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Starch Gel Templating of Spongelike Macroporous Silicalite Monoliths and Mesoporous Films

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Silicalite nanoparticles and starch gel templates have been used to fabricate zeolite materials with a hierarchical micro/meso/macropore organization. Two methods were investigated. First, macroporous monoliths consisting of a continuous mesoporous framework of microporous silicalite were prepared by incorporating 50-nm-sized zeolite nanoparticles into freshly prepared viscous starch gels, followed by air-drying and calcination. Macropore sizes between 0.5 and 50 μm were achieved by varying the amount of starch and the starch/silicalite weight ratio. Mesoporous thin films of microporous silicalite, 2−15 μm in thickness, were also prepared by using gels containing low concentrations (2 wt %) of starch. Second, starch sponges with high internal macroporosities were prepared by freezing and thawing of starch gels and were then infiltrated with colloidal suspensions of silicalite nanoparticles and air-dried to produce silicalite−starch foams with pores up to 100 μm across depending on the starch concentration and the silicalite loading. The zeolite nanoparticles were deposited as coherent layers on the thin walls of the starch framework, which could be removed by calcination without significant disruption of the silicalite framework. In general, the methods described are facile, low in cost, and environmentally benign and can be readily extended to other inorganic materials with macroporous architectures, provided that suitable nanoparticle building blocks are available.

Introduction

Materials with ordered multimodal pore size distributions have attracted much attention recently,[1−19] because they combine the benefits of high surface area micro- and mesoporosity with the accessible diffusion pathways of macroporous networks. The tailored synthesis of hierarchically porous systems from materials such as crystalline zeolites, amorphous silica, metallic gold, and elemental carbon should therefore lead to higher separation and catalytic efficiency and new applications in large-molecule catalysis, biomolecule separations, miniaturization of electronic devices, and chromatographic supports.[4] To date, hierarchical materials with combinations of micro-/mesopores,[6,12,14] meso-/macropores,[1,2,4,13,15] micro-/macropores;[3,5,8−11,16] and micro-/meso-/macropores[7] have been prepared usually by employing dual templates with appropriate reaction solutions or nanoparticle building blocks. In general, the control of the bimodal porosity is achieved by combining suitable templates for the required length scale organization; for example, tetraalkylammonium ions are used for directing microporosity (<2 nm), long-chain surfactant or block copolymer micelles for mesoporosity (2−50 nm), and polystyrene latexes or organized bacterial threads for macroporosity (>50 nm).

Zeolite monoliths and thin films with hierarchical porosity are expected to have important and wide-ranging applications in the catalytic conversion of automobile exhaust gases and other catalytic processes.[19] Some efforts have been made to synthesize zeolite monoliths with controlled morphologies by heating shaped powders or gels under hydrothermal conditions,[20,21] using sodium bentonite as a binder,[22] or

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employing a bulk materials dissolution technique.[23] However, these shaped zeolite monoliths do not exhibit higher-ordered architectures, and the fabrication of zeolite monoliths with hierarchical pore systems has only recently being reported. Composites consisting of microporous ZSM-5 and macroporous mullite have been prepared by in situ crystallization of ZSM-5 utilizing glass from sintered kaolin clay,[19] and a similar method has been used to synthesize monolithic TS-1/cordierite catalyst.[24] In other work, macroporous monoliths of zeolites have been produced by zeolite coating of ceramic foam supports such as α-Al_2O_3, SiC/Al_2O_3, and ZrO_2/Y_2O_3 foam.[25]

Several groups have reported the preparation of macroporous zeolite monoliths with microporous walls by dual templating methods.[3,5,7−11] For example, macroporous inverse opal frameworks of silicalite have been synthesized under hydrothermal conditions by combining polystyrene latex sphere templating with synthesis mixtures containing tetrapropylammonium hydroxide (TPAOH) as a structure-directing agent.[3] A similar strategy, involving the use of polyurethane foams, has been employed to prepare macroporous silicalite architectures.[11] Alternatively, preformed zeolite nanoparticles have been employed as building blocks to construct hierarchically ordered pore systems using bacterial superstructures[5] or polystyrene beads[7−10] as secondary templates.

In this paper, we describe a new approach in which we use starch gels and sponges in combination with preformed silicalite nanoparticles to produce hierarchical architectures in the form of macroporous spongelike monoliths or thin films with meso-/macroporosity. Because starch is readily available, inexpensive, and easy to process, our method has the advantages of being facile, low-cost, environmentally benign, and amenable to scale-up.

