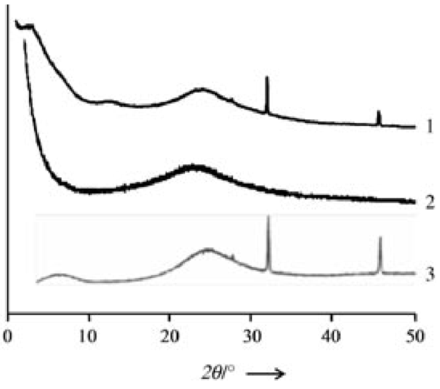

Figure 4. XRD patterns of extracted nanoslab samples prepared according to procedure 1 of Table 1 (curve 1); prepared by us according to the procedure reported by Kragten et al. (procedure 2 of Table 1, curve 2);[4] the spectrum reported by Kragten et al. (curve 3).[4]

Experimental Section

TEM samples for extracted material were prepared as dilute suspensions in methanol. A few drops of suspension were allowed to dry on perforated carbon-coated copper grids. Samples were imaged and analyzed by EDX on a Philips CM20 operating at 200 kV. XRD patterns of extracted powders loaded in capillaries were recorded in Debye-Scherrer mode on a STOE StadiP, equipped with a linear position sensitive detector.

Tabelle 1: Nanoslab isolation procedures.

Procedure	Reference	Clear solution, cooled at 0 °C	Acidification		Organic solvent		
		Volume [mL]	Acid, cooled at 0 °C	Quantity [mL] or final pH	Solvent	Volume [mL]	Elimination procedure
1	this work[c]	5	HCl (8.5 M)	15	*t*BuOH	60	evaporation; $T = 20\,^{\circ}\mathrm{C}$, $P = 60$ Pa
2	Kragten et al.[c] (ref. [4])	7	HCl (0.5 M)	15[d]	THF[a]	15	evaporation; $T = 60\,^{\circ}\mathrm{C}$
3	Schoeman[b] (ref. [3])	?	H-form of ion exchange resin	pH 2	*t*BuOH	?	freeze drying
4	Ravishankar et al.[c] (ref. [1b])	?	HCl (?)	pH 3	*t*BuOH	?	freeze drying
5	Ravishankar et al.[c] (ref. [2])	5	HCl (0.5 M)	15	THF[a]	20	evaporation

[a] Tetrahydrofuran. [b] Molar ratio TEOS:TPAOH:H_2O of 25:9:490. [c] Molar ratio TEOS:TPAOH:H_2O of 25:9:440. [d] 5 mL of clear solution was added to the acid.

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