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Solvothermal removal of the organic template from L_3 ("sponge") templated silica monoliths

Daniel M. Dabbs[1], Norbert Mulders[2] and Ilhan A. Aksay[1,*]
[1]*Department of Chemical Engineering, Princeton University, Princeton, NJ, 08544, USA;* [2]*Department of Physics and Astronomy, University of Delaware, Newark, DE, 19716, USA; *Author for correspondence (Tel.: +1-609-2584393; Fax: +1-609-2586835; E-mail: iaksay@princeton.EDU)*

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Abstract

We compare the methods of continuous solvent (Soxhlet) and supercritical solvent extractions for the removal of the organic template from nanostructured silica monoliths. Our monoliths are formed by templating the L_3 liquid crystal phase of cetylpyridinium chloride in aqueous solutions with tetramethoxy silane. The monoliths that result from both Soxhlet and supercritical extraction methods are mechanically robust, optically clear, and free of cracks. The Soxhlet method compares favorably with supercritical solvent extraction in that equivalent L_3-templated silica can be synthesized without the use of specialized reactor hardware or higher temperatures and high pressures, while avoiding noxious byproducts. The comparative effectiveness of various solvents in the Soxhlet process is related to the Hildebrand solubility parameter, determined by the effective surface area of the extracted silica.

Introduction

The removal of organic substances from porous ceramic materials using supercritical solvent extraction (SSE) is a well-known and generally effective process (McHardy & Sawan, 1998). A supercritical fluid combines the high solvating power of a liquid with the high permeability of a vapor. Supercritical drying is a preferred method for processing crack-free monoliths: the absence of the liquid–vapor interface prevents differential capillary pressures within the monolith, reducing drying stresses. But there are limitations and disadvantages to the application of SSE to surfactant-templated ceramics such as our L_3-templated silica (Prakash et al., 1995). For example, supercritical carbon dioxide extraction, although known to be an environmentally friendly extraction technique, is not as effective in removing polar surfactants, whose solubility is high in water but low in supercritical CO_2 (Dale Spall & Laintz, 1998; Brennecke, 1997). Solubility can be increased by adding co-solvents, but the nature of these can off-set the benign aspects of the CO_2 process. A more effective, although less benign, supercritical extraction method uses an organic solvent such as methanol as the supercritical fluid, a process that involves higher temperatures and pressures to achieve criticality, concomitant with higher solvating capability (Darr & Poliakoff, 1999). We have successfully used high temperature solvent extraction to produce physically robust nanostructured silica monoliths (Malik et al., 2006). The principal drawbacks to this method of SSE include the need for special equipment, high pressures combined with high temperatures (P_c, T_c respectively), long processing times (up to 1 week), careful control of processing parameters to protect the sample during extraction, and byproducts that are frequently noxious (Malik et al., 2006).

Interest in removing the organic component of self-assembled materials, the structure-directing agent (SDA), via methods utilizing solvents centers on two goals: preserving the structure of the templated inorganic phase and removing the SDA as completely as possible (Patarin, 2004). Calcination to remove the organic can lead to densification of the porous structure, network collapse and loss of the mesostructure (Patarin, 2004). Further, the organic component is destroyed in the process, adding to the cost of processing (Lee et al., 2003). Solvent extraction avoids high temperatures and, as we have observed in our monolithic samples, coloration of the sample due to the retention of partially oxidized organic (McGrath et al., 1997, 2000). Solvent-based recovery of the SDA has been achieved via supercritical extraction using CO_2, (Kawi & Lai, 2002; van Grieken et al., 2003) and solvent recovery (Whitehurst, 1992). Lee et al. (2003) extended the efficacy of solvent recovery by designing an SDA that can be disassembled within the mesostruture. The fragments are then removed by extraction and may be reassembled for reuse. Most of the extant literature appears to deal with removing the organic from powders, although this is not always noted in the experimental descriptions, and does not describe the potential for use with larger monolithic structures.

In this paper, we compare two methods to remove the organic component of an isotropic nanostructured silica monolith: continuous solvent (Soxhlet) and high temperature supercritical solvent extraction. The principal advantages of Soxhlet extraction include the simplicity of the apparatus (Figure 1), processing under atmospheric pressure in an open system, and processing temperatures no higher than the boiling point of the solvent (for methanol, $T_b = 64.7°C$ at one atmosphere). We show that extraction efficiencies within nanostructured silica that have undergone Soxhlet extraction, as determined by weight loss measurements and surface area measurements, approach that measured for similar materials extracted using high temperature SSE.

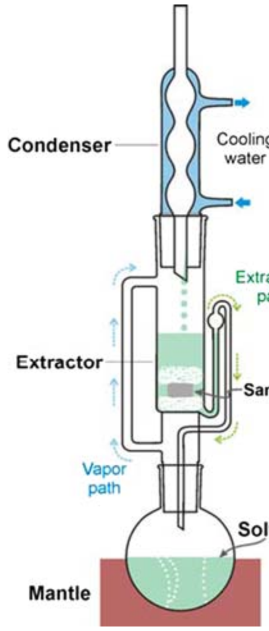

Figure 1. Schematic of a Soxhlet extraction apparatus indicating the vapor and liquid extractant paths. The sample under extraction is cushioned by loosely packed ceramic fibers.