Experimental Section

Preparation of Silicalite−Starch Gel Monoliths and Films. Silicalite−starch composites were prepared from a mixture of a freshly prepared starch gel and colloidal silicalite suspension. The latter was synthesized as described elsewhere.[5] Typically, 0.5 g of potato starch (Sigma) was mixed with 15.7 g of deionized water in a beaker with stirring to form a lump-free suspension. The suspension was then heated on a paraffin oil bath at 85 °C, and the stirring was continued until the starch gelatinized. The viscous starch paste was kept at 85 °C for 10 min without further stirring. After being allowed to cool to room temperature, 1 g of a colloidal silicalite suspension (pH 9; solid content, 4%) was added to the starch paste with stirring. The mixture was then poured into Petri dishes, or other plastic containers of the desired shape, and left to gel. Spreading of the viscous mixture on flat substrates produced composite films. After air-drying, the starch template was removed by calcination at 600 °C for 6 h.

Preparation of Starch Sponges. Starch gel sponges were prepared as follows. Potato starch (5.0 g) was added to 50.0 g of deionized water in a glass container with stirring. The starch slurry was placed on a paraffin oil bath preheated to 95 °C and manually stirred until gelatinization occurred. The gelatinized starch paste was kept at 95 °C for an additional 10 min without stirring and was then removed from the oil bath and transferred to Petri dishes. It was left to age at room temperature for ca. 15 h, after which it was frozen in a freezer at −20 °C for 15 h. Thawing of the gel at room temperature produced an intact macroporous starch gel sponge. Materials prepared without the room-temperature aging or freezing/dehydrating steps did not show well-defined sponge architectures.

Preparation of Silicalite−Starch Sponges. Silicalite−starch sponge monoliths were prepared by the following method. A preformed starch sponge gel was cut to produce a ~5-mm-thick slice that was subsequently immersed in a silicalite colloidal solution (pH 10; solid content, 19%) with gentle stirring for 12 h. The silicalite-loaded sponge was then removed from the solution, washed with deionized water, and allowed to dry in air. The inorganic loading of the silicalite−starch sponge monolith could be increased further by reimmersion of the hybrid composite into the silicalite sol for an additional 12 h, and this cycle could be repeated several times. The starch template was removed by calcination at 600 °C for 6 h.

Characterization. X-ray diffraction (XRD) experiments were carried out on a Siemens D500 diffractometer with a Cu Kα source. Scanning electron micrographs were recorded on a JEOL JSM 5600LV instrument operating at an accelerating voltage of 20 or 25 kV. Samples were mounted onto circular carbon adhesive pads attached to cylindrical aluminum stubs and were gold-coated using an Edwards S150A sputter coater. Energy-dispersive X-ray analysis (EDXA) was performed on a JEOL JSM 5600LV scanning electron microscope equipped with an Oxford Instruments microanalysis system and Link ISIS software. Thermogravimetric analysis (TGA) was carried out on Netzsch TG409EP instrument at a heating rate of 5 °C/min from room temperature to 800 °C in air with a flow rate of 90 mL/min. BET surface area measurements were carried out at 77 K on Quantachrome Autosorb-1 and Micromeritics ASAP 2000 instruments.

Results

Silicalite−Starch Gel Monoliths and Films. Monoliths and thin films of a silicalite−starch composite were prepared in situ by incorporating preformed silicalite nanoparticles[5] (mean diameter, ca. 50 nm; micropore area, 240 $m^2\ g^{-1}$) into freshly prepared viscous starch gels and drying them in air. A range of materials was prepared by varying the amount of starch and the starch/silicalite weight ratio. The films were usually prepared from gels containing low concentrations (2 wt %) of starch, whereas concentrations of up to 40 wt % were used for the monoliths. In most cases, the monoliths and thin films were prepared using starch/silicalite weight ratios greater than 1.0, up to a value of 33.

Although the as-synthesized gel monoliths were relatively hard compared with the flexible films, both types of composites could be cut to desired sizes or shapes and calcined at a temperature of 600 °C without significant shrinkage or loss of structural integrity. In all cases, TGA indicated complete removal of the starch and TPAOH templates after calcination (Figure 1). The percentage weight losses associated, for example, with a silicalite−starch composite film prepared from 2% starch and low zeolite loading (starch/silicalite ratio = 33) were 11.4% (<70 °C, water), 63.1% (150−380 °C, starch carbonization and TPAOH desorption), and 20.6% (380−500 °C, TPA-OSi decomposition, loss of

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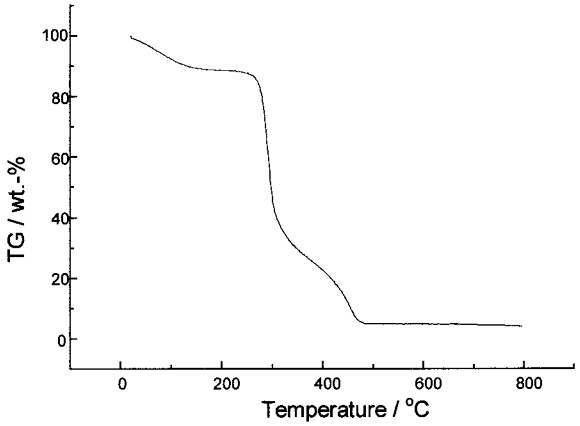

Figure 1. TGA data for a starch−silicalite composite film prepared from 2 wt % starch and a starch/silicalite weight ratio of 3.

