

Synthesis and Properties of 1,3,5-Benzene Periodic Mesoporous Organosilica (PMO): Novel Aromatic PMO with Three Point Attachments and Unique Thermal Transformations

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Abstract: A new aromatic periodic mesoporous organosilica material containing benzene functional groups that are symmetrically integrated with three silicon atoms in an organosilica mesoporous framework is reported. The material has a high surface area, well-ordered mesoporous structure and thermally stable framework aromatic groups. The functional aromatic moieties were observed to undergo sequential thermal transformation from a three to two and then to a one point attachment within the framework upon continuous thermolysis under air before eventually being converted to periodic mesoporous silica devoid of aromatic groups at high temperatures and longer pyrolysis times. The mesoporosity of the material was characterized by powder X-ray diffraction (PXRD), transmission electron microscopy (TEM), and nitrogen porosimetry, whereas the presence and transformation of the aromatic groups in the walls of the materials were characterized by solid-state NMR spectroscopy, mass spectrometry, and thermogravimetric analysis. The attachment of a benzene ring symmetrically onto three siloxanes of the framework was used advantageously as a cross-linker to enhance the thermal stability of the organic group. Some of these properties are investigated in comparison with other aromatic PMOs that have only two point attachments and an amorphous phenylsilica gel that has only one point attachment. The successful synthesis of the first aromatic PMO with its organic group attached within the framework through more than two points is an important step toward the synthesis of PMOs having organic groups with more complex and multiple attachments within the framework.

Introduction

Inorganic mesoporous materials synthesized through surfactant-mediated self-assembly methods have attracted much attention in recent years due to their high surface area and well-ordered porous structures.^{1–4} The incorporation of organic groups on the surfaces of ordered mesoporous silicas through co-condensation of organotrialkoxysilanes that have terminal organic groups with tetraalkoxysilanes (Si(OEt)₄ or Si(OMe)₄) that have no organic functional group can be carried out to obtain organic-functionalized ordered mesoporous silica materials.⁵ However, when this method is used, a loss or a significant

reduction in the degree of long range order of the materials is often observed particularly when the amount of organotrialkoxysilane with a pendant organic functional group exceeded ca. 40 molar % of the total silicon source. Two recent successful attempts to reach up to 50–65% functionalization level^{5h,i} are exceptions from the aforementioned typical behavior, but even in these two cases, the degree of structural ordering was quite low and the adsorption capacity was reduced for materials with the highest organic group loadings. In 1999, a novel approach for making ordered surfactant-templated periodic mesoporous organosilicas (PMOs) with bridging organic groups in the framework by using bridging organosilane precursors was reported in the literature (Scheme 1).^{6–14} Furthermore, control over the relative proportion of the bridging organic groups in these materials has been made possible by employing co-

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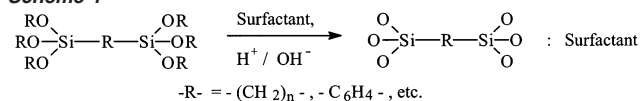
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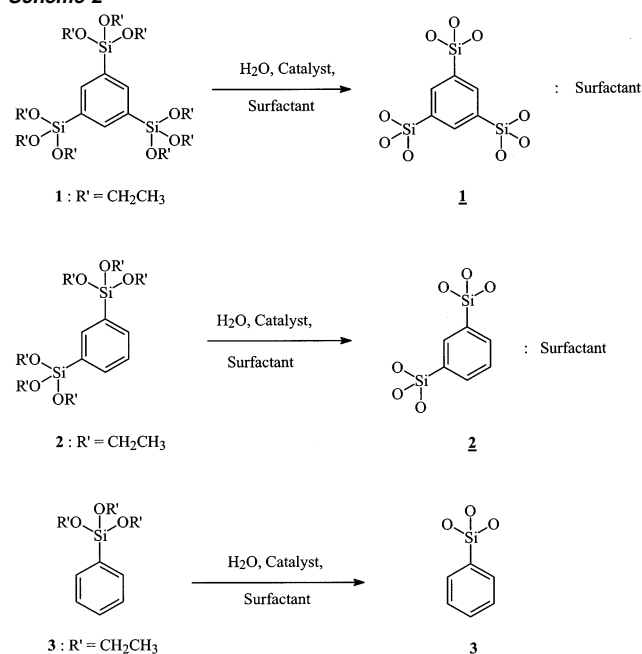
Scheme 1



condensation methods in the presence of tetralkoxysilanes.^{6a,b} This new method allowed the synthesis of various ordered PMO materials that have hybrid organic–inorganic channel walls as well as unique physical, surface, and chemical properties. The synthesis of PMO materials has also opened up a broad range of research opportunities on the investigation of the chemistry of functional groups in the framework of a solid mesoporous silica host, which is dubbed “chemistry of the channel walls”.^{6a,h,8}

So far, the kinds of PMO materials reported are limited to a few types of alkane, alkene, alkyne, organometallic, and aromatic bridging functional groups.^{6–14} On the other hand, there are many papers in the literature on the synthesis of numerous different kinds of organosilica precursors^{15,16} from which many other possible new PMO materials with novel properties can be made. In all of the reported PMO materials so far, the incorporation of bridging organic groups can be thought of as a mere replacement of some of the Si–O–Si linkages of a mesoporous silica (MCM-41) material by Si–R–Si linkages. However, unlike oxygen atoms, which are bivalent, the organic functional groups can be made to bind to more than two silicon atoms allowing the opportunity to use them not only as functional groups but also as cross-linkers in the structures to form rigid hybrid organic–inorganic frameworks. In this paper,

Scheme 2



we demonstrated this possibility by using a 1,3,5-benzene group bound to three silicon atoms of the framework of a PMO material both as a functional group and a cross-linker (Scheme 2). The possibility of the synthesis and the remarkable thermal stability of the resulting ordered mesoporous materials were briefly mentioned during a recent MRS meeting.^{6k} Herein, details on the synthesis, structure, thermal stability, and thermally induced transformations are reported for the first time.

From a potential applications point of view, aromatic groups within solid supports are important for anchoring various catalytic reagents and for separation of toxic organic wastes.¹⁷ For instance, half-sandwich tricarbonylchromium organometallic compound have been successfully anchored within aromatic silica gels and their catalytic properties for the polymerization of phenylacetylene along with their electrochemical properties have been reported.^{17a} Corriu et al. also reported various types of aromatic functionalized xerogels from organosilane precursors containing mono-, di-, and trisubstituted benzenetricarbonylchromium(0) complexes. Some of these materials were also successfully used for preparing chromium nanocluster-containing nanocomposites. The presence of aromatic groups in ordered mesoporous materials might give additional advantages for controlling the size and shapes of such nanostructures and during size and shape selective catalysis. Ozin et al. reported the first aromatic PMO containing a bridging benzene group,^{6c} followed by a paper on several other functional aromatic group containing PMOs along with some preliminary evidence of the ordering of the aromatic moieties in the channel walls.⁶ⁱ Very recently, detailed work on similar materials with complete ordering of aromatic functional groups throughout the channel walls was reported by Inagaki and co-workers.^{7c} These are the first examples of mesoporous materials with crystalline-type frameworks. However, in all these previously reported aromatic PMO

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materials except for *p*-benzyl-methylene PMO briefly discussed in a recent work,^{6j} the aromatic ring containing functional group is directly attached to only two silicon atoms with a simple bridging topology.^{6c,i,9} The successful synthesis of this PMO with more than two-point attachment described here also provides evidence that rigid organosilicate units with multiple-point attachments can be assembled to form periodic mesoporous materials with high adsorption capacity, unique thermal properties, and potentially useful properties for various applications.

