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Large-Pore Ethylene-Bridged Periodic Mesoporous Organosilicas with Face-Centered Cubic Structure

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Low-temperature ($\sim 15^\circ\text{C}$) Pluronic-F127-templated synthesis of periodic mesoporous organosilicas (PMOs) with ethylene ($-\text{CH}_2-\text{CH}_2-$) framework groups and a face-centered cubic structure of spherical mesopores ($Fm3m$ symmetry) was greatly enhanced through the use of judiciously chosen swelling agents and the optimization of synthesis conditions. The resulting materials were characterized by using small-angle X-ray scattering (SAXS), nitrogen adsorption, transmission electron microscopy (TEM), and thermogravimetry. While it was confirmed that 1,3,5-trimethylbenzene is a facile swelling agent for F127-templated ethylene-bridged PMOs with cubic $Fm3m$ structure and our optimization of the synthesis afforded hitherto unreported unit-cell size and pore size, it was also shown that swelling agents predicted to have a higher extent of solubilization in Pluronics provide vast new opportunities. In particular, xylene was found to afford highly ordered PMOs with large unit-cell size and pore diameter, and a wide range of moderately or weakly ordered organosilicas with very large unit-cell parameters (up to ~ 50 nm) and pore diameters (up to ~ 18 nm). In the case of xylene, the pore size and unit-cell size were tunable by adjusting the amount of inorganic salt (KCl) in the synthesis mixture. The use of toluene allowed us to obtain unprecedented well-ordered PMOs with large unit-cell size (~ 42 nm), very large mesopores (nominal diameter 16–17 nm; capillary condensation pressure up to $\sim 0.87\text{ }p/p_0$), and enhanced primary mesopore volume, and also afforded large-pore (nominal diameter ~ 15 nm) PMO in the absence of an inorganic salt. The use of benzene also afforded large-pore PMO under salt-free conditions. Ethylene-bridged PMO was successfully converted to closed-pore ordered mesoporous silica at a temperature as low as 400°C . The identification of new swelling agents for large-pore ethylene-bridged PMO with spherical mesopores is likely to be extendable on PMOs of other framework compositions and on other related materials.

Introduction

Periodic mesoporous organosilicas (PMOs) with bridging organic groups homogeneously distributed in the silica-analogous frameworks were first reported in 1999.^{1–4} Since then, PMOs have continued to attract the attention of scientists and engineers because of their fascinating properties, such as a uniform distribution of organic groups throughout the inorganic framework, which affords interesting physical and chemical properties, as well as tunable surface properties associated with different organic bridging groups.^{5–11} The unique nanoscale environment of mesopores of PMOs is attractive in applications involving adsorption of biomolecules, and controlled release of therapeutic substances.^{12–16} First PMOs were synthesized with bis(trialkoxysilyl)organic precursors and cationic alkylammonium surfactants as templates^{1–4,17} and a remarkable tendency to the formation of highly ordered structures with spherical mesopores was observed.^{1,17} More specifically, common alkylammonium surfactants (cetyltrimethylammonium, octadecyltrimethylammonium) known from their tendency for templating 2-D hexagonal structures of silicas (MCM-41,¹⁸ FSM-16¹⁹) afforded 3-D hexagonal ($P6_3/mmc$) and cubic $Pm3n$ organosilica structures. Since then, a variety of alkylammonium surfactants

were successfully used to template the aforementioned PMO architectures and other PMOs with spherical mesopores, including face-centered cubic ($Fm3m$) structures.^{20–23} The resulting materials showed pore sizes up to ~ 7 nm.^{21,24} Oligomeric surfactants also afforded PMOs with spherical mesopores of size comparable to that achievable with alkylammonium surfactants.²⁵

The introduction of block copolymers as templates for PMO synthesis^{26–29} opened new opportunities, but the use of these templates in the synthesis of PMOs with spherical pores proved to be challenging. An initial work with Pluronic copolymers indicated that the use of commercially available Pluronic F127 ($\text{EO}_{106}\text{PO}_{70}\text{EO}_{106}$) surfactant affords well-defined organosilica structures when the bridged organosilane precursor is mixed with a majority of the silica precursor.³⁰ It was argued³⁰ that the properties of the hydrophobic block of the copolymer template have a crucial effect on the synthesis of well-defined PMOs. This contention was soon confirmed by the successful synthesis of PMO with spherical mesopores templated by poly(ethylene oxide)-poly(butylene oxide)-poly(ethylene oxide) triblock copolymer (PEO-PBO-PEO),²⁸ whose middle block was more hydrophobic than the PPO block in Pluronics. The resulting PMO had large mesopores (~ 10 nm) with narrow size distribution, and a periodic structure, as seen from small-angle X-ray scattering (SAXS) and TEM. Although the structure was originally not assigned,²⁸ the reported SAXS reflections cor-

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respond to the interplanar spacing ratios of 1:1.64:2.60:2.88, which can be identified as (111), (220), (331), and (422) reflections of *Fm3m* structure, matching reflections observed later³¹ for ethylene-bridged Pluronic-templated PMO synthesized at low initial temperature in the presence of 1,3,5-trimethylbenzene (TMB). On the basis of the identification as *Fm3m* structure, the unit-cell parameter of the PEO-PBO-PEO-templated PMO can be estimated as 24 nm. Unfortunately, block copolymer templates with suitable hydrophobic blocks (such as PBO) are not readily available commercially. Therefore, an important breakthrough in the synthesis of copolymer-templated PMOs with spherical mesopores was the use of inorganic salts to facilitate the formation of the periodic nanostructure, which first led to ethylene-bridged PMO with body-centered cubic (*Im3m*) structure and pore diameter ~ 10 nm templated by Pluronic F127.^{32,33} A similar synthesis approach afforded ethylene-bridged PMO with *Fm3m* structure under somewhat lower acid concentration.^{34,35} Subsequent syntheses of ethylene-bridged PMO (pore diameter ~ 6 nm)³⁶ as well as highly ordered phenylene- and thiophene-bridged PMOs (pore diameter 6–9 nm) with *Im3m* structure³⁷ showed that the use of inorganic salts is not necessary for the formation of Pluronic-templated PMOs with spherical mesopores. Phenylene-bridged PMO with spherical pores was also synthesized by Inagaki et al.,³⁸ but the structure was not assigned. Mixed-phase ethenylene-bridged PMO with very large pores (18.5–28.3 nm) containing a fraction of *Fm3m* structure was also reported, although in this case, Pluronic P123 (EO₂₀PO₇₀EO₂₀) was used as a template in the presence of TMB as a swelling agent.³⁹

