

Mesoporous Silicate–Surfactant Composites with Hydrophobic Surfaces and Tailored Pore Sizes

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Received: June 6, 2002; In Final Form: July 29, 2002

Mesoporous silicate–surfactant composites were prepared via washing of as-synthesized silicate–surfactant–expander materials in appropriate solvents. The expander can be generated in situ from the surfactant decomposition under high-temperature conditions, or supplied externally at the stage of the synthesis or postsynthesis hydrothermal treatment. The washing removed the expander as well as a minor part of the surfactant ions present and thus opened the mesopores whose walls were covered by a relatively dense layer of surfactant ions. Depending on the synthesis method for silicate–surfactant–expander composites, both ordered and disordered mesoporous silicate–surfactant composites were obtained with narrow pore size distributions and a wide range of adjustable pore sizes (4–12 nm). Despite the fact that these materials contained 25–35 wt % of surfactant, they exhibited large BET specific surface areas (360–550 m² g^{−1}) and total pore volumes (from 0.4 to as large as 1.8 cm³ g^{−1}). It is postulated that the surfactant retained in the silicate–surfactant composites is bonded to the silicate walls via electrostatic interactions, which are originally responsible for the formation of silicate–surfactant or silicate–surfactant–expander mesophases. The mesoporosity of the composites is mostly constituted by the space initially occupied by expander, which was later removed upon washing. The synthesis approach described herein is the first successful method for synthesis of ordered and disordered mesoporous silicate–surfactant composites with hydrophobic surfaces, the latter being predominantly formed by long alkyl chains of surfactant ions.

Introduction

Recently, there has been considerable interest in the synthesis of mesoporous materials with well-defined pore structures and narrow pore size distributions through surfactant templating approaches. This led to the synthesis of mesoporous silicas,^{1–7} metallosilicates,^{1,8–10} and a variety of other mesoporous oxides^{11–14} with high specific surface areas, tailored pore sizes, and many different ordered and disordered structures. In addition, hybrid mesoporous structures with (i) organic groups covalently bonded to silicate frameworks,^{1,5,15,16} (ii) silicate–organic frameworks,^{17–19} and (iii) organic groups covalently bonded to organosilicate frameworks^{20,21} have been reported. In most cases, the mesoporosity of the materials synthesized via surfactant templating approaches becomes accessible after removal of the template via calcination,¹ solvent extraction,^{4,6,7} ion-exchange,²² or postsynthesis modification.^{23,24} As far as we know, the only exception is the case of disordered silicates templated by surfactant L₃ phases,^{25,26} whose pore walls consist of bicontinuous surfactant bilayers covered by silicate layers and whose pores are filled with water and therefore accessible after drying of the sample.

It would be interesting and potentially useful to be able to synthesize silicate–surfactant and, in general, inorganic–surfactant composites with readily accessible hydrophobic

(surfactant-covered) pores. It has already been reported that as-synthesized (surfactant-containing) MCM-41 is promising as an adsorbent of organics from the liquid^{27,28} and gas²⁹ phase, as well as a basic catalyst for liquid-phase reactions.³⁰ As-synthesized MCM-41 has also been reported to exhibit high mechanical stability,³¹ which is a desirable feature for a prospective adsorbent and catalyst. However, surfactant–silicate composites of the MCM-41 type are in most cases essentially low-surface-area macroporous materials, as illustrated by data reported in refs 28 and 30. This may limit readily accessible interfacial area and may restrict diffusion within the surfactant phase of the composite. These limitations can be circumvented if high-surface-area surfactant–silicate composites can be synthesized. It was reported that the MCM-41 samples prepared without expanders and washed with ethanol may exhibit some mesoporosity or microporosity, and their surface properties clearly indicate that the silicate pore walls are covered by a relatively dense layer of surfactant molecules.³² However, materials prepared using this approach have very low mesopore volumes and/or poor pore accessibility. Herein, we report the method for synthesis of silicate–surfactant composites with surfactant-covered surfaces, tailored pore size, large pore volume, and large specific surface area.

Experimental Section

Materials. As-synthesized silicate–surfactant and silicate–surfactant–expander composites used for this study were synthesized as already reported elsewhere. Sample 1 was MCM-41 synthesized directly at 343 K without addition of amines, as described in ref 33. This synthesis is analogous to that originally

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reported in ref 34. Sample 2 was MCM-41 synthesized directly at 343 K with a dimethylhexadecylamine/cetyltrimethylammonium (DMHA/CTMA⁺) molar ratio of 0.5:1.³³ Sample 3 was synthesized similarly, but with DMHA/CTMA⁺ = 1.5 (the sample was denoted DS-DMHA-1.5 in ref 35). Sample 4 was synthesized via hydrothermal restructuring of sample 1 in the presence of dimethyldecylamine (DMDA) at 393 K and was denoted HR-DMDA-1.5–393 in ref 35. Samples 5 and 6 were synthesized via postsynthesis hydrothermal restructuring in mother liquor^{33,36} and were denoted TR3–24h (5C) and TR1–2d (6C) in ref 36. Samples 1–4 were extracted with ethanol under reflux and the resultant samples are denoted 1E–4E. Sample 4 was also extracted at room temperature and the resulting material is denoted 4ELT. Samples 5 and 6 were extracted with heptane under reflux for 12–15 h, and the resulting materials are denoted 5H and 6H. Calcined samples 1–6 are denoted 1C–6C, whereas calcined sample 4E is denoted 4EC.

