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Synthesis of Periodic Mesoporous Ethylenesilica under Acidic Conditions

Wenhui Wang,[†] Songhai Xie,[‡] Wuzong Zhou,[‡] and Abdelhamid Sayari*,[†]

*Department of Chemistry and Centre for Catalysis Research and Innovation (CCRI),
University of Ottawa, Ottawa, Ontario, Canada K1N 6N5, and School of Chemistry,
University of St. Andrews, St. Andrews, Fife, UK KY16 9ST*

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High-quality mesoporous ethylenesilicas were prepared for the first time under acidic conditions using alkylpoly(ethylene oxide) oligomers or polyalkylene oxide triblock copolymers as supramolecular templates. Depending on the synthesis conditions, materials with medium (4−5 nm) and large (8−9 nm) mesopores were obtained. Addition of butanol in conjunction with P123 under acidic condition had a dramatic effect on the pore-size distribution, which became much narrower, indicating the occurrence of a porous system with enhanced ordering.

Introduction

The discovery in 1992 of ordered M41S silica mesophases using a supramolecular self-assembly approach[1,2] was the starting point of a new era in porous materials. Within 10 years, more than 3000 papers and several books and special journal issues appeared in the area of periodic (and disordered) mesoporous materials with narrow pore size distributions. Figure 1 shows the main experimental parameters that have been explored in the design and synthesis of such materials. On average, every 2 years, a novel and exciting development occurs in this field giving a renewed impetus for further innovations. As far as the synthesis of mesostructured materials is concerned, the most important milestones are (i) generalization of synthesis strategies (wide range of pH, temperature, and amphiphilic template molecules), (ii) framework- and surface-modified silicas, (iii) non-silica mesostructured materials via supramolecular templating pathways (e.g., metals, transition-metal oxides, and chalcogenides) and via silica mesophase replication (e.g., mesoporous carbons, metals, alloys and polymers), (iv) mesoporous organosilicates, and (v) assembly of zeolite seeds into mesoporous structures. This remarkable progress in synthesis was accompanied by the development of a wide variety of potential applications in adsorption, catalysis, separation, environmental cleanup, drug delivery, sensing, and optoelectronics. A number of authoritative reviews dealing either with the overall area of mesoporous materials[3−10] or with specific segments of this field such as catalysis[11] and adsorption[12−14] by mesoporous materials were published. In addition, reviews devoted to specific types of periodic

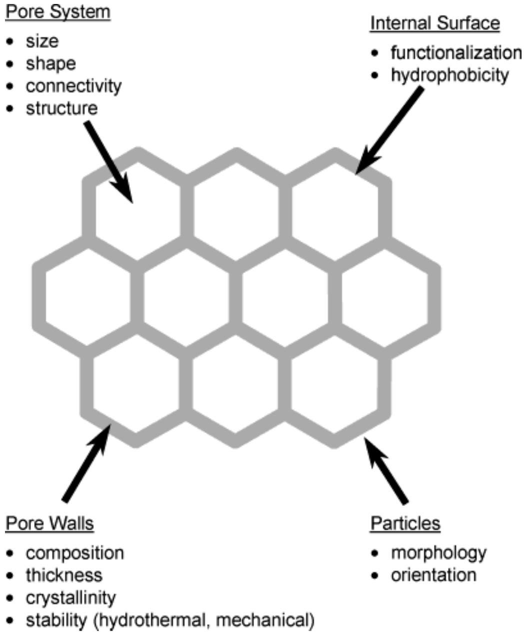

Figure 1. Structural parameters for the design of periodic mesoporous materials.

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* Corresponding author: Tel: (613) 562 5483. Fax: (613) 562 5170. E-mail: abdel.sayari@science.uottawa.ca.

[†] University of Ottawa.

[‡] University of St. Andrews.

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mesoporousmaterials such as aluminophosphates,[15] aluminosilicates,[16] non-silica materials,[17−19] inclusion materials,[20,21] surface-modified mesoporous silica,[22,23] and organic−inorganic mesoporous nanocomposites[24,25] are also readily available.

