

Nanoporous Organosilicas: Periodic Materials Synthesized with Surfactant Templates in Acidic Media

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Nanoporous organosilicas have been synthesized by the acid-catalyzed hydrolysis and condensation of bis-(triethoxysilyl)ethane (BTSE) using a hydrothermal approach. Cetyltrimethylammonium chloride (CTAC), polyoxyethylene(10) cetyl ether (Brij 56), and polyoxyethylene(10) stearyl ether (Brij 76) were employed as structure directors using the surfactant template method. The surfactants were extracted from the nanoscopic composite precipitates with acidified ethanol. The resulting nanoporous organosilicas have been characterized by nitrogen gas sorption, powder X-ray diffraction, and high-resolution thermogravimetric analysis. While the organosilicas synthesized with CTAC exhibit large surface areas (1000 m²/g) and pore volumes (1.0 cm³/g), they form relatively disordered matrixes as evidenced by broad pore size distributions and X-ray diffraction patterns. Brij 56 gives periodic nanoporous organosilicas with pore diameters 36–39 Å. The use of brij 76 as the structure director gave better quality organosilicas, with large surface areas, sharp pore size distributions, and pore diameters of 43–45 Å. X-ray diffraction patterns exhibit three well-defined peaks typical of hexagonal (*p6mm*) mesoporous materials. The effects of initial HCl concentrations on the chemical and structural properties of the final products are examined.

Introduction

Polysilsesquioxanes with large surface areas and ordered pore structures were first reported by Inagaki and co-workers.¹ These porous organosilicas are comprised of siloxane units bridged by organic groups. Ordered polysilsesquioxane materials containing a variety of organic functional groups have been reported.^{2–6} Supramolecular assemblies of surfactants are used as structure directing agents to engineer the porosity of these materials using a templating approach. The micellar assemblies, which are first formed in solution, are encapsulated by the polymerization of silsesquioxane precursors containing alkoxysilyl groups. This polymerization results in the formation of nanoscopic composites that precipitate out of solution. Subsequent extraction of the surfactants gives porous organosilicas. The siloxane linkages impart these materials with structural rigidity following the template removal. The ordered pore structures formed by this process allow ready access of diffusing molecules to the large internal surface areas and organic groups. With both structural rigidity and organic functionality, these materials exhibit some of the favorable properties of both organic and inorganic materials.

Despite the successful synthesis and characterization of periodic nanoporous organosilicas containing a variety of organic groups, the number of available silsesquioxane precursors limits the organosilicas that can be made in this way. Also, not all silsesquioxane precursors can be used to create periodic nanoporous organosilicas. The lack of structural rigidity in the organic portion of the silsesquioxane precursor is a limiting factor. Too much flexibility will result in a material (similar to an organic polymer) that does not hold its shape once the surfactant templates are extracted. The resulting materials are amorphous. An attractive alternative for functionalizing pol-

ysilsesquioxanes is the co-condensation of trialkoxy organosilanes with the silsesquioxane precursors during material formation.^{7–10} The wide variety of functional groups commercially available as trialkoxy organosilane derivatives makes this synthetic route a particularly versatile one.

The use of an acid catalyst to synthesize large pore organosilicas has generated great interest.^{11–14} We recently reported the effects of acidic media on the preparation of a series of nanoporous organosilicas by the co-condensation of bis(triethoxysilyl)ethane (BTSE) with *N*-(2-aminoethyl)-3-aminopropyltrimethoxysilane (AAPTS) using cetyltrimethylammonium chloride (CTAC) as the structure director.⁹ The chemical and structural properties of these organosilicas were compared to those of organosilicas synthesized with the same precursors via base-catalyzed synthesis.¹⁰ The acid-catalyzed organosilicas were found to form much faster, with a higher yield, and a higher incorporation of the diamine-containing functional silane than the corresponding base-catalyzed organosilicas. The higher reaction rate for acid-catalyzed nanostructured materials templated with alkylammonium halide surfactants is not unprecedented. Huo, et al.¹⁵ reported faster reaction rates for acid-catalyzed mesoporous silicas than for those synthesized under basic conditions. Despite these advantages, the acid-catalyzed organosilicas formed amorphous matrixes that exhibited relatively poor diffusion kinetics compared to the base-catalyzed materials with ordered pore structures. We feel that although the highly acidic media led to fast reactions and high yields, it may have also disrupted the self-assembly process needed to form well-ordered nanoporous organosilicas. Less acidic conditions may result in organosilicas with ordered pore structures.

