Colloid Polym Sci (2004) 282: 728–733
DOI 10.1007/s00396-003-1004-0

ORIGINAL CONTRIBUTION

Mark C. Burleigh
Shalini Jayasundera
Chris W. Thomas
Mark S. Spector
Michael A. Markowitz
Bruce P. Gaber

A versatile synthetic approach to periodic mesoporous organosilicas

Received: 27 June 2003
Accepted: 2 September 2003

Electronic Supplementary Material Supplementary material is available in the online version of this article at http://dx.doi.org/10.1007/s00396-003-1004-0

M. C. Burleigh · S. Jayasundera
C. W. Thomas · M. S. Spector
M. A. Markowitz (✉) · B. P. Gaber
Laboratory for Molecular Interfacial
Interactions, Center for Bio/Molecular
Science and Engineering,
Naval Research Laboratory,
Washington, DC 20375, USA
E-mail: mam@cbmse.nrl.navy.mil
Tel.: +1-202-4046072
Fax: +1-202-7679594

Abstract A synthetic protocol for the preparation of a variety of high-quality periodic mesoporous organosilicas (PMOs) is presented. These nanostructured organosilicas have been synthesized by the acid-catalyzed hydrolysis and condensation of bis(triethoxysilyl) precursors containing different organic bridging groups. Polyoxyethylene(10) stearyl ether (Brij 76) is employed as the structure director using the surfactant template approach. Methylene, ethylene, ethenylene, and phenylene-bridged PMOs have been synthesized. Surfactant extraction is accomplished by refluxing the mesoscopic composite precipitates in acidified ethanol. The resulting PMOs have been characterized by nitrogen gas sorption, powder X-ray diffraction, ^{13}C and ^{29}Si solid-state NMR, and high-resolution thermogravimetric analysis. These organosilicas exhibit large surface areas, narrow pore size distributions, and large total pore volumes. This is the first report of a synthetic protocol with the versatility to make high-quality PMOs containing aliphatic, aromatic, or olefinic carbon functional groups. This versatility is discussed in terms of template and precursor structures under the acidic reaction conditions.

Introduction

A new class of ordered mesoporous materials containing organic functional bridging groups and synthesized from bisalkoxysilyl precursors $(R'\mathrm{O})_3\mathrm{Si}–R–\mathrm{Si}(\mathrm{O}R')_3$ with surfactant templates have recently been reported [1, 2, 3]. These periodic mesoporous organosilicas (PMOs) exhibit a number of distinct advantages over other organosilica hybrid materials. Traditional routes to ordered organosilicas include postsynthetic grafting of terminally functionalized organosilanes $(R'\mathrm{O})_3\mathrm{Si}–R$ to existing ordered mesoporous silicas [4] or co-condensation [5] of these molecules with silica precursors such as tetraethoxysilane (TEOS). Postsynthetic grafting decreases pore sizes and the smaller pores block the diffusion of large molecules through such mesostructures. When high concentrations of functional groups are grafted, these materials tend to be hydrophobic, with all organic functional groups located on the mesopore surfaces. This can lead to slower adsorption of molecules for applications in aqueous media because of poor wettability, when all the hydrophobic groups are located at the solid–water interface. This problem can be solved by co-condensation reactions that give a homogeneous distribution of organic functional groups throughout the silica matrix [6]. This is only effective when low concentrations of organosilanes are used, since phase separation between precursors and disordered materials with amorphous microstructures results when high concentrations of functional silanes are used. The ability to produce materials with both high loading of organic functional groups homogeneously distributed throughout a silica matrix and highly ordered mesoporous structures for fast molecular diffusion is best accomplished using the PMO methodology [7]. Since every monomer unit of a PMO contains an organic functional group, highly ordered pore structures and a homogeneous distribution of organic functional groups are accomplished with relatively high functional group incorporation. Perhaps the most promising aspect of these materials is the opportunity to tailor the chemical nature of their large surface areas by changing the organic bridging functionalities that are coupled to the inorganic silicates. PMOs are very promising materials for advanced adsorbents, sensors, and catalyst supports. The synthesis of PMOs can be challenging owing to the differences in reactivity between precursors that contain different organic groups and the efficient encapsulation of surfactant supramolecular assemblies required to produce products with ordered pore structures.

