Synthesis of Large-Pore Face-centered-cubic Periodic Mesoporous Organosilicas with Unsaturated Bridging Groups

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Abstract

Periodic mesoporous organosilicas (PMOs) with ethenylene (-CH=CH-) bridging groups in the framework and large spherical mesopores of tunable size arranged in face-centered-cubic structures (Fm3m symmetry) were synthesized using Pluronic F127 (EO₁₀₆PO₇₀EO₁₀₆) as a surfactant and xylene (isomer mixture) as a swelling agent at low temperature (7 °C) under moderately acidic conditions (0.1 M HCl). The resulting PMOs were characterized by small-angle X-ray scattering, nitrogen adsorption, transmission electron microscopy and solid-state ²⁹Si NMR. The unit-cell parameters were enlarged from 31 to 42 nm and the pore diameters increased from 14 nm to as much as 22 nm while increasing the amount of the swelling agent in the reaction mixture, until these two structural parameters reached a plateau. The enlargement was not accompanied by a loss

of structural ordering, which is exceptional for not only PMOs, but also other surfactant-templated materials. While the extraction of the surfactant was ineffective in generating readily accessible mesopores for samples prepared with low relative quantities of the swelling agent, extracted samples prepared with higher proportions of the swelling agent exhibited good mesopore accessibility. On the other hand, the calcination under argon at 350 °C afforded well accessible mesopores in all cases, even though the unit-cell shrinkage was significant and a substantial fraction of Si-C bonds was cleaved.

Keywords: periodic mesoporous organosilica, ethenylene-bridged organosilica, pore size control, micelle swelling agent, Pluronic block copolymer

Introduction

Periodic mesoporous organosilicas (PMOs) are a special class of surfactant-templated ordered mesoporous materials having organic moieties embedded in the silica-type framework through the condensation of bridged organosilane precursors [1-3]. The high surface areas, uniform mesopore sizes, well-defined structures and the presence of different organic groups make PMOs attractive materials for various applications [4]. Over the past sixteen years, PMOs with different bridging groups, such as methylene [5-7], ethylene [1,2,8,9], ethenylene [2,3,6,10,11], phenylene [6,12-14], biphenylene [15,16], thiophene [12,17] and so on, have been synthesized. Different structures, such as 2-dimensional (2-D) hexagonal [1,18], 3-dimensional hexagonal (P6₃/mmc symmetry)

[1], cubic Pm3n [19], body-centered cubic (Im3m symmetry) [20], face-centered cubic (Fm3m) [21,22] and gyroidal cubic Ia3d structure [23], have been reported, although most of these structures were obtained for ethylene-bridged PMOs, with a much more limited set of structures demonstrated for other PMO compositions. The presence of different organic groups in the framework presents an opportunity to facilely tailor various physical and chemical properties. Up to now, PMOs have been studied for various potential applications, including low-dielectric-constant materials [24,25], catalysis [26-29], light harvesting [28,30], drug delivery [31,32], environmental technology [33,34] and so forth.

Among the aforementioned PMOs, ethenylene-bridged PMOs have been studied with keen interest [2,3,6,10,11,35-43], primarily because of their unsaturated bridging groups that can be chemically modified. Various studies have been conducted in this direction, resulting in the introduction of functional groups [3,40,42,43]. Some of the potential applications of the ethenylene-bridged periodic mesoporous organosilicas include catalysis [40] and adsorption [2,42]. Although there have been a number of studies focused on ethenylene-bridged PMOs with cylindrical mesopores arranged in a 2-D hexagonal structure, reports on ethenylene-bridged PMOs with spherical mesopores were few [36,38], and only in one case, a product was primarily a single phase [38]. The latter was large-pore ethenylene-bridged PMO with a face-centered cubic structure prepared at low temperature (7 °C) and moderate acid concentration (0.1 M HCl) using Pluronic F127 as a surfactant template and an appropriate micelle swelling agent, namely 1,3,5-trimethylbenzene (TMB), xylene or toluene. The maximum mesopore diameters