TPA^+, and carbon burn off). Corresponding XRD measurements showed strong reflections for orthorhombic silicalite at 1.092 nm (011), 0.987 nm (200), 0.381 nm (501), 0.369 nm (033), and 0.363 nm (133) in both the noncalcined and calcined materials, as well as additional silicalite reflections in the latter for 2θ between 13 and 22°. EDXA confirmed the presence of Si in the calcined monoliths, along with trace levels of K that originated from impurities in the starch gel.

SEM images of calcined monoliths showed intact macroporous frameworks with continuous walls that consisted of closely packed aggregates of microporous silicalite nanoparticles (Figure 2). Although the pore sizes were heterogeneous, increasing the starch/silicalite weight ratio generally produced inorganic replicas with larger voids. For example, monoliths prepared with a starch content of 3 wt % produced dense replicas without macroporosity for high silicalite loadings (starch/silicalite = 0.1), whereas pores up to 500 nm and 50 μm were observed for materials fabricated with starch/silicalite ratios of 1.0 and 32, respectively. Other factors, such as increasing the stirring rate and setting times involved in the preparation of the composite gels, also increased the macroporosity of the silicalite monoliths formed after calcination.

Nitrogen adsorption/desorption isotherms from the calcined monoliths showed type 1 behavior with nearly identical horizontal adsorption and desorption branches (Figure 3), indicating the presence of both micro- and mesopores. The BET total surface area of the calcined sample was 273 m^2/g, with micropore and mesopore areas of 193 and 80 m^2/g, respectively. The micropore volume was determined to be 0.09 cm^3/g. The hysteresis loop observed at high relative pressures was of H1 type and typical of a mesoporous material consisting of agglomerates of spherical particles with approximately uniform size, consistent with high-magnification SEM images of the calcined monoliths (Figure 2d). BJH methods showed a narrow distribution of mesopores with an average diameter of 40 nm.