In this paper, we describe the preparation of a series of nanoporous organosilicas by the acid-catalyzed hydrolysis and condensation of bis(triethoxysilyl)ethane (BTSE) around supramolecular assemblies of cetyltrimethylammonium chloride

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(CTAC) using a hydrothermal approach. The effects of varying the initial HCl concentration on the chemical and structural properties of the final products are examined. We also report the first syntheses of periodic nanoporous organosilicas with the nonionic polyoxyethylene(10) cetyl ether (Brij 56) and polyoxyethylene(10) stearyl ether (Brij 76) surfactants as structure directors using the template methodology.

Experimental Section

Chemicals. All organosilanes were obtained from Gelest, Inc. NaOH, HCl, CTAC, Brij 56, Brij 76, and EtOH were obtained from Aldrich. All chemicals were used as received. Water used in all synthetic procedures was deionized to 18 M Ω cm.

General Acidic Synthesis. Supramolecular assemblies of surfactants were formed under acidic conditions in aqueous media, followed by the addition of BTSE. The synthesis mixtures were covered and stirred at 50 °C for 12 h, followed by heating at 90 °C under static conditions for 24 h. The precipitates were recovered by suction filtration and air-dried.

Brij 56. The method described by Zhao¹⁶ was modified by the use of BTSE and aqueous solutions of various acid concentrations. Concentrated HCl was added to deionized water to make the initial aqueous solutions. Concentrations were varied from 0.4 to 1.6 M. The Brij 56 (4.0 g) was added to 100 mL solutions upon stirring, and the mixtures were covered and heated at 50 °C for 12 h. BTSE (10.50 mL) was then added to the resulting clear solutions. The synthesis mixtures were covered and stirred at 50 °C for 12 h, followed by heating at 90 °C under static conditions for 24 h. The precipitates were recovered by suction filtration and air-dried. A portion of these as-synthesized mesoscopic composites were characterized, while the remaining amount was extracted with acidified ethanol, to produce mesoporous organosilicas. The reactant molar ratios were as follows:

0.14 Brij 56:133 H₂O:0.96–3.84 HCl:0.67 BTSE.

Brij 76. A protocol similar to that used to synthesize organosilicas with Brij 56 was followed, with the exception that 200 mL of acidic solutions were used. The corresponding reactant molar ratios were:

0.13 Brij 76:267 H₂O:1.92–7.67 HCl:0.67 BTSE

CTAC. The procedure of Huo et al.¹⁵ for the synthesis of ordered mesoporous silica under acidic conditions was modified by using BTSE in place of TEOS and different acid concentrations. The desired acid strength was achieved by slowly adding concentrated HCl to deionized water under stirring in a polypropylene vessel. HCl concentrations were varied from 0.5 to 3.9 M. Surfactant templates were formed by the addition of 6.6 mL of CTAC (25% w/w) to 100 mL of solutions upon stirring. BTSE (10.50 mL) was then added to the resulting clear solutions. Synthesis mixtures were covered and stirred at 50 °C for 12 h, followed by heating at 90 °C under static conditions for 24 h. The precipitates were recovered by suction filtration and air-dried. A portion of these as-synthesized mesoscopic composites were characterized, while the remaining amount was extracted with acidified ethanol, to produce mesoporous organosilicas. The reactant molar ratios were as follows:

0.12 CTAC:133 H₂O:1.2–9.2 HCl:0.67 BTSE

The molar compositions of all organosilicas synthesized with CTAC, Brij 56, and Brij 76 are listed in Table 1.