Measurements. Nitrogen adsorption measurements were carried out at 77 K on a Micromeritics ASAP 2010 volumetric adsorption analyzer. Before the measurements, the extracted samples were outgassed under vacuum at room temperature in the port of the adsorption analyzer until the residual pressure was equal to or below 6 μ m Hg, which usually required several hours. The calcined samples were outgassed for 2 h at 473 K. The weight change curves were recorded under flowing nitrogen using a TA Instruments TGA 2950 high-resolution thermogravimetric analyzer in a high-resolution mode with a maximum heating rate of 5 K min^{−1}. Solid state ²⁹Si MAS NMR experiments were performed on a Bruker 400DMX spectrometer operating at a resonance frequency of 79.49 MHz at room temperature using a 7 mm zirconia rotor with a spinning frequency of 2.5 kHz. Prior to quantitative experiments the standard saturation recovery experiments were performed to obtain the spin–lattice relaxation times, T_1 , for different silicon sites and samples. Subsequently, the relaxation delays of 200–600 s ($5T_1$) were used in the single pulse experiments with high-power decoupling during acquisition. The total number of scans was 500–800, and chemical shifts were externally referenced to TMS.

Calculations. The BET specific surface area³⁷ was calculated from data in the relative pressure range from 0.04 to 0.2. The total pore volume³⁷ was estimated from the amount adsorbed at a relative pressure of 0.99. The α_s plots³⁸ were obtained using the reference adsorption data for a strongly hydrophobic surface (octyldimethylsilyl-modified silica)³⁹ and for a silica surface.⁴⁰ The pore size distributions (PSDs) were calculated using a method described in ref 39, which was developed for materials with strongly hydrophobic surfaces covered by hydrocarbon chains. The pore size is defined as the position of the maximum on PSD.

Results and Discussion

Weight change curves for silicate–surfactant and silicate–surfactant–expander samples used to prepare porous surfactant–silicate composites are shown in Figure 1, whereas the corresponding weight change derivatives are shown in Figure 2. These data have already been discussed in some detail elsewhere.^{35,41} The weight change curves exhibited a major weight loss at temperatures between 323 and 573 K, which is attributable to the decomposition and/or thermodesorption of surfactant template and expander (if present). As originally reported by Beck and co-workers,¹ alkyltrimethylammonium surfactants decompose primarily via Hoffmann elimination. Our

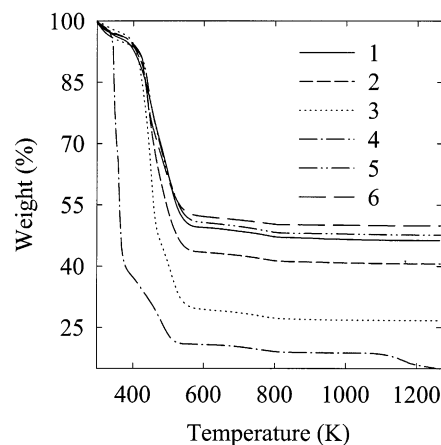


Figure 1. Weight change patterns for as-synthesized silicate–surfactant and silicate–surfactant–expander samples used for the preparation of the mesoporous silicate–surfactant composites (data taken from refs 35 and 41).

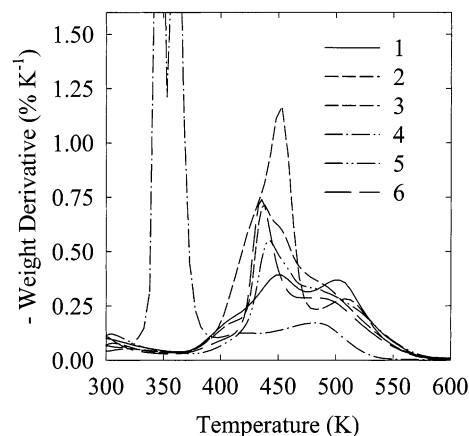


Figure 2. Weight change derivatives for as-synthesized silicate–surfactant and silicate–surfactant–expander samples used for the preparation of the mesoporous silicate–surfactant composites (data taken from refs 35 and 41).