A recently developed low-temperature approach to the Pluronic-copolymer-templated synthesis of ordered mesoporous materials^{31,40–49} brought new opportunities in the PMO synthesis.^{31,47} As was originally shown for large-pore SBA-15 silica with 2-D hexagonal symmetry ((100) interplanar spacing up to 15 nm)^{41–43} and large-pore FDU-12 silica with *Fm3m* symmetry (unit-cell parameter up to 44 nm),⁴⁰ the low initial synthesis temperature (~ 15 °C) combined with the use of a suitable swelling agent (hexane for SBA-15; TMB for FDU-12) allows one to appreciably increase the unit-cell size and pore size. A judicious selection of a swelling agent (such as 1,3,5-triisopropylbenzene (TIPB) for SBA-15 or xylene for LP-FDU-12) led to a further increase in the unit-cell size achievable at low temperature for SBA-15 (d_{100} up to 26 nm)^{45,50} and FDU-12 (unit-cell parameter up to 53 nm).⁵¹ The low-temperature synthesis originally developed for silicas has been extended first on ethylene-bridged PMO with *Fm3m* structure,³¹ then on weakly ordered methylene-bridged PMO,⁴⁶ and more recently on 2-D hexagonal PMOs (d_{100} up to at least 20 nm) with a variety of framework compositions.⁴⁷ In particular, it was shown³¹ that TMB is suitable as a swelling agent in the Pluronic-F127-templated synthesis of ethylene-bridged PMOs with spherical mesopores, affording well-ordered *Fm3m* structures. It should be noted that the use of TMB and Pluronic P123 at or above room temperature affords disordered^{29,52} or inhomogeneous³⁹ organosilica products. While the synthesis with F127 template³¹ afforded well-ordered PMOs at 15 °C, which is typically used in low-temperature syntheses, the largest unit-cell parameter of 37 nm and the pore diameter (BdB, spherical model) of 14.7 nm (as determined from N₂ adsorption isotherm with capillary condensation at a relative pressure of ~ 0.81) were achieved at 10 °C. Moreover, a weakly ordered organosilica with unit-cell size of 39 nm (assuming *Fm3m* structure), and pore diameter of 18.5 nm (BdB, spherical model, as determined from N₂ adsorption isotherm with capillary condensation at a

relative pressure of ~ 0.85), was synthesized at 5 °C with use of somewhat reduced acid concentration (1.5 M). The weakly ordered methylene-bridged PMO reported in another study⁴⁶ was presumably a face-centered cubic structure with the unit-cell parameter of 41 nm (based on SAXS) and the pore diameter (KJS-cylindrical) of 13.0 nm (capillary condensation pressure 0.83 p/p_0).

The judicious selection of the swelling agents for the surfactant-templated synthesis of ordered mesoporous materials can be based on the following principles.⁴⁵ First, swelling agents of a moderate extent of solubilization in the surfactant micelles are preferable, as they provide an opportunity for achieving an appreciable pore size enlargement without the loss of the structural ordering of the templated material. Second, the selection of a swelling agent can be based on the knowledge of (i) the extent of solubilization of compounds (swelling agent candidates) in micellar solutions (or extrapolation within families of related compounds, if experimental data for a particular compound are not available) and (ii) the performance of the known swelling agents in the surfactant-templated synthesis of materials. In particular, the notion that the extent of solubilization of alkyl-substituted benzenes in Pluronics decreases as the size and number of alkyl substituents increases led to the identification of TIPB as a less strongly solubilized alternative to TMB in the synthesis of Pluronic P123-templated SBA-15 silica and PMOs with 2-D hexagonal structure.^{45,47} On the other hand, the realization that the use of a more strongly solubilized swelling agent can improve the previously developed TMB-based synthesis of LP-FDU-12 silica involving F127 surfactant³¹ led to the identification of xylene and toluene as swelling agents for ultralarge-pore FDU-12 synthesis.⁵¹

Herein, the synthesis and characterization of large-pore ethylene-bridged PMOs with unprecedented structural properties are reported. Our low-temperature synthesis involved either TMB, which was used by others in a similar synthesis,³¹ or other appropriately selected swelling agents, namely xylene, toluene, and benzene, which were predicted⁵¹ to solubilize more strongly in Pluronics than TMB does. The use of the selected swelling agents, combined with an optimization of the amount of an inorganic salt, afforded highly ordered PMOs with *Fm3m* structures and unit-cell parameters ~ 40 nm, as well as a range of PMOs with even larger unit-cell sizes (up to ~ 50 nm) and with gradually diminishing degree of structural ordering. The highly ordered products had a nominal (KJS-cylindrical) pore diameter of ~ 14 –17 nm. To the best of our knowledge, these are the largest unit-cell sizes and pore diameters reported for well-ordered PMOs with spherical mesopores.

Materials and Methods

Materials. In a typical experiment, 0.50 g of Pluronic F127 (EO₁₀₆PO₇₀EO₁₀₆) was dissolved in 30 g of 2.0 M HCl solution under mechanical or magnetic stirring at 15 °C. Then, 0.50 g (or 1.00 g, see below) of the swelling agent (TMB, 1,3,5-triisopropylbenzene (TIPB), 1,3,5-triethylbenzene (TEB), xylenes—mixture of isomers (referred to herein as xylene), toluene, or benzene) and 2.50 g (or other amount) of KCl was added (except for benzene, in which case no salt was used). It should be noted that for TMB, TEB, and TIPB, a mechanical stirrer set at a moderate stirring speed was used and the reaction mixture was prepared in a polypropylene (PP) bottle with its mouth taped with parafilm leaving a small hole for the stirrer. For xylene, toluene, and benzene, a magnetic stirrer (set at 300 rpm) was used and the reaction mixture was in a glass container whose mouth was taped with parafilm. After 2 h, 2.90 g of

bis(trimethoxysilyl)ethane (BTME) was added. The reaction mixture was stirred for 1 day at 15 °C (in a semiclosed container, as described above). Then, the reaction mixture was treated hydrothermally at 100 °C for 1 day in a closed PP bottle. The product was filtered out, washed with deionized water, and dried at ~60 °C under vacuum. Finally, the surfactant was removed from the sample via the Soxhlet extraction with ethanol. One of the PMOs was calcined under argon or air at 350 and/or 400 °C (ramp 2 deg/min, dwell time 5 h).