Nanostructured materials have high potential for use in applications such as filtration, catalysis, and composite processing, (Pinnavaia & Thorpe, 1996) applications requiring access to the void volume and channel wall surfaces. The resulting silica matrix lends itself to *in-situ* polymerization of infiltrated monomers, a method of fabrication particularly well-suited to optical storage composites (Malik et al., 2006). We use L_3 phase-templated silica as the test matrix, a nanostructured silica formed by templating silica onto the surfaces of a surfactant bilayer that forms the isotropic L_3 or “sponge” liquid crystalline phase (Figure 2) (McGrath et al., 1997, 2000). A significant advantage in the use of the L_3 phase in templation is that the organic components of the L_3 phase (including the co-surfactant hexanol) compose the interior of the bilayer (Figure 2). [The L_3 structure has been viewed as a distortion of either lamellar or cubic structures and as an intermediate phase between the two ordered phases. (Porte, 1992; Kim et al., 1998)] The dual interconnectivity of the L_3 structure provides a

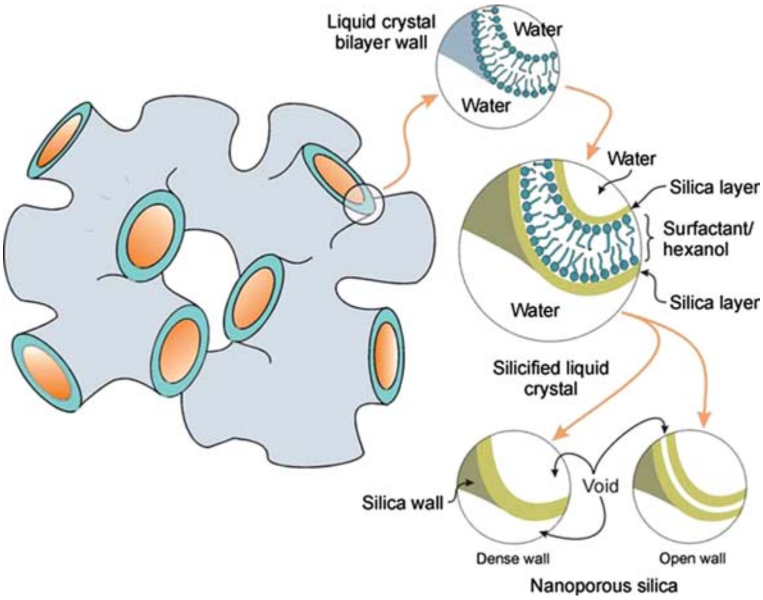

Figure 2. Schematic of the L_3 sponge phase and the templation of the bilayer by silica (McGrath et al., 1997; 2000).

continuous channel volume while providing structural integrity to the resulting nanostructured silica following templation and conversion.

The L_3 liquid crystal is a thermodynamically stable phase (Strey et al., 1990; Skouri et al., 1991) composed of the surfactant cetylpyridinium chloride monohydrate ($CpCl \cdot H_2O$, 1-hexadecylpyridinium chloride mono-hydrate, $C_{16}H_{33}(N^+)C_5H_5(Cl^-) \cdot H_2O$), the co-surfactant hexanol ($C_6H_{13}OH$), and hydrochloric acid (0.2 M, aqueous). This system was adapted from the system described by McGrath (1997), replacing the original brine solution (aqueous NaCl) with dilute HCl (aq) as the chloride source (McGrath et al., 1997). The source of silica for silicification of the L_3 phase remained tetramethoxysilane (TMOS).

A disordered structure such as the L_3 phase does not form interfaces such as the grain boundaries typically observed in materials synthesized by templating the more ordered liquid crystals (e.g., hexagonal arrays or lamella, Figure 3) (McGehee et al., 1994; Dabbs & Aksay, 2000). The formation of interfaces within the more ordered systems result in powders or granules following deposition of the inorganic phase (McGehee et al., 1994). In contrast, lacking either ordered or intergranular surfaces, L_3-templated silica remains optically transparent throughout silicification. The disordered channels of the L_3 liquid crystalline phase permeate the entire volume of its solution, separating the water fraction into two equal volumes (Porte, 1992). This structure gives rise to the "dilution effect", in which an increase in the primary solvent content expands the characteristic channel size as the bilayer membrane stretches to maintain continuity throughout the solution (Porte, 1992; Strey et al., 1990). The effect of increasing the solvent content while fixing the amount of organic can be followed using small angle X-ray scattering (SAXS) and is interpreted as proof that the L_3 phase exists in solution (Lei et al., 1997). For those applications in which access to the void volume and continuity of the channel network is vital in large continuous structured materials [such as in membranes, catalyst supports, and optical storage matrices (Malik et al., 2006)], syntheses that involve templating a disordered phase are more readily applied to larger scale structures.