TABLE 1: Molar Composition of Nanoporous Organosilicas (mole, BTSE = 0.67)

sample	surfactant (mol)	water	acid (HCl)
B56(1)	Brij 56 (0.14)	133	0.96
B56(2)	Brij 56 (0.14)	133	1.92
B56(3)	Brij 56 (0.14)	133	2.88
B56(4)	Brij 56 (0.14)	133	3.84
B76(1)	Brij 76 (0.13)	267	1.92
B76(2)	Brij 76 (0.13)	267	3.84
B76(3)	Brij 76 (0.13)	267	5.76
B76(4)	Brij 76 (0.13)	267	7.67
CT(1)	CTAC (0.12)	133	1.2
CT(2)	CTAC (0.12)	133	2.3
CT(3)	CTAC (0.12)	133	3.5
CT(4)	CTAC (0.12)	133	4.7
CT(5)	CTAC (0.12)	133	9.2

Control Samples. Control blanks were prepared according to the protocols described above, without the addition of surfactants.

Postsynthetic Treatment. As-synthesized mesoscopic composites were placed in excess (350 mL/g) acidified ethanol (1 M HCl) and refluxed for 6 h. The products were recovered by filtration, washed with absolute ethanol, and dried under vacuum at 60 °C for 10 h. The extraction procedure was repeated twice.

Characterization. X-ray diffraction measurements were made on an Enraf-Nonius FR591 rotating-anode operating at 13 kW. A singly bent graphite monochromator selected Cu K α radiation and provided in-plane resolution of 0.014 Å⁻¹ full width at half-maximum. Powder samples were placed in 1.0 mm quartz capillary tubes. Gas sorption experiments were performed using a Micromeritics ASAP 2010. Nitrogen gas was used as the adsorbate at 77 K. Thermogravimetric analyses were performed with a TA Instruments TGA 2950 thermogravimetric analyzer. All measurements were made in high-resolution dynamic mode.

Results and Discussion

X-ray Diffraction. Powder X-ray diffraction analyses were performed on both the as-synthesized composites and the extracted organosilicas. Typical diffraction patterns of extracted organosilicas synthesized with Brij 56, Brij 76, and CTAC are shown in Figure 1a–c. The use of Brij 56 as the structure director gave products that exhibit a single peak in their diffraction patterns centered at $2\theta \sim 1.5^\circ$ that corresponds to a $d(100)$ spacing of approximately 60 Å. The diffraction patterns of the extracted Brij 76 organosilicas all exhibit three peaks at $2\theta = 1.45^\circ$, 2.5° , and 2.9° . These peaks can be indexed as (100), (110), and (200) Bragg reflections. This pattern is indicative of materials with a two-dimensional hexagonal ($p6mm$) pore structure.¹⁷ The as-synthesized materials exhibit similar d spacings as the extracted samples, giving no evidence of matrix expansion or contraction as a result of the extraction process. No well-defined peaks were resolved in the diffraction patterns of the CTAC samples 1 and 5, although the CTAC(2), CTAC(3), and CTAC(4) samples exhibit a broad peak at $2\theta \sim 1.5^\circ$. The $d(100)$ spacings of the extracted organosilicas are given in Table 2.

Powder X-ray diffraction analyses were also performed on all blank samples synthesized without surfactant templates. No peaks were resolved in their diffraction patterns, indicating the amorphous structure of these materials.