Measurements. The small-angle X-ray scattering (SAXS) patterns were recorded on a Bruker Nanostar U instrument equipped with Cu K α radiation source, which was a rotating anode operated at 50 kV and 24 mA. Samples were placed in the hole of an aluminum sample holder and secured on both sides with Kapton tape. Nitrogen adsorption measurements were carried out at -196 °C on a Micromeritics ASAP 2020 volumetric adsorption analyzer. The samples were outgassed at 140 °C in the port of the adsorption analyzer before being analyzed. Transmission electron microscopy (TEM) images were recorded on an FEI Tecnai G2 Twin microscope operated at an accelerating voltage of 120 kV. The samples were first sonicated in ethanol, and then drop-casted on carbon-coated copper grid and dried under air before the analysis.

Calculations. The BET specific surface area was determined from the nitrogen adsorption isotherm in a relative pressure range of 0.04–0.2.⁵³ The total pore volume was determined from the amount adsorbed at a relative pressure of 0.99.⁵³ The pore size distribution (PSD) was determined from the adsorption branch of the isotherm, using the Barrett–Joyner–Halenda (BJH) method⁵⁴ with the KJS correction for cylindrical mesopores (calibrated for diameters 2–7 nm)⁵⁵ and the statistical film thickness curve for a macroporous silica gel LiChrospher Si-1000.⁵⁶ The maximum of PSD is referred to as a nominal pore diameter. As expected from an earlier study,⁴⁴ the considered method underestimates the diameter of spherical 2 mesopores in the considered size range by ~3 nm. The micropore volume (V_{mic}) was calculated by using the α_s plot method in the standard reduced adsorption range of 1–1.2 or similar. The sum of V_{mic} and the primary mesopore volume (V_p) was calculated from α_s values (typically 1.9–2.4 or 2–2.4) above the capillary condensation range. V_p was extracted from the results of the aforementioned calculations. In the α_s method, the macroporous silica was used as a reference adsorbent.⁵⁶

Result and Discussions

Optimization of Synthesis with TMB As Swelling Agent.

As shown earlier by others,³¹ TMB is a suitable swelling agent for low-temperature Pluronic-F127-templated synthesis of ethylene-bridged PMO with well-ordered *Fm3m* structure. Our study showed that the use of a similar synthesis mixture composition (2 M HCl, 2.5 g of KCl per 0.5 g of F127 and 0.5 g of TMB) and the typical initial temperature (15 °C), but with an increased relative amount of the organosilica precursor, combined with the optimization of the stirring speed (moderate speed worked best, while higher speed resulted in a decrease in the unit-cell size), afforded a well-ordered PMO of *Fm3m* structure (see the SAXS pattern in Figure 1) and the unit-cell parameter of 41 nm (Table 1). The PMO had an adsorption isotherm (Figure 2) with a steep capillary condensation step centered at a relative pressure of 0.85 and a nominal pore diameter of 14.6 nm (Figure 2 and Table 1). The hysteresis loop was broad with a steep decline of the desorption branch at the lower pressure limit of adsorption–desorption hysteresis (0.48 p/p_0), which indicates that the entrances to the mesopores

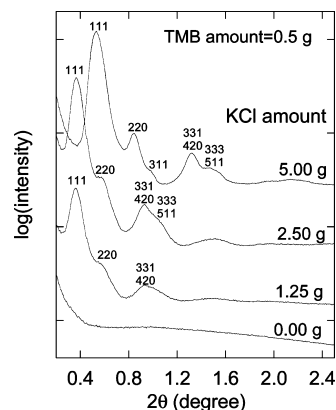


Figure 1. SAXS patterns of extracted ethylene-bridged organosilicas prepared in the presence of different amounts of KCl per 0.50 g of TMB as swelling agent.

were of diameter below 5 nm. These results show that the optimization of TMB-based synthesis affords well-ordered ethylene-bridged PMO with unprecedented unit-cell size and with pore diameter similar to that of the poorly ordered counterpart reported earlier³¹ (based on the capillary condensation pressure, which is the primary basis of the mesopore size assessment).

Selection of Swelling Agent for Pluronic-F127-Templated

PMO Synthesis. It was predicted and confirmed elsewhere⁵¹ that low-temperature Pluronic-F127-templated synthesis of silicas can be improved by using swelling agents (such as xylene and toluene) that are expected to solubilize more strongly in Pluronics than TMB does. It is shown herein that the same approach is applicable to PMOs. In particular, a series of aromatic swelling agents was examined, including 1,3,5-triisopropylbenzene (TIPB), 1,3,5-triethylbenzene (TEB), TMB, xylene, toluene, and benzene with decreasing number and/or size of alkyl substituents on the benzene ring and hence with known^{57,58} (or predicted by extrapolation)^{45,51} increase in the extent of solubilization in Pluronics micelles in aqueous solutions. The structure of the swelling agent significantly affected the quality of the product, as seen from SAXS patterns (Figure 3) for samples prepared with the same composition of the synthesis mixture, except for the use of a different swelling agent (and the absence of salt in the case of benzene). In all cases, well-resolved (or very well resolved) SAXS patterns were obtained, which could be indexed on face-centered cubic (*Fm3m*) structure. The differences in heights of the capillary condensation steps, which can be used as a rough measure of the volume of the ordered mesopores for the considered PMOs, were quite dramatic (see Figure 4). While PMOs prepared in the presence of benzene, toluene, xylene, and TMB featured well-pronounced capillary condensation steps of similar height, PMOs obtained in the presence of TEB and TIPB exhibited much smaller steps and thus much lower mesopore volumes. These differences were also clearly visible from pore size distributions, which revealed smaller pore volumes (areas of PSD peaks) and smaller pore sizes for the considered two samples (Figure 4). Among the series, the largest unit cell parameter ($a = 41.4$ nm) was exhibited by PMO (discussed above) synthesized with TMB as a swelling agent, but this synthesis was already optimized in this regard. On the other hand, the degree of structural ordering of PMOs obtained with xylene and toluene as swelling agents was somewhat better, as seen from SAXS patterns, while their unit-cell parameters were 39.2 and 34.4 nm, respectively. It is clear that TMB, xylene, toluene, and benzene swelling agents afford well-ordered face-