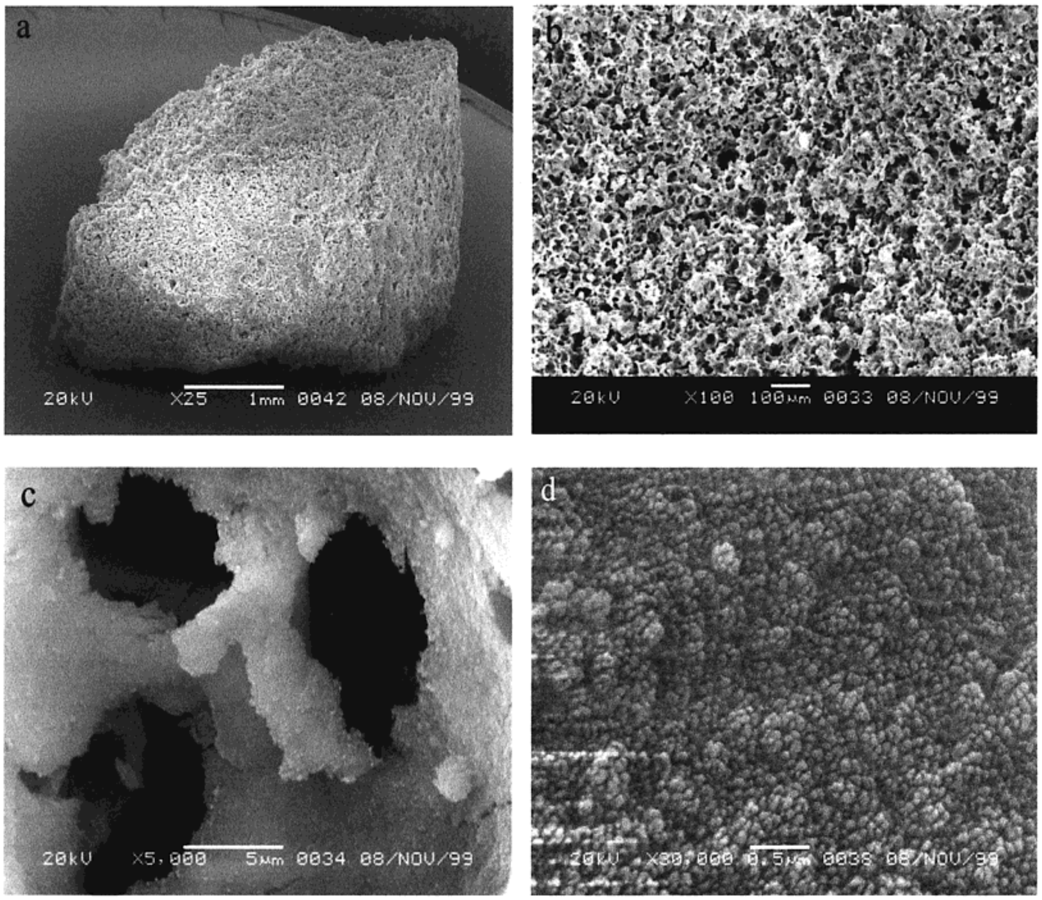

Figure 2. SEM images of a calcined macroporous silicalite monolith prepared from a starch−silicalite gel template (38 wt % starch, starch/silicalite weight ratio = 2.6). (a) Low-magnification image showing a fragment of the intact monolith (scale bar = 1 mm). (b−d) Higher-magnification images of a showing (b) macroporous texture (scale bar = 100 μm), (c) individual macropores (scale bar = 5 μm), and (d) mesoporous wall structure of aggregated silicalite nanoparticles (scale bar = 0.5 μm).

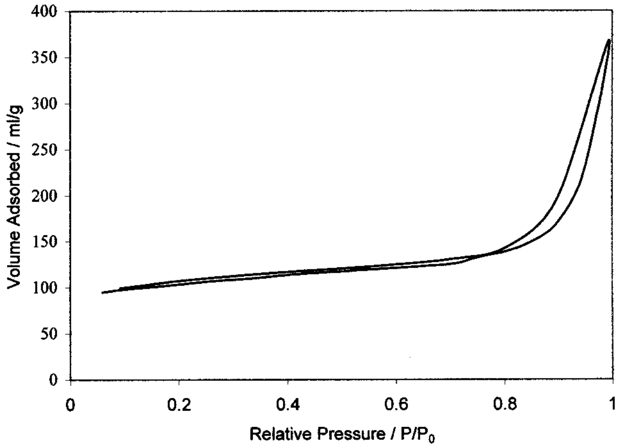

Figure 3. BET adsorption isotherm for a calcined silicalite monolith prepared from a starch−silicalite gel.

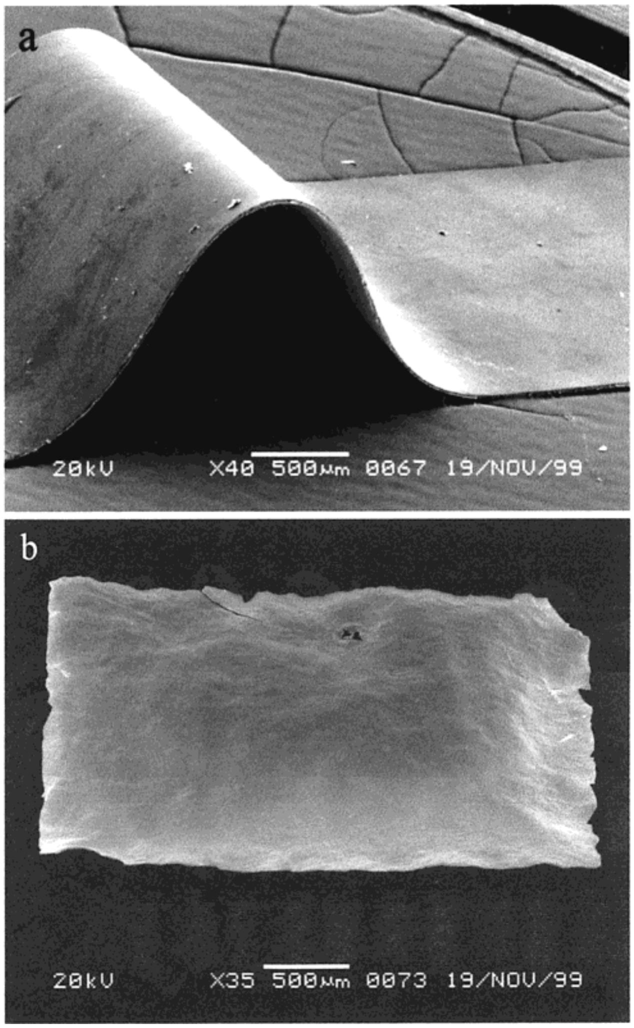

Figure 4. Silicalite−starch films (a) before and (b) after calcination. The films were prepared from 2 wt % starch gels with a starch/silicalite weight ratio of 3.9 and a typical thickness of 15 μm. Scale bars = 500 μm in both micrographs.