The great majority of reports to date describe the synthesis and characterization of one specific PMO [8, 9, 10]. Often, the reported synthetic procedure does not produce ordered organosilicas when different PMO precursors are substituted. Cationic alkylammonium templates that produce highly ordered mesoporous silica in acidic media [11] result in amorphous materials when more hydrophobic PMO precursors are used [12]. Yoshina-Ishii et al. [13] reported that a protocol employing cationic templates under basic conditions produced ethylene ($–CH_2–CH_2–$) and ethenylene ($–CH=CH–$) bridged PMOs but led to extensive Si–C bond cleavage, effectively disconnecting the rings when phenylene- and thiophene-bridged precursors were used [13]. The triblock copolymer P123 has been successfully employed for the synthesis of both ethylene-bridged [8] and phenylene-bridged [14] PMOs under acidic conditions. According to these reports the ethylene-bridged PMO requires approximately 24 times as much HCl per mole of precursor. Several other synthetic protocols for PMOs have been reported recently, but all describe the synthesis and characterization of only one PMO [15, 16, 17]. It follows that there is a present need for a general procedure that can be used to prepare a variety of high-quality PMOs with different organic bridging groups.

We recently reported the synthesis and characterization of ethylene-bridged PMOs prepared with cationic cetyltrimethylammonium and alkylethylene oxide (Brij 56, Brij 76) templates in acidic media [12]. Synthetic parameters such as template-to-precursor ratio and reactant mixture acidity were optimized to produce high-quality ethylene-bridged PMOs. The alkylethylene oxides were efficient templates, producing hexagonal mesostructures in high yield. Subsequently, the synthesis of an ethylene-bridged PMO using this procedure was confirmed by others [10, 17]. We have since discovered that, unlike many protocols that produce ordered mesostructures from one specific precursor and disordered products from others, our synthetic procedure can be used to make many different PMOs. Herein, we report the successful synthesis of a variety of PMOs with this versatile technique. This is the first report of a synthetic procedure used to make high-quality PMOs containing aliphatic, aromatic, or olefinic carbon functional groups. A highly ordered pure silica analog was also synthesized using this same procedure.

Experimental

Materials

The PMO precursors used include bis(triethoxysilyl)ethylene, bis(triethoxysilyl)methylene, bis(triethoxysilyl)ethenylene, and 1, 4-bis(triethoxysilyl) benzene (Fig. 1). The 1,4-bis(triethoxysilyl)benzene monomer was synthesized in our laboratory (see the following subsection) while the other organosilanes were obtained from Gelest. Ligroin (Fisher) was used without further purification. All other chemicals were obtained from Aldrich and were used as received. The water used in all the synthetic procedures was deionized to 18 MΩ cm.

Monomer synthesis. 1,4-Bis(triethoxysilyl)benzene

A N_2-purged three-necked round-bottomed flask with a stirrer bar and magnesium turnings (15 g, 0.62 mol) was flame-dried before adding TEOS (450 ml, 2 mol), dry tetrahydrofuran (THF, 250 ml), and a few crystals of iodine. The solution was brought to reflux (65 °C) and *p*-dibromobenzene (48 g, 0.20 mol) in THF (125 ml) was added dropwise to the flask during a 2-h period. This solution was allowed to reflux for another 1.5 h, becoming dark yellow. Cooling to room temperature, we removed the THF by rotary evaporation and about 200 ml ligroin was added to precipitate MgBr; it was removed by vacuum filtration. The liquor was condensed by rotary evaporation and subjected to vacuum distillation to remove excess TEOS (65 °C, 0.5 Torr) followed by the product (130 °C, 0.2 Torr), which appeared as a colorless oil (30 g, recovered yield 37%). ^{1}H NMR (400 MHz, $CDCl_3$/TMS, δ) 7.68 (s, 4H), 3.87 (quartet, 12H), 1.24 (t, 18H). ^{13}C NMR (100.7 MHz, $CDCl_3$/TMS, δ) 134.0, 133.2, 58.7, 18.1.