The structures of ordered-phase templates, such as hexagonally arranged micellar nanotubules (Figure 3), have their channel volume (e.g., the diameter) defined and filled by the amphiphilic surfactant (Kresge et al., 1992; Beck et al., 1992). Access to the primary void volume and channel

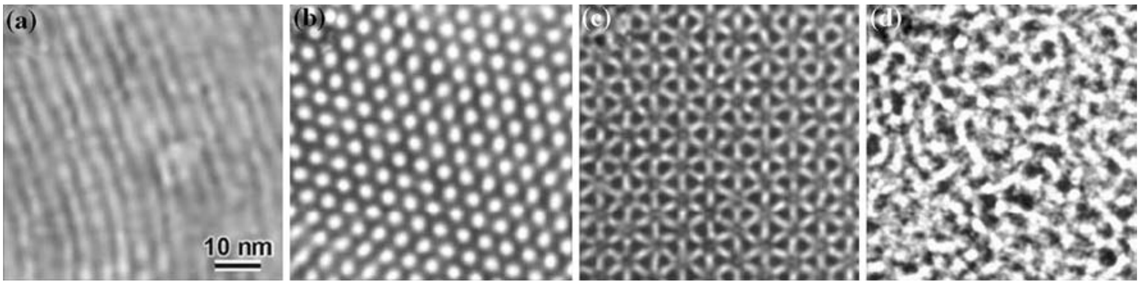

Figure 3. Nanostructured silica formed by the interaction of silicon alkoxides with structured surfactant liquid crystals: (a) lamellar, (b) hexagonal, (c) cubic (McGehee et al., 1994; Dabbs & Aksay, 2000) and (d) L_3 (Dabbs & Aksay, 2000). All samples shown were heat-treated to remove the organic component after gelation and drying. Cubic and L_3 morphologies are seen to have 3D channel structure.

surfaces requires removal of the organic component. In the case of the L_3 structure, channel access is readily available through the aqueous regions without first removing the organic phase, a characteristic we have used to our advantage in reinfiltrating the matrix phase with solutions (McGrath et al., 1997; Darr & Poliakoff, 1999).

We have previously shown that the underlying structure of an L_3 silica does not appear to change appreciably when comparing air-dried, supercritical CO_2 extracted, or heat-treated (600°C for one hour) L_3 silica powder samples, although the measured surface areas were shown to increase with decreasing organic content (McGrath et al., 2000). Heat-treated samples were typically discolored, ranging in appearance from opaque when heated under air to black when heated under nitrogen. Coloration is thought to be the result of the partial decomposition of retained organics within the matrix, whereas the degree of opacity is assumed to be a result of fracturing within the samples. Since the degree of coloration would be determined by the efficiency of extraction prior to heat treatment, (McGrath et al., 2000) we sought methods for the efficient removal of the organic from L_3 silica, a process that could be complicated by the encapsulation of the organic within the silica-coated bilayer walls (Figure 2). We have shown that efficient drying and extraction strengthens the silica by increasing the extent of cross-linking within the solid, allowing for the fabrication of larger nanostructured monoliths (Malik et al., 2006).

Here, we show that concomitant to the removal of the organic component, both the Soxhlet and the high temperature supercritical solvent extraction methods appear to enhance the condensation of free silanols ($\equiv$ Si–OH), which, combined with the removal of the organic component, results in a mechanically robust, optically transparent silica monolith containing a continuous nanostructured channel network. These monoliths are strong enough to withstand infiltration by solutions, presaging use as matrices for composite materials, especially in those materials for which optical clarity would be a marked advantage.

Experimental

L_3 solutions of 65 wt.% and 90 wt.% solvent fractions were used as the templates for forming the silica monoliths; the solvent was 0.2 mol dm^{-3} hydrochloric acid. The ratio of hexanol to $CpCl{\cdot}H_2O$[1] was fixed at approximately 1.15 (by weight) for all templating solutions.[2]

To ensure consistency in the synthesis of L_3 solutions, we followed a strict procedure described

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[1] The high reactivity of tetramethoxysilane (TMOS) to the mucous membranes and the cornea of the eye require that any synthesis involving TMOS must be done in a well-ventilated fume hood.

[2] Cetylpyridinium chloride and hexanol were purchased from Sigma Chemical Co. Concentrated hydrochloric acid was standard chemical stores grade and was diluted to the appropriate concentration prior to use. Distilled deionized water was used for all dilutions and solutions; measured conductivities ranged between 1 and 10 MΩ cm for the pure water. Tetramethoxysilane (TMOS, $(CH_3O)_4Si$, $\geq 97\%$ pure) was from Fluka Chemica-BioChemika. The TMOS was checked for evidence of prehydrolysis that may have occurred prior to use; otherwise, it and all other chemicals were used as received.

elsewhere (Malik et al., 2006; McGrath et al., 1997, 2000) and summarized here. First, the CpCl surfactant and hexanol co-surfactant were carefully measured to a ratio of 1.15 hexanol/CpCl by weight. These were gently mixed at very low speed using a Teflon-coated stir bar to form a homogeneous paste. The appropriate amount of 0.2 mol dm^{-3} hydrochloric acid was then added to the paste, the volume corresponding to the solvent fraction of interest. To reduce errors in measuring quantities, no less than 5 g total solution was made for each sample. For example, to prepare 5 g of L_3 phase solution containing 65 wt.% solvent, the following amounts of materials were used: 0.814 g CpCl, 0.936 g hexanol, and 3.250 g of the 0.2 mol dm^{-3}HCl solvent.

After adding the hydrochloric acid, each sample was stirred using a Teflon-coated stir bar over a magnetic stirrer, taking care not to heat the solution (a water bath at room temperature was used as necessary to avoid heating the sample) or create bubbles in the solution. After 20–30 min. of continuous stirring, a "good" solution would be optically clear, with an apparent viscosity similar to that of water. The solutions were then tightly sealed and set aside for no less than 2 h at room temperature. [The insistence on solution aging is not arbitrary; as determined in another study, the cetylpyridinium chloride is received as a dry powder of the lamellar phase (Bhansali et al., 2006). To ensure that the L_3 solution was phase-pure, it was necessary to allow sufficient time for the lamellar phase to swell, dissolve and completely convert to the L_3 phase].