The use of bridged silsesquioxane molecules $(R'O)_3Si-R-Si(OR')_3$ as precursors for the synthesis of xerogel or aerogel nanocomposites via sol−gel techniques has been known for quite some time.[26,27] However, it is only in 1999 that researchers had the clever idea of combining the use of bridged silsesquioxane precursors and the supramolecular templating synthetic approach to obtain periodic mesoporous organosilicates (PMOs).[28−30] In addition to the unique features of periodic mesoporous materials, such as their high surface area, tunable pore sizes, and narrow pore size distributions, PMOs open a wide range of new and exciting opportunities for designing materials with controlled surface properties at the molecular level.[24,25] However, owing to the required rigidity of the PMO pore walls, the range of suitable bridged silsesquioxane precursors is limited compared to those used for the synthesis of organosilicate xerogels or aerogels.[26,27] To date, PMOs with organic spacers R originating from methane, ethane, ethylene, acetylene, butene, benzene, biphenyl, toluene, xylene, dimethoxybenzene, thiophene, bithiophene, and ferrocene have been achieved.[24,25] Successful syntheses of PMOs have been reported to take place under basic,[28−37] acidic,[38−42] or neutral[43] conditions. Several PMO mesophases have been obtained, including the following cubic structures ($Pm\bar{3}n$) akin to SBA-1,[28,31] ($Fm\bar{3}m$) similar to FDU-1,[42,44] and ($Im\bar{3}m$) isostructural to SBA-16;[45] 2D hexagonal structure ($P6mm$) similar to MCM-41[28−32,36,37] or SBA-15;[39,41] and a 3D hexagonal mesophase[28,31] whose space group is yet to be determined. Early work[28−31] used alkytrimethylammonium surfactants as structure-directing agents. Then other cationic,[46] neutral,[43] and nonionic surfactants[38−42,47−49] and even surfactant mixtures[50] were used.

Nonionic oligomeric and triblock copolymers have proven to be versatile supramolecular templates for silica[51−56] and transition-metal oxide[57] mesophases. Their use led to the discovery of a variety of new silica mesophases such as SBA-*n* (n = 11−16),[51] FDU-1,[52] FDU-12,[56] and MSU-*n* (n = 1−4).[53,54] Some of these amphiphilic molecules were used as structure-directing agents for organosilica mesophases. Fröba et al.[39] used 1,2-bis(trimethoxysilyl)ethane (BTME) as organosilica source under acidic conditions in the presence of neutral Pluronic P123 ($EO_{20}PO_{70}EO_{20}$) triblock copolymer, where EO and PO stand for ethylene oxide and propylene oxide, respectively. Their material exhibited hexagonal symmetry akin to SBA-15 silica with high surface area (900 m^2/g) and a relatively broad pore size distribution with a maximum at ca. 6.5 nm. Guo et al.[58] found that addition of salts such as NaCl improves the degree of ordering of the material. Likewise, Burleigh et al.[41] used the same triblock copolymer in addition to trimethylbenzene micelle-swelling agent under acidic conditions in the presence of 1,2-bis(triethoxysilyl)ethane (BTEE) to synthesize a series of PMOs with pore sizes ranging from 6 to 20 nm. Using a lyotropic liquid crystal Pluronic P123 triblock copolymer as template, Zhu et al.[40] obtained highly ordered, large pore ethanesilicas with pore sizes ranging from 5.8 to 7.7 nm. Alkylpoly(ethylene oxide) oligomers, namely Brij 56 [$C_{16}H_{33}(OCH_2CH_2)_{10}$-OH,[38,47−49] denoted $C_{16}EO_{10}$] and Brij 76 ($C_{18}EO_{10}$)[38,47] were also used to obtain ethanesilicas with two-dimensional hexagonal symmetry. The more hydrophobic poly(butylenes oxide) containing triblock copolymer B50−6600 ($EO_{39}BO_{47}EO_{39}$) afforded, under acidic condi-

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tions, a well-ordered organosilicate with large cagelike pores whose diameter was ca. 12 nm[42] with similar structure as FDU-1.[44,52] More recently, Guo et al.[45] reported that addition of large amounts of K_2SO_4 to a synthesis mixture containing BTME and Pluronic F127 ($EO_{106}PO_{70}EO_{106}$) under acidic conditions affords a high-quality cubic ($Im\bar{3}m$) ethanesilica mesophase with large cavities of 9.8 nm in diameter.

Except for few investigations, the overwhelming majority of literature reports on PMOs dealt with the preparation of ethanesilica, most likely because bis(trialkoxylsilyl)ethane is the only widely available silsesquioxane precursor. Unfortunately, the ethane linker offers very little in terms of further chemistry within the material pore walls. On the contrary, periodic mesoporous ethylenesilica may offer a wide range of opportunities for further surface modifications based on olefin chemistry. However, only two reports dealt with the synthesis of such materials. Using cetyltrimethylammonium bromide (CTAB) and bis(triethoxysilyl)ethylene (BTSENE) under basic conditions, Stein et al.[59] obtained mesoporous ethylenesilica with 2.4 nm wormlike channels. In the presence of gaseous bromine, only about 29% of C=C double bonds were found to be accessible to bromination reaction. Likewise, Ozin et al.[60] used mixtures of TEOS and BTSENE in the presence of CTAB to synthesize a series of PMOs under basic conditions. The pure ethylenesilica mesophase exhibited well-ordered 4 nm pores with hexagonal symmetry. Treatment with bromine in CH_2Cl_2 under reflux showed that only 10% of the C=C double bonds were brominated, and the remainder was hydrogenated, presumably through reaction with the solvent. In both cases, the pore structure was preserved during bromination.[59,60] Nonetheless, the surface area, pore volume, and size decreased.