PMO synthesis

The method previously described for the synthesis of periodic nanoporous ethane–silica [12] was modified by the use of a specific amount of HCl and the appropriate organosilane precursor (Fig. 1). Concentrated HCl (13.1 ml, 12.2 M) was added to deionized water (186.9 ml) to make the initial aqueous solutions. The Brij 76 surfactant (4.0 g) was added to the 200 ml solutions upon stirring, and the mixtures were covered and heated at 50 °C for

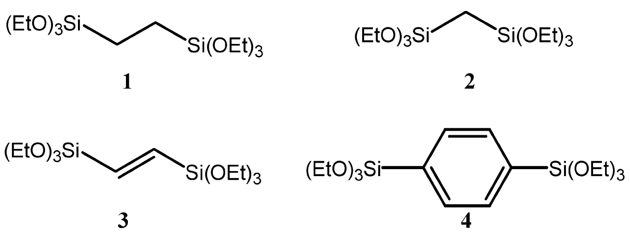

Fig. 1 Structures of the periodic mesoporous organosilica (*PMO*) precursors. *1* Bis(triethoxysilyl)ethane, *2* bis(triethoxysilyl)methane, *3* bis(triethoxysilyl)ethene, and *4* 1, 4-bis(triethoxysilyl)benzene

12 h. The precursors were then added to the resulting clear solutions. The reactant molar ratios were as follows: 0.11 Brij 76:222 H_2O:3.20 HCl:0.56 organosilane

The synthesis mixtures were covered and stirred at 50 °C for 12 h, followed by heating at 90 °C under static conditions for an additional 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 amounts were extracted with acidified ethanol, to produce mesoporous organosilicas. Composites were placed in excess (350 ml g^{-1}) acidified ethanol (1 M HCl) and refluxed for 12 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. A pure silica analog was synthesized by substituting an equimolar amount of TEOS in place of the organosilane.

Characterization

X-ray diffraction measurements were made using a Enraf-Nonius FR591 rotating-anode operating at 13 kW. A singly bent graphite monochromator selected Cu Kα radiation and provided an 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. Solid-state cross-polarization magic angle spinning (CP MAS) ^{13}C and ^{29}Si NMR experiments were performed at room temperature using a Bruker DMX-500 MHz at resonance frequencies of 125.77 and 99.36 MHz, respectively, with a 4.0-mm MAS probe. The samples were packed in 4-mm zirconia Bruker rotors fitted with Kel-F end caps for MAS at 10–12.5 kHz for ^{13}C NMR and 5 kHz for ^{29}Si NMR analysis. A two-pulse phase modulation decoupling [18] was used for proton decoupling. A ^{13}C CP contact time of 2 ms was used for all the samples with up to 1,000 scans and 10 s delays. The ^{13}C reference was set to external tetrakis(trimethylsilyl) silane at 3.5 ppm with respect to tetramethylsilane (TMS) at 0 ppm. A ^{29}Si contact time of 3 ms was used for all the samples with up to 6,000 scans and 2–5 s delays. The ^{29}Si reference was set to external tetrakis(trimethylsilyl) silane at −9.9 ($SiMe_3$) and −135.6 ppm (297 K) with respect to TMS at 0 ppm.