Two visual tests were sufficient to confirm that the solutions were single phase: Samples that were observed to be turbid or viscous were assumed to contain multiple phases. Polarized light microscopy confirmed the presence of other phases in that phase-pure solutions were transparent when viewed between polarizing filters while the presence of ordered phases was indicated by opalescent regions within the solution (McGrath, 1997; Bhansali et al., 2006). Only optically clear solutions were used in forming the silica monoliths.

TMOS was used as the silica source in each L_3 solution. To ensure complete hydrolysis of the alkoxide, the amount of TMOS added to the L_3 solution was determined by the amount of solvent in the solution. The molar ratio of water to TMOS was fixed at 4:1, a practice based on standard sol-gel processing using silicon alkoxides. For example, 6.87 g of TMOS was added to 5 g of 65 wt.% solvent L_3 solution. TMOS was added drop-wise without stirring[1]. (The solution warms significantly upon adding the TMOS due to the rapid hydrolysis of the alkoxide by the acidic solution.) The samples were tightly sealed following TMOS addition.

After complete hydrolysis (taken as the point at which the temperature of the sample returned to ambient), the solutions were set aside to gel. Samples gel within 2–5 h after adding TMOS if incubated at 60°C, within 48 h if held at room temperature. In all the solutions used in this work, the gels were optically clear, colorless, and molded to the shape of the container. There was little change in volume during the transition from fluid to gel and no free liquid was observed on the surface of the gel.

Before any extraction, each gelled sample was treated with successive solvent exchanges with increasingly methanol-rich solutions of methanol and water. Eventually the gel would be covered by pure methanol. The first exchange medium was a solution of 1:1 water-to-methanol (by volume). The sample was covered with methanol/water shortly after the sample gelled. The gels did not swell with the addition of the exchange solution. After several hours, the water/methanol solution was poured off and replaced with a fresh solution containing 60% methanol and 40% water by volume. The process of adding progressively methanol-rich solutions would be repeated three or four times, until the gel was under pure methanol. The gels could then be stored for several days under methanol without noticeable shrinkage and/or cracking.

Continuous Soxhlet extraction was used as one method for removing the organic materials from the L_3 silica gel. A cylindrical monolith of L_3 silica, approximately 2 cm in diameter and 1.5 cm in height, would be placed in the extraction chamber of the Soxhlet extraction apparatus cushioned on both sides by glass wool (Figure 1). A 500-ml boiling flask was half filled with extracting solvent and heated to boiling. Heating the solvent in the Soxhlet apparatus resulted in a continuous stream of hot solvent flowing over and through the sample. Extractions were run continuously for four days, to ensure complete drying and to remove as much of the organic component as possible. The samples were then allowed to air dry, then removed to a vacuum drying oven and held at 50°C under low pressure.

High temperature supercritical methanol extraction was also used as a procedure to remove the organics from two L_3-templated silica of different volume fractions. The critical points of methanol ($T_c = 240.1°C$ and $P_c = 8.096$ MPa) are much higher than those of CO_2 ($T_c = 31.04°C$ and $P_c = 7.38$ MPa). In the high temperature process, the sample is immersed in methanol contained within a pressure reaction vessel (Parr model #4761), sealed, and heated to the critical temperature, allowing the internal pressure to build up to the critical point. The reactor was left at the critical point for at least 4 h, then the seal was gradually broken and the extracting fluid was allowed to slowly escape the containment vessel, carrying with it the solubilized organic component of the gel.[3] Further details on the extraction apparatus are given in the companion paper (Malik et al., 2006). A successful extraction was marked by the removal of complete monoliths (2 cm diameter, 1.5 cm thick) from the reactor vessel.

Surface area measurements were made on dried samples using a Micromeritics Flowsorb II 2300 single-point Brunauer, Emmett and Teller (BET) gas-adsorption apparatus (Norcross, GA). Samples were first dried in air, vacuum dried at 50°C for at least 8 h, then degassed at 100°C under a flowing 70/30 He/N_2 gas mixture for several hours prior to measurement. Surface areas were determined from the amount of nitrogen gas adsorbed onto the silica surfaces from a flowing stream of 70/30 He/N_2 gas at liquid nitrogen temperature (−196°C).

Simultaneous differential scanning calorimetry (DSC) and thermogravimetric analysis (TGA) were performed using a Rheometrics STA1500 (Piscataway, NJ). Typical furnace runs were done under streaming air. The standard furnace run consisted of the following steps: (i) ramp from ambient temperature to 600°C at 5°/min; (ii) hold at 600°C for 1 h; and (iii) furnace cool at 20°C/min back to ambient temperature.

Results and discussion

It was assumed for the purposes of this study that the source of chloride (e.g., HCl instead of NaCl) did not significantly change the nature of the L_3 solution. The effect of changing the solution's ionic strength upon the L_3 phase region will be addressed in a future publication (Bhansali et al., 2006).

Solvent fractions selected for the L_3 solutions were restricted to those most likely to yield phase-pure solutions (determined by optical clarity and the absence of opalescence in the solution when viewed between crossed polarizing filters). Our experience with solutions covering a wide range of solvent fractions has demonstrated that low solvent fractions (less than or equal to 55 wt.%) and high solvent fractions (greater than 90 wt.%) were difficult to synthesize consistently. The mid-range 65 wt.% solvent fraction is an ideal fraction for ensuring consistency among different solutions and has been observed to be less affected by the slight deviations in concentrations when several solutions are made. The 90 wt.% solvent fraction is a more sensitive composition and it is important that the empirical process described for synthesizing the L_3 solution is followed exactly.