TABLE 1: Structural Parameters of the Organosilicas^a

swelling agent (mass in g), mass of KCl (in g) ^b	<i>a</i> (nm)	<i>S</i> _{BET} (m ² /g)	<i>V</i> _t (cm ³ /g)	<i>V</i> _{mic} (cm ³ /g)	<i>V</i> _p (cm ³ /g)	<i>w</i> _{KJS} (nm)
TMB (0.5), KCl (5.0)	28.6	397	0.26	0.13	0.12	9.5
TMB (0.5), KCl (2.5)	41.4	688	0.39	0.24	0.13	14.6
TMB (0.5), KCl (1.25)	41.9	576	0.30	0.24	0.05	14.4
TMB (0.5), KCl (0)	— ^c	807	0.40	— ^d	— ^d	— ^e
xylene (0.5), KCl (2.5)	39.2	405	0.27	0.16	0.10	14.1
xylene (0.5), KCl (1.25)	41.9	632	0.36	0.26	0.09	13.9
xylene (0.5), KCl (0.94)	45.0	610	0.35	0.24	0.09	15.0
xylene (0.5), KCl (0.63)	47.8	413	0.25	0.16	0.06	14.9
xylene (0.5), KCl (0)	51 ^f	733	0.37	0.33	0.02	18.7
xylene (1.0), KCl (2.5)	38.7	414	0.29	0.16	0.11	14.4
xylene (1.0), KCl (1.25)	45.0	361	0.23	0.14	0.08	15.2
xylene (1.0), KCl (0.94)	45.7	750	0.41	0.31	0.08	15.0
xylene (1.0), KCl (0.63)	47.8	439	0.24	0.19	0.04	14.8
xylene (1.0), KCl (0)	49.4	786	0.42	0.33	0.05	17.5
toluene (0.5), KCl (2.5)	34.4	422	0.30	0.15	0.13	12.6
toluene (0.5), KCl (1.25)	41.9	449	0.34	0.15	0.16	15.7
toluene (0.5), KCl (0.94)	41.9	305	0.24	0.11	0.11	15.5
toluene (0.5), KCl (0.63)	39.2	453	0.31	0.16	0.13	13.7
toluene (0.5), KCl (0)	41.9	433	0.28	0.17	0.10	14.6
toluene (1.0), KCl (2.5)	36.0	400	0.29	0.14	0.13	13.7
toluene (1.0), KCl (1.25)	42.5	647	0.46	0.24	0.19	16.0
toluene (1.0), KCl (0.94)	43.1	578	0.43	0.20	0.19	17.1
toluene (1.0), KCl (0.63)	42.5	599	0.42	0.22	0.17	16.7
toluene (1.0), KCl (0)	41.9	378	0.29	0.13	0.14	15.9
benzene (0.5), KCl (0)	36.9	453	0.37	0.13	0.19	13.7
no swelling agent, KCl (2.5)	— ^c	794	0.39	— ^d	— ^d	— ^e
no F127	— ^c	430	0.65	~0.00	— ^g	— ^e

^a Notation: *a*, unit cell parameter for extracted sample; *S*_{BET}, BET specific surface area; *V*_t, total pore volume, *V*_{mic}, micropore volume; *V*_p, volume of ordered (primary) mesopores; *w*_{KJS}, KJS pore diameter—calculated using a procedure calibrated for cylindrical mesopores; underestimation of the pore diameter by ~3 nm is expected. ^b Amount of swelling agent and KCl per 0.5 g of Pluronic F127. ^c No clear peak on SAXS pattern, so the unit-cell parameter is not defined. ^d No good separation between micropore and mesopore ranges, *V*_t has a major contribution from the micropore volume. ^e No peak on mesopore size distribution. ^f Pattern not well resolved; the main SAXS peak is tentatively assigned as the (111) reflection of the *Fm3m* structure. ^g Mesopore volume essentially equal to *V*_t.

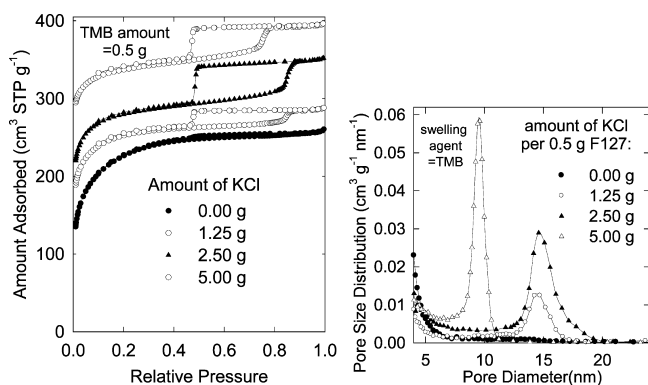


Figure 2. Nitrogen adsorption isotherms (left) and pore size distributions (right) for organosilicas prepared with 0.5 g of TMB and different amounts of KCl per 0.5 g of F127. For clarity, the isotherms were offset vertically by 90, 100, and 225 cm³ STP g⁻¹ for samples synthesized with 1.25, 2.5, and 5.0 g of KCl.

centered cubic PMOs with appreciable mesopore volume and large pore size, whereas TEB and TIPB afford cubic PMOs with much lower mesopore volume and smaller pore dimensions. It is shown below how the PMO synthesis involving xylene and toluene can be optimized, while maintaining high quality of the products. It is important to note that among the considered swelling agent candidates, only TMB was used before³¹ in the synthesis of PMOs with spherical mesopores.