Results and discussion

Powder X-ray diffraction analyses were performed on the as-synthesized composites and the extracted organosilicas, as well as the pure silica analog. The diffraction pattern of the ethenylene-bridged PMO shown in Fig. 2 is typical. Three peaks are resolved at $2\theta = 1.45$, 2.55, and 2.95°. These peaks can be indexed as (100), (110), and (200) Bragg reflections, indicative of materials with 2D hexagonal (*p*6*mm*) pore structures [13]. Ethylene and phenylene PMOs, as well as the pure silica material, exhibited similar diffraction patterns. Nitrogen gas sorption analyses performed on all the extracted PMOs show type IV isotherms with a large step in the mesoporous range, and narrow Barrett–Joyner–Halenda pore size distributions. The adsorption/desorption isotherm and the pore size distribution for the phenylene-bridged PMO, shown in Fig. 3, are typical. The pore sizes of the PMOs range from 35 to 50 Å. Thermogravimetric analyses of the as-synthesized composites indicate an approximate weight loss of 35% due to surfactant decomposition centered at 390 °C. Elemental analyses of the extracted pure silica analog indicate a residual carbon content of less than 2.7%, indicating both a high degree of precursor hydrolysis and efficient template extraction. The physicochemical properties of the PMOs are shown in Table 1.

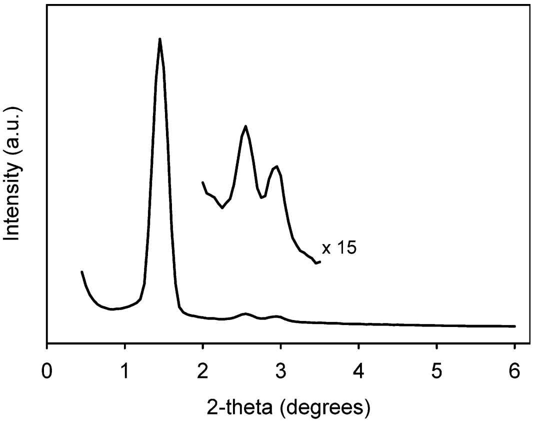

Fig. 2 Powder X-ray diffraction pattern of extracted ethenylene-bridged PMO

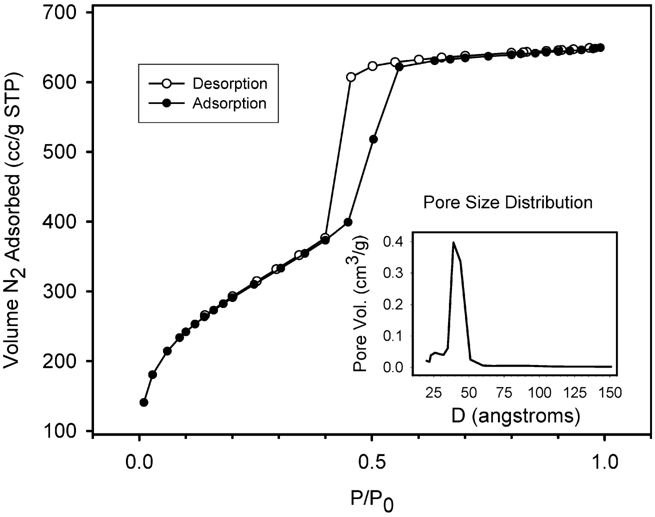

Fig. 3 Nitrogen gas adsorption/desorption isotherm and pore size distribution (*inset*) of the phenylene-bridged PMO

Solid-state ^{13}C and ^{29}Si CP MAS NMR spectroscopy was used to characterize a number of important features of the PMOs. These features include the efficient hydrolysis and condensation during synthesis, the successful removal of the surfactant templates during the postsynthetic extraction, and the stable Si–C bonding throughout the synthesis. The ^{13}C CP MAS NMR spectra of the as-synthesized and extracted methylene,

Table 1 Physicochemical properties of periodic mesoporous organosilicas

Sample	*d*(Å)[a]	Brunauer–Emmett–Teller surface area ($m^2\ g^{-1}$)	Total pore volume ($cm^3\ g^{-1}$)	Pore size (Å)[b]	Wall thickness(Å)[c]
Methylene periodic mesoporous organosilica	74	930	1.00	50	35
Ethylene periodic mesoporous organosilica	63	1,120	1.20	43	30
Ethenylene periodic mesoporous organosilica	61	1,070	1.10	39	25
Phenylene periodic mesoporous organosilica	57	850	0.70	35	31
Nanoporous silica	61	990	1.40	46	24