Experimental Section

Reagents. Cetylpyridinium chloride (CPCI), cetyltrimethylammonium bromide (CTABr), ammonium fluoride, sodium bicarbonate (NaHCO₃), anhydrous ethanol, and phenyltriethoxysilane were obtained from Aldrich and used without further purification. Hydrochloric acid (HCl, 35.5 wt. %) solution was obtained from BDH Inc. and methanol was received from ACP Chemicals Inc. Tetrahydrofuran (THF) was also received from ACP and was dried over CaH₂ and molecular sieves before being distilled further over Na/benzophenone. Chlorotriethoxysilane (ClSi(OEt)₃) was synthesized following a literature procedure¹⁸ from the reaction between tetrachlorosilane (SiCl₄) and anhydrous ethanol followed by repeated fractional distillation.

Synthesis. 1,3,5-Tris(triethoxysilyl)benzene (**1**) was synthesized through Grignard reaction as reported by Shea et al.¹⁹ Typically, 1.90 g Mg (78 mmol) was activated by stirring it with iodine in a three-neck round-bottom flask for 2 h, after which 61.4 mL of freshly distilled anhydrous THF and 6.72 g (43 mmol) chlorotriethoxysilane were added into it. A solution of 4.09 g (13 mmol) 1,3,5-tribromobenzene in 61.4 mL THF was prepared and about 15 mL of this solution was added dropwise at room temperature. After the reaction turns mildly exothermic (after ca. 20 min), the reaction mixture was cooled to 0 °C, and the remaining solution was added dropwise over 30 min. The solution was stirred overnight at room temperature. Then, the solvent was pumped off and the residue was extracted with *n*-hexane. After pumping off the *n*-hexane, the residue was fractionally distilled (125 °C/0.035 mmHg) and stored under dry nitrogen (typical yield, 0.79 g, 10.8%). ¹H NMR (300 MHz, CDCl₃) δ 1.22 (t, 27 H, CH₃), 3.8 (q, 18 H, CH₂), 8.1 (s, 3 H, Ar-H). ¹³C NMR (75.48 MHz, CDCl₃) δ 19.27 (CH₃), δ 59.67 (CH₂O), δ 130.11, 143.89 (CH aromatic).

1,3-Bis(triethoxysilyl)benzene (**2**) was synthesized similarly by using 1,3-dibromobenzene as a reagent with chlorotriethoxysilane.¹⁹ In a typical synthesis, 8.24 g Mg (0.34 mol) was activated with iodine under vigorous stirring in a three-neck round-bottom flask for 2 h. Then 250 mL of freshly distilled anhydrous THF and 29.6 g (0.19 mol) chlorotriethoxysilane were added into it. A solution of 16 g (67.8 mmol) 1,3-dibromobenzene in 150 mL THF was prepared and about 20 mL of this solution was added dropwise at room temperature. After the reaction turns mildly exothermic (after ca. 20 min), the reaction mixture was cooled to 0 °C, and the remaining solution was added dropwise over 40 min. After work up as above, the product was distilled (149 °C/0.035 mmHg), a typical yield was 4.10 g (15%). ¹H NMR (300 MHz, CDCl₃) δ 1.17 (t, 18 H, CH₃), 3.88 (q, 12 H, CH₂), 7.29 (t, 1 H, Ar-H), 7.89 (d, 2H, Ar-H), 8.34 (s, 1H, Ar-H). ¹³C NMR (75.48 MHz, CDCl₃) δ 19.10 (CH₃), δ 59.42 (CH₂O), δ 127.47, 130.98, 136.96, 141.05 (CH aromatic).

Synthesis of Aromatic PMOs and Silica Gels. The syntheses of organosilicas were carried out in the presence of CPCI or CTABr surfactant solutions in a plastic bottle. Three materials were prepared in CPCI solution from precursors **1**, **2**, and **3** (phenyltriethoxysilane) and are denoted as **1**, **2** and **3**, respectively. A 1,3,5-benzene PMO

sample was also prepared in CTABr solution from precursor **1** and the resulting material is denoted by **1'**.

For a typical synthesis in CPCI solution, 0.11 g (0.3 mmol) of CPCI was taken and mixed with water (4.36 g, 0.24 mol) under mild stirring at ca. 40 °C. To this solution was added 0.81 g HCl (35.5 wt. %, 8.1 mmol), and the temperature of the solution was adjusted to 32 °C. Then 0.90 g (1.6 mmol) of **1** or 0.96 g (2.4 mmol) of **2** or 0.77 g (3.2 mmol) of **3** was added and the solution was left under moderate stirring for 15 min. Initially, a phase separation was observed, which then immediately disappeared, and a white precipitate formed while the organosilane underwent hydrolysis and condensation. The resulting solution was neutralized to pH ≈ 8 with portion-wise addition of NaHCO₃ after ca. 10 min. Soon after, 0.1 mg NH₄F (2.7 μmol) was added and the slurry was allowed to age at room temperature for 2–4 d. The white powder was then collected by filtration, washed thoroughly with water, and air-dried under ambient conditions (yield = 0.45 g for **1**). For the synthesis of materials from precursor **3**, a similar procedure was employed and the resulting material **3** was recovered as a chunk of soft solid, which was ground later into fine powder for analysis.

For the synthesis of 1,3,5-benzene PMO (**1'**) using CTABr as a template, a solution composed of molar ratio Si:CTABr:H₂O:NH₄OH of 1.0:0.12:130.1:35.7 was prepared. Typically, a solution was made of water (4.8 mL, 0.27 mol), ammonium hydroxide (10.9 g, 30 wt. % in water) and CTABr (0.24 g, 0.658 mmol). The surfactant was dissolved by warming the solution to 40 °C. Then, 1,3,5-tris(triethoxysilyl)benzene (**1**) (1 g, 1.77 mmol) was added dropwise to this solution with rapid stirring. Once the solution had homogenized, the stirring was slowed for an additional 10 min. After aging at 80 °C for 4 d, the product **1'** was isolated by filtration as a white powder; yield = 0.41 g.

As a control sample, a 1,3,5-benzenesilica gel material with the same composition of reactants as **1'** above was prepared but in the absence surfactant. It was also aged for 4 d and was collected as a chunk of glassy precipitate.

Surfactant-Extraction. The surfactant template was removed from the organosilica materials through solvent extraction. An as-synthesized sample (0.5 g) was gently stirred for 2 h in a solution of ca. 5 g HCl (36 wt. %) and 100 g of methanol in 50 °C water bath. The powder was filtered, washed with methanol, and air-dried at room temperature.

Calcination under Air and Pyrolysis under Nitrogen. The calcined materials were obtained by putting ca. 0.5 g surfactant-extracted material on a quartz crucible inside a temperature-programmable furnace under air or under a flow of nitrogen, by raising the temperature from room temperature to 350 or 450 °C over a period of 1 h and holding the temperature at 350 or 450 °C for 6 h. The resulting materials are denoted as **1C350A** (sample **1** calcined at 350 °C under air), **1C450A** (sample **1** calcined at 450 °C under air), **1C350N** (sample **1** calcined at 350 °C under nitrogen), **1C450N** (sample **1** calcined at 450 °C under nitrogen), **1'C350A** (sample **1'** calcined at 350 °C under air) and **1'C450A** (sample **1'** calcined at 450 °C under air).

