

## Fabrication of Ordered Porous Structures by Self-Assembly of Zeolite Nanocrystals

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Zeolites are a class of microporous crystalline materials with uniform and molecular-sized pores and have been widely used as catalysts and separation media. At present, all of these applications use zeolites in the form of pellets or granules with their microstructures largely uncontrolled. Construction of zeolite structures in other geometries such as thin films<sup>1</sup> and fibers<sup>2</sup> with designed microstructures, and of zeolite materials with ordered macropore systems<sup>3</sup> promises to improve the separation and catalysis efficiency of zeolites and open doors for zeolites to new applications<sup>4</sup> such as in microelectronic devices. In this report, we attempt to demonstrate that complex porous architectures, such as micropatterned zeolite films, micro-macroporous zeolite structures, self-standing zeolite membranes, and long zeolite fibers, can be fabricated by using zeolite nanocrystals as "building blocks" through a novel, convenient, and versatile materials-processing approach.

We have synthesized nanocrystals of silicalite, ZSM-5, TS-1, Beta, A, and FAU according to reported hydrothermal procedures.<sup>5–11</sup> Only our effort on silicalite is reported in detail here as an example, however. Silicalite nanocrystals with adjustable diameters ranging from 30 to 80 nm and with narrow particle size distributions were typically synthesized as follows. A synthesis solution was prepared by dropwise adding aqueous tetrapropylammonium hydroxide (TPAOH, 20–25 wt %) solution into tetraethyl orthosilicate (TEOS, 98 wt %) with strong agitation followed by 3 days of aging at 30 °C under stirring. The final gel molar composition is 1 TPAOH:2.8 SiO<sub>2</sub>:11.2 EtOH:40 H<sub>2</sub>O. The clear solution was then transferred to a Teflon-lined autoclave and heated at 80 °C for 3 days, with a constant stirring at 250 rpm. The resulting solids were retrieved by centrifugation (15 000 rpm). The solid product was thoroughly washed with distilled

water until pH < 8 by repeated dispersion and separation using ultrasonication and centrifugation. The washed nanocrystals were eventually dispersed in neat ethanol for subsequent morphological constructions at ambient temperature. All structures were calcined at 550 °C in air for 5 h (Figure 1).

X-ray diffraction (XRD) pattern of as-synthesized and calcined nanosilicalite matches that of a typical 100% crystalline nanosilicalite sample.<sup>6,7</sup> Transmission electron microscope (TEM) images show uniform spherical nanoparticles with diameters of 30–80 nm. Fourier transform infrared (FT-IR) spectra show that the samples are of MFI type structure (band at 550 cm<sup>-1</sup>)<sup>12</sup> with 97% crystallinity<sup>12</sup> and with high concentrations of terminal Si–OH groups (band at 972 cm<sup>-1</sup>).<sup>10</sup> N<sub>2</sub> adsorption measurement on calcined nanosilicalite sample reveals micropore volume of 0.19 cm<sup>3</sup>/g and BET equivalent micropore area of 342 m<sup>2</sup>/g, consistent with reported values for crystalline nanosilicalite.<sup>6,7</sup>

Combining micromolding<sup>13,14</sup> and self-assembly of monodisperse zeolite nanoparticles, zeolite thin films with two-scale ordering are fabricated according to a procedure described in Figure 1. A drop of nanosilicalite suspension was first placed on a smooth surface such as a silicon wafer. Then, a patterned polydimethylsilane (PDMS) stamp was applied facedown with a compression pressure of  $\sim(1-2) \times 10^5$  Pa. The mold was left in place for at least 12 h to allow ethanol to evaporate and the nanoparticles to self-assemble. Figure 2a shows a representative SEM image of a dual scale-ordered zeolite structure in which zeolite nanoparticles are self-organized into a continuous close-packed network, whereas the structural ordering observed at the micrometer level is imparted by the micromolding operation using the PDMS stamp. Micromolding with aqueous sol of nanocrystals were attempted, but produced zeolite films with less well-defined patterns. Ethanol is advantageous over water as a dispersion medium in several aspects. First, ethanol is more volatile and thus easier to remove from the self-assembled structures. Second, ethanol wets both hydrophilic and hydrophobic surfaces, leading to molded structures with well-defined features. It is also speculated that ethanol stabilizes zeolite nanocrystals by partially grafting them with ethyl groups through esterification/hydrogen bonding.<sup>15</sup> Surface grafting reduces cohesive forces between zeolite nanocrystals and thus prevents premature aggregation during the self-assembly process. As ethanol evaporates, the nanoparticles are driven by capillary forces to move close to each other and eventually hydrogen bonds form,<sup>2</sup> locking the nanocrystals in place. A variety of patterns can be obtained by simply choosing an appropriate PDMS mold. The largest patterned area and the smallest line feature obtained with micromolding are 0.8 × 0.8 cm and 200 nm, respectively. After calcination at 550 °C, the features are retained, and the zeolite nanocrystals are further cross-linked by condensation of external surface silanol groups. XRD shows that patterned zeolite film retains MFI structure after calcination. To the best of our knowledge, this is the first report on zeolite films with micropatterns. Zeolite films with micropatterned structures are promising for microelectronic and optoelectronic applications.<sup>4</sup>

Polystyrene latex templating has been successfully used for preparing macroporous materials.<sup>16,17</sup> Very recently, macroporous

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(1) Yan Y.; Davis M. E.; Gavalas G. R. *Ind. Eng. Chem. Res.* **1995**, *34*, 1652–1661.