Nitrogen Sorption. Nitrogen gas sorption analyses were performed on the extracted organosilicas. The Brij 56 organosilicas all exhibit type IV isotherms with a large step in the mesoporous range, and sharp pore size distributions. The

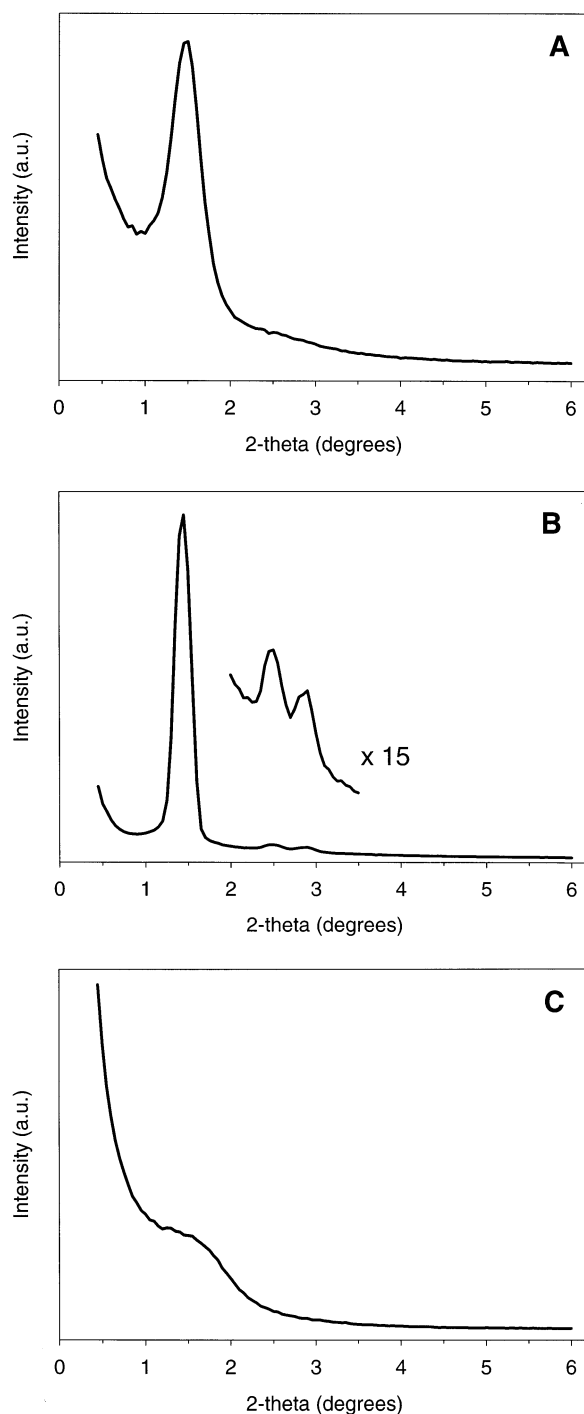


Figure 1. X-ray diffraction patterns of (a) Brij 56(2), (b) Brij 76(2), and (c) CTAC(3) templated organosilicas.

measured adsorption/desorption isotherm and BJH pore size distribution (inset) for sample B56(2), Figure 2a, is typical. The distribution gives a pore size of 39 Å. The structural properties of the nanoporous organosilicas are listed in Table 2. Nitrogen gas sorption analysis of the Brij 76 samples, Figure 2b, show properties similar to those of the Brij 56 organosilicas, but with larger pore sizes (43 Å). In general, all of the organosilicas synthesized with Brij surfactants have surface areas of approximately 1000 m²/g and total pore volumes near 1.0 cm³/g. The nitrogen sorption analysis of the CTAC organosilicas indicate that they have different microstructures when different acid concentrations are employed. When relatively low or high concentrations of HCl were used [samples CTAC(1) and CTAC-

TABLE 2: Structural Properties of Nanoporous Organosilicas

sample	d^a (Å)	d^b (Å)	BET surface area (m ² /g)	total pore volume (cm ³ /g)	pore size ^c (Å)	wall thickness ^d
B56(1)	63	61	1100	1.1	38	32
B56(2)	59	59	980	1.0	39	29
B56(3)	61	59	1090	1.0	35	33
B56(4)	59	59	910	0.8	36	32
B76(1)	59	61	1030	1.1	44	26
B76(2)	61	61	1070	1.1	44	26
B76(3)	61	61	1050	1.1	43	27
B76(4)	63	63	900	1.0	45	28
CT(1)			1020	1.5		
CT(2)			980	1.0	26	
CT(3)			1030	1.0	26	
CT(4)			1020	1.0	26	
CT(5)			730	1.3		