Characterizations. Powder X-ray diffraction (PXRD) patterns were obtained on a Siemens D5000 diffractometer using a high power Ni-filtered Cu-K_α radiation with λ = 1.541 78 Å source operating at 50 kV/35 mA. Transmission electron microscopy (TEM) images were recorded on a Philips 430 microscope operating at an accelerating voltage of 100 kV. The nitrogen adsorption measurements for samples **1**, **2**, and **3** were obtained at McMaster University Powder Processing Facility using a Quantachrome Autosorb 1. Samples were outgassed at 200 °C before the measurements were done at 77 K. Nitrogen adsorption isotherms for sample **1'** and the corresponding calcined samples were measured at 77 K on a Micromeritics ASAP 2010 volumetric adsorption analyzer. Before the measurements, the samples were outgassed under vacuum at 140 °C. Thermogravimetric analysis (TGA) data for PMO samples **1**, **2**, and **3** were obtained at a heating rate of 10 °C min⁻¹ under a flow of nitrogen on a Perkin-Elmer TGA-7 instrument. The TGA analysis for samples **1'** and the corresponding

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calcined samples was recorded under air and nitrogen on a TA Instruments TGA 2950 thermogravimetric analyzer in a high-resolution mode with a maximum heating rate of $5\text{ }^{\circ}\text{C min}^{-1}$. Solution phase nuclear magnetic resonance spectra were taken with a Varian VXR 300 spectrometer using tetramethylsilane (TMS) as an internal reference. Solid-state magic-angle spinning nuclear magnetic resonance (MAS NMR) spectra were obtained using a Bruker DSX 400 spectrometer on samples packed into a zirconia rotor spinning at 6 kHz. The experimental parameters were as follows: for ^{13}C (100.6 MHz) cross polarization magic angle spinning (CP-MAS) NMR, 3 s recycle delay, 2.5 ms contact time, $\pi/2$ pulse width of $5.5\text{--}7.0\ \mu\text{s}$, and 2000–5000 scans; for ^{13}C nonquaternary suppression (NQS) CP-MAS NMR experiment, 3 s recycle delay, $50\ \mu\text{s}$ dephasing delay, and 2000–3000 scans; and for ^{29}Si (79.5 MHz) CP-MAS NMR, 3 s recycle delay, 10 ms contact time, $\pi/2$ pulse width of $6.0\text{--}7.5\ \mu\text{s}$, and 10 000–150 000 scans. Adamantane (major peak, 38.4 ppm vs. TMS) and $\text{Si}[\text{Si}(\text{CH}_3)_3]_4$ (major peak, -9.98 ppm vs. TMS) were used as external references for ^{13}C - and ^{29}Si -NMR spectra, respectively.

Results and Discussion

Sol–Gel Processing of 1 (Synthesis of 1,3,5-benzene PMO). It is known that mesoporous silica materials can be synthesized from tetraalkoxysilane precursors both under acidic and basic conditions in a wide concentration range. On the contrary, synthesis using some organosilane precursors should be done more carefully during self-assembly and sol–gel processing as the Si–C bonds are more vulnerable to cleavage under certain synthetic conditions in acidic and basic solutions. For instance, Si–C bonds were reported to cleave significantly in 1,1'-bis(triethoxysilyl)ferrocene and slightly in 1,4-bis(triethoxysilyl)benzene during sol–gel processing and self-assembly in aqueous HCl or ammonia solutions while those of bis-triethoxysilylated ethylene, methylene, and ethane precursors remained intact under the same conditions.⁶ To avoid or minimize these problems, the self-assembly of some PMO precursors under neutral conditions could be done successfully.^{6c,i,j} In this study, the hydrolysis and self-assembly of 1,3,5-tris(triethoxysilyl)benzene, **1**, was therefore carried out under acidic conditions followed by immediate neutralization to avoid the possible cleavage of one or more of the Si–C bonds. Additionally, the self-assembly of **1** in basic solution was performed.

Structural Characterization. The PXRD pattern of the as-synthesized PMO sample **1** (Figure 1A) showed a strong and sharp low angle diffraction corresponding to the presence of an ordered mesostructured material. The position of the XRD peak (arbitrarily denoted here as (100) peak) corresponds to the interplanar spacing of $\sim 37\ \text{\AA}$. The PXRD pattern (Figure 1A) of the surfactant-extracted material also revealed the presence of the 100 reflection with its d -spacing position remaining unchanged but its intensity increased, which is a clear indication that the ordered structure of the material was intact after template removal in acid/methanol solution. The slight increase in the intensity of the peak after template removal is probably due to an increase in electron contrast between the pores and the channel wall, a case that is common to as-synthesized surfactant containing and surfactant-free PMO materials.⁶ Interestingly, the 100 reflection on the PXRD pattern of the 1,3,5-benzene PMO remained observable after the material was pyrolyzed under nitrogen up to $800\text{ }^{\circ}\text{C}$ (Figure 1B). The variable temperature PXRD patterns of surfactant-extracted PMO **1** under nitrogen atmosphere (Figure 1B) also showed an initial increase in the intensity of the diffraction peak as the material was heated,

