Langmuir–Blodgett Deposited Monolayers of Silicalite-1 Seeds for Secondary Growth of Continuous Zeolite Films

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Recently, the use of more powerful characterization techniques has produced new insights into the mechanism of zeolite crystallization, and a number of “non-conventional” preparation methods aimed at the synthesis of microporous materials of desired size, morphology, chemical composition, and pore structure have been developed.[1,2] This new knowledge has been applied to the synthesis of zeolite films[3,4] with applications such as membranes,[5,6] sensors,[7,8] and insulators with low dielectric constant.[9,10] Many of these advanced applications require a continuous defect-free thin film, and a considerable research effort has been directed toward achieving this aim. The assembly of zeolite crystals on a support in a controlled manner is of particular importance, as often the presence of such densely packed crystals is required as seeds for the preparation of continuous zeolite films by secondary growth. Methods for assembling zeolite crystals on supports at present include electrostatic deposition through a polymer layer,[11–13] spin-coating,[14,15] and arrangement through well-defined covalent and ionic linkages.[16–19] The Langmuir–Blodgett (LB) technique is a widely used method for the preparation of mono- and multilayer films of a vast number of materials.[20–22] Surprisingly, we found only one brief report in the literature about LB zeolite films, and this study was limited to micrometer size crystals.[23] Herein, we present for the first time the formation of a dense monolayer of methanol treated Silicalite-1 (pure silica zeolite with MFI type structure) nanocrystals (95 nm) on Si wafer using the LB technique and demonstrate its successful use as a seed layer to prepare a continuous zeolite film by subsequent secondary growth.

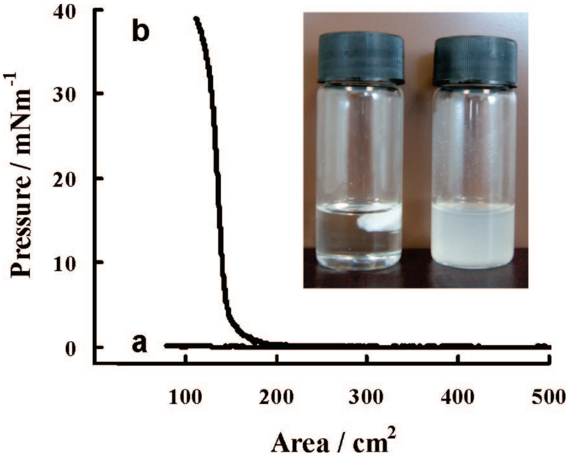

Figure 1. Pressure–area isotherms for (a) aqueous and (b) methanol modified Silicalite-1. Inset shows image of methanol treated Silicalite-1 in water (left) and chloroform (right).

The Silicalite-1 crystals were prepared using a synthesis solution based on the literature report.[24] Dynamic light scattering (DLS) analysis confirmed that the mean hydrodynamic diameter of the aqueous Silicalite-1 crystals was 95 nm with monomodal distribution (not shown). Purified aqueous Silicalite-1 was spread on the water surface in an LB trough. However, upon compression, only a minimal increase in the surface pressure was detected, indicating that a stable film was not formed (Figure 1). It has previously been reported that small zeolite particles contain surface

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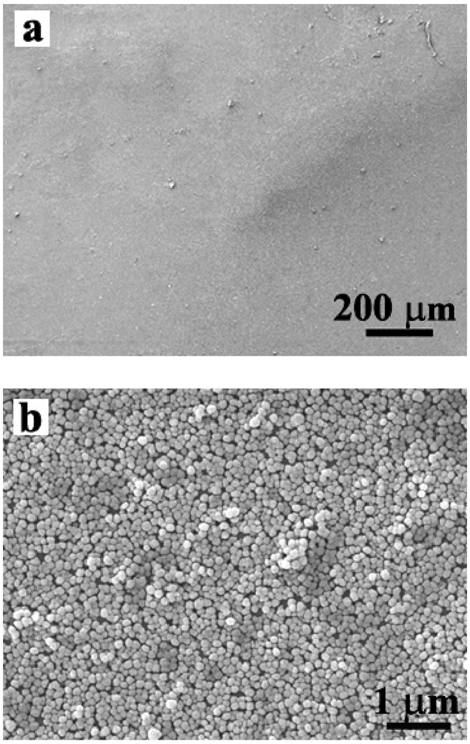

Figure 2. SEM images of Silicalite-1 films transferred onto silicon wafer.