obtained for this kind of materials were around 14 nm and the unit-cell parameters were around 30 nm. The synthesis of this very interesting product was based on a strategy involving a moderate acidic synthesis medium combined with a sub-ambient temperature, which was also found suitable for the synthesis of ethylene- and phenylene-bridged PMOs with face-centered cubic structures [38,44]. In comparison to typical conditions of the synthesis of PMOs with spherical mesopores using Pluronics as templates, which involve ~2 M HCl solution as the synthesis medium [9,45], the synthesis under moderately acidic conditions affords remarkably high mesopore volumes.

The pore size control is a crucial opportunity in surfactant-templated syntheses of mesoporous materials [46-48]. Hydrophobic organic additives have been recognized as agents capable of swelling surfactant micelles, thus opening an opportunity to tailor the pore diameter of surfactant-templated materials simply by changing a quantity of the swelling agent [46,47]. While this potential has been recognized at the inception of the surfactant-templated materials research field [46,47], cases resembling an ideal swelling action, in which the pore size and unit-cell size can be systematically tuned without the loss of the structural ordering, have been rare [49-51]. Instead, one typically observed a pore size increase accompanied by a major loss of ordering [52] or a change in the structure type (among which the change from 2-D hexagonally ordered SBA-15 silica with cylindrical mesopores to mesocellular foams, MCFs, with spherical mesopores being perhaps the best known example [53]). While a systematic and appreciable pore size control through the adjustment of the quantity of the swelling agent has not been reported for well-ordered PMOs (to the best of our knowledge), other methods of the

pore size control were found operational in the swelling-agent-based syntheses. In particular, the selection of the initial synthesis temperature [6,45] or the adjustment of the salt concentration in the synthesis mixture [9] afforded tunable unit-cell sizes and some degree of the pore diameter adjustability for block-copolymer-templated PMOs. Moreover, different swelling agents could afford different pore diameters [9]. Finally, the use of surfactants with different molecular sizes (in the absence of a swelling agent) yielded PMOs with pore diameters increasing with the size of the surfactant molecule [54,55].

The present study of ethenylene-bridged PMO demonstrates a substantial pore size and unit-cell size increases with a preservation of a high degree of structural ordering upon increasing the quantity of the swelling agent, representing an embodiment of the ideal swelling agent concept. The considered case is especially appealing, because block-copolymer-templated organosilicas with ordered arrangements of spherical mesopores do not form readily and the ethenylene-bridged organosilica framework with the face-centered cubic structure is known to form only in a moderate acidic synthesis mixture employed herein [38]. While other conditions are likely to emerge as suitable for the formation of this structure, still it is surprising that such an uncommon framework composition/structure combination is amenable to such a straightforward pore size and unit-cell size engineering.

Experimental Section

Synthesis. The synthesis procedure was analogous to that reported by us earlier (with 0.5 g xylene per 0.5 g Pluronic F127) [38], but different quantities of the swelling agent were used and in some cases, different hydrothermal treatment temperature was employed. 0.5 g of Pluronic F127 triblock copolymer $\text{EO}_{106}\text{PO}_{70}\text{EO}_{106}$ (BASF) was dissolved in 30 mL of 0.1 M aqueous HCl solution at 7 °C under magnetic stirring until the polymer dissolved. Then a selected mass of xylene isomer mixture (Aldrich) (0.25, 0.5, 1, 2, 4, 6 or 7 g) and 2.5 g of KCl were added. After 2 hours, 1.73 mL of bis(triethoxysilyl)ethylene, BTEEn (Gelest), was added. The reaction mixture was stirred at 7 °C for one day in a covered container. Then the reaction mixture was transferred to a polypropylene (PP) bottle and treated hydrothermally at 100 °C for 1 day or the mixture was divided into two parts, one of which was treated for 1 day at 100 °C in a PP bottle and another one at 130 °C in a Teflon-lined autoclave. The resulting as-synthesized material was filtered, washed with deionized water, and dried at ~60 °C in a vacuum oven. Finally, the material was either calcined at 350 °C under argon for 5 hours (heating ramp 2 °C/min) or extracted using 60 mL ethanol and 5 mL HCl at 50-60 °C to remove the surfactant.