This contribution is concerned with the synthesis of high-quality ethylene-bridged organosilicas under acidic conditions in the presence of nonionic alkylpoly(ethylene oxide) oligomers or polyalkylene oxide triblock copolymers. Moreover, recent literature data indicate that additives such as cosolvents and salts may have dramatic effects on the morphology and structure of the obtained mesophases.[45,61−65] Two striking examples on the effect of additives during the preparation of periodic mesoporous silica in the presence of P123 triblock copolymer have been reported recently. Addition of butanol was found to give rise to a large pore cubic ($Ia\bar{3}d$) mesophase instead of the more familiar SBA-15 hexagonal structure.[63] Moreover, depending on the synthesis temperature, the pore size could be adjusted from 4 to 12 nm. Likewise, the use of salts, in particular sodium iodide, afforded a highly ordered cubic ($Ia\bar{3}d$) silica mesophase.[64] We found it interesting to investigate whether this dramatic effect occurs when BTSENE is used as precursor.

Experimental Section

Vinyltriethoxysilane (VTES) and $RuCl_2(PPh_3)_3$ used for the preparation of the bis(triethoxysilyl)ethylene precursor were obtained from Aldrich. All surfactants were also purchased from Aldrich. These included the following oligomeric surfactants: Brij 56 [$C_{16}H_{33}(OCH_2CH_2)_{10}OH$, designated as $C_{16}EO_{10}$]; Brij 76 ($C_{18}EO_{10}$); Brij 58 ($C_{16}EO_{20}$); and Brij 78 ($C_{18}EO_{20}$), as well a poly(alkylene oxide) triblock copolymer Pluronic P123 ($EO_{70}PO_{20}EO_{70}$).

Bis(triethoxysilyl)ethylene (BTSENE) was prepared via metathesis of VTES according to Marciniec et al.'s method.[66] In a 50 mL three-necked flask, VTES (7.9 g, 0.05 mol) and $RuCl_2(PPh_3)_3$ (0.048 g, 0.00005 mol) were added. After stirring and refluxing for 24 h, unreacted VTES was distilled off. The product was vacuum distilled to give a clear colorless liquid, which was identified by ^1H and ^{13}C NMR and mass spectrometry as BTSENE.[66]

Preparation of Mesoporous Ethylenesilicas in the Presence of Oligomeric Surfactants. All materials were prepared using mixtures with the following composition: BTSENE:oligomer:HCl:H_2O = 1:0.27:7.7:53. In a typical preparation, 2 g of Brij 76 was dissolved in 10 g of distilled water and 50 g of 2 M hydrochloric acid at 50 °C. After complete dissolution, BTSENE (3.52 g) was added, and the mixture stirred at 50 °C for 20 h, followed by another 20 h period at 50 °C under static conditions. A white precipitate was recovered by filtration, washed thoroughly with water, and dried. The surfactant was removed by two consecutive solvent extractions using 150 mL of ethanol and 2 g of concentrated HCl for 1 g of sample at 50 °C for 5 h. Using the same preparation procedure, other samples were prepared in the presence of Brij 56 (1.92 g), Brij 58 (3.16 g), and Brij 78 (3.24 g) oligomers. The amount of surfactant was adjusted to keep the overall molar composition of the synthesis mixture constant. The obtained samples will be referred to as BRxx-ES, where BRxx indicates the oligomer used, e.g. BR76 means Brij 76; and ES stands for ethylenesilica.

Preparation of Mesoporous Ethylenesilica in the Presence of Triblock Copolymer P123. The synthesis was carried out using a mixture with the following molar composition: BTSENE:P123:HCl:H_2O = 1:0.033:11.76:81.4. The triblock copolymer P123 (2 g) was dissolved in 15 g of distilled water and 60 g of 2 M HCl. The mixture was stirred for 1 day at 35 °C, then 3.6 g of BTSENE was added. A white precipitate appeared. The mixture was kept at 35 °C for an additional period of 20 h and then at 90 °C for 2 days. The solid was recovered by filtration, washed, dried, and solvent-extracted as described above. This sample will be designated P-ES.