earlier studies showed that under TGA conditions employed herein, DMDA expander thermodesorbs at a relatively low temperature (about 333–383 K),³⁵ whereas DMHA thermodesorbs at temperatures somewhere within the range from 393 to 573 K.^{35,41} Cetyltrimethylammonium surfactant bonded to the silicate surface decomposes and thermodesorbs primarily at temperatures from 393 to 573 K, so the thermal events reflecting the release of DMHA expander and surfactant template are not well-separated.^{35,41} Above 573 K, the further weight loss can be attributed to the surface dehydroxylation and thermodesorption of some residual products of template decomposition, and the residue at 1273 K consists primarily of silica (see ref 41 and references therein). On the basis of the aforementioned assignment of the weight change events, one can conclude that the samples under study exhibit a wide variation of silica contents (from about 20 to 50 wt %), and total contents of surfactant and expander (from 40 to 75 wt %). Sample 1 was synthesized in relatively low temperature conditions without application of expander and therefore its weight change behavior is related primarily to the decomposition of CTMA⁺ template.³⁵ Samples 2 and 3 were synthesized in the presence of DMHA expander, whereas samples 5 and 6 were prepared under conditions that promote in situ formation of DMHA expander via decomposition of CTMA⁺ surfactant.^{42,43} Therefore, the weight change behavior of these materials is primarily related to the decomposition and/or thermodesorption of CTMA⁺ and

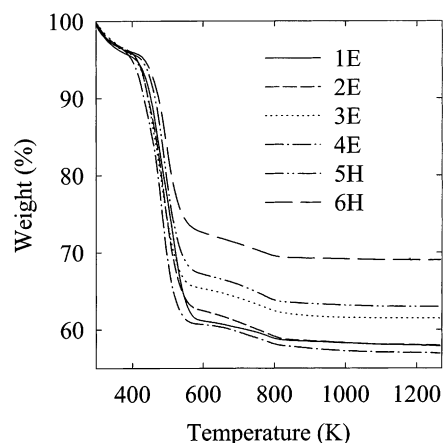


Figure 3. Weight change curves for the silicate-surfactant composites.

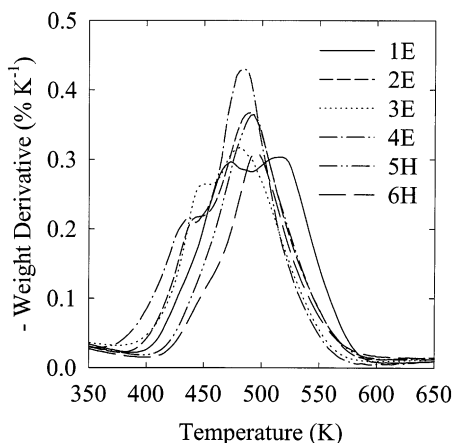


Figure 4. Weight change derivatives for the silicate-surfactant composites.

DMHA.⁴¹ Sample 4 was prepared from sample 1 using DMDA as an expander, and consequently its weight change pattern results mostly from the loss of CTMA⁺ and DMDA.³⁵ As determined from nitrogen adsorption measurements, the as-synthesized samples discussed above were primarily macroporous or nonporous, and their BET specific surface areas were below 40 m² g⁻¹, as expected from earlier studies of as-synthesized samples.^{45,46} It should be noted that nitrogen adsorption behavior of sample 1 was discussed in some detail elsewhere.⁴⁴

After extraction with polar (ethanol) or nonpolar (heptane) solvents, the thermogravimetric behavior of the samples changed (see Figures 3 and 4). The residue at 1273 K (that is, an approximate silica content) substantially increased (see Figure 3), which was particularly pronounced for samples that were originally prepared using DMDA or DMHA as expanders. Interestingly enough, the weight loss in the temperature range of template decomposition/thermodesorption for the extracted samples was approximately proportional to the BET specific surface area of the corresponding calcined materials. More specifically, calcined samples 1–6 had S_{BET} equal to 1210, 1100, 1050, 1160, 890, and 770 m² g⁻¹, respectively, which mirrored the weight losses for extracted materials, as listed in Table 1. Moreover, the overall decomposition pattern of the extracted samples was quite close to that for sample 1 before and after extraction. Sample 1 was prepared without the presence of an expander, and the low-temperature synthesis conditions employed were unfavorable for in situ generation of an expander via surfactant decomposition. Therefore, sample 1 can be regarded as a surfactant-silicate composite. The similarity in the weight change behavior among samples 1 and 1E, and the

TABLE 1: Properties of the Silicate-Surfactant Composites

sample	wt loss between 323 and 623 K (%)	BET specific surf area (m ² g ⁻¹)	pore size (nm)	total pore vol (cm ³ g ⁻¹)
1E	37	60	2.4	0.18
2E	36	470	4.4	0.60
3E	33	510	9	1.4
4E	38	540	12	1.8
4ELT	35	550	12	1.8
5H	31	370	4.4	0.42
6H	26	360	5.5	0.46