[a] *d*(100) spacing of the extracted products (± 2 Å)
[b] Calculated from the adsorption branch
[c] Estimated from a_0 pore size, where $a_0 = (2\sqrt{3}/3) \times d(100)$

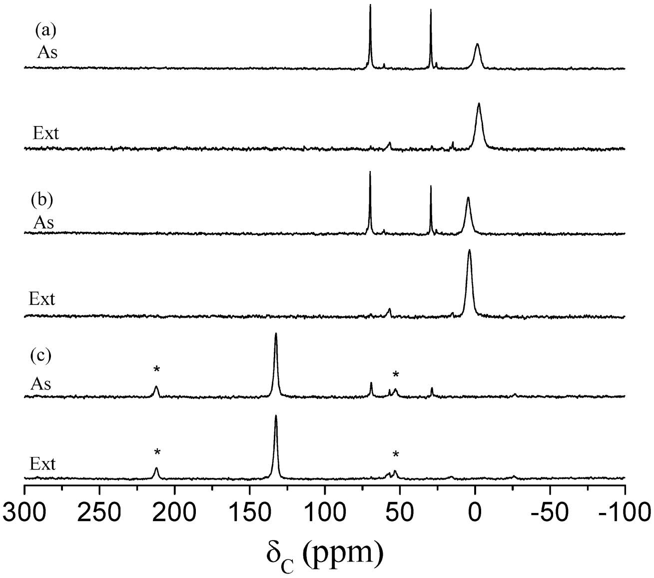

Fig. 4 ^{13}C cross-polarization magic angle spinning (*CP MAS*) NMR spectra of as-synthesized (*As*) and extracted (*Ext*) *a* methylene-bridged, *b* ethylene-bridged, and *c* phenylene bridged PMOs

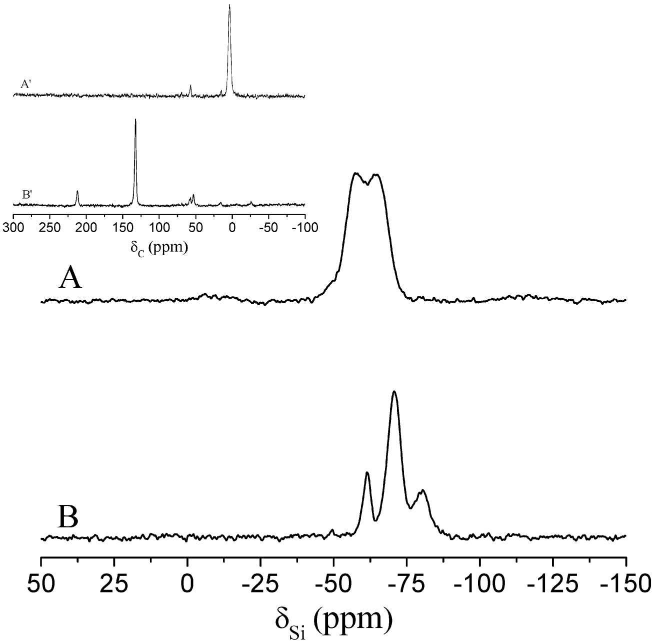

Fig. 5 ^{29}Si CP MAS NMR spectra of *a* ethylene-bridged and *b* phenylene-bridged PMOs. The *inset* shows the respective ^{13}C CP MAS NMR spectra of the PMOs

ethylene, and phenylene organosilicas are shown in Fig. 4. All three sets of spectra show the disappearance of the primary surfactant resonances located at $\delta \approx 30$ and 70 ppm after extraction, indicating nearly complete removal of the surfactant using the acidified ethanol extraction method. Very small resonances observed at $\delta \approx 18$ ppm (methyl) and $\delta \approx 58$ ppm (methylene) in the spectra taken after extraction are characteristic of trace amounts of ethanol used in the extraction process. Before and after extraction, the ^{13}C frequency assignments of all the samples show only a single carbon peak assigned to the methylene, ethylene, and phenylene groups (around –2, 5, and 134 ppm, respectively) covalently linked to Si nuclei. This shows that the C–Si bonds of the PMOs are stable during the synthesis and extraction processes.

