Zeolite Nanoslabs?

On the TEM and AFM Evidence of Zeosil Nanoslabs Present during the Synthesis of Silicalite-1**

*Harikrishnan Ramanan, Efrosini Kokkoli und Michael Tsapatsis**

Stichwörter:
nanoblocks · nanoslabs · silicates · zeolites

The mechanism of formation of synthetic zeolite structures has been a subject of many recent investigations.[1–3] One of the commonly studied zeolites is silicalite-1 (siliceous ZSM-5). Recent studies on the synthesis of tetrapropylammonium (TPA) silicalite-1 have reported the formation of zeosil nanoparticles (termed *nanoslabs* or *nanoblocks*) during the early stages of silicalite-1 crystallization.[4–6] The zeosil nanoparticles are believed to agglomerate into larger tablets and eventually form silicalite-1 crystals.[4–6] Transmission electron microscopy (TEM) analysis of samples prepared by evaporation of a clear solution prepared by hydrolyzing tetraethylorthosilicate (TEOS) in the presence of aqueous TPA hydroxide (TPAOH) solution at 20 °C has been claimed to reveal the existence of such nanoparticles.[6] More specifically, TEM images that are provided in ref. [6] are interpreted as „conglomerated" nanosized particles with an average in-plane dimension of 4×4 nm^2 and thickness of approximately 1.2–1.3 nm. It is mentioned that „occasionally larger particles are observed with in-plane dimensions corresponding to multiples of 4 nm", suggesting they are formed through sidewise coalescence of elementary nanoslabs of dimension 4×4 nm^2. Figure 1a and Figure 2a herein are, respectively, Figure 1a and 1b of ref. [6]. It is interesting to note the tetragonal shape of the so-called „conglomerate" and the oriented arrangement of the so-called 4×4 nm^2 nanoblocks with their faces parallel to each other. Such an arrangement indicates oriented aggregation of the nanoslabs by simple evaporation on a TEM grid. Even more interesting is that despite the authors' claim that they are not able to obtain a diffraction pattern from these particles, close inspection of the images in Figure 1a and Figure 2a (Figure 1a and 1b in ref. [6]) clearly shows the presence of approximately 3 Å spaced fringes indicating crystalline order. Optical diffractograms (fast Fourier transform (FFT)) of Figure 1a and Figure 2a (shown in Figure 1b and Figure 2b) clearly show that the entire particle is a single crystal with unambiguous fourfold symmetry. The 3 Å spacing and fourfold symmetry are not discussed in ref. [6]. Such a small spacing and symmetry do not agree with the

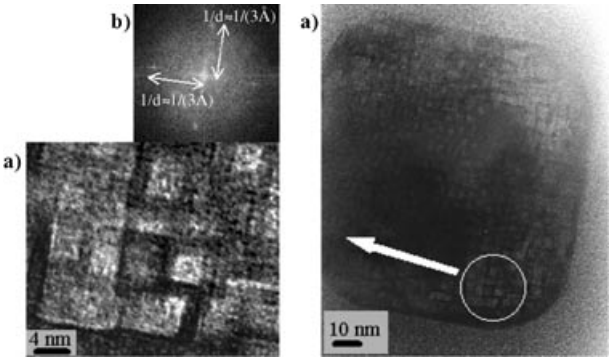

Figure 1. Parts a) Figure 1a in ref. [6], TEM images of nanoslabs prepared from TEOS/TPAOH/water system, b) our FFT of Figure 1a revealing fourfold symmetry with $d \approx 3$ Å.

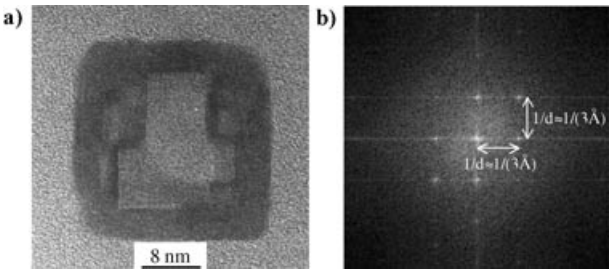

Figure 2. a) Figure 1b in ref. [6], an occasionally observed larger block in nanoslab sample, b) our FFT of Figure 2a confirming crystalline nature of observed particle with $d \approx 3$ Å and fourfold symmetry.