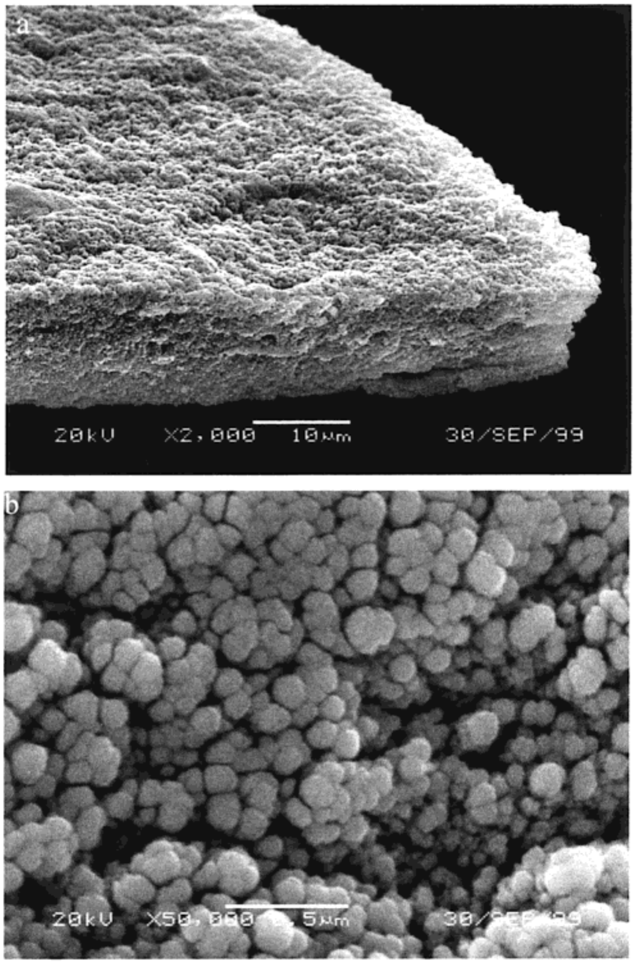

Figure 5. Silicalite−starch composite film after calcination showing (a) surface and internal texture of silicalite aggregates (scale bar = 10 μm) and (b) cross section of the film with silicalite aggregates and interparticle mesopores (scale bar = 0.5 μm).

Silicalite−starch gels with thicknesses between 2 and 15 μm were prepared as flexible composite films. Except for materials prepared at a high starch/silicalite ratio (= 33), the films showed no cracking and remained intact after calcination (Figure 4). The calcined films did not disintegrate when placed in water, ethanol, or acetone. Because the films were prepared from low starch contents, the resulting textures were denser than the monolithic materials (Figure 5a), and continuous macroporous frameworks were not observed. However, high-magnification SEM images showed that the calcined films consisted of loosely packed aggregates of silicalite nanoparticles with meso- and macroscale pores, 20−500 nm in size (Figure 5b).

Silicalite−Starch Sponges. Starch sponges with high internal porosities were prepared by a novel method that involved the freezing and thawing of starch gels (see Experimental Methods). The sponges consisted of intact 3-D bicontinuous macroporous networks with pore sizes that were dependent on the starch concentration used. For example, sponges prepared from a starch concentration of 9 wt % consisted of 50−200-μm-sized pores with wall thicknesses of 5−10 μm (Figure 6), whereas increasing the starch concentration to 16.7 wt % produced sponges with smaller openings (<100 μm) and thicker walls (10−20 μm). When moist, the starch sponges could be stored without loss of structure at room temperature and were easy to handle and cut into desired shapes. Once dried, the sponges were tough and hard but not brittle or crispy.