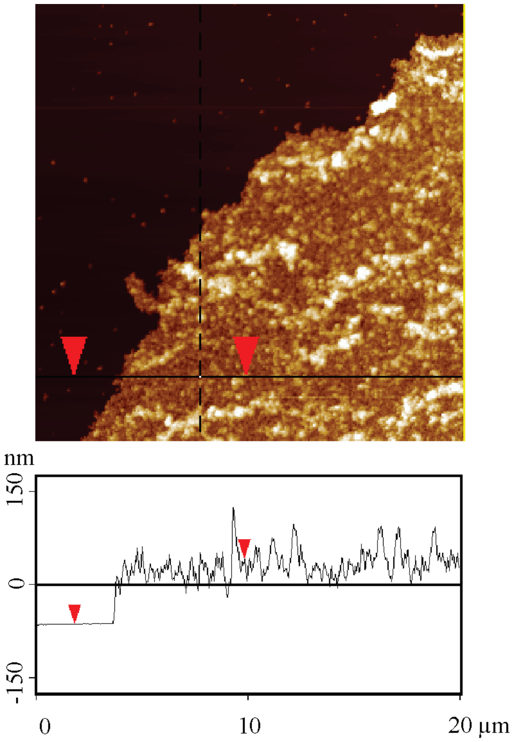

Figure 3. AFM image and cross-section analysis for Silicalite-1 film transferred onto silicon wafer.

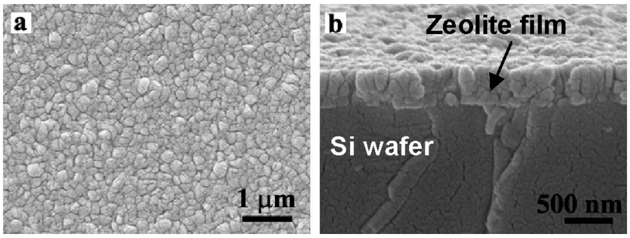

Figure 4. SEM top (a) and cross-section (b) view images of calcined Silicalite-1 film prepared by secondary growth of zeolite LB monolayer.

hydroxyl groups making them hydrophilic.[25,26] In contrast, when compressing Silicalite-1 after ultrasonic treatment in methanol, a relatively stable film was formed, shown in curve b, indicating a change in the Silicalite-1 hydrophobicity. The increased hydrophobicity of the methanol-treated Silicalite-1 was further confirmed by its low dispersibility in water and high dispersibility in chloroform (Figure 1 inset).

Brewster angle microscopy (BAM) images were taken during the course of compression of the methanol treated Silicalite-1 spread in the LB trough (Figure 1S, Supporting Information). At the beginning, the film consisted of islands of aggregated particles (a), which densified upon further compression, and the films were not very homogeneous (b, c). High magnification SEM images of deposited LB layers clearly show smooth and continuous Silicalite-1 monolayers with high density extending to millimeter dimensions (Figure 2). The characteristics of the LB film were further confirmed by AFM cross-section analysis (Figure 3). The vertical distance between the two points shown on the section analysis was 104 nm, reinforcing the monolayer nature of the film. The improved ordering of the film after deposition on the substrate may be due to the effect of capillary forces in the meniscus similar to the enhanced ordering of nanospheres observed during vertical evaporative colloidal crystal deposition.[27] Similar results were obtained when analyzing different areas of the sample as well as samples prepared from different batches.

The Silicalite-1 monolayer obtained by the LB technique was investigated as a seed layer for the secondary growth of zeolite films. SEM results proved that a well developed dense Silicalite-1 film was obtained, demonstrating that the LB monolayers are ideal seeds on which to grow continuous zeolite films. Figure 4 shows the SEM top (a) and cross-section (b) view images of a calcined Silicalite-1 film and the underlying Si substrate. The Silicalite-1 film is smooth, continuous, and crack free with a thickness of about 500 nm. It should be noted that some of the crystals extend from the support to the film surface and that the gaps between the nanocrystals were completely filled by competitive lateral and vertical growth during the secondary synthesis steps.