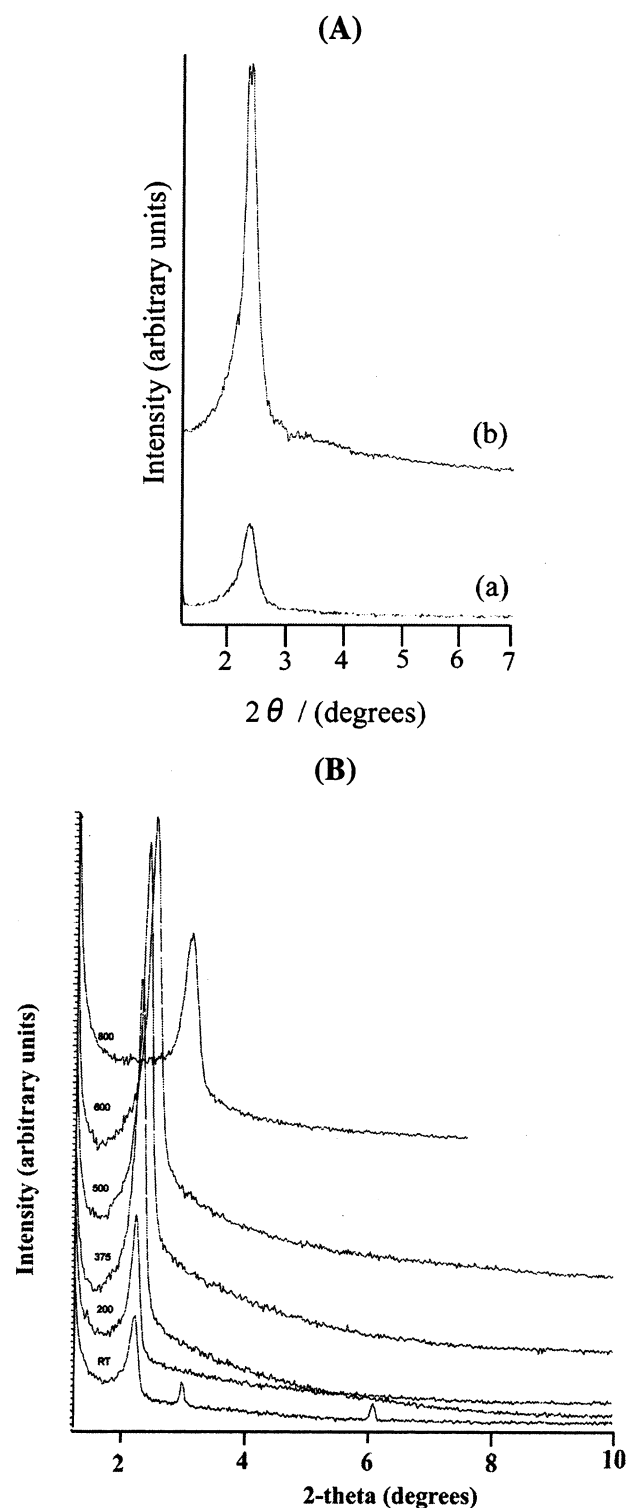


Figure 1. (A) PXRD of 1,3,5-benzene PMO materials, (a) as-synthesized and (b) surfactant-extracted. (B) Variable temperature powder X-ray diffraction of surfactant-extracted 1,3,5-benzene PMO, heated under nitrogen. The temperatures from bottom to top indicate RT (room temperature), 200, 375, 500, 600, and 800° .

probably due to the loss of water adsorbed inside the channel and the increase in electron contrast between the channel walls and the pores. But the peak position did not start to change until $375\text{ }^{\circ}\text{C}$. Above $500\text{ }^{\circ}\text{C}$, the peak position started to shift significantly to high angle and the mesoporous structure began to shrink substantially driven by the transformation and subse-

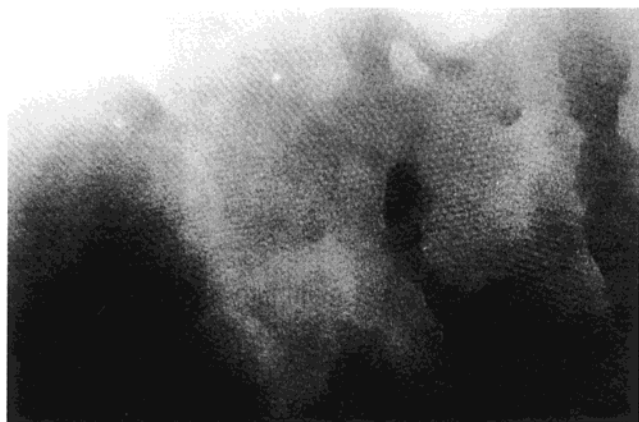


Figure 2. TEM image of surfactant-extracted hexagonal mesoporous materials obtained from **1**.

quent elimination of the benzene groups and further cross-linking through condensation of silanol groups (Si-OH). After pyrolysis at 800 °C, the (100) interplanar spacing changed from 37 to 27 Å ($\Delta d_{100} = 10$ Å) due to the overall process of condensation of silanol groups and loss of the aromatic groups.

The TEM images of both as-synthesized (not shown) and solvent-extracted materials (Figure 2) show ordered domains that appeared to have a 2-dimensional hexagonal symmetry throughout the sample. Moreover, the TEM images showed that the ordered PMO phase dominates over any disordered (amorphous) organosilicate phase. The TEM images also provided further evidence that the structural integrity of the material was maintained after the extraction of the template, a result consistent with the PXRD patterns.

For comparative purposes and for thorough investigation of the properties of 1,3,5-benzene PMO, the hydrolysis and condensation of 1,3-bis(triethoxysilyl)benzene (**2**) and phenyltriethoxysilane (**3**) in surfactant solutions were conducted under similar reaction conditions and a white power product **2** for the former and a soft chunky product **3** for the latter were obtained. Sample **3** was ground into powder and after which both materials **2** and **3** were also subjected to some characterizations (see the Experimental Section). The PXRD pattern for **2** was found to be similar to that of **1** showing a low angle reflection with similar unit cell dimension while that of sample **3**, which is expected to form stable silsesquioxane oligomers, showed no low angle reflections as expected.

The solvent-extracted 1,3,5-benzene PMO (**1'**) synthesized using CTABr as a surfactant exhibited a single, rather broad peak in its XRD pattern (see Supplementary Figure 1S). The position of the peak corresponded to the interplanar spacing of 3.4 nm. The position of the peak also shifted to higher angles and the intensity decreased upon calcination under air at 350 and 450 °C, with a decrease in the corresponding interplanar spacing to 3.3 and 3.1 nm, respectively. The TEM images (Supplementary Figure 2S) showed that this PMO is locally well ordered, but they are not sufficient to identify the structure type.

The nitrogen adsorption isotherm of 1,3,5-benzene PMO sample **1** (Figure 3) was of type I rather than type IV. This indicates that the pore size of this material is either on the borderline between the micropore and mesopore ranges, or in

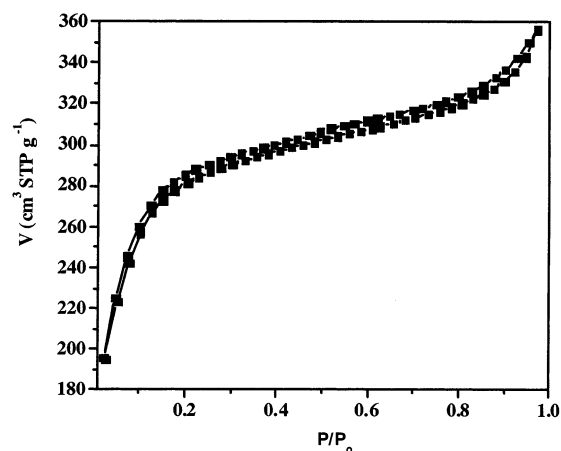


Figure 3. Nitrogen adsorption/desorption isotherms and pore size distributions of 1,3,5-benzene PMO.

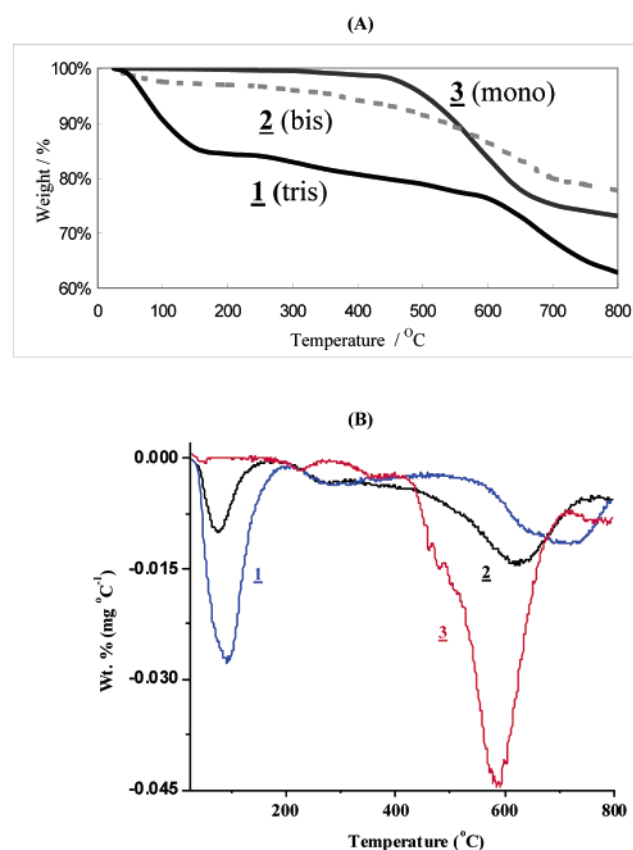


Figure 4. Thermogravimetric analysis (TGA) plot (A) and differential thermogravimetric analysis (DTGA) plot (B) of 1,3,5-benzene PMO under nitrogen.

the micropore range.²⁰ The BET surface area was 880 m² g⁻¹, the total pore volume was 0.55 cm³ g⁻¹, and the primary pore volume was 0.41 cm³ g⁻¹. The average pore diameter was found to be below 22 Å.