Measurements. Nitrogen adsorption measurements were carried out at -196 °C on a Micrometrics ASAP 2020 volumetric adsorption analyzer. The samples were outgassed under vacuum at 140 °C in the port of the adsorption analyzer before the analysis. Small angle X- ray scattering (SAXS) patterns were recorded on a Bruker Nanostar U

SAXS/wide angle X-ray scattering (WAXS) instrument equipped with a rotating anode X-ray source and a 2-D detector Vantec 2000. The instrument was in a high flux configuration and the flight path was ~73 cm. Samples were placed in the hole of an aluminium sample holder and secured on both sides using a Kapton tape. Transmission electron microscopy (TEM) images were recorded on a FEI Tecnai Spirit microscope operated at an accelerating voltage of 120 kV. The samples were first sonicated in acetone and then deposited on carbon-coated copper grid and the solvent was dried under air before the imaging. Thermogravimetric (TGA) weight change patterns were recorded under air on a TA Instruments Q500 thermogravimeter. The temperature was increased to ~800 °C at a ramping rate of 10 °C/min. ²⁹Si magic-angle-spinning (MAS) cross-polarization (CP) NMR experiments were carried out on a Varian INOVA 300 wide bore spectrometer. The operating frequency was 59.6 MHz. Samples were packed into a 5 mm zirconia rotor, loaded into a 5 mm Doty XC-5 CP/MAS probe and spun at 6-8 kHz. Total of 500-1000 scans were acquired based on the sensitivity of the sample. The recycle delay was 5 s, the contact time was 3 ms, and the 90° pulse was 4 ms. The chemical shift reference was 4,4-dimethyl-4-silapentane-1-sulfonic acid (DSS).

Calculations. The BET specific surface area (S_{BET}) was determined from nitrogen adsorption isotherm data in the relative pressure range 0.04-0.20 [56]. The total pore volume (V_t) was calculated from the amount adsorbed at a relative pressure of 0.99 [56]. The micropore volume (V_{mic}) was determined using the α_s plot method [56,57] in the standard reduced adsorption, α_s , range from 0.9 to 1.2 using LiChrospher Si-1000 as a reference adsorbent [57]. The sum of the primary mesopore volume (V_p) and the

micropore volume was evaluated in the α_s range from 2 to 2.5. The mesopore volume was calculated by subtracting V_{mi} from $V_{mi} + V_p$ calculated as mentioned above. Pore size distributions (PSDs) were calculated from adsorption branches of isotherms using the Barrett-Joyner-Halenda (BJH) method with the KJS correction for cylindrical mesopores [58] and the statistical film thickness curve for a macroporous silica gel LiChrospher Si-1000 [57]. This method is likely to underestimate the diameter of spherical mesopores by ~2 nm in the considered pore size range [59]. The pore diameter for most of the samples was calculated using a geometrical relation for materials with face-centered-cubic structures of spherical mesopores [60]:

$$w_d = a \left(\frac{6}{\pi v} \frac{V_P \rho}{1 + V_P \rho + V_{mic} \rho} \right)^{1/3} \quad (1)$$

where a is the unit-cell parameter calculated from the position of (311) peak [61] on the SAXS pattern, v is the number of spherical mesopores in the unit cell (4 for the face-centered cubic structure), and ρ is the framework density. The framework density for ethenylene-bridged PMOs was assumed to be 1.52 g cm^{-3} [38].