(2) Jung, K. T.; Hyun, J. H.; Shul, Y. G.; Kim, D. S. *Zeolites* **1997**, *19*, 161–168.

(3) Holland, B. T.; Abrams, L.; Stein, A. *J. Am. Chem. Soc.* **1999**, *121*, 4308–4309.

(4) Ozin, G. A. *Adv. Mater.* **1992**, *4*, 612–649.

(5) Boudreau, L. C.; Kuck, J. A.; Tsapatsis, M. *J. Membr. Sci.* **1999**, *152*, 41–59.

(6) Persson, A. E.; Schoeman, B. J.; Sterte, J.; Otterstedt, J. E. *Zeolites* **1994**, *14*, 557–567.

(7) Schoeman, B. J.; Sterte, J.; Otterstedt, J. E. *Zeolites* **1994**, *14*, 110–116.

(8) Mintova S.; Olson, N. H.; Valtchev, V.; Bein, T. *Science* **1999**, *283*, 958–960.

(9) Zhu, G.; Qiu, S.; Yu, J.; Sakamoto, Y.; Xiao, F.; Xu, R.; Terasaki, O. *Chem. Mater.* **1998**, *10*, 1483–1486.

(10) Cambior, M. A.; Corma, A.; Mifsud, A.; Perez-Pariente, J.; Valencia, S. In *Progress in Zeolite and Microporous Materials; Studies in Surface Science and Catalysis*; Chon, H., Ihm, S.-K., Uh, Y. S., Eds.; Elsevier: Amsterdam, 1997; Vol. 105, Part A, pp 341–348.

(11) Castagnola, N. B.; Dutta, P. K. *J. Phy. Chem. B* **1998**, *102*, 1696–1702.

(12) Coudurier, G.; Naccache, C.; Vadrine, J. C. *J. Chem. Soc., Chem. Commun.* **1982**, 1413–1415.

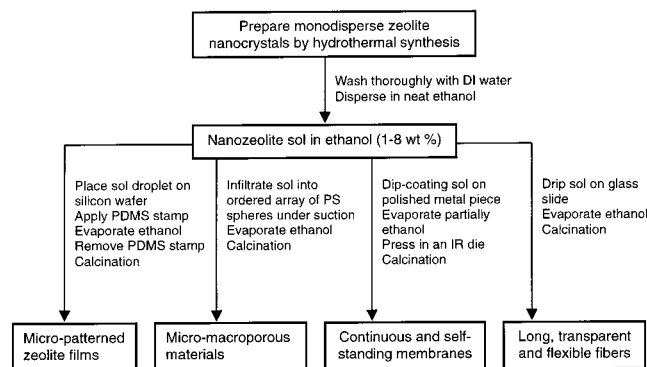
(13) Yang, P.; Deng, T.; Zhao, D.; Feng, P.; Pine D.; Chmelka, B. F.; Whitesides, G. M.; Stucky, G. D. *Science* **1998**, *282*, 2244–2246.

(14) Trau, M.; Yao, N.; Kim, E.; Xia, Y.; Whitesides, G. M.; Aksay, I. A. *Nature* **1997**, *390*, 674–676.

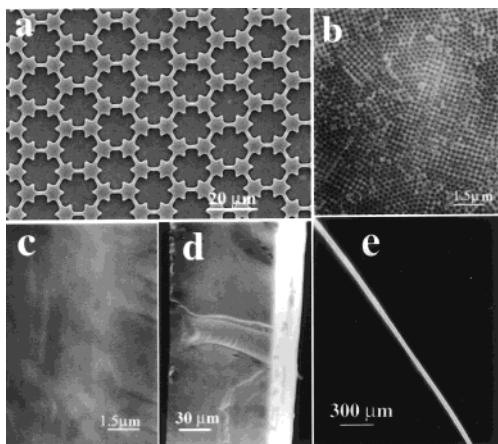
(15) Kawai, T.; Tsutsumi, K. *Colloid Polym. Sci.* **1998**, *276*, 992–998.

(16) Holland, B. T.; Blanford, C. F.; Stein, A. *Science* **1998**, *281*, 538–540.

(17) Velev, O. D.; Tessier, P. M.; Lenhoff, A. M.; Kaler, E. W. *Nature* **1999**, *401*, 548.