Xylene As Swelling Agent for PMO Synthesis. As can be seen in Figure 4, the replacement of TMB with xylene while keeping other conditions constant (except for a better protection from swelling agent evaporation and a different mode of stirring)

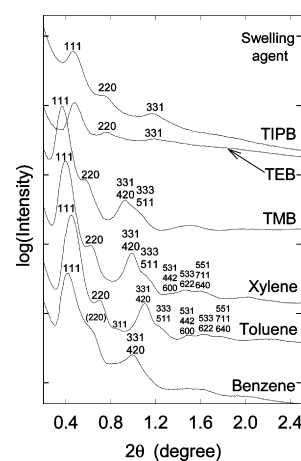


Figure 3. SAXS patterns of extracted ethylene-bridged PMOs prepared with different swelling agents.

afforded PMOs with quite comparable unit-cell size and pore diameters, while increasing the degree of structural ordering. Moreover, the reduction of the amount of salt in the synthesis mixture led to a marked unit-cell size increase (up to ~50 nm) in the case of xylene (see Table 1 and SAXS patterns in Figure 5), while in the case of TMB, a similar change in synthesis conditions led to the decrease in quality (without any appreciable unit-cell size increase) and eventually, the loss of periodic mesoporous structure. Because of the fact that the increase in the amount of xylene tends to improve the quality of SAXS patterns while maintaining a similar pore diameter, the discussion is primarily focused herein on samples prepared with 1.0 g

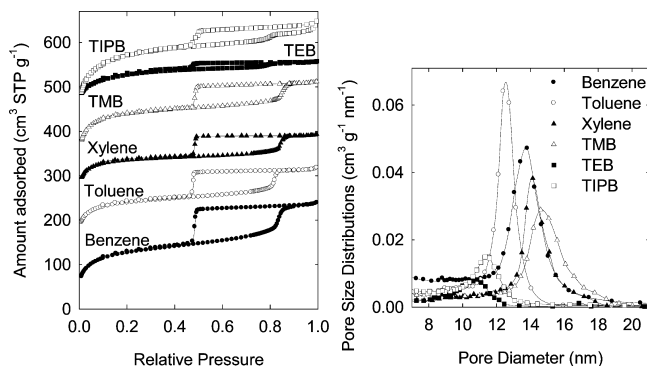


Figure 4. Nitrogen adsorption isotherms (left) and pore size distributions (right) of extracted ethylene-bridged PMOs prepared with different swelling agents. The isotherms for samples prepared with toluene, xylene, TMB, 1,3,5-triethylbenzene (TEB), and 1,3,5-triisopropylbenzene (TIPB) were offset vertically by 120, 220, 260, 440, and 350 $\text{cm}^3 \text{STP g}^{-1}$, respectively, for the sake of clarity.

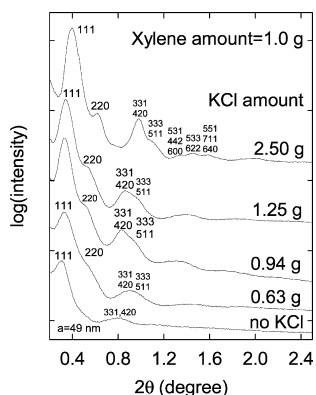


Figure 5. SAXS patterns of extracted ethylene-bridged PMOs prepared in the presence of different amounts of KCl with 1.0 g of xylene per 0.5 g of F127.

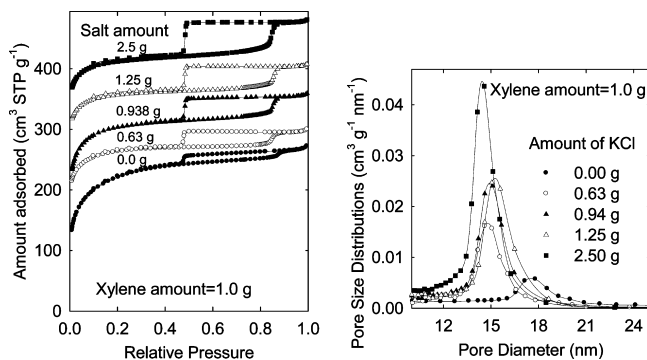


Figure 6. Nitrogen adsorption isotherms (left) and pore size distributions (right) for PMOs synthesized with different amounts of KCl and 1.0 g of xylene as a swelling agent. For clarity, isotherms were offset vertically by 140, 90, 255, 295 $\text{cm}^3 \text{STP g}^{-1}$ for samples synthesized with 0.63, 0.938, 1.25, and 2.5 g of KCl.

of xylene per 0.5 g of F127 (Figures 5 and 6), while data for samples prepared with a regular amount of xylene (0.5 g), which show a similar trend, are presented in Figure S1 in the Supporting Information. It should be noted that the observed effect of the relative amount of the swelling agent on the PMO structure indicates that the micelles of Pluronic F127 are essentially saturated with xylene, the latter being in appreciable excess (similarly to the case of LP-FDU-12 silica),⁵¹ and perhaps the larger excess of the swelling agent (1 g per 0.5 g of F127) makes the distribution of the swelling agent more uniform throughout the micelles.

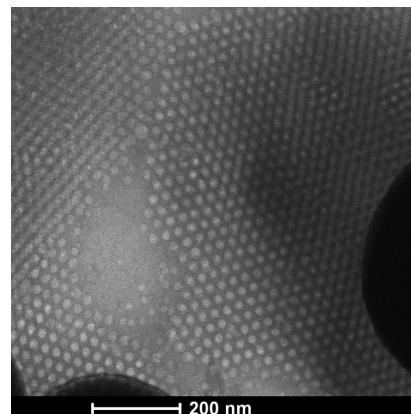


Figure 7. TEM image of PMO synthesized with xylene as a swelling agent (0.5 g of xylene and 2.5 g of salt per 0.5 g of F127), which can be identified as [110] projection of the face-centered cubic structure.

The decrease in the relative amount of salt resulted in a shift of reflections on SAXS patterns toward lower angles, thus indicating the increase in the unit-cell size. This increase was paralleled by the decrease in the resolution of the SAXS patterns. The largest unit-cell size for which the SAXS pattern was clearly indexable as a pattern of the face-centered cubic structure was 45–46 nm (for 0.94 g of KCl), but similar, although somewhat less well-resolved patterns were recorded, in which the position of the first peak would correspond to the unit-cell parameter of 48 nm (for 0.63 g of salt). If the salt was not added, the SAXS patterns still resembled the patterns for other samples from the series, but the main peak was at even lower angles, and the corresponding unit-cell parameter was ~ 50 nm, assuming $Fm3m$ structure. Nitrogen adsorption isotherms (Figure 6 and in the Supporting Information Figure S1) exhibited steep capillary condensation steps and hysteresis loops with desorption at the lower limit of adsorption–desorption hysteresis ($\sim 0.48 p/p_0$), indicating the presence of uniform cage-like mesopores. The pore diameter was similar (14–15 nm, capillary condensation pressure $\sim 0.85 p/p_0$) for all the samples, except for the ones prepared in the absence of the salt, which exhibited much larger pore diameters (~ 18 nm, capillary condensation pressure 0.88–0.89 p/p_0). The primary (ordered) mesopore volume exhibited a tendency to decrease as the amount of salt was lowered (see Table 1). The same trend was observed for TMB, although it was more dramatic, and the salt was needed to form the periodic structure under the considered conditions. TEM confirmed the well-defined periodic structure of the PMO prepared in the presence of xylene (see Figure 7). It is clear that xylene offers an opportunity to achieve well-ordered PMOs with unprecedented unit-cell dimensions, and weakly ordered PMOs with very large mesopores.