Fourier transform infrared analysis was used to investigate the colloidal Silicalite-1 surface properties and showed that identical spectra were recorded for powders obtained following drying of aqueous and methanol modified Silicalite-1 (Figure 2S, Supporting Information). The X-ray diffraction (XRD) powder pattern of methanol modified Silicalite-1, following drying, also confirmed that the treatment in alcohol did not alter the zeolite crystal structure (Figure 3S, Supporting Information). In a further investigation, a Silicalite-1 methanol suspension was repeatedly recorded upon exposure to air over a period of 1 h, and selected attenuated total reflection (ATR)-IR spectra are shown in Figure 5a. The first measured spectrum (spectrum 2) was similar to the spectrum

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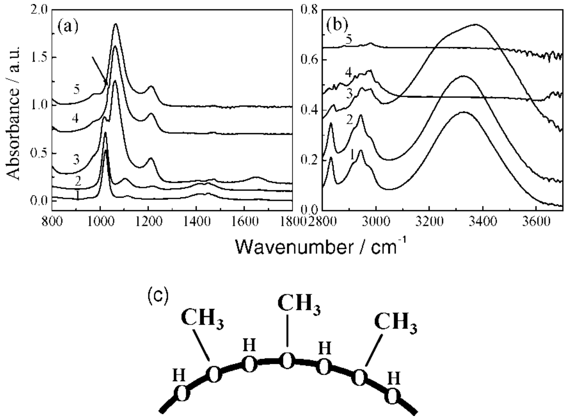

Figure 5. (a, b) ATR-IR spectra of methanol (1) and methanol treated Silicalite-1 (images 2–5 recorded over a 1 h period in chronological order) and (c) schematic illustration of modified Silicalite-1.

of pure methanol (spectrum 1). Spectrum 3 represents an intermediate state of the suspension, in which the zeolite compound is predominant, as revealed by the intensity of the characteristic Silicalite-1 peaks at 1062 and 1210 cm^{-1} and the C–O methanol stretch band at 1020 cm^{-1}.[28] The methanol has not completely evaporated as best seen from the peaks due to C–H bond stretching vibrations between 2800 and 3000 cm^{-1}. The change in the shape of the peak near 3330 cm^{-1}, which results from the O–H bond stretching, and the appearance of a peak at 1650 cm^{-1}, which is typical for H–O–H bond bending vibrations, indicate the presence of water.[29] At the same time, an additional peak at 1033 cm^{-1} is observed, the position of which cannot be related to either Silicalite-1 or methanol. We attribute this peak to –OCH$_3$ groups coated on the Silicalite-1 surface as schematically represented in Figure 5c via reaction between methanol and the terminal OH groups. The increased hydrophobicity of the modified Silicalite-1 crystals is therefore due to methoxylation of the particle surface. Spectrum 4 still contains features related to the methanol modification, a shoulder at 1033 cm^{-1}, and additional peaks in the 2800–3000 cm^{-1} region. However, these features are no longer visible in spectrum 5 recorded after 1 h of exposure time, which is similar to the IR spectra of Silicalite-1 powder.

In summary, a simple methanol treatment has been used to successfully increase the hydrophobicity of Silicalite-1 nanocrystals via the formation of methyl group shells. The LB technique was shown to be a useful means of preparing high quality smooth and homogeneous monolayer films of closely packed Silicalite-1 crystals, which were excellent seed layers for the secondary growth of continuous defect-free Silicalite-1 films. It is possible that this finding may be applied to a range of other zeolite systems, and, therefore, Silicalite-1 modification by other alcohols, as well as alcohol modification of other zeolite type nanocrystals, is currently under investigation.

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Supporting Information Available: BAM images of Silicalite-1 at the air–water interface (Figure 1S), IR spectra (Figure 2S), XRD powder pattern of Silicalite-1 (Figure 3S), and experimental details (PDF). This material is available free of charge via the Internet at http://pubs.acs.org.

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