**Figure 1.** Flowchart of fabrication procedures of ordered porous structures.



**Figure 2.** SEM images of calcined (a) a micro-patterned silicalite film, (b) zeolite structure with ordered macropores, (c) self-standing silicalite membrane, top view, (d) self-standing silicalite membrane, cross-sectional view, (e) a long silicalite fiber

silica with partially zeolitic walls was obtained by hydrothermally converting preformed dry gel at high temperature (130 °C).<sup>3</sup> Here we report a new procedure that produces completely crystalline macroporous zeolites by combining self-assembly of monodisperse zeolite nanocrystals at room temperature with polystyrene latex templating (9.9 wt %, 300 nm diameter, Bangs Laboratory) (Figure 1). SEM micrographs show that the close packing order of the latex spheres are imprinted into the zeolite matrix (Figure 2b). Two distinct [100] and [110] faces can be observed, resembling cubic close packing of latex spheres. The spherical voids have a uniform diameter of  $\sim 160$  nm. The macropore size (80–250 nm) can be tuned with the size of the latex sphere. The average wall thickness estimated from SEM measurements is  $\sim 150$  nm, which corresponds to at least three layers of silicalite nanocrystals. Because of the assistance of ethanol dispersant, the filling of the voids between latex spheres with nanocrystals is complete and continuous. FT-IR spectra show a significant decrease of  $972\text{ cm}^{-1}$  band after the sample is calcined, suggesting cross-linking of external surface silanol groups of the nanocrystals. It is also noticed that the macroporous structures obtained here are much more uniform than those reported previously, where high temperature gel conversion results in a partially disordered array of polystyrene sphere templates.<sup>3</sup> Microporous materials with regular macropores are expected to have improved diffusion, leading to higher separation and catalysis efficiency of zeolites.

Continuous, optically transparent, and self-standing silicalite membranes are prepared by dip-coating nanocrystal suspension on polished metal surface followed by drying and high-pressure

compression (about 100 MPa) (Figure 1). SEM images of the membrane surface and cross-section are shown in Figure 2c,d. The thickness of zeolite membranes can be adjusted from  $20\text{ }\mu\text{m}$  to several tens of micrometers by changing the concentration of the nanocrystal suspension or the number of dip-coating processes. After calcination, the membrane is still transparent and crack-free. FTIR spectra for the calcined silicalite membrane reveal total loss of the  $972\text{ cm}^{-1}$  peak, indicating that high-pressure compression leads to closer packing and better cross-linking between the nanocrystals. TEM image confirms that the membrane is compact after high-pressure compression and calcination.  $\text{N}_2$  adsorption measurement on calcined membrane reveals a micropore volume of  $0.19\text{ cm}^3/\text{g}$  and BET equivalent surface area of  $340\text{ m}^2/\text{g}$ . Self-standing zeolite membranes are of great interest as model systems for studies of gas diffusion in zeolites.<sup>18</sup>

Optically transparent, flexible, and long zeolite fibers were obtained without using glass capillary as template<sup>2</sup> according to the procedure described in Figure 1. A drop of ethanol suspension of nanosilicalite was first placed on a glass slide. As ethanol evaporated, the monodisperse nanocrystals were self-assembled into many long cylindrical fibers with a diameter of about  $27\text{--}33\text{ }\mu\text{m}$  (Figure 2e). Fibers with semi-square cross-section were also produced. The average length of the fibers is 1.5 cm, which is much longer than the average length of 2.2 mm for TS-1 fibers reported in the literature using aqueous sol of TS-1 crystals.<sup>2</sup> It is also observed that small nanocrystals ( $<80$  nm) with narrow particle size distribution are essential for the formation of longer fibers, because they are much more inclined to self-assembly than larger and nonuniform particles. In addition, both before and after calcination at  $550\text{ }^\circ\text{C}$ , the fibers are optically transparent and show good flexibility when twisted. Zeolite fibers are potentially useful as advanced photoconductive materials and as advanced adsorbents and catalysts that offer faster diffusion and lower pressure drop than zeolite pellets or granules.<sup>2</sup>

We have demonstrated that complex porous structures can be fabricated by taking advantage of the ethanol-assisted self-assembly of zeolite nanocrystals. The high concentration and reactivity of external surface silanol groups of the zeolite nanocrystals are critical for hydrogen bonding formation and for subsequent cross-linking (Si–O–Si covalent bond) during calcination. This simple processing scheme separates crystallization of zeolite nanocrystals from the morphological construction, allowing preparation of complex structures that are otherwise difficult to obtain by direct hydrothermal synthesis. The processing has no effect on the crystallinity, micropore area, and volume of the nanocrystals. Additionally, by using nanocrystals as the building blocks, this approach provides the possibility of exploiting the properties of the individual nanocrystals as well as those of the specific morphologies. Similar porous structures have been constructed using other monodisperse colloidal nanocrystals such as ZSM-5 (Si/Al = 25), TS-1, Beta (Si/Al = 8–50), FAU (Y (Si/Al = 2–4) and X (Si/Al = 1–2)) and LTA (Si/Al = 3). Work on constructing three or four scale-ordered zeolite materials by combining polystyrene latex templating and micromolding are under way.

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**Supporting Information Available:** XRD, IR,  $\text{N}_2$  adsorption, SEM, and TEM (PDF). This material is available free of charge via the Internet at <http://pubs.acs.org>.

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(18) Lewis, J. E.; Gavalas, G. R.; Davis, M. E. *AIChE J.* **1997**, *43*, 83–90.