The ^{29}Si CP MAS NMR spectra of the bridged PMOs (Fig. 5) also indicate that the C–Si bonds are stable and no cleavage occurred. Each spectrum showed only one major region of ^{29}Si peaks representing the –RSi(OSi)$_n$(OH)$_{3-n}$ or T_n units, where *R* is the bridging organic group in each case. The phenylene-bridged silica spectrum (Fig. 5, spectrum b) displays three resolved peaks at −80, −70, and −61 ppm which can be assigned to the T_n structural units within the silica matrix, where $n = 3$, 2, and 1, respectively. The ethylene-bridged silica spectrum (Fig. 5, spectrum a) displays the T_n structural unit peaks at −64, −57, and −50 ppm for $n = 3$, 2, and 1, respectively. The absence of any signals centered around −105 ppm, where the characteristic Si(OSi)$_n$(OH)$_{4-n}$ units generally appear, confirms that the C–Si bonds of the precursors did not cleave and that these bonds were stable. The ^{13}C MAS NMR resonances associated with the ethoxy groups of the PMO precursors were undetectable, indicating that a high degree of hydrolysis was achieved during synthesis.

The powder X-ray diffraction, nitrogen sorption, and solid-state NMR characterization clearly indicate the successful synthesis of PMOs containing a variety of organic bridging groups. The unprecedented versatility of this synthetic protocol over many others reported for PMOs is due to a combination of key factors that affect the surfactant template approach to synthesizing porous materials. These include the precursor molecular structure and reactivity, interactions between the template surfaces and hydrolyzed precursors, the overall stability of the Brij 76 supramolecular assemblies, and the acidic reaction conditions.

In comparing our synthetic procedure to other reported syntheses, we first note that other procedures often employ strongly basic conditions {1, 2, 3]. While this is generally not a problem during the formation of mesoporous silicas, the siloxane linkages formed during these reactions are relatively stable to base-catalyzed hydrolysis compared to the Si–C bonds in PMO precursors. The silicon to sp^2 carbon bonds in organically bridged PMO precursors containing aromatic rings are the most susceptible to hydrolytic cleavage under basic conditions [13]. The Si–C bonds of the PMO precursors are hydrolytically stable under the acidic reaction conditions employed in our synthetic procedure.

Many reported PMO protocols employ alkylammonium halide (CTA^+X^-) surfactants as templates [1, 3, 15, 16]. The mechanism behind the encapsulation of these cationic surfactants involves charge-matching between the positively charged supramolecular assemblies, negatively charged halide anions, and positively charged $Si–OH_2^+$ groups of the hydrolyzed and protonated precursors produced under acidic conditions $(S^+)(X^-)(I^+)$ [19]. When these surfactants are used in basic conditions, the positively charged ammonium groups match with the negatively charged $Si–O^-$ groups from the precursors [20]. This charge-matching is a very efficient process during the synthesis of mesoporous silicas and other metal oxides, where hydrolyzed precursors are both charged and polar. PMO precursors containing nonpolar organic bridging groups may not be as strongly attracted to the charged template surfaces. In fact, thermogravimetric analyses indicate that under acidic conditions ethylene-bridged PMO precursors polymerized in the aqueous media and encapsulated only a small amount (5–6 wt%) of the surfactant normally incorporated (30–40 wt%) into mesoscopic composites produced by surfactant templating syntheses [12]. The supramolecular assemblies of nonionic Brij 76 in water may be constituted primarily of the hydrophobic 18 carbon alkyl chains in the core and the many oxyethylene groups on the surface. The many ethylene groups that populate the surface may interact better with the nonpolar groups of the PMO precursors than the highly charged surfaces produced by the CTA^+ surfactants.