Preparation of Mesoporous Ethylenesilica in the Presence of Triblock Copolymer P123 and Additives. The synthesis of ethylenesilica in the presence of butanol was carried out as follows.[66] Pluonic P123 (0.986 g) was dissolved in 35.1 g of distilled water, 1.9 g of concentrated HCl, and 0.932 g of butanol at 35 °C. BTSENE (1.76 g) was added to the solution and stirred vigorously for 5 min. The mixture composition was BTSENE:P123:HCl:water:BuOH = 1:0.034:3.66:390:2.62. The white precipitate that appeared immediately was kept under stirring for 1 day at 35 °C, followed by another day at 100 °C without stirring. The preparation of periodic mesoporous ethylenesilica in the presence of NaI was as follows:[67] Pluronic P123 polymer (0.96 g) was added to a solution containing 22.5 g of water, 5.62 g of NaI, and 15 g of 4 M HCl. The mixture was heated to 55 °C before addition of BTSENE (1.22 g) under stirring. The mixture composition was BTSENE:P123:HCl:water:NaI = 1:0.048:17.4:362:10.8. After 1 day at 55 °C, the mixture was heated for another day at

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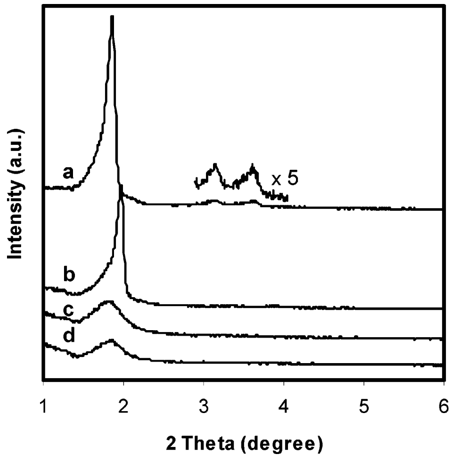

Figure 2. XRD Patterns for (a) BR76-ES, (b) BR56-ES, (c) BR58-ES, and (d) BR78-ES.

80 °C under static conditions. In both cases, separation of the material and removal of the surfactant was carried out as described above. The obtained samples will be referred to as P-ES-But and P-ES-NaI, respectively.

Bromination. The accessibility of the C=C double bond in BR76-ES and P-ES was probed using bromine addition. The white ethylenesilica material (0.05 g) was treated under vacuum and exposed to bromine vapor for 24 h at room temperature. The now brown material was washed with dichloromethane until it turned white again. Using the overall formula for brominated samples $Si_2O_3(CHBr{=}CHBr)_x(CH{=}CH)_{1-x}$, the percentage of C=C double bonds that reacted with bromine was calculated on the basis of the carbon content, which was obtained using a CHNS elemental analyzer (Carlo Erba EA1100).

Characterization. X-ray powder diffraction (XRD) patterns were collected on a Scintag X_2 Advanced Diffraction System using Cu Kα radiation with 0.15418 nm wavelength, a step size of 0.02° 2θ, and a counting time per step of 4.0 s over a $0.7° < 2\theta < 8°$ range. Nitrogen adsorption experiments were performed at 77 K using a Coulter Omnisorp 100 gas analyzer. The specific surface area, S_{BET}, was determined from the linear part of the BET plot ($P/P_0 = 0.05-0.15$). The pore size distribution (PSD) was calculated from the adsorption branch using the KJS (Kruk, Jaroniec, Sayari) method.[67] Since all the obtained mesophases were of hexagonal symmetry, the pore wall thickness (b) was calculated using $b = a - w$, where a and w are the unit cell dimension and pore size, respectively. Transmission electron micrographs (TEM) were obtained using a JEOL-2010 instrument operated at 200 kV. Before examination, the specimen were dispersed in anhydrous ethanol and deposited on a holey carbon film on a Cu grid. Scanning electron microscopy (SEM) images were collected on a JEOL-6400 instrument. ^{29}Si and ^{13}C CP MAS NMR spectra were collected as reported previously.[31,32] Spectra were recorded at room temperature on a Bruker ASX200 instrument in a magnetic field of 4.7 T (the resonance frequencies were 50.3 and 39.7 MHz, respectively), using a 7-mm Bruker probe. ^{13}C spectra were obtained using a 2 s relaxation delay, 2 ms contact time, and 3.6 μs ^{1}H 90° pulse with 31505 accumulations. ^{29}Si spectra were acquired using a 2 s relaxation delay, 2 ms contact time, and 5.6 μs ^{1}H 90° pulse with 29400 accumulations.