other extracted samples (despite dramatic differences in the weight change behavior of as-synthesized, unextracted materials) suggests that expanders were removed via extraction, whereas the surfactant was retained. This is not surprising because the surfactant used herein is an ionic one and thus it is electrostatically bonded to the silicate framework, whereas expanders are not bonded to the framework but solubilized in the micelles. Therefore, as can be seen for sample 1, the extraction led only to a minor change in the template content, showing that most of the surfactant template is difficult to remove using ethanol extraction. Acidified ethanol extraction or ion exchange have been commonly employed for the purpose of surfactant extraction, whereas ethanol itself is not a good extraction medium for the electrostatically bonded surfactant template. It was reported that ethanol washing under conditions somewhat milder than those employed herein did not remove a significant part of the surfactant template and did not open to any significant extent the pores of MCM-41 synthesized without expanders.³² The only exception was MCM-41 synthesized using as short-chain surfactant template (dodecyltrimethylammonium), for which somewhat larger pore volume was accessible to nitrogen at 77 K after ethanol washing. However, the pore volume and specific surface area of the resulting surfactant-silicate composite were still low and the kinetics of nitrogen adsorption appeared to be slow, thus showing that the resulting material did not have good adsorption properties. This study also demonstrated that surfaces of the surfactant-silicate composites obtained via ethanol washing of as-synthesized MCM-41 interacted very weakly with nitrogen adsorbate, resembling polymeric octyl phases. Because of the fact that primary mesopores of these composites were in most cases largely inaccessible, the observed hydrophobic surface properties reflected mostly the behavior of the external surfaces of the composites. This led to the conclusion that the external surfaces of MCM-41 particles are covered with relatively dense layers of electrostatically bonded surfactant ions with hydrophobic tails pointing out to the exterior of the particles, thus forming the very outermost part of the particles. As will be shown later, the aforementioned conclusions are consistent with the results of the current study.

Nitrogen adsorption isotherms for the extracted samples are shown in Figures 5 and 1S. It can be seen that the extraction of the expander-free material (sample 1) opened only a very small amount of porosity of average size of 2.4 nm (see Figure 2S) and led to a moderate increase in BET specific surface area. The resulting silicate-surfactant composite was essentially macroporous. Others also reported that ethanol-extracted MCM-41 prepared without expanders has low specific surface areas and low adsorption capacity.⁴⁷ In contrast, the extraction of expander-containing materials (samples 2–6) led to the development of significant amount of accessible mesoporosity. The average pore sizes for the extracted samples studied herein ranged from 4 to 12 nm (see Figures 6 and 2S). Ordered mesoporous silicate-surfactant composites of the pore sizes 4.4 and 5.5 nm were obtained from hydrothermally restructured

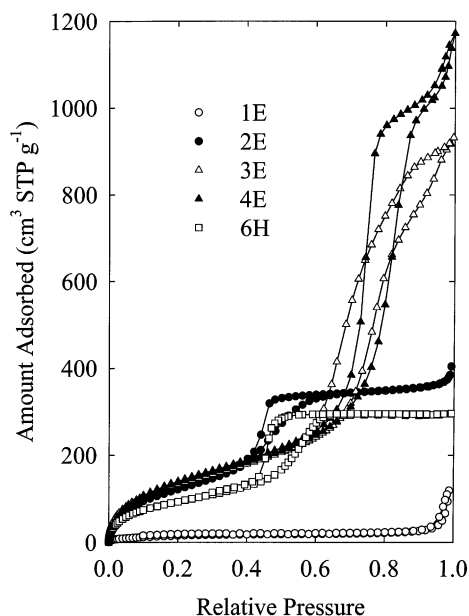


Figure 5. Nitrogen adsorption isotherms for the silicate–surfactant composites.

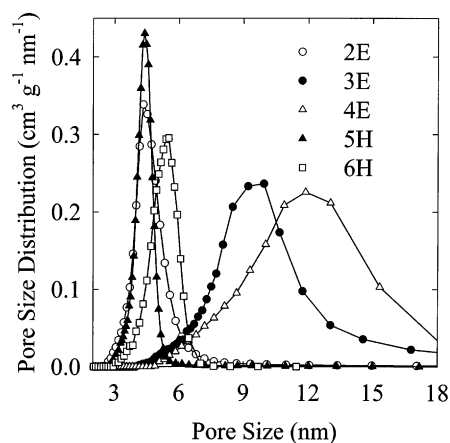


Figure 6. Pore size distributions for the silicate–surfactant composites.

MCM-41 (samples 5H and 6H). Their pore sizes and pore volumes were comparable to octyldimethylsilyl-modified large-pore MCM-41.³⁹ A similar mesoporous material (sample 2) was also obtained via extraction of MCM-41 synthesized using DMHA as an expander. Disordered large-pore mesoporous silicate–surfactant composites (samples 3E, 4E, and 4ELT) were obtained from disordered materials synthesized using a direct synthesis or postsynthesis hydrothermal restructuring with large amounts of amines. The pores of samples 4E and 4ELT were as large as 12 nm and pore volumes were as large as $1.8 \text{ cm}^3 \text{ g}^{-1}$, the latter being mostly constituted by the volume of mesopores of quite uniform size (see Figure 5). There were no major differences between the results of extraction under reflux conditions and at room temperature. This, and the fact that extraction can be achieved using nonpolar heptane, demonstrates that expander can be readily removed from silicate–surfactant–expander composites, thus affording silicate–surfactant composites with accessible porosity. The pore size can be tailored by a judicious choice of the preparation method for the silicate–surfactant–expander composite. The composites prepared at high temperature via in situ generation of expander formed as a result of surfactant decomposition are expected to have pore diameters below about 5.5 nm, as can be seen from results for sample 6H, because the calcined sample 6 had the unit-cell size