^a $d(100)$ spacing of the as-synthesized materials (± 2 Å). ^b $d(100)$ spacing of the extracted products (± 2 Å). ^c Calculated from adsorption branch. ^d Estimated from a_0 -pore size; where $a_0 = (2\sqrt{3}/3)*d(100)$.

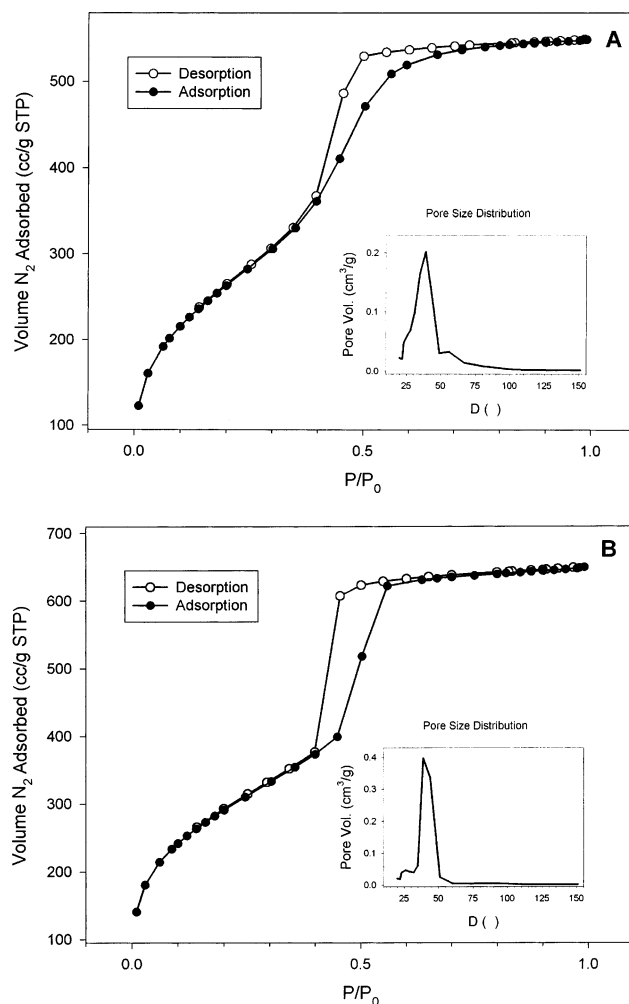


Figure 2. Nitrogen gas adsorption/desorption isotherms and pore size distributions (insets) of (a) Brij 56(2) and (b) Brij76(2) periodic organosilicas.

(5)] the resulting products were primarily macroporous, Figure 3a, with total pore volumes as large as 1.5 cm³/g. At moderate acid concentrations the CTAC organosilicas are mesoporous. The nitrogen adsorption isotherms, Figure 3b, of these materials exhibit a small step in the mesoporous range and a broad pore size distribution. The pore size distribution maximum is located at precisely the value (26 Å) normally exhibited by base-