Results and Discussion

Ethylenesilicas Prepared in the Presence of Oligomeric Surfactants. Figure 2 shows the XRD pattern for the BRxx-ES series of samples. Materials prepared in the presence of Brij 56 and Brij 76 revealed a strong peak at $2\theta \approx 2°$, attributable to the (100) diffraction peak from 2D hexagonal unit cells. Moreover, the Brij 76-derived material exhibited two minor, but well-resolved, peaks attributable to (110) and (200) reflections. This assignment is consistent with occurrence of a mesophase with well-ordered hexagonal symmetry. However, materials prepared in the presence of oligomers with a larger headgroup, namely Brij 58 and Brij 78, showed a single, relatively weak diffraction peak at $2\theta \approx 1.6°$, most likely due to a disordered pore structure.

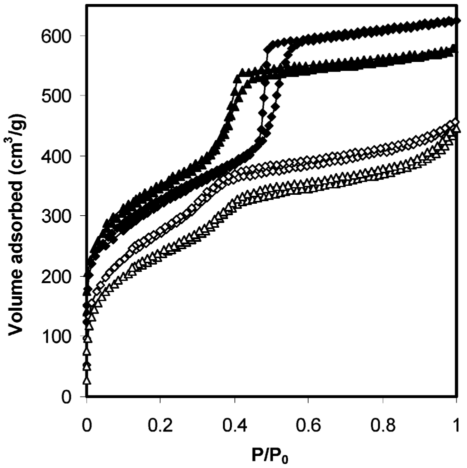

Figure 3. Nitrogen adsorption–desorption isotherms for (◆) BR76-ES, (▲) BR56-ES, (◇) BR58-ES, and (△) BR78-ES. Traces for BR76-ES and BR56-ES were shifted along the *y* axis by −110 and −100 units, respectively

Table 1. Structural Properties of BRxx-ES Samples

sample	surface area (m^2/g)	pore volume (cm^3/g)	pore size (nm)	pore wall thickness (nm)
BR76-ES	868	0.83	5.1	1.75
BR56-ES	894	0.73	4.0	2.18
BR58-ES	981	0.66	3.5	2.95
BR78-ES	847	0.63	3.8	2.78

Nitrogen adsorption–desorption isotherms for BRxx-ES samples are shown in Figure 3. The KJS pore diameter, BET surface area, pore volume,and pore wall thickness for BRxx-ES samples are shown in Table 1. Consistent with XRD data, samples prepared in the presence of Brij 56 and Brij 76 exhibited a steep adsorption uptake due to capillary condensation of nitrogen in a mesopore system with narrow pore size distribution (PSD). The capillary condensation for BR58-ES and BR78-ES takes place over a wider range of relative pressures, indicative of a broader PSD. Previous work[67,68] showed that materials with pore sizes larger than 4 nm exhibit N_2 adsorption–desorption isotherms with hysteresis loops. Consistent with this observation, BR58-ES and BR78-ES with pore sizes below 4 nm showed N_2 adsorption–desorption isotherms with reversible condensation–evaporation steps. Sample BR56-ES exhibited a pore size at the borderline of 4 nm, consistent with the occurrence of a very small hysteresis loop. Conversely, BR76-ES with 5.1 nm pores showed a sizable adsorption–desorption hysteresis loop. As suggested by the shape of nitrogen adsorption isotherms, and in agreement with XRD data, Figure 4 shows that BR56-ES and BR76-ES exhibit much narrower PSDs

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(68) Sayari, A.; Liu, P.; Kruk, M.; Jaroniec, M. *Chem. Mater.* **1997**, *9*, 2499.

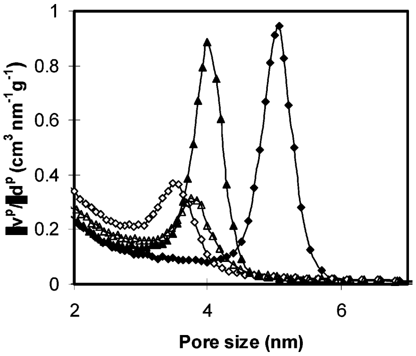

Figure 4. Pore size distributions (◆) BR76-ES, (▲) BR56-ES, (◇) BR58-ES, and (△) BR78-ES.