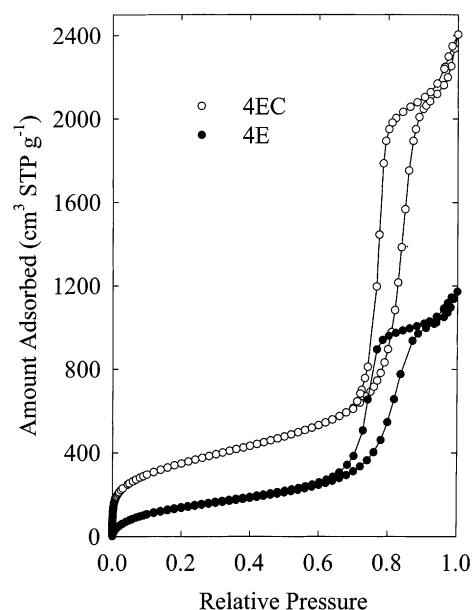


Figure 7. Comparison of nitrogen adsorption isotherm for a silica–surfactant composite 4E and a mesoporous silica 4EC obtained via calcination of the composite.

in the upper range of those obtainable using this method. The composites prepared using externally supplied expanders may exhibit much larger pore sizes, as seen for samples 4E and 4ELT. It should be noted that the mesopore size of the silicate–surfactant composite is governed by the distance between the silicate walls of the material and the thickness of the surfactant layer on the pore walls. Because the silicate backbone of the considered materials shrinks substantially upon calcination, it may happen that a calcined (surfactant-free) sample has a smaller pore size than the silicate–surfactant composite prepared via extraction of the same silicate–surfactant–expander material. This is possible, because the pore size decrease related to shrinkage upon calcination may exceed the effect of the presence of surfactant on the pore walls.

As expected, calcination of silicate–surfactant mesoporous composites prepared via extraction may lead to dramatic pore volume and surface area increase related to the elimination of surfactant. For instance, calcination of sample 4E afforded a large-pore material with total pore volume as large as $3.6 \text{ cm}^3 \text{ g}^{-1}$ and exceptionally high volume of relatively uniform mesopores (about $3 \text{ cm}^3 \text{ g}^{-1}$). This pore volume appears to exceed that of the silica prepared via direct calcination of the silicate–surfactant–expander composite.³⁵

In the case of sample 4, changes in the degree of framework cross-linking upon extraction and calcination were studied by ^{29}Si MAS NMR. The as-synthesized material had approximately the same population of Q^3 and Q^4 silicons (Q^n is defined as a silicon atom bonded to n other silicons through oxygen atoms and to $(4 - n)$ silanol groups), thus indicating a rather low degree of framework condensation. The framework cross-linking was significantly higher after calcination. After as-synthesized sample 4 and extracted sample 4E were calcined, the resulting samples 4C and 4EC had a $\text{Q}^4:(\text{Q}^3 + \text{Q}^2)$ ratio of about 2:1, but 4EC had a noticeable percentage of Q^2 silicons (about 5%). Similarly to calcination, the ethanol extraction was found to improve framework cross-linking, as $\text{Q}^4:(\text{Q}^3 + \text{Q}^2)$ ratio was 3:2 and 2:1 for 4E and 4ELT, respectively. For the latter, a larger fraction of Q^2 sites were observed (about 4%).

The silicate–surfactant composites clearly have highly hydrophobic surfaces. Shown in Figure 8 are relative adsorption

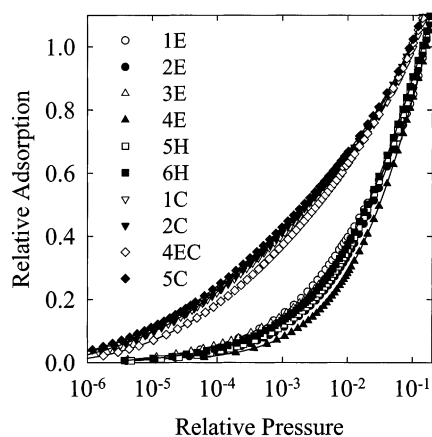


Figure 8. Low-pressure relative adsorption curves for the silicate-surfactant composites under study and for representative silicas obtained via calcination of the as-synthesized samples or mesoporous silicate-surfactant composites.