The molecular structures of PMO precursors (Fig. 1) contain six alkoxy groups as compared to only four in typical silica precursors such as TEOS. The significance of this is that 50% more alcohol is produced during PMO polymerization. This is another disadvantage for those attempting to mimic the synthesis of mesoporous silica by using CTA^+ surfactants to make PMOs [1, 3, 15, 16]. The CTA^+ surfactants have a much higher solubility in alcohol than the Brij-type alkylethylene oxide surfactants. The increased alcohol content of the reactant mixtures during PMO polymerization may destabilize the CTA^+ templates.

Conclusions

A versatile synthetic protocol for the preparation of a variety of high-quality PMOs using alkylethylene oxide templates in acidic media has been presented. The alkylethylene oxide surfactant Brij 76 is an ideal choice for a PMO template. In addition to the favorable attributes of the products (high surface areas and ordered pore channels), Brij 76 is inexpensive, nontoxic, and biodegradable [21]. The primary reasons for the unprecedented versatility of our synthetic procedure are:

1. Acidic conditions that do not break the hydrolytically labile sp^2 carbon to silicon bonds, allowing the synthesis of PMOs with stable aromatic bridging groups.
2. Better precursor-to-template interactions by use of the nonionic alkyloxy ethylene (Brij 76) surfactant with the hydrophobic PMO precursors as opposed to highly charged CTA^+ templates.
3. Better template stability during synthesis owing to the relatively low solubility of Brij 76 in ethanol.

PMOs with aliphatic, aromatic, and olefinic carbon functional groups can all be made using this simple technique. Tailoring the chemical nature of the large surface areas of PMOs by using different organic bridging groups may lead to advanced materials for adsorbent, sensor, and catalytic applications.

Acknowledgements S.J. and C.W.T. are National Research Council Fellows. This project was funded by the Office of Naval Research through a Naval Research Laboratory Accelerated Research Initative.

References

1. Inagaki S, Guan S, Fukushima Y, Ohsuna T, Terasaki O (1999) J Am Chem Soc 121:9611
2. Melde BJ, Holland BT, Blanford CF, Stein A (1999) Chem Mater 11:3302
3. Asefa T, MacLachlan MJ, Coombs N, Ozin GA (1999) Nature 402:867
4. Feng X, Fryxell GE, Wang LQ, Kim AY, Liu J, Kemner KM (1997) Science 276:923
5. Burkett SL, Sims SD, Mann S (1996) Chem Commun 1367
6. Fowler CE, Burkett SL, Mann S (1997) Chem Commun 1769
7. MacLachlan MJ, Asefa T, Ozin GA (2000) Chem Eur J 6:2507
8. Muth O, Schellbach C, Froba M (2001) Chem Commun 2032
9. Zhu H, Jones DJ, Zajac J, Roziere J, Dutartre R (2001) Chem Commun 2568
10. Hamoudi S, Kaliaguine S (2002) Chem Commun 2118
11. Huo Q, Margolese DI, Stucky GD (1996) Chem Mater 8:1147
12. Burleigh MC, Markowitz MA, Spector MS Gaber BP (2002) J Phys Chem B 106:9712
13. Yoshina-Ishii C, Asefa T, Coombs N, MacLachlan MJ, Ozin GA (1999) Chem Commun 2539
14. Goto Y, Inagaki S (2002) Chem Commun 2410
15. Yang Q, Kapoor MP, Inagaki S (2002) J Am Chem Soc 124:9694
16. Kapoor P, Yang Q, Inagaki S (2002) J Am Chem Soc 124:15176
17. Sayari A, Yang Y (2002) Chem Commun 2582
18. Bennet AE, Rienstra CM, Auger M, Lakshmi KV, Griffin RG, (1995) J Chem Phys 103:6951
19. Huo Q, Margolese DI, Ciesla U, Feng P, Gier T, Sieger P, Leon R, Petroff PM, Schuth F, Stucky GD (1994) Nature 368:317
20. Beck JS, Vartuli JC, Kennedy GJ, Kresge CT, Roth WJ, Schramm SE (1994) Chem Mater 8:2068
21. Zhao DY, Feng JL, Huo QS, Melosh N, Fredrickson GH, Chmelka BF, Stucky GD (1998) Science 279:548