Preparation of silicalite−starch sponge monoliths was achieved by immersing thin (5-mm) slices of the preformed starch gel sponge into colloidal dispersions of

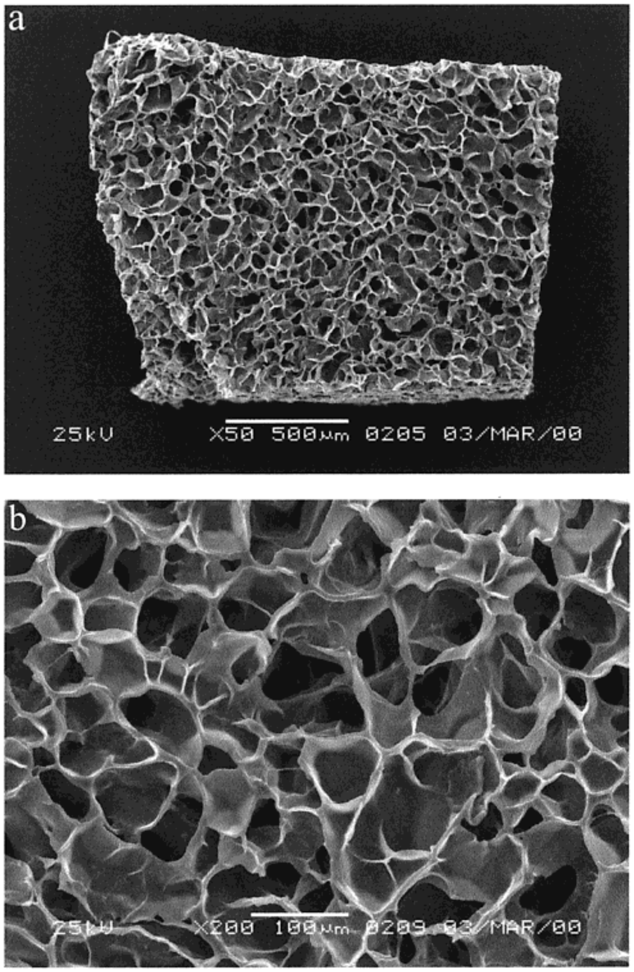

Figure 6. (a) Macroporous structure of a starch gel sponge prepared from 9 wt % starch (scale bar = 500 μm). (b) Higher-magnification SEM image showing individual pores and wall structures (scale bar = 100 μm).

silicalite nanoparticles. After air-drying, the zeolite nanoparticles were deposited preferentially on the thin walls of the sponge framework to produce an intact macroporous silicalite–starch composite (Figure 7). The silicalite layers were smooth and continuous and between 5 and 20 μm in thickness, depending on the duration of immersion (often 12 h) and the porosity of the sponge, which increased with decreasing starch weight percentage. For example, TGA studies indicated that silicalite loadings of 42.4 and 26.2 wt % were obtained using sponges prepared from starch concentrations of 9 and 16.7 wt %, respectively. Moreover, because the loading process was irreversible, the total amount of silicalite in the starch sponge could be significantly increased by successive repeats of the infiltration/air-drying cycle, provided that sufficient void space was still present within the mineralized composites. For example, the silicalite loading was increased from 26.2 to 44.8 wt % when a second infiltration cycle was undertaken on the mineralized sponge composite prepared from 16.7 wt % starch.