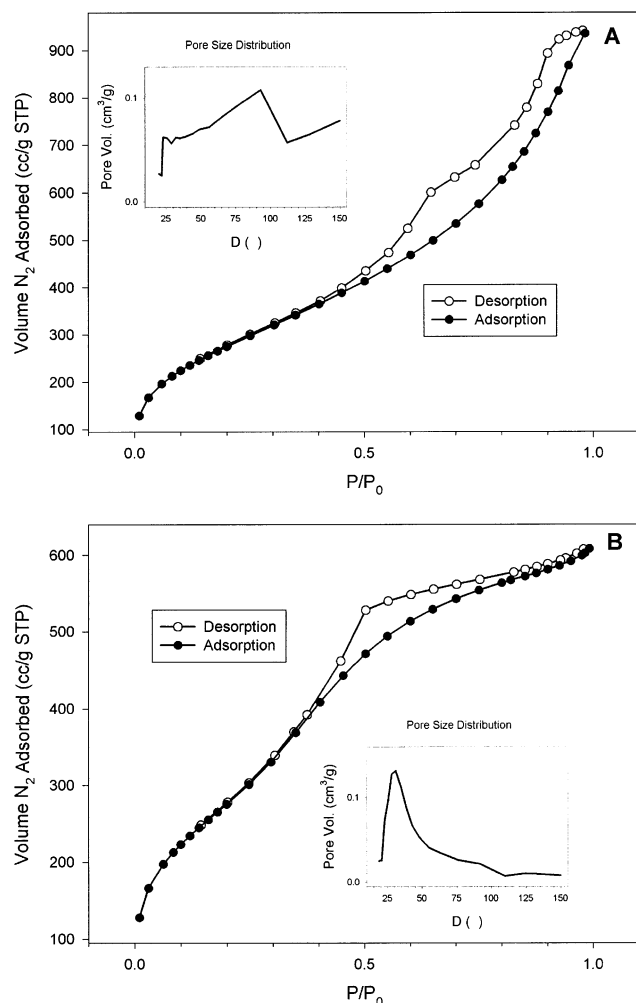


Figure 3. Nitrogen gas adsorption/desorption isotherms and pore size distributions (insets) of (a) CTAC(1) and (b) CTAC(3) nanoporous organosilicas.

catalyzed periodic nanoporous organosilicas synthesized with CTAC.¹⁰ Although this gives some evidence for the utility of CTAC as the porogen/structure director in these materials, the broad pore size distributions do not.

Thermogravimetric Analysis. Thermogravimetric analyses of the as-synthesized composites and extracted organosilicas were conducted from room temperature to 720 °C. The weight loss curves and corresponding derivative plots of the as-synthesized Brij 56 and Brij 76 organosilicas (Figure 4a,b), are dominated by the relatively large losses (34 and 39 wt %) due to the decomposition of the surfactants centered at 360 and 308 °C, respectively. A loss of 1–2 wt % at temperatures below 120 °C is due to the loss of residual ethanol and water. The weight loss curve of the as-synthesized CTAC organosilica shows a loss of only 2 wt % due to surfactant decomposition centered at 268 °C. This result is unexpected, since periodic nanoporous organosilicas synthesized under basic conditions with CTAC templates exhibited weight losses of 30–35 wt % due to decomposition of the alkylammonium surfactant.¹⁰ The loss due to residual water and ethanol (about 4 wt %) is larger than that shown by the organosilicas containing the nonionic surfactants.

The weight loss curves and corresponding derivative plots of the extracted organosilicas (Figure 5a–c) show gradual matrix decomposition from 200 to 700 °C that accounts for weight loss of approximately 7.5 wt %. The extracted Brij 56 and Brij