Extracting the organic phase

After the L_3 phase has been silicified through the addition and conversion of TMOS to silica, the retention of organic materials within the nanostructured matrix is indicated by the complex burnout path for the volatile phases (Figure 4) removed from a solvent-exchanged and air-dried L_3 silica powder (McGrath et al., 2000). For the 65 wt.% solvent samples used in this study, an ideal, completely dried L_3-templated silica monolith would be composed of about 61 wt.% SiO_2 and 39 wt.% surfactant (18 wt.% $CpCl{\cdot}H_2O$ and 21 wt.% hexanol). In this ideal dried monolith, all of the TMOS added to the system has converted to SiO_2 and all water has been removed. The thermal extraction profile shown in Figure 4 shows that this is not the case, both in the total weight loss

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[3] This process is inherently hazardous due to the high pressures involved, and the products of methanol extraction are themselves extremely dangerous. Any such extractions must be done with the strictest control and containment procedures in place. Suitable measures for collecting the waste products and preventing their escape to the atmosphere must be used. Refer to Malik et al., 2006 for details of the procedure.

(32% of the initial sample weight) and in the appearance of the weight loss profile. Below 200°C the more volatile elements of the system are removed. These include water, methanol, hexanol, and partially hydrolyzed TMOS molecules. Above 200°C the decomposition of the CpCl surfactant is primarily responsible for the remaining weight loss (McGrath et al., 2000).

The burnout profiles for methanol-extracted (as opposed to solvent-exchanged) materials, whether done using continuous Soxhlet extraction (Figure 5) or SSE (Figure 6), demonstrate the effectiveness of the more intensive extraction processes. Attempted extraction using a poor solvent such as heptane (Figure 5(a)) leaves a sample whose burnout profile closely resembles that of the methanol-exchanged sample (Figure 4), indicating little effective extraction occurred. The total weight loss in the heptane-extracted sample was 24%, perhaps due to partial drying of the monolith either by liquid partitioning into the heptane or perhaps just the result of being exposed to higher temperature in the extraction vessel (Figure 1) leading to the loss of some of the more volatile components. In comparison, the weight loss profiles for methanol-extracted (Figure 5(b)) and SSE (Figure 6) samples indicate that the remaining components of the respective extracted monoliths were the inorganic phase and CpCl·H_2O surfactant. Total weight loss in methanol-extracted monoliths were near 18% and in the SSE samples 7% of the original sample weight. In both materials the abrupt weight loss above 200°C is due to the decomposition of the surfactant. Clearly the SSE process was the more effective in removing the CpCl·H_2O based on the total weight loss. Both Figures 5(b) and 6 show a ~4% loss in weight above 300°C.

The utility of an extraction process in the fabrication of a mesoscopic material cannot be adequately demonstrated simply by the efficiency of the extraction (nor by the measured surface areas); we were most interested in extraction techniques that yielded large, uncracked, and optically clear monoliths of L_3 silica, avoiding the powders and granules that were heretofore the product of simple air-drying and thermolysis (McGrath et al., 2000). In the work by Whitehurst, over 90% by weight of the SDA is removed through solvent extraction (Whitehurst, 1992). Modified CO_2 extraction of SDAs from mesoporous powders achieved over 80% by weight of the original SDA content (Whitehurst, 1992). However, these highly effective means of extraction focused on powders, not on the monoliths used in our study.

Thermolysis of L_3 silica can be used to remove the organic components and increase the effective surface area of the sample (McGrath et al., 2000). When heated to 600°C, the measured surface areas in dried L_3-templated silica were measured at more

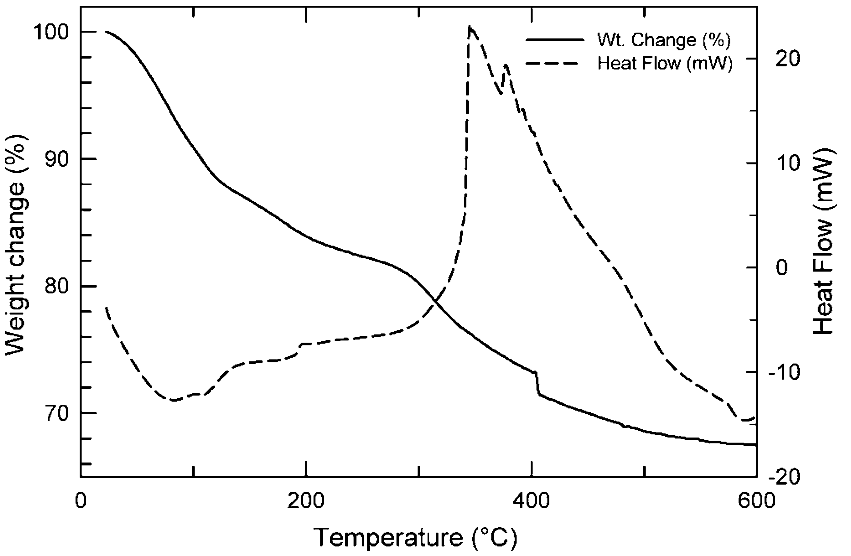

Figure 4. Thermal extraction profile from L_3 silica (McGrath et al., 2000).