Toluene As Swelling Agent for PMO Synthesis. In the case of toluene as a micelle expander, well-resolved SAXS patterns (Figure 8) were obtained, which can be indexed on the $Fm3m$ structure, even for the sample prepared without the addition of salt. The amount of salt analogous to that used in the standard TMB- or xylene-based synthesis (2.5 g of KCl per 0.5 g of F127) afforded a sample with somewhat lower unit-cell parameter of 34 nm (Table 1), which was slightly increased by doubling the amount of the swelling agent. The resulting PMOs had nominal pore diameter of ~ 13 nm, which is slightly smaller than the pore size of their counterparts prepared with TMB and xylene. However, when the amount of salt was reduced to about half of the original amount (0.94–1.25 g KCl per 0.5 g of F127), PMOs with large unit-cell parameters (up to 42–43 nm),

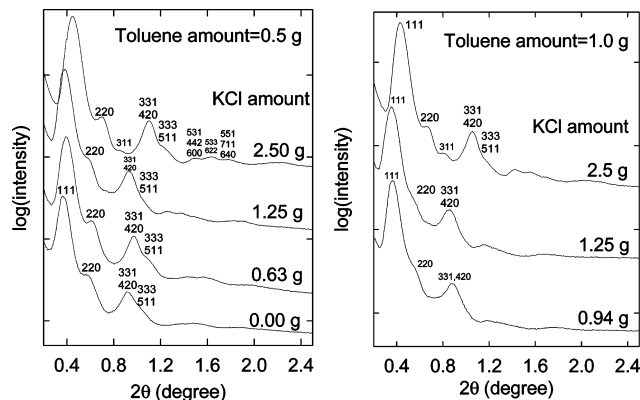


Figure 8. SAXS patterns of extracted ethylene-bridged PMOs prepared in the presence of different amounts of KCl with (left) 0.5 g and (right) 1.0 g of toluene as a swelling agent.

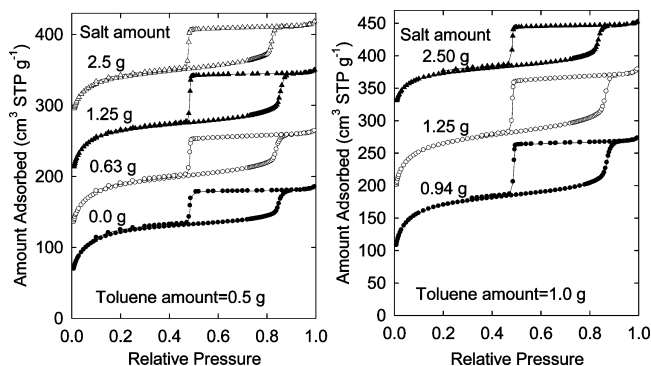


Figure 9. Nitrogen adsorption isotherms for PMOs synthesized with different amounts of KCl and (left) 0.5 g and (right) 1.0 g of toluene as a swelling agent. For clarity, (left) the isotherms were offset vertically by 60, 130, and 220 cm³ STP g⁻¹ for samples synthesized with 0.63, 1.25, and 2.5 g of KCl, respectively, and (right) the isotherms were offset vertically by 100 and 260 cm³ STP g⁻¹ for samples synthesized with 1.25 and 2.5 g of KCl, respectively.

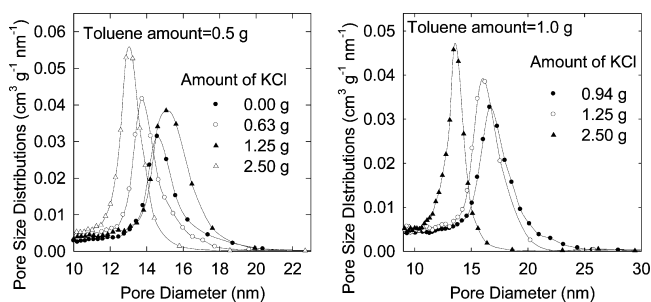


Figure 10. The pore size distributions of PMOs synthesized with different amounts of KCl and (left) 0.5 g and (right) 1.0 g of toluene as a swelling agent per 0.5 g of F127 block copolymer.

unprecedented nominal mesopore diameter (15–17 nm; capillary condensation pressure 0.86–0.88 p/p_0 , see Figure 9 and in the Supporting Information Figure S2) and enhanced mesopore volume were obtained (see Figure 10, Figure S2 in the Supporting Information, and Table 1). The aforementioned capillary condensation pressures correspond to the pore diameters of 21–25 nm according to the BdB spherical model.⁵⁹ Clearly, these values are much larger than the BdB-based pore diameters reported earlier for well-ordered (or even weakly ordered) PMOs with $Fm3m$ structure.³¹ While the BdB spherical pore model is likely to significantly overestimate the pore diameter, the use of a geometrical relation proposed for the $Fm3m$ structure²⁴ suggests that the actual pore diameter for our PMOs reached 18–19 nm. It should be noted that in cases of

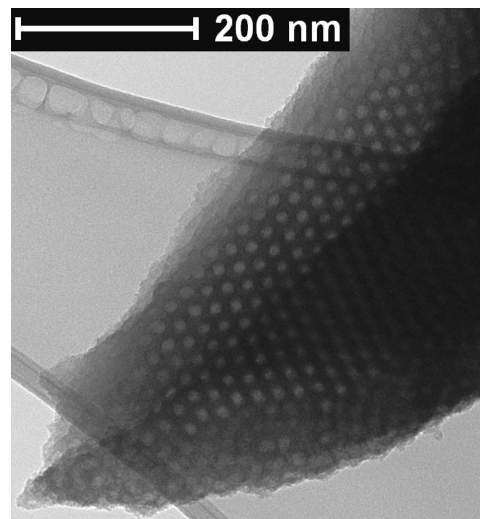


Figure 11. TEM image of PMO synthesized with 0.5 g of toluene and 1.25 g of KCl per 0.5 g of F127.