Results and Discussion

Ethenylene-bridged PMOs prepared with different quantities of xylene and hydrothermally treated at 100°C exhibited well-resolved SAXS patterns characteristic of the face-centered cubic structure (see Figure 1 as well as Supporting Figures S1 and S2). The second strongest peak on the patterns can be indexed as a (311) reflection and is the most suitable for the calculation of the unit-cell parameters for samples that exhibit

SAXS patterns similar to those considered herein [61]. A (331) reflection can be identified at somewhat higher angles. A subsequent peak or shoulder appears at a position that allows to index it as either (531) or (442)/(600) reflection, or their superposition. The first and typically the most intense peak can be identified as a (111) reflection overlapped with unresolved (200) reflection and therefore its position was not used for the unit-cell size evaluation [61]. The as-synthesized and calcined sample prepared with the lowest xylene content exhibited a shoulder on its SAXS patterns that appears to correspond to the (220) reflection. This reflection is often seen for face-centered cubic PMOs that have a quite low mesopore volume [9]. The fact that this reflection is not seen for other samples is consistent with the increase in the volume of ordered mesopores as the quantity of the swelling agent increased. A similar trend was seen for FDU-12 silicas prepared without and with a hydrothermal treatment [62]. Such changes in the pattern are a manifestation of the XRD/SAXS peak intensity dependence on the ratio of the mesopore size (and thus mesopore volume) to the unit-cell size (and thus unit-cell volume), which was modeled for 2-D hexagonal structures [63].

Unit-cell parameters of as-synthesized samples increased from 30.6 to 42.7 nm as the mass of the micelle swelling agent (xylene) in the synthesis mixture increased from 0.25 to 4 g per 0.5 g of Pluronic F127 surfactant (Table 1). It should be noted that the unit-cell size of the sample prepared with 0.5 g of xylene was similar to that reported earlier for this particular synthesis mixture composition and mass of the swelling agent (33.2 vs. 31.2 nm) [38]. While swelling agents are well known from their ability to enlarge the unit cells and mesopores of micelle-templated materials [46,47], the

enlargement is typically associated with a decrease in the degree of structural ordering [52] or with the change in the structure type [53], as discussed above. Herein, the unit cell enlargement was not accompanied by any noticeable decrease in ordering (even if the relative peak intensities changed somewhat), which is remarkable. It is also notable that the unit-cell parameter ceased to increase once a certain level of xylene (4 g) in the synthesis mixture was reached, while a further increase in the quantity of the swelling agent did not compromise the structural ordering. As is evident from the pore volumes discussed hereafter, in all synthesis mixtures, only a part of xylene was taken up by the micelles. Possibly, the micelles were so much saturated with xylene in the cases involving higher proportions of this swelling agent that a further increase in its quantity in the synthesis mixture had no effect on the micelle size. Interestingly enough, no or little unit-cell size increase was typically observed in the synthesis of ethylene-bridged PMO with face-centered cubic structure using Pluronic F127/xylene pair (the same as that used herein) in 2 M HCl solution when the quantity of the swelling agent was increased from 0.5 to 1 g per 0.5 g of Pluronic F127 [9]. Apparently, either the aforementioned synthesis of a different organosilica framework under a much higher acid concentration was less amenable to the control of the pore size via the adjustment of the quantity of the swelling agent, or the adjustment would take place for quantities of xylene below 0.5 g (per 0.5 g of Pluronic F127), which would be much lower than the limiting value of 4 g of xylene observed herein.

The as-synthesized materials were subjected to extraction in order to remove the surfactant. The resulting samples had unit-cell sizes close to those of as-synthesized

samples. If a decrease in the unit-cell parameter was observed, it was not more than 3 % for the samples hydrothermally treated at 100 °C. The resulting unit-cell parameters ranged from 31.3 to 41.7 nm (see Table 1). Among the reported PMOs with cubic structures, only ethylene-bridged PMOs prepared under certain conditions exhibited similarly large unit-cell sizes [9,44].