Nitrogen adsorption isotherms for 1,3,5-benzene PMO samples synthesized using the CTABr template, **1'**, are shown in Supplementary Figure 3S and the corresponding pore size distributions are shown in Supplementary Figure 4S. The solvent-extracted PMO exhibited an adsorption capacity that was very high for an ordered mesoporous material with such a

(20) Kruk, M.; Jaroniec, M. *Chem. Mater.* **2001**, *13*, 3169–3183.

Table 1. Chemical Shift Data for Various Aromatic PMO **1** and **2** and Phenylsilica Gel **3** (see Scheme 3)

compd	carbon	chemical shift/ppm
1 ^a	Si-C	130.2
	α-C	141.7
2 ^a	Si-C	130.2
	α-C	140.4
	α'-C	136.4
	β-C	127.6
3 ^b	Si-C	130.8
	α-C	134.6 ^c
	β-C	128.2 ^c
	γ-C	128.2 ^c

^a Its chemical shift assignment was further supported by ¹³C NQS CP-MAS NMR experiment. ^b Attempted ¹³C NQS CP-MAS NMR measurement for it did not give clear results. ^c Overlapping peaks.

small pore diameter (2.6 nm, see Supporting Table 1S). The BET specific surface area was 1110 m² g⁻¹, and the primary pore volume was 0.62 cm³ g⁻¹. The calcination of solvent extracted sample **1'** at 350 °C resulted in a decrease in the BET specific surface area, primary pore volume and pore diameter to 1010 m² g⁻¹, 0.52 cm³ g⁻¹, and 2.5 nm, respectively, whereas the calcination at 450 °C led to a more dramatic decrease to 800 m² g⁻¹, 0.37 cm³ g⁻¹, and 2.1 nm, respectively. The heat treatment also led to a decrease in low-pressure nitrogen adsorption (see Supplementary Figure 5S). This decrease can be related to some extent to the increase in the degree of exposure of organic groups on the surface of the PMO caused by the transformation of these groups to the species with two-point and one-point attachment (see below). In particular, the latter groups can be fully located on the pore surface and would be likely to weakly interact with nitrogen molecules, which are known to interact much more weakly with the surface organic groups than with the hydroxylated silica surface.²⁰ However, it needs to be kept in mind that the 1,3,5-benzene PMO samples were found to exhibit a strong low-pressure adsorption, which is quite unexpected for mesoporous organosilicas. This behavior may be related to surface roughness or framework microporosity that arise from a low degree of pore wall consolidation. Another possibility is that the ordered material is contaminated with a disordered phase that would exhibit a strong low-pressure adsorption. Therefore, a 1,3,5-benzene gel that was synthesized in the absence of surfactant template was indeed found to exhibit a strong low-pressure adsorption related to its primarily microporous nature (see Supplementary Figures 6–8). These results indicate that contamination of the 1,3,5-benzene PMO with a disordered phase may contribute to the unexpectedly strong low-pressure adsorption observed for this PMO. However, the remarkably large adsorption capacity for this PMO suggests that the content of the disordered phase, if any, is likely to be low. Therefore, other factors considered here, such as surface roughness or framework microporosity, are likely to lead to a strong low-pressure adsorption in this PMO. In particular, the thermally induced decrease in low-pressure adsorption is consistent with the notion that the walls of the solvent-extracted material are unconsolidated, perhaps microporous, or rough to a significant extent and they become more consolidated or smooth only after the thermal treatment.

Thermal Properties. TGA analysis of surfactant-extracted samples (Figure 4) showed that air-dried sample **3** after storage under ambient atmosphere showed a very low amount of

physisorbed water, compared to **1** and **2** as seen from the higher weight loss at ca. 85–100 °C for the former than the latter two. This is probably due to the more highly cross-linked structure (see ²⁹Si NMR spectra below), nonporous nature and strong hydrophobic character caused by the pendant phenyl groups in material **3** compared to materials **1** and **2**. The larger amount of physisorbed water in samples **1** and **2** may also suggest that the benzene groups enclosed within the walls by the surrounding hydrophilic siloxane moieties are not as accessible and hydrophobic as the pendant phenyl group that lie on the surface of the channels of sample **3**. The decrease in weight at 200–400 °C for surfactant-templated materials may in general be attributable to the decomposition of residual surfactant. The lack of any substantial weight losses in this range for surfactant-extracted samples **1** and **2** indicated that the surfactant was successfully removed via solvent extraction. In the case of sample **3**, there was not much surfactant even before the solvent extraction, as this material was amorphous and did not seem to have self-assembled with the surfactant. Interestingly, weight losses corresponding to benzene groups in 1,3,5-benzene PMO (**1**) were observed to start at ca. 600 °C, whereas those in 1,3-benzene PMO (**2**) and 1-benzenesilica xerogel (**3**) at ca. 500 and ca. 450 °C, respectively. The differences in the decomposition temperature for benzene rings clearly indicate the increase in thermal stability of the organic functional group when anchored onto three rather than two or one siloxane. Furthermore, the decomposition temperature for the benzene groups in **3** also appeared much lower than those for the other two samples, **1** and **2**. It is important to keep in mind that other organosilica xerogels with benzene groups attached in one point (similarly as in **3**) and two points (similarly as in **2**) are known to exhibit exceptionally high thermal stability,^{7c,21} so further enhancement of stability observed for 1,3,5-benzene PMO reported herein is remarkable. It will be shown later that the thermal transformation of benzene groups with three-point attachment proceeds via intermediates with two-point or one-point attachment, so the differences in the decomposition temperatures may be in part due to the slower kinetics of decomposition processes that require the cleavage of a relatively higher number of bonds.