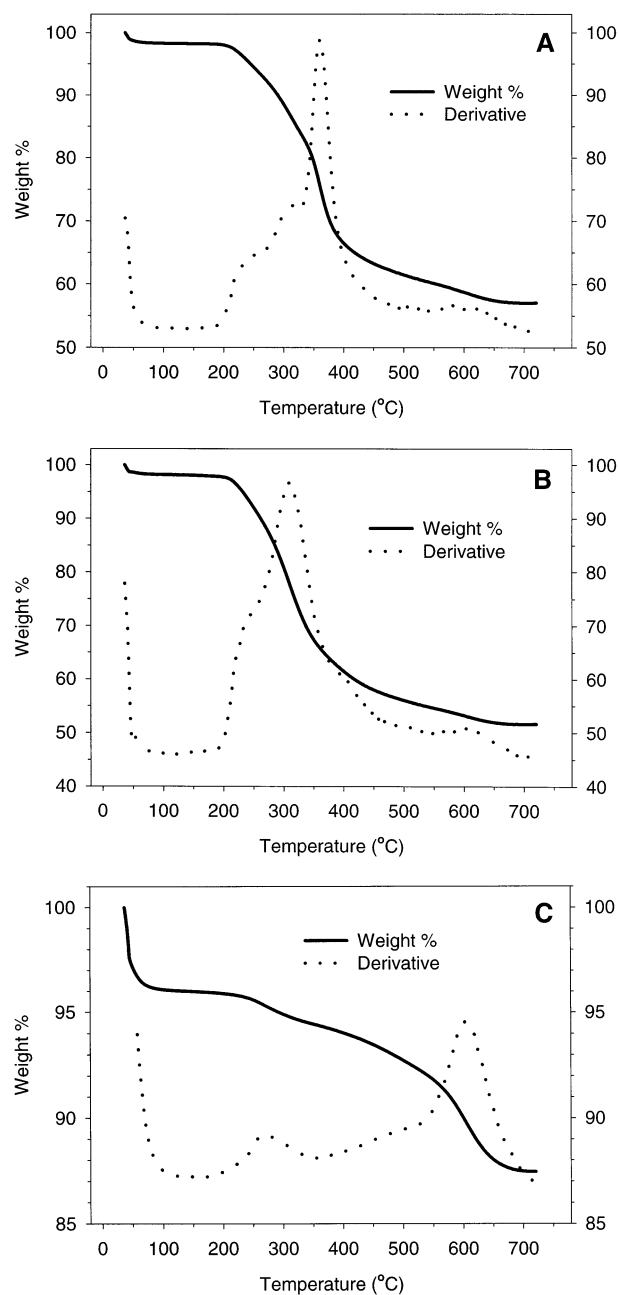


Figure 4. Thermogravimetric weight loss curves and derivative plots of as-synthesized (a) Brij 56(2), (b) Brij 76(2), and (c) CTAC(3) organosilicas.

76 templated materials exhibit losses of 4 and 3 wt % centered at 400 and 380 °C, respectively. These losses may be due to residual surfactants in these materials. The elevated temperatures of these losses, compared to those of surfactant decomposition in the as-synthesized materials, may indicate that these residual surfactant molecules are located within the pore walls of the organosilicas and not in the mesopores. This would explain the difficulty in removing them by simple extraction.

Conclusions

We have reported the synthesis and characterization of nanoporous organosilicas under acidic conditions. These materials have been synthesized by the hydrolysis and condensation of bis(triethoxysilyl)ethane (BTSE) using a hydrothermal approach. The cationic cetyltrimethylammonium chloride (CTAC), and nonionic polyoxyethylene(10) cetyl ether (Brij 56), and poly-