As will be discussed below, the extraction in some cases afforded materials with mesopores that were not readily accessible to nitrogen molecules, which are used in the porosity characterization. On the other hand, the removal of the surfactant via calcination rendered samples with well-accessible mesopores, even though Si-C bonds in the framework were degraded to an appreciable extent (as reported earlier [38] and additionally shown below). In the case of the calcined samples, the unit-cell parameters increased from 27.7 to 38.0 nm as the mass of xylene in the synthesis mixture increased from 0.25 to 4 g (Supporting Table S1 and SAXS patterns in Supporting Figure S2). The samples discussed above were prepared by employing a hydrothermal treatment at 100 °C. Some of the synthesis mixtures were also treated at a higher temperature of 130 °C, which resulted in similar or slightly larger unit-cell parameters for as-synthesized, extracted or calcined samples (see Table 1, Supporting Table S1 and SAXS data is Supporting Figures S3 and S4).

TEM images of the samples prepared with different quantities of the swelling agent are shown in Figure 2. In all cases, well-ordered structures were observed. Figure 2(b) and (d), as well as the lower right part of Figure 2(c) can be identified as [110] projections of the face-centered cubic (fcc) structure. Figure 2(f) appears to show [110]

projection of the fcc structure with stacking faults characteristic of stacking sequences of 3-D hexagonal structure [59]. Figure 2(e) and a top part of Figure 2(c) can be identified as [100] projections of the fcc structure. However, some parts of the samples appeared disordered (see for instance top of Figure 2(a)), which was minor for the samples prepared with higher quantities of xylene (2 g or more), but more visible in the sample prepared using its lower quantity (1 g). The TEM images confirm that the ordering has been preserved, or perhaps even enhanced, when larger quantities of the swelling agent were present in the synthesis mixture. Also, some areas imaged by TEM (see Figure 2(a), (b), (d) and (e)) were dark and no nanoscale structure could be discerned therein, especially when a lower quantity of xylene was used, but mesopore structures were often observed on the edges of the particles. The observation of disordered domains, which are quite prominent in TEM images for the sample prepared with a lower quantity of the swelling agent (1 g), can be reconciled with a very well resolved SAXS pattern if one envisions that many large ordered domains may be too thick to allow electrons to pass through them and be detected and thus would render dark areas on TEM images [38].

Most of the extracted samples exhibited adsorption isotherms (Figure 3(a)) characteristic of materials with large, uniform cage-like mesopores [64], that is, with steep capillary condensation steps at quite high relative pressures (p/p_0 between 0.8 and 0.95) and with very steep capillary evaporation steps at a relative pressure corresponding to the lower limit of adsorption-desorption hysteresis (that is, a relative pressure of ~ 0.5). As a result, broad hysteresis loops were observed. The desorption at the lower limit of the hysteresis suggests that the mesopores were accessible to the surrounding gas phase

through passages of diameter not larger than ~5 nm [65]. The isotherm for the sample prepared with the lowest quantity of the swelling agent (0.25 g) exhibited a very low uptake of nitrogen, which combined with its well-resolved SAXS pattern characteristic of the fcc structure of mesopores, suggests that the material had mesopores inaccessible to nitrogen at -196 °C. Thermogravimetric analysis (TGA) indicated that an appreciable fraction of the surfactant was not extracted from the sample. As seen in Supporting Figure S5, the weight loss between 100 and 790 °C, which can be attributed to the surfactant decomposition and volatilization as well as the degradation of the bridging groups, decreased after extraction, and was reduced even more via calcination. Assuming that the organosilica (with an average of one silanol group per two silicon atoms) is converted to silicon dioxide during the heating process, one can estimate that the original template (primarily surfactant, because xylene would have evaporated at a lower temperature) content was 34 wt.%. The latter was reduced to 23 and 13 wt.% after extraction and calcination, respectively. It is clear that only 1/3 of the surfactant was removed by extraction, while the calcination appeared to be more efficient, even if it did not lead to a quantitative surfactant removal. The residual surfactant may be present in some micropores in the framework, and therefore it may restrict the mesopore connectivity and cause their inaccessibility to nitrogen at -196 °C. The sample prepared with the second-lowest quantity of xylene (0.5 g) exhibited an adsorption capacity lower than those for the samples prepared with higher quantities of xylene. For the former, some mesopores might have been inaccessible to nitrogen as well, which may be at least in part due to the residual surfactant. It should be noted that an analogous sample reported