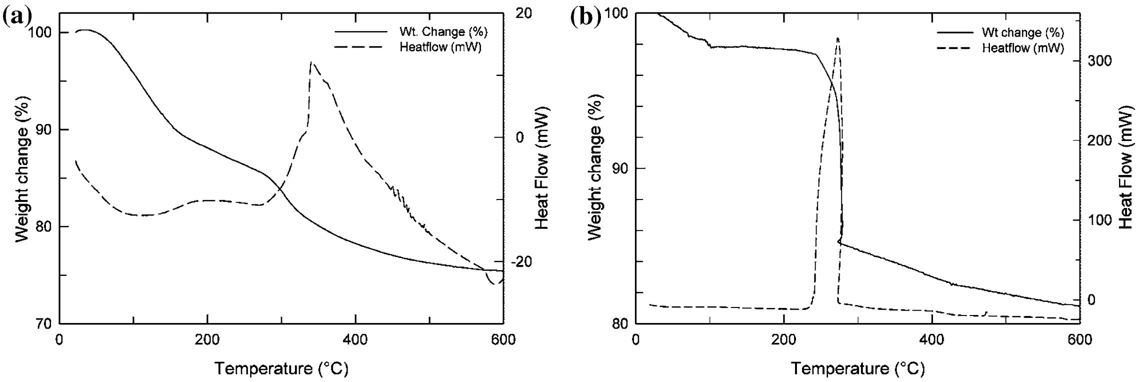

Figure 5. Thermal analysis on samples extracted by the Soxhlet process under (a) heptane and (b) methanol. Solvation of the organic component is much higher in methanol, apparent in the reduced weight loss and the shape of the weight loss curve. Although a significant portion of organic remains in the monolith following methanol extraction, the efficiency of thermolytic extraction is significantly improved by active solvent extraction beforehand.

than 900 m^2 g^{-1} (Figure 7(a)). But thermolysis results in discoloration and loss of transparency due to the large amount of residual organic in the matrix and, as we have noted before (McGrath et al., 2000), our monoliths were invariably reduced to granules or powders during drying and thermolysis, probably due to internal stresses arising from differential pressures created by the presence of the air/liquid interface in the porous matrix (Brinker & Scherer, 1990). Eliminating or reducing these internal stresses while strengthening the walls of the silica matrix are obvious methods to prevent cracking during drying. The SSE process avoids the liquid/vapor interface completely (McHardy & Sawan, 1998). Solvothermal extraction methods such as the Soxhlet technique reduces the liquid/vapor interface energy using solvents other than water and increases the extent of cross-linking within a templated silica matrix as shown by ^{29}Si magic angle spinning nuclear magnetic resonance (MAS-nmr) spectroscopy (Tanev & Pinnavaia, 1996).

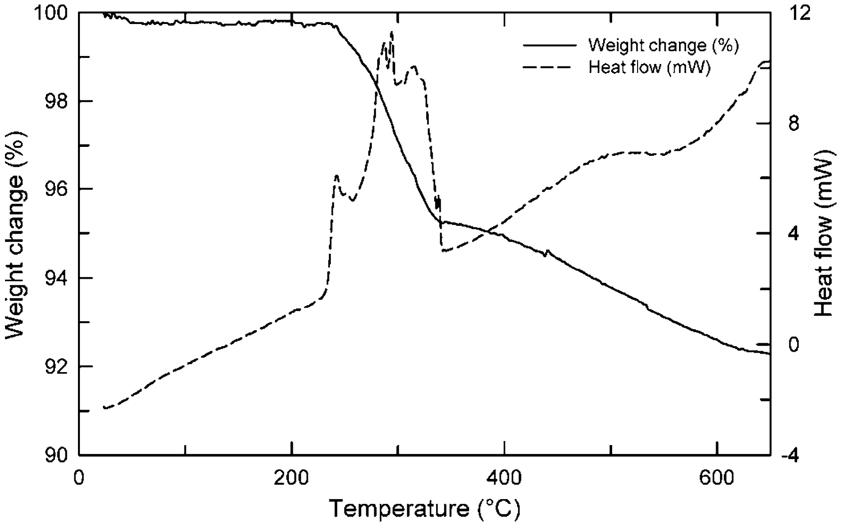

Figure 6. Thermal analysis of SSE material. Small amounts of organic surfactant are retained in the sample, evident in the thermal profiles. Although the effectiveness of the SSE process in removing the organic materials is better than that observed when Soxhlet extraction is used (for comparable extraction periods), the relative simplicity of the latter with respect to SSE is a strong advantage.

In Figure 7(b), the effect of different solvents on the measured surface area of the resulting silica is shown as a function of the respective Hildebrand solubility parameter (McGrath et al., 2000), a measure of the cohesive energy density of the solvent (Burke et al., 1984). Extracting solvents (water, methanol, ethanol, acetone, THF, and *n*-heptane) were chosen to cover a range of solubility parameters, from 48.0 (water) to 15.3 $\mathrm{MPa}^{1/2}$ (*n*-heptane). Thermal analysis of methanol-extracted samples (Figure 5(a)) revealed the effectiveness of solvent extraction with respect to the structure of the monolith: the resulting thermal profile closely resembles the pyrolysis of the surfactant in air in the onset of pyrolysis, the rapidity with which mass is lost, and the complete loss of material by oxidation (McGrath et al., 2000). We remain unable to determine if the observed increase in effective surface area is due to opening the channel network through extraction of byproducts, removing the surfactant and hexanol from the volume between the silica layers (Figure 1), or through some combination of the two processes.