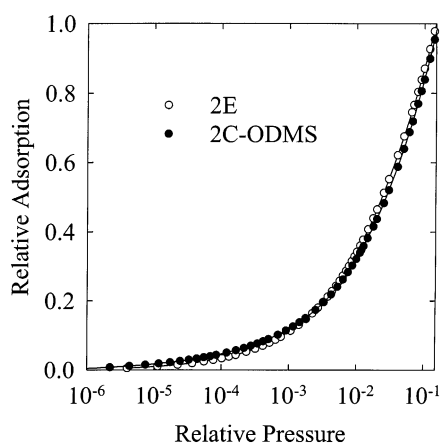


Figure 9. Comparison of relative adsorption curves for a silicate-surfactant composite and a silica chemically modified with octadecyldimethylsilyl groups of the bonding density $1.7 \mu\text{mol m}^{-2}$ (the latter sample was described in ref 48).

curves for these mesoporous composites and the corresponding calcined silicas. It can be seen that the silicate-surfactant composites exhibited a much weaker low-pressure adsorption, similar to the alkylsilyl-modified silica surfaces (see Figure 9). The α_s plot analysis also shows that the comparative plot obtained using an octyldimethylsilyl-modified silica reference adsorbent exhibits much better linearity than that obtained using the silica reference adsorbent (see Figure 3S). Therefore, the surfaces of silicate-surfactant composites clearly interact with nitrogen adsorbate in a way more similar to long alkyl chains than to a bare silica surface. This provides strong evidence that the surfaces of mesoporous silicate-surfactant composites are covered with a relatively dense layer of electrostatically bonded surfactant ions with alkyl tails pointing outward, similarly to as-synthesized MCM-41 and to MCM-48.^{32,46} Thus we demonstrated that the mesoporous silicate-surfactant composites of large specific surface area and pore volume, tailored pore size, and surfaces covered with surfactant ions can be synthesized via extraction of silicate-surfactant-expander composites using appropriate solvents suitable for expander removal and yet incapable of removing most of the surfactant ions.

This study also sheds light on some controversial topics regarding the formation of large-pore MCM-41 under high-temperature conditions. It was suggested that water partially fills the space in the enlarged pores.³⁴ This is highly unlikely, because water will be removed upon sample drying and the

pores of as-synthesized material would be accessible to nitrogen adsorbate, which is not the case as verified for samples 5 and 6 prepared as described in ref 36. Others suggested that the pore size expansion is related to the fact that alkyl chains of the surfactant become more extended⁴⁹ as the high-temperature pore enlargement proceeds. If so, the pores would still be essentially inaccessible after extraction (as in the case of sample 1 and an MCM-41 sample reported in ref 47), which is in contrast with experimental data reported herein for samples 5 and 6. So the change of configuration of surfactant alkyl chains is not likely to be a major factor in high-temperature pore size enlargement, although it can certainly play some minor role in the pore size expansion process, as inferred from the recently reported study on thermal behavior of silicate-surfactant composites.⁵⁰ However, the results reported herein are in accord with the unified mechanism of pore size enlargement under high-temperature conditions, which involved in situ generation of amine expander via surfactant decomposition.^{33,42} This mechanism is consistent with findings about the role of small cations, such as tetramethylammonium, in the process,⁵¹ because their incorporation in the silicate-surfactant composites may facilitate the surfactant decomposition process.⁴² It should also be noted that our findings do not support the contention that the pore size enlargement under high-temperature conditions is related to the incorporation of additional surfactant molecules in the pores during the process.^{49,52,53} This surfactant would have to either be bound to silicate interface or be accompanied with counterions. In the former case, the surfactant would be difficult to extract using both polar and nonpolar solvents; in the latter case, it would be difficult to extract using a nonpolar solvent, such as heptane used herein. In contrast, our data show that a significant amount of organics can be extracted using heptane from as-synthesized large-pore MCM-41 obtained via the high-temperature synthesis procedure. This strongly indicates that these organics are primarily constituted by nonpolar species, such as DMHA, rather than the ionic surfactant. So, under high-temperature conditions, micelle diameter enlargement is related primarily to the swelling by nonpolar species rather than polar surfactant ions (the latter was proposed in refs 49, 52, and 53).

The results discussed herein allow one to speculate about a possible reason of degradation of MCM-41 during extended hydrothermal syntheses at high temperatures. It is suggested that the pore size enlargement can take place as long as the surfactant layer on the pore surface has a sufficient bonding density, being thus capable to accommodate the nonpolar expander molecules and to shield the silicate structure from water that readily destroys ordered silica structures under hydrothermal conditions.⁵⁴ The significant depletion of the surfactant layer that takes place after prolonged hydrothermal treatment at temperatures of 423 K or higher would eventually make the silicate framework unprotected against water and thus susceptible to collapse, which is actually observed under such conditions.³⁶ Moreover, the current study provides evidence that the pore size enlargement during the postsynthesis treatment of as-synthesized MCM-41 in the presence of amines³³ preserves the layer of electrostatically bonded surfactant on the silicate surface. Because ordered surfactant-silicate composites are known to undergo various phase transitions from one ordered phase to another,⁵ the pore size enlargement during the aforementioned pore size expansion can be viewed as a transformation from ordered silicate-surfactant composite to a disordered silicate-surfactant-expander composite. Such a transformation may completely change the topology and connectivity of the silicate framework while preserving the specific

surface area. We have speculated earlier that the specific surface area conservation during this process provides evidence for a substantial degree of preservation of the original silica framework structure.⁵⁵ The current study suggests that the preservation of framework structure is in fact not necessary to explain the specific surface area conservation. Thus, it is not unlikely that large-pore silicas synthesized via the postsynthesis hydrothermal treatment with amines in fact exhibit large departures from cylindrical pore geometry. One of the structures that can be envisioned would be a foamlike structure, which was reported to form in silica–polymeric–surfactant–expander systems.⁵⁶

Acknowledgment. The donors of the Petroleum Research Fund administered by the American Chemical Society are gratefully acknowledged for support of this research. The funding was also provided by the NSF Grant CHE-0093707. A.S. thanks the Natural Sciences and Engineering Research Council (NSERC) of Canada for generous financial support.