Weight change curves acquired under air for the CTABr-templated 1,3,5-benzene PMO (solvent-extracted **1'** and calcined **IC350A** and **IC450A**) and the corresponding weight change derivatives are shown in Supplementary Figure 9S. The weight loss observed below 100 °C can be attributed to the thermodesorption of water (and perhaps some solvents left after surfactant-extraction in the case of the solvent-extracted material **1'**) from the surface of the samples. It appears that the heat treatment led to an increased hydrophobicity of the surface of the PMO. A minor weight loss at about 250 °C for the solvent-extracted sample can be attributed to the decomposition and thermodesorption of the residual surfactant left after the extraction. The small magnitude of this weight loss indicates that the solvent-extraction procedure employed was successful in removing almost all of the surfactant from the as-synthesized material. A major weight loss observed at 570 °C can be attributed to the burnout of the organic bridging groups. This event mostly took place in a narrow temperature range for the solvent-extracted PMO, whereas some broadening of the decomposition range

(21) Babonneau, F.; Leite, L.; Fontlupt, S. *J. Mater. Chem.* **1999**, *9*, 175–178.

was observed after calcination at 350 °C and especially at 450 °C. On the basis of the extensive NMR study of the 1,3,5-benzene PMO sample templated by cetylpyridinium surfactant, this broadening is attributable to a partial transformation of the benzene groups with three-point attachment in the framework to benzene groups attached with two points and one point attachment. Clearly, such a bonding heterogeneity is likely to lead to a wider temperature range for the decomposition. The decomposition behavior of solvent-extracted 1,3,5-benzene PMO was found to be similar to that for a disordered material synthesized from the same organosilica precursor in the absence of surfactant structure-directing agent (see Supplementary Figure 10S). However, the disordered sample exhibited a somewhat broader temperature range for the organic group decomposition. As can be seen from the comparison of Supplementary Figures 9S and 11S, the organic groups were more thermally stable under nitrogen than they were under air atmosphere. The weight loss related to the removal of the organic groups under nitrogen was observed at ca. 650 °C. It is interesting to note that the weight loss observed under air for the solvent-extracted *I'* and calcined *I'C350A* correlated very well with their formulas assessed on the basis of NMR data. Under the assumption that the product of the decomposition of these samples under air is SiO₂ and that the surfactant content is negligibly small, the ratio of the weight loss between ca. 150–200 and 1000 °C (surface dehydroxylation and organic group decomposition) to the weight at ca. 150–200 °C was predictable with absolute accuracy of 1–2% on the basis of the formulas derived from NMR data below. This excellent agreement between TGA and NMR data allowed us to estimate the amount of organic groups lost for the sample heated at 450 °C from the TGA data. This estimate suggests that less than 50% of benzene groups were removed from the PMO as a result of calcination at 450 °C for 6 h under air.

NMR Characterization. The solid-state ²⁹Si CP-MAS NMR spectra (Figure 5) of the as-synthesized aromatic PMOs and gel samples described here showed virtually no Q_n signals (Si sites attached to four oxygen atom) between –98 and –111 ppm. This clearly indicated that all the Si–C bonds of the materials remain uncleaved during the sol–gel processing and under the synthetic conditions employed. The samples, however, showed characteristic T_n signals attributed to CSi(OSi)₃ (T₃ at –79 ppm), CSi(OSi)₂(OH) (T₂ at –71 ppm) and CSi(OSi)(OH)₂ (T₁ at –62 ppm) (Figure 5). The peak corresponding to T₂ in *I* and *2* was found to be the major signal indicating the presence of significant number of SiOH groups and a rather low degree of polymerization in the materials. This is probably caused by the mild sol–gel processing condition and the low aging temperature used as well as the higher number of cross-linkable SiOH groups available from *1*, (9 cross-linkable SiOH groups per each molecule of precursor *1* compared to only 4 in TEOS or 3 in precursor *3*) that the structure of the solid may remain stable even for very low degrees of framework condensation. The ²⁹Si NMR spectra also revealed that surfactant-extraction from the materials under dilute acidic condition did not cause cleavage of the Si–C bonds.

The ²⁹Si MAS NMR spectra of the 1,3,5-benzene PMO synthesized using CTABr as a template (*1'*) (Supplementary Figure 12S), were very similar to those of PMO materials templated with cetylpyridinium chloride surfactant. There was

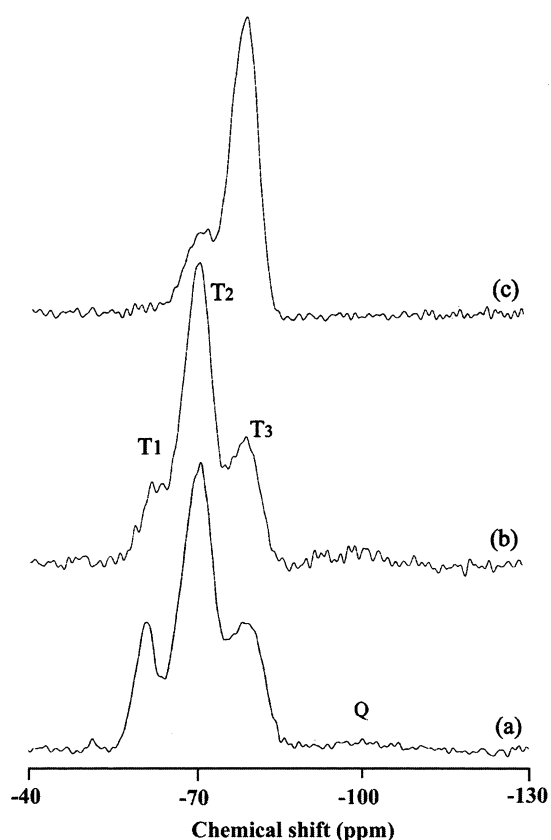
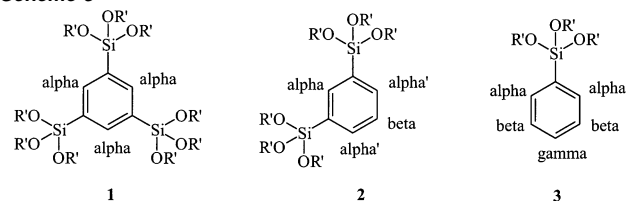


Figure 5. ²⁹Si CP-MAS NMR spectra of surfactant-extracted 1,3,5-benzene PMOs (a) and 1,3-benzene PMOs (b) and 1-benzene gel (c).

Scheme 3



essentially no evidence for cleavage of Si–C bonds during the synthesis, as the population of Q_n sites was found to be negligible. The degree of framework condensation was low, as seen from the presence of 18.5% of T₁ silicon sites, 57.4% of T₂ silicon sites and only 24.1% of fully cross-linked T₃ silicon sites. A small amount of Q_n silicon sites appeared after calcination at 350 °C (2.9% of Q₂ sites and a total of 12.7% of Q₃ and Q₄ sites, in addition to 7.0% of T₁ sites, 48.9% of T₂ sites and 28.7% of T₃ sites), so the heating at this temperature already caused some cleavage of Si–C bonds. After calcination at 450 °C, more than half of the Si–C bonds were cleaved, as inferred from the occurrence of 10.8% of Q₂ sites, 18.1% of Q₃ sites and 25.3% of Q₄ sites, in addition to 9.3% of T₁ sites, 16.9% of T₂ sites and 19.7% of T₃ sites. These NMR data allowed us to derive the following formula of the solvent-extracted 1,3,5-benzene PMO: SiO_{1.03}(OH)_{0.94}(C₆H₃)_{0.33}. If we further assume that the sample calcined at 350 °C did not lose any organic groups (although some of the bonds that connected them into the framework were severed) and the organic groups present would be exclusively of types shown in Scheme 3, then the following approximate formula is obtained: SiO_{1.21}(OH)_{0.75}-(C₆H_{3.47})_{0.33}. It can be seen that the thermal treatment did reduce the amount of silanols (OH groups), but the latter amount is