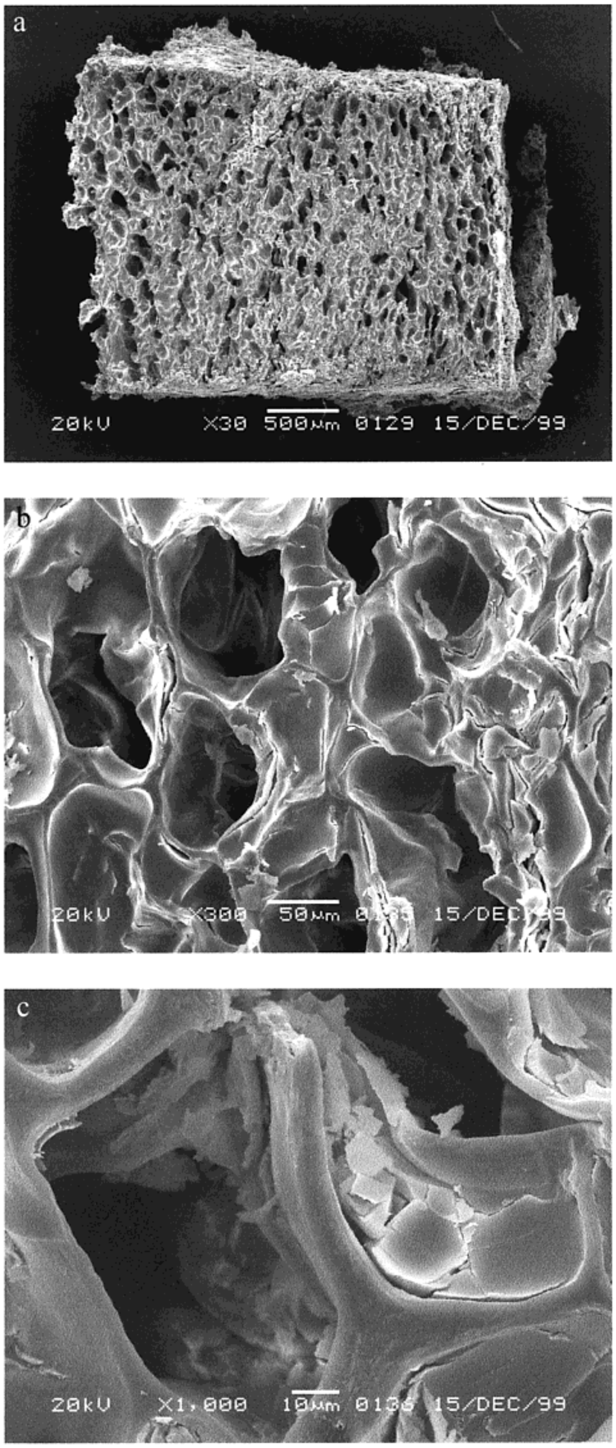

Figure 7. (a) As-synthesized starch–silicalite macroporous sponge composite prepared with a starch concentration of 9 wt % (scale bar = 500 μm). (b and c) Higher-magnification SEM images showing internal silicalite coating of the starch walls (scale bars = 50 and 10 μm, respectively).

Removal of the starch sponge and TPA templates by calcination produced macroporous monoliths of microporous silicalite (Figure 8). SEM images indicated a reasonable level of fidelity between the starch gel sponge template and the corresponding zeolite monolith, although some degree of local collapse and disorganization of the structure was also observed (Figure 8c). High-magnification images of the fractured sections of the pore walls confirmed the presence of aggregated zeolite nanoparticles, and XRD confirmed that the macroporous replica consisted of crystalline silicalite.

Discussion

In this paper, we have illustrated how a nanotectonics[26] approach involving the use of preformed silicalite

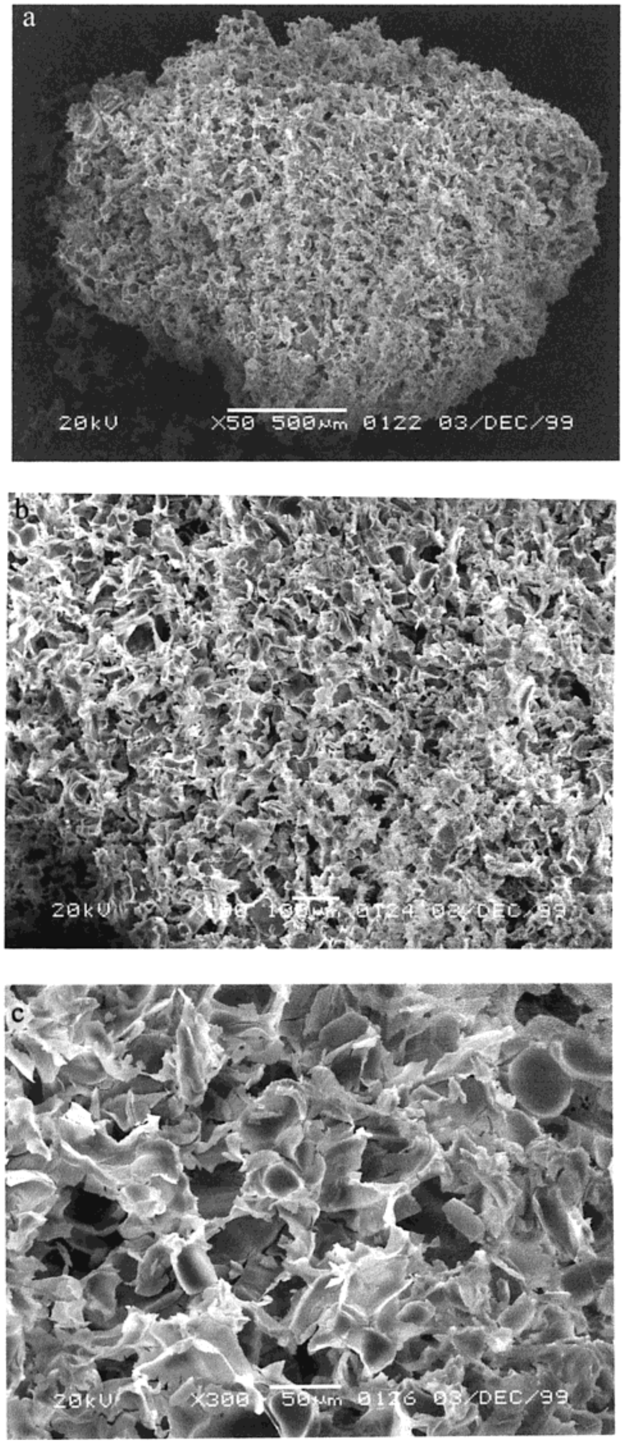

Figure 8. (a) Calcined macroporous monolith prepared from a silicalite-loaded starch sponge (16.7 wt % starch) (scale bar = 500 μm). (b and c) Higher-magnification SEM images showing disorganized porous framework of curved silicalite sheets (scale bars = 50 and 10 μm, respectively).