earlier [38] had well-accessible mesopores, but a similar sample prepared with a different swelling agent (toluene; 0.5 g) clearly suffered from some limitations in the pore accessibility, which appears to be reflected in a slow diffusion of nitrogen molecules to the mesopores. In the case of extracted samples prepared with 1 g or more of xylene, the BET specific surface areas were 230-320 m² g⁻¹ and the total pore volumes were 0.26-0.38 cm³ g⁻¹, having a tendency to increase as the quantity of the swelling agent increased. The mesopore volumes of these samples ranged from 0.21 to 0.30 cm³ g⁻¹, which are quite large as for PMOs with fcc structures of spherical mesopores (compare with data reported in [9,38]). The micropore volumes were quite low (0.05-0.08 cm³ g⁻¹). The pore size distributions (Figure 3(b)) revealed an appreciable pore size enlargement (from about 15 to as large as 20 nm) taking place as the mass of the swelling agent was increased from 0.5 to 2 g. Calculations based on Equation 1 rendered similar pore size values. The pore diameter of 20 nm is exceptionally high for well-defined PMOs with spherical mesopores, and only ethylene-bridged PMOs were reported to reach such high pore sizes [44]. In the case of ethenylene-bridged PMOs, the highest pore diameter value was 15 nm [38]. The subsequent increase in the quantity of the swelling agent did not lead to any significant further pore size increase, and also the pore size distributions (Figure 3(b)) for the pertinent samples were of similar width. The isotherms were quite flat at pressures approaching the saturation vapor pressure (relative pressure of 1), indicating the lack of any appreciable population of pores of size on the borderline between the mesopore (pore diameter 2-50 nm) and macropore (diameter > 50 nm) ranges.

Selected synthesis mixtures were also hydrothermally treated at 130 °C. After extraction, the resulting samples exhibited higher BET specific surface areas (340-510 m² g⁻¹), total pore volumes (0.38-0.61 cm³ g⁻¹), mesopore volumes (0.27-0.48 cm³ g⁻¹) and micropore volume (0.09-0.13 cm³ g⁻¹) (see Table 1 as well as adsorption isotherms and pore size distributions in Supporting Figure S6). The pore diameters also increased, reaching the values of w_d equal to 22-24 nm and w_{KJS} of 21 nm (see Supporting Figure S6). Surprisingly enough, the hydrothermal treatment at 130 °C still did not enlarge entrances to the mesopores beyond ~5 nm, as seen from the capillary evaporation at the lower limit of adsorption-desorption hysteresis (relative pressure of ~0.50).

The characterization of calcined samples allowed us to appreciate even more the pore size adjustment potential of the considered synthesis, because all calcined samples had readily accessible mesopores. The adsorption isotherms (Supporting Figure S7) were similar to those of the corresponding extracted samples for xylene masses from 0.5 to 7 g. Moreover, the sample prepared with 0.25 g of xylene had an isotherm quite similar to those of the other samples. The capillary condensation was observed at relative pressures of 0.8-0.9. The position of the capillary condensation step moved to higher relative pressures as the swelling agent quantity in the reaction mixture increased from 0.25 to 4 g, which provided evidence of the pore diameter increase from ~11 to 20 nm (see Supporting Figure S7), while the use of Equation 1 rendered values from ~13 to 20 nm. An increase in the amount of xylene beyond 4 g did not cause any major further pore size increase, as discussed above. In comparison to the extracted samples, the calcined samples typically had lower unit-cell parameters and pore diameters, apparently as a

result of a higher shrinkage upon calcination. On the other hand, the calcined samples had higher BET specific surface areas and pore volumes (see Table 1 and Supporting Table S1), which may be due to a more complete removal of surfactant during calcination [38]. This behavior did not extend over the calcined samples hydrothermally treated at 130 °C, in which case the calcined and extracted samples exhibited comparable mesopore volumes (see Table 1 and Supporting Table S1, as well as adsorption isotherms and pore size distributions in Figure 3 and Supporting Figure S8). Apparently, the efficiency of the extraction improved as the hydrothermal treatment temperature was increased.