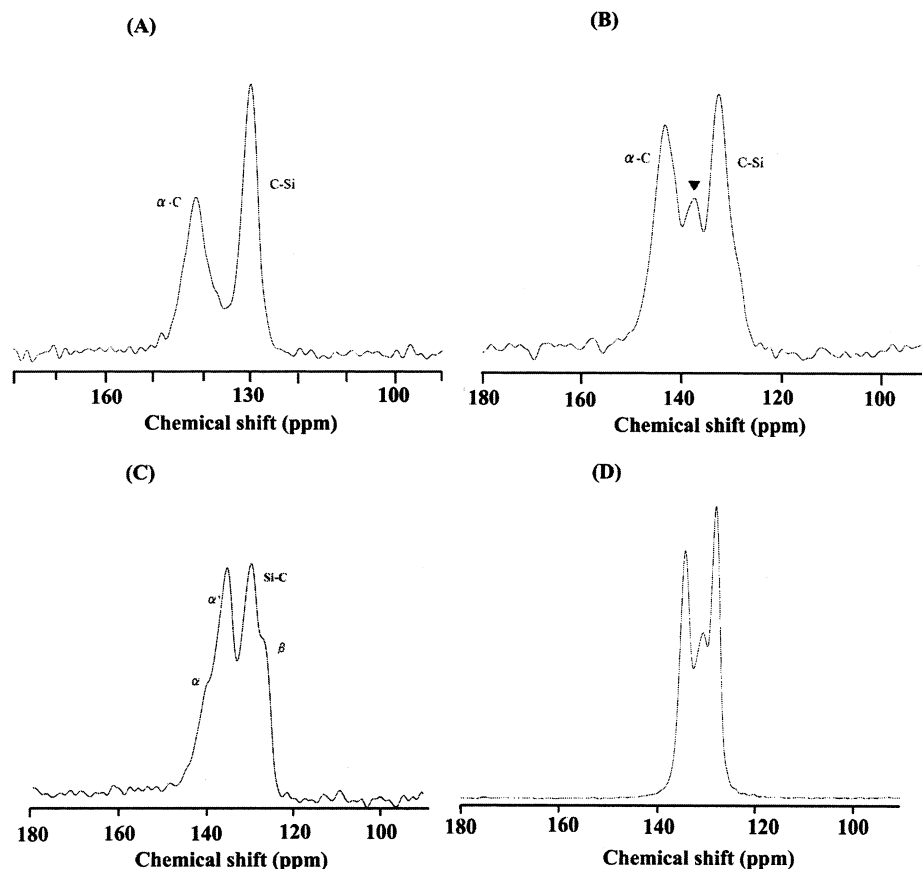
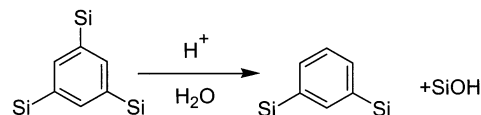


Figure 6. ^{13}C CP-MAS NMR spectra of (A) once and (B) thrice surfactant extracted PMO **1** (\blacktriangledown indicates new peak formed due to cleavage of Si–C bond), (C) once solvent-extracted PMO **2** and (D) gel **3**.

high even after the heat treatment. It should be noted that it does not seem to be possible to derive the formula for the material calcined at 450 °C (sample *I'*C450A) on the basis of NMR data alone, because this material exhibited a significant loss of organic groups upon the thermal treatment, as discussed above on the basis of the TGA data.

The ^{13}C CP-MAS NMR spectra (Figure 6) of the PMOs and gel materials showed that the aromatic groups were indeed intact after the sol–gel processing and surfactant-extraction. The molecular structures of the precursors and the final samples **1**, **2**, and **3** show that the benzene rings contain 2, 4 and 4 different kinds of carbons, respectively (Si–C and α -C for **1**, Si–C, two kinds of α -C and one β -C for **2** and Si–C, α -C, β -C, γ -C for **3**) (Scheme 3). The ^{13}C CP-MAS NMR spectrum of **1** contains two peaks at 130.2 and 141.7 ppm corresponding to Si–C and α -C (Si–C–C) carbons of the benzene ring, respectively. These assignments were further corroborated by ^{13}C NQS CP-MAS NMR experiments in which case only the quaternary carbons were observable (spectra not shown). Moreover, an additional new peak at 137.5 ppm and a shoulder peak at ca. 128.6 ppm appeared after PMO **1** underwent repeated solvent-extraction (at least three times) resulting most likely from the cleavage of some of the Si–C bonds after successive acid leaching (Scheme 4). This hypothesis was also supported by the very close proximity of the position of these new peaks to those of PMO **2** which has resonance peaks at 130.2, 140.4, 136.4, and 127.6 ppm corresponding to Si–C, α -C, α' -C, and β -C carbons (Scheme 3). The chemical shifts for the phenyl group in ^{13}C CP-MAS NMR spectrum for **3** appeared at 130.8, 136.4, and 128.2 ppm and these were assigned to Si–C, α -C, and

Scheme 4



overlapping β -C and γ -C carbons, respectively. It is also noteworthy that the NMR peaks for sample **3** appeared much sharper than those for samples **1** and **2** due to the fact that the phenyl group in the former is more mobile on its Si–C axis. Furthermore, the ^{13}C CP-MAS NMR spectra of a bifunctional PMO (BPMO) prepared from mixtures of precursors **1** and **3** as well as **2** and **3** (25% **3** based on the molar ratio of phenyl group and their syntheses were conducted under the same conditions as the other PMOs) also showed signals corresponding to the various carbons of the aromatic groups indicating the quantitative incorporation of the two differently bonded aromatic functional groups. The method of incorporating terminal and bridging organic groups simultaneously into mesoporous materials has actually been described and demonstrated recently to offer an opportunity to make materials with unprecedented tunable bifunctional and multifunctional properties that are potentially useful for various applications.^{6h,14}

Stepwise Channel Metamorphosis of **1 (Pyrolysis of **1** under Air and Nitrogen).** 1,3,5-benzene PMO was found to show interesting channel metamorphosis in a stepwise fashion during thermolysis in air (Scheme 5). Figure 7 shows the ^{13}C CP-MAS NMR spectra of surfactant extracted PMO **1** before and after calcination under air and nitrogen at 350 and 450 °C for 6 h. The spectra showed that most of the aromatic signals

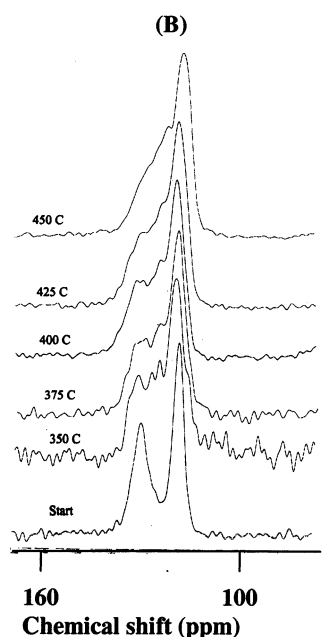
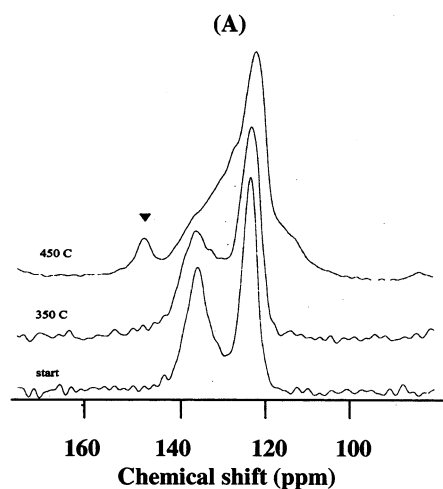
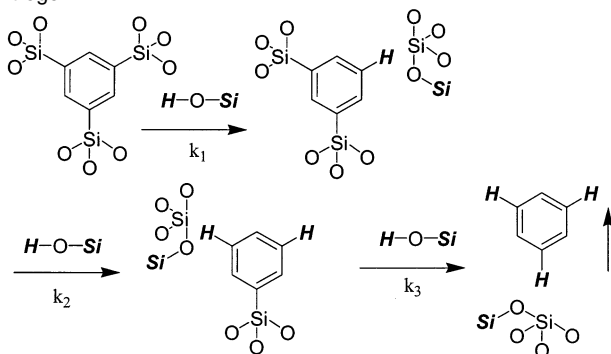