nanoparticles and starch gel templates can be applied to fabricate zeolite materials with hierarchical pore organization. The in situ preparation of macroporous silicalite monoliths and films from starch gels is, to a large extent, dependent on the facile incorporation of the zeolite nanoparticles into the biopolymeric matrix. Starch $(C_6H_{10}O_5)_n$ is generally composed of two types of polysaccharides: amylose, a linear species formed from D-glucose units linked α-1→ 4 to each other, and amylopectin, a branched species containing D-glucose units linked α-1→ 4, along with 5% of α-1→ 6 linkages. At temperatures around 85 °C, aqueous dispersions of starch become gellike as a result of swelling and disruption of the starch granules. The resulting gel, which consists of a hydrated 3-D porous network of predominantly amylose molecules, is thixotropic and negatively charged at neutral pH because of a small number of carboxyl groups.[27] Because the pore size distribution in the starch gel primarily depends on the starch content,[28] silicalite monoliths with varying macroporosities can therefore be readily prepared by changing the starch concentration or the starch/silicalite weight ratio, or both, in the as-synthesized composite. In general, the calcined monoliths consist of continuous mesoporous walls of aggregated silicalite nanoparticles, which indicates that the extent of particle coalescence is sufficient to produce a self-supporting architecture while still maintaining a significant number of interparticle voids.

The use of preformed starch sponges to produce macroporous silicalite monoliths has several advantages. First, the method allows direct control of the inorganic architecture through systematic modification of the pore network of the organic foam. Second, pores of up to 100 μm are possible, whereas the maximum pore size produced by calcination of the silicalite–starch gel monoliths is ca. 50 μm. Third, relatively high levels of zeolite loading are attained using the sponge templates, and these levels can be increased further by repeated cycles of silicalite infiltration to produce walls in the range 5–20 μm. The high level of colloidal infiltration is probably facilitated by repulsive electrostatic interactions between the anionic starch gel and negatively charged silicalite nanoparticles. These interactions prevent the initial deposition of nanoparticles onto the external surface or in the near-surface regions of the sponge so that the colloid penetrates deep into the biopolymeric architecture. Similar observations were reported for silica and silicalite infiltration into swollen bacterial templates,[1,5] whereas positively charged nanoparticles such as TiO_2 did not penetrate the organic structure because of the formation of a thick surface coating. In the case of silicalite, the increased ionic strength associated with evaporation of the solvent upon air-drying gives rise to particle aggregation and the formation of a continuous zeolite layer on the internal surfaces of the spongelike starch monolith.

In general, macroporous silicalite–starch hybrid sponges could have certain advantages over the corresponding calcined replicas in terms of increased structural organization and enhanced mechanical properties. We have prepared colloids of calcined 50-nm-sized silicalite nanoparticles with extracted TPA templates (unpublished data), and it should be possible therefore to use these colloids directly as building blocks along with organic scaffolds such as starch sponges to prepare

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inorganic–organic hybrid materials with hierarchically organized porosity. This approach alleviates the need to remove the macroporous starch template and could therefore give rise to biocompatible and bioactive materials that, to some extent, resemble biominerals such as bone. Future work will aim to extend our current studies using starch templates to other zeolite colloids and inorganic materials with potential applications in catalysis, separations technology, and bioengineering.

Conclusions

Silicalite–starch gel monoliths and films, as well as spongelike starch foams infiltrated with silicalite nanoparticles, have been used for constructing macroporous architectures of the zeolite silicalite. Two methods are described: first, the in situ preparation silicalite–starch gel composites and their subsequent calcination and, second, the use of preformed starch sponges. In both cases, the materials exhibit at least two levels of hierarchy in pore organization, viz. the microporosity of the silicalite walls and the macroporous voids of the open-framework monoliths. A third level of mesoporosity is also present in some materials as a result of incomplete coalescence of the silicalite nanoparticles. Modifications in the starch concentration or the starch/silicalite weight ratio can be used to control the size of the macropores and the thickness of the silicalite deposits. The methods are facile, low-cost, and environmentally benign, and they can be readily extended to other inorganic materials with macroporous architectures, provided that suitable nanoparticle building blocks are available.

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