As seen from these results, the increase in the quantity of the swelling agent leads to the formation of ethenylene-bridged PMOs with larger unit-cell sizes and mesopore diameters. It can be hypothesized that the uptake of the swelling agent by the micelles increased as the quantity of the swelling agent was increased in the reaction mixture, leading to larger pore volumes, pore sizes and unit-cell parameters. When the quantity of the swelling agent reached the point in which its uptake by the micelles no longer increased to any appreciable extent with the increase of its quantity in the reaction mixture, the unit-cell size and pore size reached a plateau (for 4 g or more of xylene). It should be noted that the pore volume did not scale with the combined volume of the block copolymer and swelling agent, and was much lower than the latter volume (per gram of the framework formed; especially for higher quantities of the swelling agent), thus suggesting that in all cases considered herein, an excess (or even a large excess) of the swelling agent was used.

^{29}Si CP MAS NMR spectrum of a sample calcined at 350 °C under argon featured peaks between -65 to -85 ppm corresponding to T^n sites ($-\text{C}_2\text{H}_2-\text{Si}(\text{OSi})_n(\text{OH})_{3-n}$). The spectra also featured peaks between -100 and -120 ppm corresponding to Q^n sites ($\text{Si}(\text{OSi})_n(\text{OH})_{4-n}$), which may arise from Si-C bond cleavage (Supporting Figure S9). On the basis of earlier studies of ethenylene-bridged PMOs [39], it is expected that the Si-C bond cleavage involves a conversion of the bridging ethenylene groups to pendant vinyl groups. This contention is consistent with TGA of calcined samples, which showed the weight loss exceeding that predictable for the framework organic groups, although the inability to resolve the weight loss related to the framework/pendant organic groups and the residual surfactant makes the quantification difficult. The extraction with ethanol combined with HCl was performed to remove the surfactant while preserving the integrity of ethenylene bridging groups [45]. In this case, only peaks corresponding to T^n sites were seen on the NMR spectrum and thus the cleavage of Si-C bonds was not observed (see Supporting Figure S8).

The above results show that under the considered conditions (0.1 M HCl solution; initial temperature of 7 °C) xylene is an excellent swelling agent for the synthesis of ethenylene-bridged PMOs with a face-centered cubic structure. It was hypothesized that ethylbenzene is likely to exhibit a similar swelling action to xylene, which was experimentally confirmed earlier for silicas and organosilicas with fcc structures prepared in 2 M HCl solution [66,67]. As seen in Supporting Figure S10, the use of ethylbenzene (4 and 7 g) afforded highly ordered face-centered-cubic materials with similar unit-cell parameters (see Supporting Table S2) as in the case of xylene. They also exhibited

similar adsorption isotherms and pore diameters. The pore diameter did not increase when the mass of ethylbenzene was increased from 4 to 7 g, similarly as in the case of xylene discussed above. These results suggest that ethylbenzene works similarly to xylene in the synthesis of fcc ethenylene-bridged PMOs under the considered conditions. It should be noted that the ethylbenzene-swollen samples discussed above were calcined under argon at 350 °C, so an appreciable degradation of Si-C bonds can be suspected, and the extraction would need to be used to avoid the Si-C bond cleavage (as discussed above).