[*] Dr. H. Ramanan, Prof. E. Kokkoli, Prof. M. Tsapatsis
Department of Chemical Engineering and Materials Science
University of Minnesota
151 Amundson Hall
421 Washington Ave SE
Minneapolis, MN 55455-0132 (USA)
Fax: (+1) 612-626-7246
E-mail: tsapatsi@cems.umn.edu

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proposed structure of the nanoslabs. We will show (see below) that the Figure 1a and 1b of ref. [6] are most likely from a small amount of sodium chloride (NaCl) crystals contaminating the extracted material.

Atomic force microscopy (AFM) studies on evaporated suspensions of the extracted silica species reported in ref. [5] were also used to support the discovery of zeosil nanoslabs in ref. [6]. Step sizes determined by AFM were reported to be a multiple of approximately 1.2 ± 0.3 nm and interpreted as nanoslabs present either as single or stacked entities.[6] We also performed AFM measurements to compare our findings with those of ref. [5]. We summarize below our results from the TEM and AFM analysis and compare our findings on the existence of nanoslabs or nanoblocks with earlier studies.[4–6]

The procedure for synthesizing a clear suspension of the nanoparticles and their subsequent isolation or extraction has been adopted from earlier studies.[4–6] Samples prepared from the as-synthesized clear suspension as well as the extracted phase were investigated by TEM imaging, electron diffraction (ED), and energy dispersive X-ray (EDX) analysis. Images and diffraction patterns were captured under conditions of low electron-beam intensity. The as-synthesized clear suspension upon evaporation on a TEM grid forms extended platelike deposits (Figure 3a). Closer examination along the edges of the plates reveals a laminated deposit. In addition to such extended areas with laminated appearance, agglomerates of smaller globular shaped particles approximately 3–5 nm in size (Figure 3b) were also observed, but only rarely. The extended platelike deposits and the globular particles do not exhibit any diffraction. This result, along with the absence of any regular pattern of fringes within the particles confirms their amorphous nature. In contrast to the results reported in ref. [6], no material similar to that shown in Figure 1a and Figure 2a could be found in the powder prepared by evaporation of the as-synthesized suspension though we analyzed a number of representative samples. Note that previous studies, including one report by some of the authors of ref. [6], show similar results,[5]

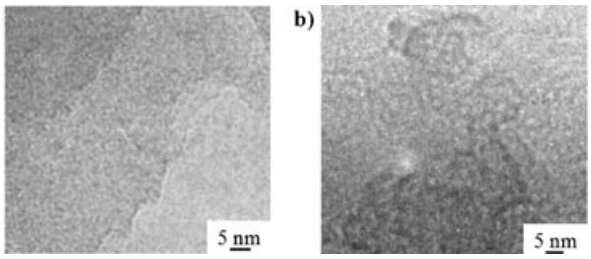

Figure 3. TEM images of amorphous silica powder from as-synthesized clear solution, a) extended laminated deposit, b) globular shaped particles.

that is, evidence of amorphous laminated deposits. The question then remains: what are the particles in Figure 1a and Figure 2a? TEM studies of the powder extracted in the organic phase (tetrahydrofuran (THF)) revealed crystalline particles (Figure 4a and b) that are very similar to the nanoslabs in ref. [6]. Figure 4c shows the FFT of the image in Figure 4b indicating fourfold symmetry and a spacing of 2.8 Å. ED and EDX studies of the crystalline particles confirmed them to be NaCl crystals. Figure 4d shows the ED pattern indexed as a ⟨001⟩ projection of a face-centered cubic unit cell of NaCl with lattice dimension $a = 5.6$ Å.[7] Figure 4e shows the EDX analysis of the particles with the corresponding Cl (strong) and Na (weak) peaks in agreement with the EDX analysis of a pure NaCl crystal (Figure 4f). The presence of NaCl crystals in the sample extracted from the organic phase indicates that not all the water has been salted out during the extraction stage. In addition to the NaCl particles, large amorphous agglomerates (Figure 5a and 5b) were also found in the extracted sample. The agglomerates appear to be similar to the laminated deposit observed in Figure 3a as well as those in the reported TEM studies (Figure 2 in ref. [5]). The EDX scan of