Supporting Information Available: Figures of N₂ adsorption isotherms, pore size distributions, and α_s plot. This material is available free of charge via the Internet at <http://pubs.acs.org>.

References and Notes

- Beck, J. S.; Vartuli, J. C.; Roth, W. J.; Leonowicz, M. E.; Kresge, C. T.; Schmitt, K. D.; Chu, C. T.-W.; Olson, D. H.; Sheppard, E. W.; McCullen, S. B.; Higgins, J. B.; Schlenker, J. L. *J. Am. Chem. Soc.* **1992**, *114*, 10834.
- Yanagisawa, T.; Shimizu, T.; Kuroda, K.; Kato, C. *Bull. Chem. Soc. Jpn.* **1990**, *63*, 988.
- Inagaki, S.; Fukushima, Y.; Kuroda, K. *J. Chem. Soc., Chem. Commun.* **1993**, 680.
- Tanev, P. T.; Pinnavaia, T. J. *Science* **1995**, *267*, 865.
- Huo, Q.; Margolese, D. I.; Stucky, G. D. *Chem. Mater.* **1996**, *8*, 1147.
- Bagshaw, S. A.; Prouzet, E.; Pinnavaia, T. J. *Science* **1995**, *269*, 1242.
- Zhao, D.; Huo, Q.; Feng, J.; Chmelka, B. F.; Stucky, G. D. *J. Am. Chem. Soc.* **1998**, *120*, 6024.
- Corma, A.; Navarro, M. T.; Perez-Pariente, J. J. *J. Chem. Soc., Chem. Commun.* **1994**, 147.
- Tanev, P. T.; Chibwe, M.; Pinnavaia, T. J. *Nature* **1994**, *368*, 321.
- Reddy, K. M.; Moudrakovski, I.; Sayari, A. *J. Chem. Soc., Chem. Commun.* **1994**, 1059.
- Antonietti, D. M.; Ying, J. Y. *Angew. Chem., Int. Ed. Engl.* **1996**, *35*, 426.
- Liu, P.; Liu, J.; Sayari, A. *Chem. Commun.* **1997**, 577.
- Tian, Z.-R.; Tong, W.; Wang, J.-Y.; Duan, N.-G.; Krishnan, V. V.; Suib, S. L. *Science* **1997**, *276*, 926.
- Yang, P.; Zhao, D.; Margolese, D. I.; Chmelka, B. F.; Stucky, G. D. *Nature* **1998**, *396*, 152.
- Burkett, S. L.; Sims, S. D.; Mann, S. *Chem. Commun.* **1996**, 1367.
- Macquarrie, D. J. *Chem. Commun.* **1996**, 1961.
- Inagaki, S.; Guan, S.; Fukushima, Y.; Ohsuna, T.; Terasaki, O. *J. Am. Chem. Soc.* **1999**, *121*, 9611.
- Melde, B. J.; Holland, B. T.; Blanford, C. F.; Stein, A. *Chem. Mater.* **1999**, *11*, 3302.
- Yoshina-Ishii, C.; Asefa, T.; Coombs, N.; MacLachlan, M. J.; Ozin, G. A. *Chem. Commun.* **1999**, 2539.
- Asefa, T.; Kruk, M.; MacLachlan, M. J.; Coombs, N.; Grondley, H.; Jaroniec, M.; Ozin, G. A. *J. Am. Chem. Soc.* **2001**, *123*, 8520.
- Burleigh, M. C.; Dai, S.; Hagaman, E. W.; Lin, J. S. *Chem. Mater.* **2001**, *13*, 2537.
- Chen, C.-Y.; Li, H.-X.; Davis, M. E. *Microporous Mater.* **1993**, *2*, 17.
- Vartuli, J. C.; Schmidt, K. D.; Kresge, C. T.; Roth, W. J.; Leonowicz, M. E.; McCullen, S. B.; Hellring, S. D.; Beck, J. S.; Schlenker, J. L.; Olson, D. H.; Sheppard, E. W. *Chem. Mater.* **1994**, *6*, 2317.
- Antochshuk, V.; Jaroniec, M. *Chem. Commun.* **1999**, 2373.
- McGrath, K. M.; Dabbs, D. M.; Yao, N.; Aksay, I. A.; Gruner, S. M. *Science* **1997**, *277*, 552.
- McGrath, K. M.; Dabbs, D. M.; Yao, N.; Edler, K. J.; Aksay, I. A.; Gruner, S. M. *Langmuir* **2000**, *16*, 398.
- Denoyel, R.; Sabio Rey, E. *Langmuir* **1998**, *14*, 7321.