selected PMOs with the largest pore diameters, Table 1 provides data for two samples prepared under the same conditions to show the unit-cell size and pore diameter reproducibility. The ordered structure in the large-pore PMO was clearly visible by TEM (Figure 11). The increase in the relative amount of toluene (from 0.5 to 1 g per 0.5 g of F127) was beneficial in obtaining the largest unit-cell sizes and pore diameters, although the differences between the two compositions were not dramatic. It appears that the increase in the relative amount of toluene in the synthesis mixture led to some increase of the amount of toluene solubilized in the micelles, which in turn led to larger unit-cell dimensions and pore sizes with concomitant slight decrease in the degree of structural ordering, as inferred from the resolution of SAXS patterns.

In the case of toluene as a swelling agent, well-ordered PMO with pore diameter ~ 15 nm and with large unit-cell size (~ 42 nm) was obtained in the absence of salt (see Figures 8–10), which is by far the largest pore diameter achieved for well-ordered PMO with spherical pores synthesized under salt-free conditions. Benzene also afforded PMO with quite large unit-cell size (37 nm) and pore diameter (14 nm) under salt-free conditions. The development of the salt-free pathway to large-pore PMOs with spherical pores may be particularly important if the present strategy is adjusted for the thin film preparation.⁶⁰ It should be noted that our attempt to enhance the structural properties of the organosilica prepared in the presence of benzene using salt did not render a good-quality PMO.

Formation of PMO under Low-Temperature Conditions.

As discussed above, ethylene-bridged PMO forms under a variety of conditions with different swelling agents, although the unit-cell size, pore diameter, and degree of structural ordering depend on the selection of the swelling agent, and the amount of salt. It is known that the presence of salt in solution leads to dehydration of micelles of Pluronic block copolymers,⁶¹ wherein water interacts with PEO blocks and may also be present to some extent in the micelle core.⁶² Apparently, the depletion of an already low amount of water from the hydrophobic PPO core and the concomitant dehydration of the hydrophilic PEO corona enhances the “contrast” between PEO and PPO domains, and promotes the formation of the PMO structure.^{32,63} However, it appears that in the case of Pluronic F127 under low-temperature conditions, the presence of a sufficiently “strong” swelling agent is also required for the PMO

structure to form, which may be related to a stronger hydrophilicity of PEO and PPO at lower temperatures.⁶⁴ No uniform mesopores were observed in organosilica formed in the absence of the swelling agent at 15 °C (see Figure S3 in the Supporting Information) and a similar material was recovered when TMB was used as a swelling agent under salt-free conditions (see Figures 1 and 2, and in the Supporting Information Figure S3). Only the replacement of TMB with a swelling agent with stronger propensity to solubilize in Pluronics (that is, xylene) afforded a sample that exhibited uniform mesopores (as seen from the occurrence of a sharp capillary condensation step at high relative pressures and from a broad hysteresis loop), but otherwise the isotherm for this material was quite similar to the nonmesostructured case described above. Eventually, swelling agents with even stronger solubilization tendency (toluene, benzene) afforded well-ordered PMOs in the absence of the salt. It is unlikely that the aforementioned organosilicas devoid of the structural ordering formed without the involvement of the Pluronic F127 surfactant, because in the absence of the latter, a disordered organosilica with very broad pore size distribution in the mesopore range and with no appreciable microporosity was recovered (see Figure S3 in the Supporting Information). In contrast, the PMOs had uniform mesopores and an appreciable volume of the micropores (see Table 1), thus having completely different porous properties. Therefore, F127 appears to mediate the formation of the organosilica framework even if no uniform mesopores can be observed. It appears that in cases where F127 block copolymer was present, the condensation of organosilica species took place around it, but only under appropriate conditions (the presence of the swelling agent and, for “weaker” swelling agents, sufficient concentration of salt) was there a partition of the organosilica structure between more hydrophilic and more hydrophobic domains of the block copolymer. As a result, there developed regions of the hydrophobic domains that were free (or largely free) of the organosilica framework, which is equivalent to the formation of mesopore spaces, whose volume exhibited a tendency to increase as swelling agents of increased “strength” were used. The present study shows that the swelling agents predicted to solubilize more strongly in Pluronics (xylene, toluene, benzene) than TMB does induce the formation of PMO under salt-free conditions, and allow one to generate an appreciable mesopore volume, in contrast to the swelling agents that are expected to solubilize to a smaller extent (TEB and TIPB). Earlier results on the use of swelling agents for the synthesis of Pluronic-copolymer-templated ordered mesoporous silicas (SBA-15, FDU-12)^{45,50,51} and other silicas templated by low-molecular-weight surfactants^{65,66} support the present conclusion about the swelling agent “strength”. At the swelling agent concentrations considered herein, the Pluronic F127 micelles appear to be saturated or nearly saturated by the swelling agent (in the case of TMB, xylene, and toluene), because the increase in the amount of the swelling agent brought at best a minor increase in the mesopore volume and unit-cell parameter. It is noteworthy that an overly large amount of salt appears to somehow hinder the incorporation of the swelling agent in the micelles, resulting in the decrease in the unit cell parameter (see Table 1 and Figures 1 and 8).