The polarity of the surfactant CpCl implies that increasingly polar solvents will better dissolve the surfactant and remove it from the silica monolith. The presence of the co-surfactant hexanol complicates the picture somewhat, acting to counter the effectiveness of highly polar solvents. This is indicated in Figure 7(b): water is seen to act as a very poor solvent (in terms of increasing surface area). At the other end of the spectrum, the much less polar solvent acetone, with a solubility parameter similar to that of hexanol, is only very slightly better in increasing channel access than is water. The efficacy of methanol extraction implies that the combined solubility of the hexanol/CpCl system is much more compatible with the more polar alcohols, ethanol and methanol, but the presence of hexanol reduces the influence of strong polar interactions.

Physical properties following extraction

The differences in the physical appearance of the samples after extraction were quite marked: water-extracted samples were cloudy white whereas methanol extracted samples were clear. The cloudiness of the water-extracted samples was attributed to internal fractures, some of which were easily seen without optical magnification. Heat treating the samples after Soxhlet extraction at 600°C for several hours did not change the appearance of either significantly. Ethanol-extracted samples were clear after extraction and following heat treatment. Acetone- and *n*-heptane-extracted samples were clear following extraction, and became colored after heat treatment. The acetone-extracted samples turned black and the *n*-heptane-extracted samples turned red. We did not determine the reasons for coloring, assuming that the partial oxidation of the retained organic was responsible.

Most significantly, the Soxhlet extracted samples were usually intact following extraction and

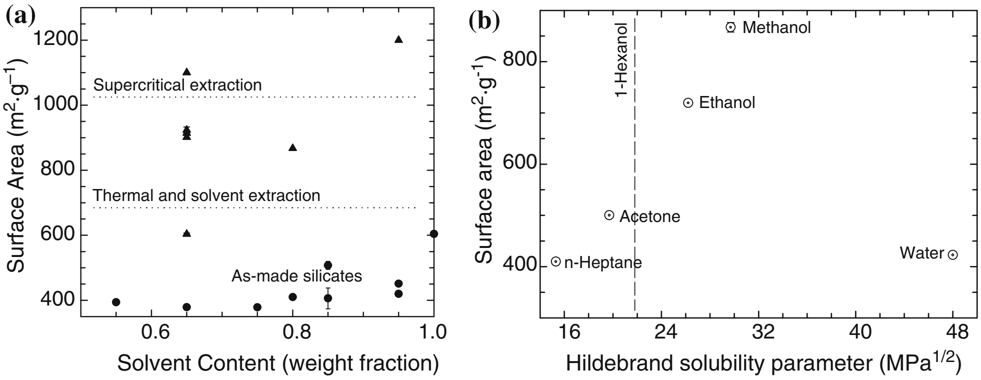

Figure 7. Single-point BET surface areas: (a) surface areas relative to treatment; (b) change in surface areas for a series of 65 wt.% samples under Soxhlet extraction, relative to the solubility parameter of the respective solvents. Soxhlet extraction is at least as effective as thermal extraction when the proper solvent is used. As shown, methanol was very effective in increasing the effective surface area of the monolith.

could be handled in air after removal from the extraction chamber. Subsequently heat treating the less well extracted samples could cause fractures within the matrix, but samples did not fall apart or granulate after heat treatment (except in the case of water-extracted samples which were far more fragile and did tend to granulate).

The exposure to higher temperatures while under organic solvent provides the likeliest explanations for the integrity of even poorly extracted samples. First, the organic solvents used in this study have lower vapor pressures than that of water (related to the solubility parameter). This simple measure implies lower solid/liquid and vapor/liquid interfacial energies in silica infiltrated with the organic solvent when compared to one filled with water or a water/organic solution. The matrix is then exposed to less stress in subsequent drying to remove the liquid phase from the matrix.

Secondly, exposing the silica to an organic solvent at elevated temperatures for extended periods improves the mechanical connectivity of the silica network through the condensation of the dangling Si-OH groups, as shown using ^{29}Si MAS-nmr spectroscopy (Tanev & Pinnavaia, 1996; Noble et al., 2003). As the free silanols are removed via condensation to form new Si–O–Si bridges, the water byproduct is removed by the action of continuous solvent extraction. The dehydration of the matrix walls increases the extent of cross-linking within the silica matrix, increasing its resistance to cracking under drying stresses. Using water as an extraction solvent is detrimental to the manufacture of stronger monoliths as it would hydrate the silica network, breaking Si–O–Si links and expanding existing defects into fractures.

The worrisome aspect of the choice of methanol as the extracting solvent of choice relates to the production of methanol in the hydrolysis of the TMOS during the silicification of the surfactant structure. We have noted before that adding methanol to a solution of the L_3 liquid crystal decreases the diffraction peak intensity with increasing methanol content, as measured by small angle X-ray scattering (SAXS) (McGrath et al., 2000). The obvious implication is that the presence of methanol degrades the L_3 structure. We do not have comparable measurements for the L_3 structure in the presence of TMOS.