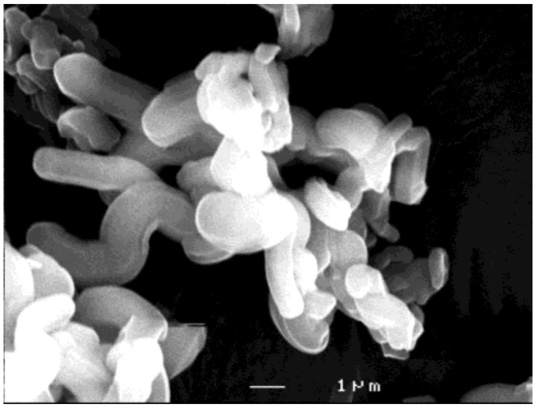

Figure 5. SEM image for BR76-ES.

than the other two samples. The morphology of BR76-ES (Figure 5), which consisted of hexagonally facetted flexible rods, provided further evidence that this material is of high-quality.

Figure 6 shows typical TEM images viewed down the [001] direction for the ethylene-bridged mesoporous organosilicas prepared in the presence of Brij 76 (Figure 7a) and Brij 56 (Figure 7b). These images provide direct evidence of the well-ordered hexagonal arrangement of the pore system. Moreover, the pore sizes estimated based on TEM images were consistent with those determined by nitrogen adsorption.

A typical ^{29}Si MAS NMR spectrum for the ethylene-bridged mesoporous materials prepared in the presence of alkyl(poly(ethylene oxide)) oligomers is shown in Figure 7a. It exhibited only two signals at −73.1 and −82.6 ppm, assigned to Si species covalently bonded to carbon atoms T^2 [C-$SiO_2(OH)$] and T^3 [C-SiO_3], respectively. The absence of Q^n species ($Si(OSi)_n(OH)_{4-n}$, $n = 2-4$) confirms that no carbon−silicon bond cleavage of the BTSENE molecules occurred during synthesis or solvent extraction. The corresponding ^{13}C CP MAS NMR spectra (Figure 7b) had a strong peak at 145.9 ppm, attributable to the ethylene carbon atoms linked to silicon. There were also two additional peaks at 16.1 and 58.2 ppm, which were assigned to non-hydrolyzed $Si-O-CH_2CH_3$ groups. Hence, the ^{29}Si and ^{13}C NMR data are consistent with each other and provide strong evidence for the occurrence of a network composed of $O_{1.5}Si-CH=CH-SiO_{1.5}$ units.

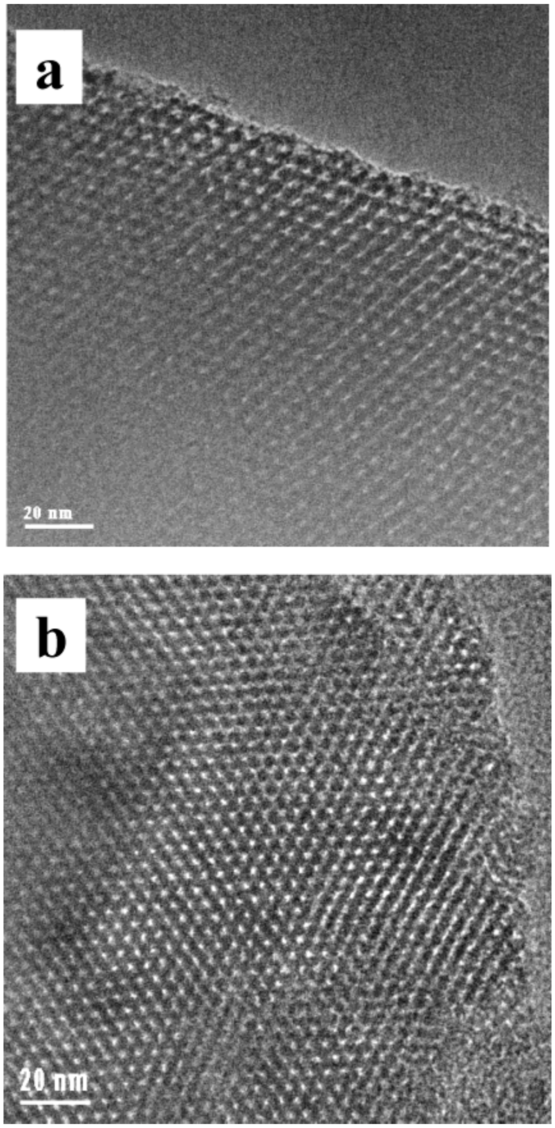

Figure 6. TEM images for (a) BR76-ES and (b) BR56-ES, both projected along the [001] zone axes.