The largest unit-cell sizes were observed in the case of xylene as a swelling agent, despite the fact that toluene and benzene were capable of generating higher mesopore volumes. For pure-silica FDU-12 materials, xylene also afforded a higher unit-cell size than toluene. Further studies will be needed to clarify if the larger unit-cell sizes observed for xylene are related to

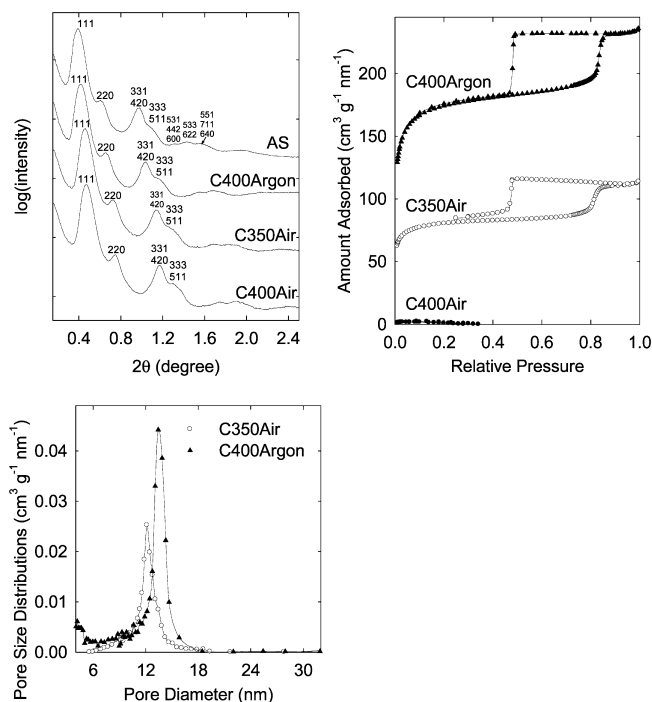


Figure 12. SAXS patterns (top left), nitrogen adsorption isotherms (top right), and pore size distributions (bottom) for materials derived from PMO via calcination at different temperatures.

inherent properties of the considered swelling agents, or are specific to the synthesis conditions explored.

Some dependence of the unit-cell size on the stirring speed was observed (see discussion for TMB-based synthesis and the data for PMOs prepared in the presence of xylene in Figure S4 in the Supporting Information). The stirring rate may have an influence on the rate of evaporation of the swelling agent (and possibly, methanol that is a product of organosilica precursor hydrolysis) from the solution, as our reaction system was at best semiclosed. To minimize this effect, the syntheses with xylene, toluene, and benzene were done in a covered container, which required magnetic stirring. Even in this case, the stirring speed had some effect, so the interactions of the swelling agent with the surfactant and the very formation of the surfactant-templated PMO may be affected by the stirring rate in a manner somewhat dependent on a particular swelling agent used. While the equilibrium solubilization of the swelling agent in the surfactant is not likely to be a function of the stirring speed, the hydrolysis of the organosilica precursor and its impact on the micelle/swelling-agent/organosilica interactions, and consequently on the uptake of the swelling agent by the micelles, may be dependent on the stirring rate.

Conversion of PMO to Closed-Pore Material. The PMO synthesized with xylene as a swelling agent (xylene (0.5), KCl (2.5)) was calcined at different temperatures under argon or air atmosphere. The calcination under argon at 400 °C, which is known to largely preserve the integrity of the organic groups,⁶⁷ afforded a sample with adsorption properties similar to those of the extracted material (see Figures 6 and 12). On the other hand, the use of air atmosphere that results in the oxidative removal of ethylene bridges with concomitant conversion to silica⁶⁸ afforded a closed-pore material at 400 °C, which is lower than the lowest temperature at which Pluronic-templated silicas or organosilicas were successfully converted to closed-pore materials in earlier studies.^{46,51} An extensive structural shrinkage observed in the case of calcination under air (Table 2) is an effect of the loss of the bridging groups. It appears that even at

TABLE 2: Structural Properties of Ordered Mesoporous Organosilicas^a

sample, calcination T (°C)	atmosphere	a (nm)	a/a _{AS}	S _{BET} (m ² g ⁻¹)	V _t (cm ³ g ⁻¹)	w _{KJS} (nm)
xylene (0.5), KCl (2.5)-AS	N/A	39.2	N/A	— ^b	— ^b	— ^b
xylene (0.5), KCl (2.5), 400	argon	36.9	0.94	606	0.36	13.5
xylene (0.5), KCl (2.5), 350	air	33.3	0.85	279	0.17	12.2
xylene (0.5), KCl (2.5), 400	air	32.6	0.83	<10	~0.00	N/A

^a T, calcination temperature; a, unit-cell parameter; a/a_{AS}, degree of shrinkage upon calcination calculated as the unit-cell parameter of calcined material divided by the unit-cell parameter of the as-synthesized (AS) material; S_{BET}, BET specific surface area; V_t, total pore volume; w_{KJS}, pore diameter. ^b Not determined. N/A, not applicable.

350 °C under air, a fraction of the mesopores may be closed, because the mesopore volume was low and the isotherm indicated slow diffusion of nitrogen through some parts of the porous structure, as seen from increase in uptake on the desorption branch above *p/p*₀ of ~0.5, and from low-pressure hysteresis. Both open-pore and closed-pore materials were highly ordered, as seen from SAXS.

Conclusions

TMB is a facile swelling agent for the F127-templated low-temperature synthesis of ethylene-bridged PMOs with face-centered cubic structures, allowing one to reach the unit-cell parameter up to 42 nm and nominal pore diameter up to ~15 nm. The use of swelling agents (TEB, TIPB) expected to have a lower extent of solubilization in Pluronics afforded inferior materials, which is consistent with the notion that the uptake of TMB by micelles of F127 is already quite limited. However, the application of swelling agents (xylene, toluene, benzene) with a higher predicted extent of solubilization in Pluronics allowed us to obtain PMOs with similar (or even larger) unit-cell size and with higher degree of structural ordering (xylene) or larger pore diameter (up to 17 nm) and mesopore volume (toluene). The decrease in the amount of an inorganic salt (KCl) in the synthesis mixture typically led to the increase in the unit-cell size, although in some cases, the effect was primarily seen for higher salt concentrations, whereas there was no clear trend at lower concentrations. In the case of xylene, the decrease in the amount of salt and its eventual elimination allowed us to increase the unit-cell size of PMOs up to ~50 nm. On the other hand, toluene and benzene rendered well-ordered large-pore PMOs in the absence of the salt, which was necessary in the TMB-based PMO synthesis under low-temperature conditions considered herein. It is clear that the use of “stronger” swelling agents induces the formation of PMOs under salt-free conditions, in which “weaker” swelling agents afford at best weakly ordered PMO product. The study demonstrated that the use of judiciously chosen aromatics as swelling agents in the block-copolymer-templated PMO synthesis provides vast new opportunities, but their realization may require an appropriate selection of synthesis conditions. The PMO synthesized using our novel procedure can be converted into a closed-pore ordered mesoporous silica at temperature as low as 400 °C.

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

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