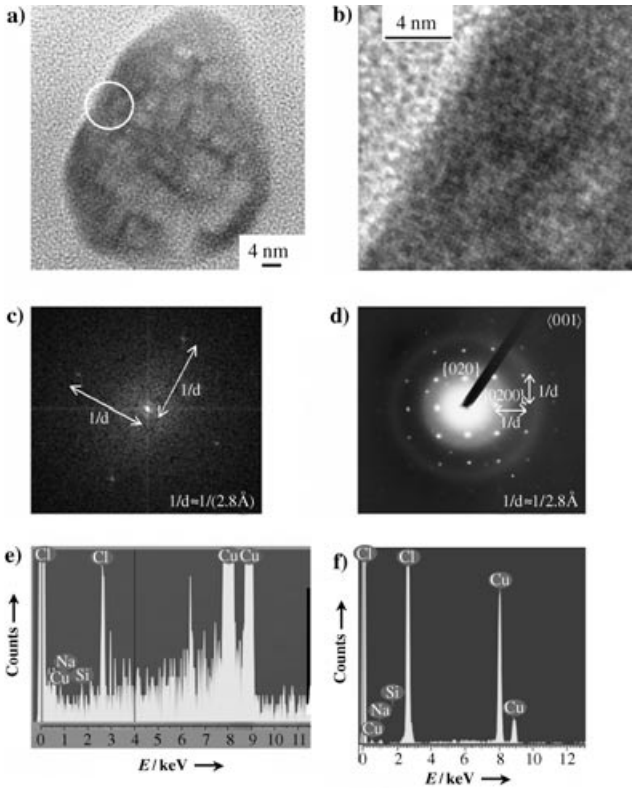

Figure 4. TEM of powder extracted in THF, a) image of particle having the agglomerate appearance reported in ref. [6], b) enlarged view of circled region in (a) revealing lattice fringes spaced at 2.8 Å, c) FFT of image shown in (b) revealing $d \approx 2.8$ Å and fourfold symmetry, d) ED pattern obtained from particle similar to that shown in (a). The fourfold symmetry and $d \approx 2.8$ Å in (c) and (d) are consistent with ⟨001⟩ projection of NaCl crystals, e) EDX analysis obtained from particle similar to that shown in (a), f) EDX analysis from a sodium chloride standard.

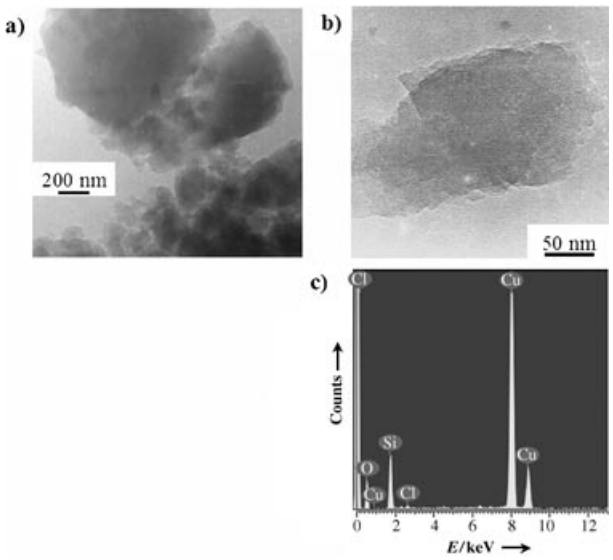

Figure 5. TEM of powder extracted in THF, a) and b) amorphous silica agglomerates, c) EDX analysis of amorphous silica agglomerate.

a representative region of the large agglomerate shown in Figure 5a confirms that the agglomerate is predominantly silica (Figure 5c). The presence of the peak for Cl in the scan suggests that some NaCl particles could be trapped in the amorphous silica (the peak for Na is relatively weak so that it is absent in this scale). The presence of significant peaks for Cu in all the EDX results are due to the use of Cu grids for TEM sample preparation.

The extracted powders were also examined by AFM. Step heights were calculated by analysis of several AFM images such as the ones shown in Figure 6a. The step heights obtained from several representative isolated agglomerates are shown in Figure 6b. Our observance of a step-height distribution centered at about 1.5 nm (Figure 6b) includes the step heights of 1.2 ± 0.3 nm reported by the authors of ref. [5]. However, the distribution measured in our samples is significantly broader and we also observed step heights that do not correspond to multiples of around 1.3 nm or to any other dimensions that have been proposed for the nanoslabs in refs. [5,6] (that is, $2.7 \times 1.0 \times 1.3$, $4 \times 2 \times 1.3$, $4 \times 4 \times 1.3$, and $8 \times 8 \times 1.3$ nm^3). We conclude that AFM analysis of the extracted samples does not confirm the existence of nanoslabs as single or stacked entities as suggested in refs. [5,6].

There are two other more recent published studies that include TEM imaging of nanoslabs.[8,9] In ref. [8], the as-synthesized suspension was used to make thin films on silicon wafers. Although fringes arising from silicon wafers were resolved, the silica–TPA film is featureless. Despite the lack of evidence for the presence of order in these films, the authors call them the thinnest zeolite film synthesized to date based on the assumption that the film is formed predominantly of nanoslabs of silicalite-1. However, this assumption is not supported by their TEM data. In another study,[9] mesoporous materials are claimed to be formed by ordered arrangement (tiling) of nanoslabs. The TEM images provided are typical of mesoporous materials with no clear evidence of order within the wall and especially for the presence of nanoslabs.