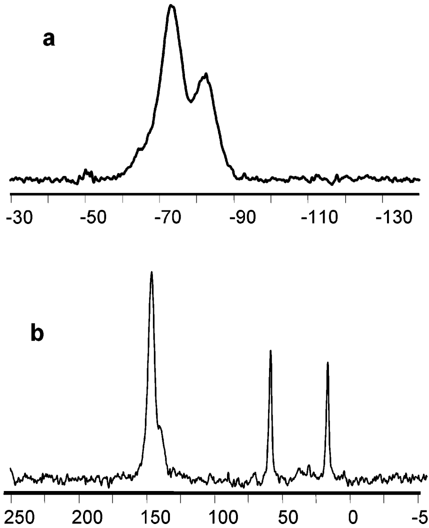

Figure 7. (a) ^{29}Si and (b) ^{13}C CP MAS NMR data for BR76-ES.

Addition of bromine generated another ^{13}C NMR peak at ca. 33 ppm attributable to *C*-Br species. However, the peak at 145.9 ppm did not vanish, indicating that a fraction of C=C bonds were presumably hidden within the pore walls and therefore not accessible to bromine. The percentage of C=C bonds that reacted with bromine was found to be 51%.

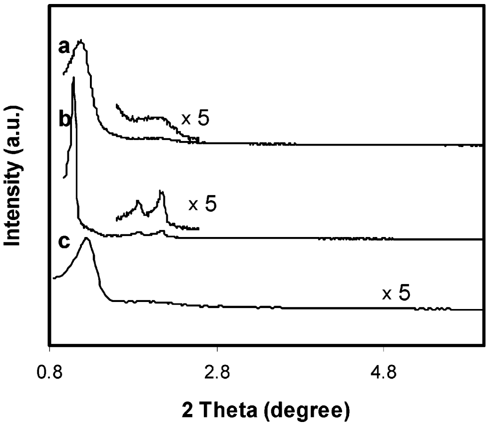

Figure 8. XRD pattern for (a) P-ES, (b) P-ES-But, and (c) P-ES-NaI.

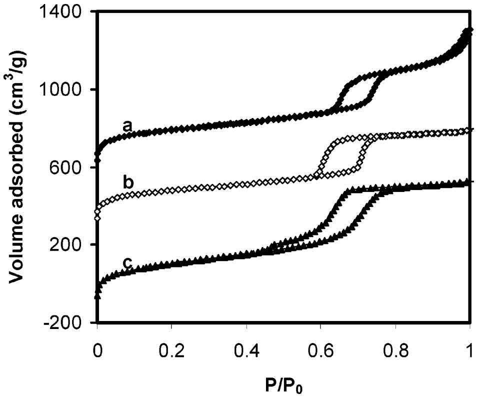

Figure 9. Nitrogen adsorption–desorption for (◆) P-ES (+600), (◇) P-ES-But (+200), and (▲) P-ES-NaI (−200). All isotherms were shifted along the y axis as indicated.

Ethylenesilica Prepared in the Presence of Triblock Copolymer P123. The powder X-ray diffraction pattern for the solvent-extracted P-ES sample is shown in Figure 8a. It reveals the occurrence of a relatively strong peak at $2\theta = 0.95°$ and a small broad peak at ca. 1.8°. These features are consistent with the occurrence of a 2D hexagonal structure whose unit cell dimension is 10.74 nm. Figure 9a shows the corresponding nitrogen adsorption–desorption isotherm. It exhibits the characteristic features of type IV adsorption isotherm with a very steep increase in adsorption at $P/P_0 = 0.72-0.77$ due to capillary condensation of nitrogen in the mesopores. It also shows a hysteresis loop, indicating that the average pore size is larger than 4 nm.[67,68] Consistent with this observation, the KJS pore diameter (Figure 10) was determined to be 8.6 nm. The BET surface area and pore volume were 676 m^2/g and 0.91 cm^3/g, respectively.

The^{29}Si MAS NMR spectrum (Figure 11a) for P-ES exhibited only two main signals at −73.1 and −82.1 ppm, assigned to Si species covalently bonded to carbon atoms T^2 [$\mathrm{C}\text{-}Si\mathrm{O_2(OH)}$] and T^3 [$\mathrm{C}\text{-}Si\mathrm{O_3}$], respectively. The absence of Q^n species (($Si\mathrm{(OSi)}_n\mathrm{(OH)}_{4-n}$), $n = 2-4$) in the range from −90 to −110 ppm confirms that, under the current synthesis conditions, no carbon–silicon bond cleavage of the BTSENE molecules occurs. The ^{13}C CP MAS NMR spectrum (Figure 11b) showed a strong single peak at 146.2 ppm, which corresponds to the ethylene carbon atoms. Hence, ^{29}Si and ^{13}C NMR data provide straightforward evidence for the occurrence of an organic–inorganic network composed of $\mathrm{O_{1.5}Si{-}CH{=}CH{-}SiO_{1.5}}$ units. The bromination test indicated that only 30% of the C═C bonds were available for reaction with bromine.