Conclusions

The unit-cell size and pore diameter of ethenylene-bridged PMOs with face-centered-cubic structure synthesized under moderately acidic concentrations (0.1 M HCl) and at low temperature (7 °C) using Pluronic F127/xylene pair is significantly enlarged in a systematic manner by increasing the quantity of the micelle swelling agent (xylene) in the synthesis mixture. The resulting maximum pore sizes and unit-cell sizes were exceptionally large. Once the quantity of the swelling agent reached a certain level, the unit-cell size and the pore diameter no longer increased. The increase in the quantity of the swelling agent did not lead to the loss of the structural ordering, while it improved the pore accessibility after the extraction of the surfactant. The PMOs had large mesopore volumes in comparison to other PMOs with spherical mesopores. The obtained results

provide another strong indication of the potential of moderately acidic conditions in the PMO synthesis.

Acknowledgements

NSF is gratefully acknowledged for support of this research (award DMR-1310260) and for funding the acquisition of SAXS/WAXS system through award CHE-0723028. PSC-CUNY grant program is also acknowledged for partial support of this research (Award # 66241-00 44). Dr. Jianqin Zhuang (CSI) is acknowledged for assistance with NMR measurements. The Advanced Imaging Facility at CSI is acknowledged for providing access to TEM. BASF is acknowledged for the donation of the Pluronic F127 triblock copolymer.

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Table 1. Structural properties of extracted PMOs synthesized using bis(triethoxysilyl)ethylene under different conditions.^a

mass of xylene (g)	hydrothermal treatment temperature (°C)	a (nm)	S_{BET} (m ² /g)	V_t (cm ³ /g)	V_p (cm ³ /g)	V_{mic} (cm ³ /g)	w_{KJS} (nm)	w_d (nm)
0.25	100	31.3 (30.6)	(34) ^b	(0.03) ^b	b	b	10.9	b
0.5	100	33.2 (33.2)	129	0.16	0.13	0.03	14.3	14.1
1	100	35.9 (36.3)	232	0.26	0.21	0.05	15.3	17.2
1	130	35.9 (37.0)	386	0.38	0.27	0.11	17.5	17.9
2	100	40.6 (40.8)	248	0.31	0.25	0.06	20.7	20.2
4	100	41.7 (42.7)	246	0.35	0.27	0.08	19.6	21.0
4	130	42.4 (42.4)	514	0.61	0.48	0.13	21.3	24.0
6	100	40.6 (41.8)	303	0.35	0.27	0.08	18.9	20.5
6	130	42.4 (42.7)	342	0.42	0.32	0.10	21.4	22.1
7	100	41.7 (42.4)	320	0.38	0.30	0.08	19.7	21.5
7	130	41.8 (43.7)	371	0.46	0.37	0.09	21.5	22.6

^a Notation: a, unit-cell parameter for extracted ethenylene-bridged sample calculated from (311) interplanar spacing (unit-cell parameter for as-synthesized sample is provided in parentheses); S_{BET} , BET specific surface area; V_t , total pore volume; V_p , primary mesopore volume; V_{mic} , micropore volume; w_{KJS} , pore diameter calculated using BJH-KJS method for cylindrical mesopores. w_d , pore diameter calculated using eq 1. ^b adsorption isotherm was distorted due to low adsorption capacity of the sample and thus the structural parameters derived from it are inaccurate or were not determined.

Figure Captions

Figure 1. SAXS patterns for extracted ethenylene-bridged PMOs synthesized in the presence of different quantities of xylene. The samples were hydrothermally treated at 100 °C.

Figure 2. TEM images of calcined ethenylene-bridged PMOs synthesized using: (a) 1, (b), 2, (c), 4, (d, e), 6 and (f) 7 g of xylene. The samples were hydrothermally treated at 100 °C.

Figure 3. (a) Nitrogen adsorption isotherms and (b) pore size distributions of extracted ethenylene-bridged PMOs synthesized using different quantities of xylene, and hydrothermally treated at 100 °C. For clarity, in (a), the isotherms were offset vertically by 70, 165, 300, 450, 600, and 750 cm³ STP g⁻¹ for materials synthesized using 0.5, 1, 2, 4, 6, and 7 g of xylene, respectively.

Figure 1

Figure 2

Figure 3