We remain concerned that the silicification process is not sufficiently rapid to completely stabilize the L_3 structure in the presence of high methanol content, especially in high solvent fraction solutions. The dilution rule that defines the L_3 phase implies that the bilayer (Figure 2) increases its surface area to accommodate the larger solvent volume and maintain continuity in the bilayer (Strey et al., 1990). Adding the TMOS to the L_3 solution raises the solvent fraction while also introducing methanol; for example, a 75 wt.% solvent fraction L_3 solution shifts to 90 wt.% solvent with the addition of the methanol formed by the hydrolysis of the TMOS. The effect of increasing the effective solvent fraction is more noticeable in the higher solvent fraction L_3 solutions as these are difficult to synthesize consistently – pushing the solvent fraction up too high moves the solution out of the L_3 phase field into a multiphase liquid crystal solution. Since we are using a fixed molar ratio of 4:1 water:TMOS, these higher solvent fraction solutions are exposed to proportionally higher amounts of methanol. Adding less TMOS or partially hydrolyzing the TMOS prior to adding it to the L_3 solution are partial remedies in that either procedure reduces the amount of added methanol.

SSE also resulted in clear monolithic samples but the results of surface area measurements were apparently inconsistent with our assumptions regarding the structure of L_3 silica (Figure 8). We have expanded on the use of supercritical extraction in the fabrication of L_3-templated silica and a corroborative paper using ethanol as the extracting solvent has been submitted (Malik et al., 2006). For the purpose of this paper, we use our methanol SSE results to compare with the results of continuous solvent extraction. First, effective surface area results were much higher in 90 wt.% solvent fraction samples, indicating that SSE was very effective in removing organic. The resulting matrix was robust, optically transparent, and free of internal fractures.

Samples made from 65 wt.% solvent fraction solutions exhibited low effective surface areas – only 600 m^2 g^{-1}. In appearance there was no obvious difference between the 65 wt.% and 90 wt.% samples, even after heat treatment. The loss of surface area is difficult to understand, especially when compared to the results of continuous solvent extraction, where surface areas were consistently higher than 800 m^2 g^{-1}. Adding to the confusion, the average channel diameter was larger in the 65 wt.% sample than in the 90 wt.% sample (1.8 vs. 1.3 nm), determined from the sorption isotherm,

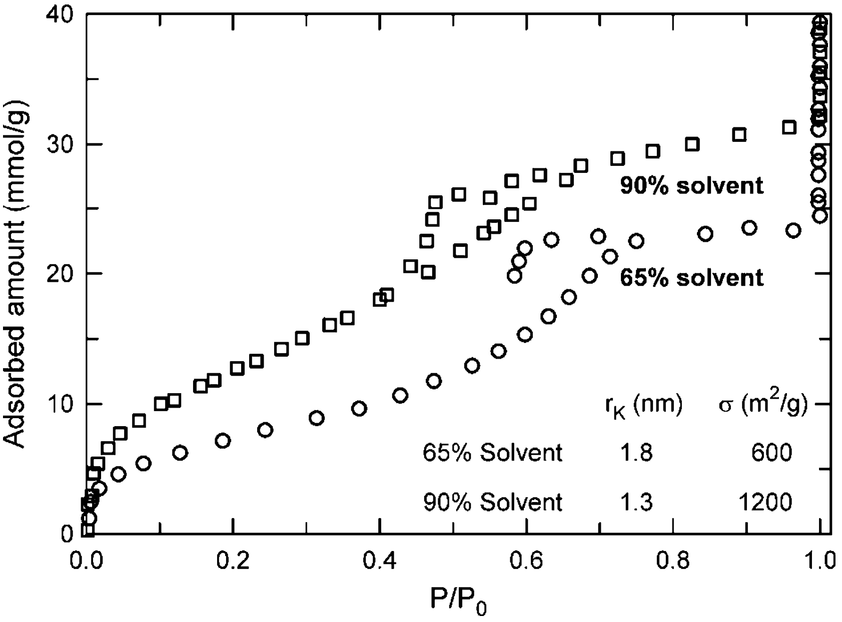

Figure 8. Isotherms from SSE samples of different solvent fractions.

but we believe this to be misleading. It is likely that the apparent average pore diameter measured for these samples was limited by the smallest diameter in the channel network and/or within the silica walls and did not measure the true channel diameter.

Both Soxhlet extracted and supercritically extracted samples could be reinfiltrated with organic solvents containing simple organic dyes without fracturing the matrices. The dyes could be removed from the monoliths by placing the sample back into pure solvent; again, the samples were sufficiently robust and did not fracture when transferred to clean solvent. This simple observation signifies perhaps the most useful aspect of these materials: Optically clear, isotropic nanostructures would be useful in many of the areas posited for applications involving nanostructure materials, including areas such as biosensors, optoelectronics, and active filters. The effectiveness of relatively simple extraction methods favors the adoption of these materials in these and related applications.

Conclusions

We have demonstrated that simple extraction techniques can be used to raise the effective surface area and perhaps the channel accessibility in a nanostructured silica. Monoliths made via continuous Soxhlet or supercritical solvent extraction yield isotropic, optically clear materials sufficiently robust to withstand reinfiltration by a simple solution after drying. Continuous solvent extraction offers the advantages of moderate temperature and ambient pressure processing without requiring specialized equipment. Much more can be done using SSE techniques, described in a companion publication, and the characterization of the channel structure in the L_3 silica is still under investigation. Despite these caveats, the silica matrix formed by the templation of the L_3 liquid crystalline phase offers a matrix suitable for the fabrication of nanostructured composites, simple separation filters, and, through activation of the channel surfaces, substrates for biosensors and solid state catalysts.

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