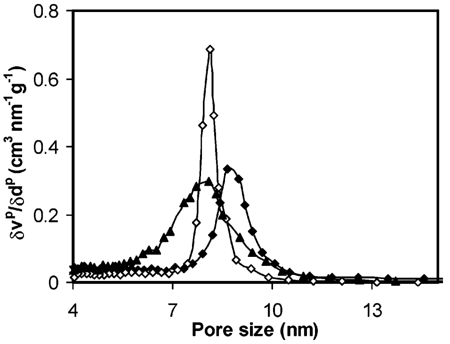

Figure 10. Pore size distributions for (◆) P-ES, (◇) P-ES-But, and (▲) P-ES-NaI.

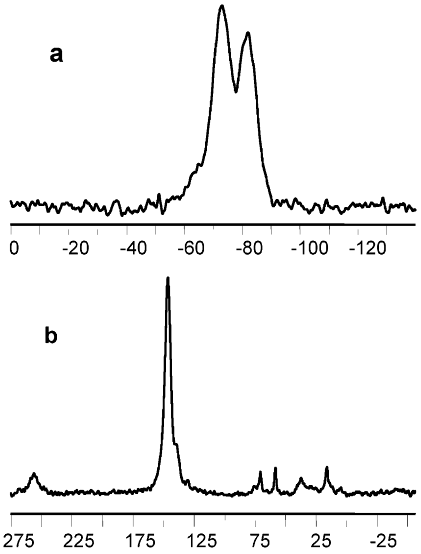

Figure 11. (a) ^{29}Si and (b) ^{13}C CP MAS NMR data for P-ES.

Table 2. Structural Properties of Samples Prepared in the Presence of P123 Triblock Copolymer with and without Additives

sample	surface area (m^2/g)	pore volume (cm^3/g)	pore size (nm)
P-ES	676	0.91	8.6
P-ES-But	624	0.75	8.0
P-ES-NaI	718	0.95	7.9

Parts b and c of Figure 8 show the XRD patterns for solvent-free P-ES-But and P-ES-NaI, respectively. Both samples exhibited a strong peak at low diffraction angles. However, P-ES-But not only had a strong and narrow (100) peak at low angle but it exhibited two additional well-resolved small peaks attributable to (010) and (200) reflections of a two-dimensional hexagonally structured mesoporous ethylenesilica. In contrast, the material prepared in the presence of NaI exhibited a somewhat weaker X-ray diffractogram with unresolved (010) and (200) peaks (Figure 8c). In both cases, no cubic mesophases were obtained.

Consistent with XRD data, the nitrogen adsorption–desorption isotherms (Figure 9b,c) show that for the material prepared in the presence of butanol, the nitrogen condensation uptake is much steeper than for

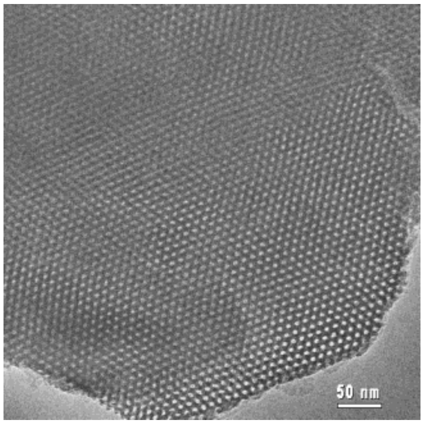

Figure 12. TEM image of P-ES-But viewed down the [001] zone axis.

the ethylenesilica prepared without additives or in the presence of NaI. These observations were also corroborated by the pore size distributions. Figure 10 shows that addition of butanol gives rise to a material with much narrower PSD than the other two materials. The physical properties of samples prepared in the presence of P123 triblock copolymer with and without additives are shown in Table 2. The high periodicity of the pore system of P-ES-But is also evidenced by TEM. A typical TEM image of P-ES-But viewed down the [001] zone axis is shown in Figure 12.

Conclusion

Highly ordered mesoporous ethylenesilicas were prepared for the first time under acidic conditions using alkylpoly(ethylene oxide) oligomers (Brij 56 and Brij 76) or polyalkylene oxide triblock copolymer Pluronic P123 as supramolecular templates. Depending on the synthesis conditions, materials with medium (4−5 nm) and large (8−9 nm) mesopores were obtained. Addition of butanol in conjunction with P123 under acidic condition afforded a material with much narrower pore size distribution, indicating the occurrence of a porous system with enhanced ordering.

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