Summarizing, we found that samples prepared by drying the as-synthesized clear suspension contain predominantly amorphous agglomerates of silica along with some nanosized globular particles. Samples prepared by drying of the extracted (by salting out with NaCl) powder in the organic phase contain crystalline NaCl particles as contaminants. Comparing our results with the reported TEM data,[6] we claim that a) NaCl crystals dispersed in the organic-rich phase have been misinterpreted as nanoblocks or nanoslabs and b) no block-shaped nanoparticles could be found in the powder obtained from drying the as-synthesized clear suspension. Our findings do not contradict the existence of nanoscopic entities during the initial stages of silicalite-1 synthesis that has been established by other characterization techniques, such as dynamic light scattering,[2,3] and small angle X-ray scattering.[10] The purpose of the current study is to re-investigate the possible existence of block-shaped nanoparticles with MFI structure during the initial stages of silicalite-1 synthesis as proposed in refs. [4–6]. From the evidence presented herein, we conclude that no such nanoslabs or nanoblocks that could be classified as building blocks for zeolite MFI structure could be unambiguously identified, a situation providing further support to the arguments presented in ref. [11].

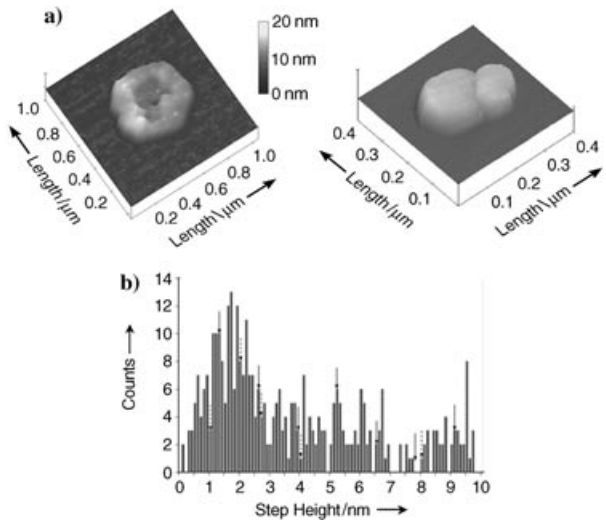

Figure 6. a) AFM images of representative agglomerates on mica substrates taken in air with an oxide-sharpened silicon nitride tip. The images show a 3D representation of the sample-height data and the gray-scale bar indicates the height variations on the topography of the surfaces. b) Histogram of step heights measured from different agglomerates. The graph shows results from 366 measurements. For comparison, arrows with solid lines show multiples of 1.3 nm for the nanoslab thickness from refs. [5,6] and the arrows with dotted lines indicate the nanoslab dimensions (1, 2, 2.7, 4, and 8 nm) from refs. [5,6].

Experimental Section

TEM samples for the as-synthesized clear silicate suspension and the extracted phase were prepared as dilute suspensions in ethanol. As the pH of the as-synthesized silicate solution was considerably high (pH > 12), TEM samples were prepared on holey carbon coated Au grids (SPI supplies, Structure Probe Inc.). Alternatively, sample preparation using holey carbon coated Cu grids (Ted Pella Inc.) also gave us identical results

though we suspected the Cu grids to be affected by the severe pH of the medium. Samples were analyzed on the JEOL JEM 3010 TEM at 300 kV for imaging and electron diffraction (ED) analysis. Energy dispersive X-ray (EDX) analysis was performed on the Philips EM 430 TEM using samples supported on holey carbon coated Cu grids (Ted Pella Inc.).

AFM characterization of the surfaces films was done with a Digital Instruments Nanoscope III system (Digital Instruments, Santa Barbara, CA). Images were obtained in contact mode in air using standard 200 μm V-shaped oxide-sharpened silicon nitride AFM cantilevers with pyramidal tips (Digital Instruments) of nominal radius 5–40 nm and nominal spring constant 0.06 $N m^{-1}$. In order to minimize the drift effects, AFM was warmed up for at least half an hour before an experiment. Samples were prepared for AFM analysis by re-dispersing a few drops of the extracted material originally dispersed in ethanol (same batch used for preparing the TEM samples) in about 10 mL of chloroform and then allowing a drop of this dispersed solution to dry on a mica plate.

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