- Zhao, H.; Nagy, K. L.; Waples, J. S.; Vance, G. F. *Environ. Sci. Technol.* **2000**, *34*, 4822.
- Vartuli, J. C.; Malek, A.; Roth, W. J.; Kresge, C. T.; McCullen, S. B. *Micropor. Mesopor. Mater.* **2001**, *44–45*, 691.
- Kubota, Y.; Nishizaki, Y.; Sugi, Y. *Chem. Lett.* **2000**, 998.
- Wu, J.; Abu-Omar, M. M.; Tolbert, S. H. *Nano Lett.* **2001**, *1*, 27.
- Kruk, M.; Jaroniec, M.; Sakamoto, Y.; Terasaki, O.; Ryoo, R.; Ko, C. H. *J. Phys. Chem. B* **2000**, *104*, 292.
- Sayari, A.; Kruk, M.; Jaroniec, M.; Moudrakovski, I. L. *Adv. Mater.* **1998**, *10*, 1376.
- Khushalani, D.; Kuperman, A.; Ozin, G. A.; Tanaka, K.; Garces, J.; Olken, M. M.; Coombs, N. *Adv. Mater.* **1995**, *7*, 842.
- Kruk, M.; Jaroniec, M.; Sayari, A. *Micropor. Mesopor. Mater.* **2000**, *35–36*, 545.
- Sayari, A.; Liu, P.; Kruk, M.; Jaroniec, M. *Chem. Mater.* **1997**, *9*, 2499.
- Sing, K. S. W.; Everett, D. H.; Haul, R. A. W.; Moscou, L.; Pierotti, R. A.; Rouquerol, J.; Siemieniowska, T. *Pure Appl. Chem.* **1985**, *57*, 603.
- Gregg, S. J.; Sing, K. S. W. *Adsorption, Surface Area and Porosity*; Academic Press: London, 1982.
- Kruk, M.; Antochshuk, V.; Jaroniec, M.; Sayari, A. *J. Phys. Chem. B* **1999**, *103*, 10670.
- Jaroniec, M.; Kruk, M.; Olivier, J. P. *Langmuir* **1999**, *15*, 5410.
- Kruk, M.; Sayari, A.; Jaroniec, M. In *Nanoporous Materials II*; Sayari, A., Jaroniec, M., Pinnavaia, T. J., Eds.; Elsevier: Amsterdam, 2000; p 567.
- Kruk, M.; Jaroniec, M.; Sayari, A. *J. Phys. Chem. B* **1999**, *103*, 4590.
- Cheng, C.-F.; Zhou, W.; Park, D. H.; Klinowski, J.; Hargreaves, M.; Gladden, L. F. *J. Chem. Soc., Faraday Trans.* **1997**, *93*, 359.
- Jaroniec, M.; Kruk, M.; Sayari, A. In *Nanoporous Materials II*; Sayari, A., Jaroniec, M., Pinnavaia, T. J., Eds.; Elsevier: Amsterdam, 2000; p 587.
- Jaroniec, M.; Kruk, M.; Shin, H. J.; Ryoo, R.; Sakamoto, Y.; Terasaki, O. *Micropor. Mesopor. Mater.* **2001**, *48*, 97.
- Kruk, M.; Jaroniec, M.; Ryoo, R.; Joo, S. H. *Chem. Mater.* **2000**, *12*, 1414.
- Park, M.; Komarneni, S. *Micropor. Mesopor. Mater.* **1998**, *25*, 75.
- Jaroniec, M.; Antochshuk, V.; Kruk, M. In *Adsorption Science and Technology*; Do, D. D., Ed.; World Scientific Publishers: River Edge, NJ, 2000; p 299.
- Zhou, W.; Klinowski, J. *Chem. Phys. Lett.* **1998**, *292*, 207.
- Gross, A. F.; Ruiz, E. J.; Tolbert, S. H. *J. Phys. Chem. B* **2000**, *104*, 5448.
- Corma, A.; Kan, Q.; Navarro, M. T.; Perez-Pariente, J.; Rey, F. *Chem. Mater.* **1997**, *9*, 2123.
- Zhou, W.; Mokaya, R.; Shan, Z.; Maschmeyer, T. *Prog. Nat. Sci.* **2001**, *11*, 33.
- Mokaya, R. *Micropor. Mesopor. Mater.* **2001**, *44–45*, 119.
- Kim, J. M.; Ryoo, R. *Bull. Korean Chem. Soc.* **1996**, *17*, 66.
- Sayari, A.; Yang, Y.; Kruk, M.; Jaroniec, M. *J. Phys. Chem. B* **1999**, *103*, 3651.
- Schmidt-Winkel, P.; Lukens, W. W., Jr.; Zhao, D.; Yang, P.; Chmelka, B. F.; Stucky, G. D. *J. Am. Chem. Soc.* **1999**, *121*, 254.