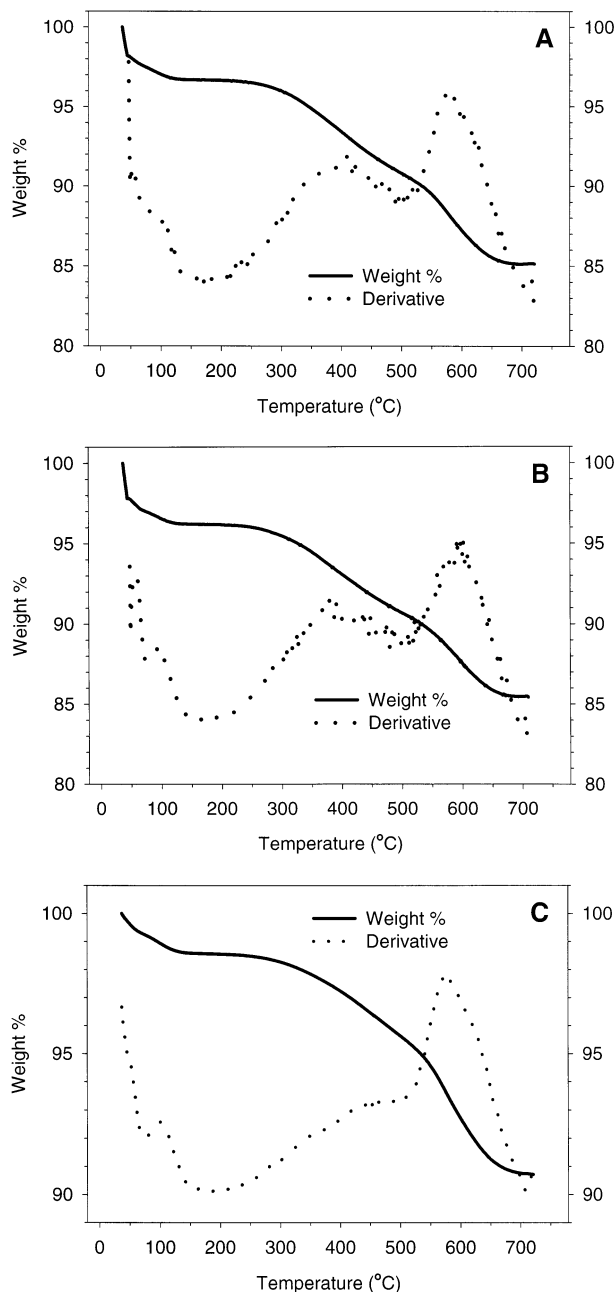


Figure 5. Thermogravimetric weight loss curves and derivative plots of extracted (a) Brij 56(2), (b) Brij 76(2), and (c) CTAC(3) nanoporous organosilicas.

oxyethylene(10) stearyl ether (Brij 76) surfactants were used as structure directors using a templating method.

Powder X-ray characterization of the acid-catalyzed organosilicas indicate the Brij 76 materials exhibit a high degree of structural ordering, giving diffraction patterns typical of 2-D hexagonal ($p6mm$) materials. Although no secondary reflections were resolved in the patterns of the Brij 56 organosilicas, their well-defined peak centered at $2\theta = 1.5^\circ$, coupled with nitrogen sorption data clearly indicate that these materials contain pores with short range hexagonal ordering. Powder XRD and nitrogen sorption data of the organosilica products indicate that the formation properties of supramolecular assemblies of the

nonionic Brij surfactants are not particularly sensitive to changes of acid concentration. The periodic nanoporous organosilicas synthesized with both Brij 56 and Brij 76 over a wide range of acid concentrations all exhibit large surface areas, large pore volumes, and sharp pore size distributions in the mesoporous range.

In contrast, the porous organosilicas synthesized with the alkylammonium halide (CTAC) surfactant exhibit significant differences in microstructure with changes in acid concentration. While the CTAC organosilicas synthesized at relatively low and high acid concentrations were primarily macroporous, those made with moderate amounts of HCl are mesoporous. Although the nitrogen adsorption isotherms of these materials do exhibit a small step in the mesoporous range, their pore size distributions are broad. None of the CTAC organosilicas synthesized under acidic conditions have periodic pore structures.

Thermogravimetric analyses of the as-synthesized composites indicate that the Brij-templated organosilicas lose approximately 35–40 wt % due to surfactant decomposition, while the CTAC-templated organosilicas lose only about 2 wt %. This is a clear indication that the alkylammonium surfactant is not being encapsulated by the BTSE during the formation of the organosilica composites. This result is consistent with both powder XRD and nitrogen sorption characterization, that indicate the relative ineffectiveness of CTAC as a structure director for nanoporous organosilicas under acidic, hydrothermal conditions. Future experiments will include the synthesis of organosilicas containing different organic bridging groups with Brij surfactants as templates.

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