Figure 7. ^{13}C CP-MAS NMR spectral change of surfactant-extracted solid from **1** heated (A) under air, 6 h, at 350 °C and 450 °C (signal at 152 ppm (▼) is attributed to a new peak formed due to oxidation of the phenyl ring) and (B) under nitrogen 6 h, from RT to 450 °C.

Scheme 5. Schematics of the Thermal Transformation of the Benzene Functional Groups from 1,3,5-benzene PMO under Nitrogen



remained intact in the material only with slight cleavage of their Si–C bonds after calcinations up to 450 °C for 6 h further proving the high thermal stability of the aromatic rings in **1**. However, the appearances of new peaks between 130 and 140

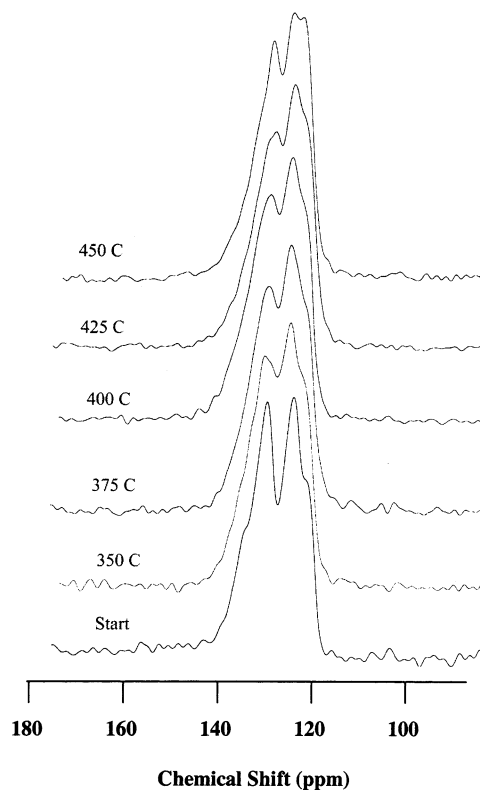


Figure 8. ^{13}C CP-MAS NMR spectral change of surfactant-extracted solid from **2** heated under nitrogen, 6 h, from RT to 450 °C.

ppm suggested the occurrence of thermal transformation of the phenyl rings during thermolysis. Moreover, new small signals at 152 and 122 ppm appeared in the material only when it was calcined in air at 450 °C and this was assigned to carbons in oxygen containing oxidized phenyl groups, O-Ph, that were likely to result due to possible oxidation of the phenyl ring under air while it was still intact in the framework or while it underwent decomposition. Similar oxidative intermediate products were reported to occur in other PMO and BPMO materials containing other organic groups when thermally treated under air.^{6b} On the other hand, the ^{29}Si CP-MAS NMR spectra of PMO **1** pyrolyzed under air shows a relatively large amount of cleavage of Si–C bonds at 450 °C as observed from the appearance of Q_n sites in its spectrum unlike the materials that were pyrolyzed under nitrogen and that underwent a much less extensive cleavage (Figure 9). The cleavage of the Si–C bonds and the transformations of the phenyl rings are believed to occur from the nucleophilic attack of silicon atoms of Si–C (benzene) by water from air and/or by residual Si–OH groups, processes which are common in PMOs during thermolysis.^{6b} The Si–C bond may also be cleaved as a result of reaction with oxygen or even with nitrogen.¹¹

Possible kinetics in the course of channel metamorphosis upon thermolysis of **1** and **2** in air assuming similar rate constants, k_1 , k_2 , and k_3 for the stepwise transformation of benzene groups in the channels shown in Scheme 5 is summarized in Supplementary Figure 13S. It was assumed that $k_1 = k_2 = k_3$, which may not be particularly accurate due to the possible differences in decomposition behavior and the decrease in the number of SiOH groups upon thermolysis and annealing of the materials. Nevertheless, the figure qualitatively represents expected changes in chemical composition during the thermal process, as expected

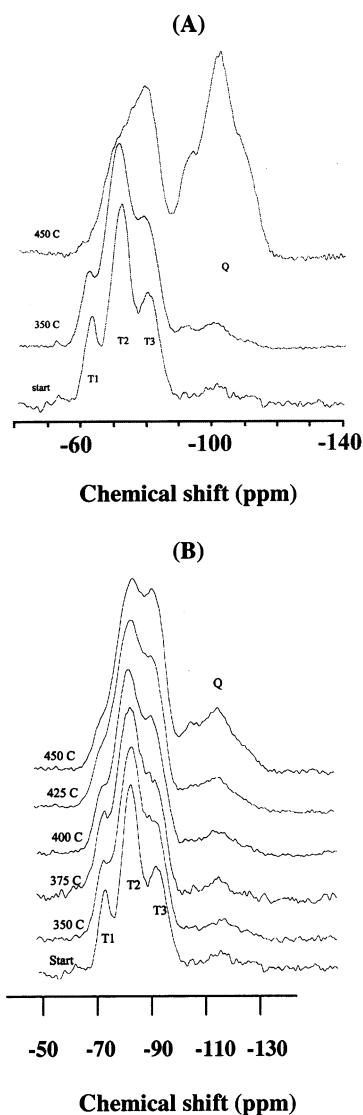


Figure 9. ^{29}Si CP-MAS NMR spectral change of PMO **1** after pyrolysis (A) under air, 6 h, at 350 and 450 °C and (B) under nitrogen, 6 h, 350 °C to 450 °C.

from changes in intensity of the various signals in the ^{29}Si and ^{13}C NMR spectra during pyrolysis (Figures 7, 8, and 9). For instance, the formation of only a little Q signal at lower calcination temperatures for sample **1** was indicative of the presence of lower amounts of disiloxylbenzene and monosiloxylbenzene groups. Continuous cleavage of Si–C bonds and the formation of mixtures of **1**, **2**, and **3** started to occur as the pyrolysis temperature and time were increased suggesting the formation of **2** and **3** at the expense of **1** (Figure 7, 8, and 9). The new ^{13}C CP-MAS NMR signals appearing in the pyrolyzed samples are at similar peak positions as those in the material made from the mixture of precursors **2** and **3**. The relatively sharper line shape of signals corresponding to monosiloxylbenzene groups on the ^{13}C CP-MAS NMR spectra also made distinguishing of many of these peaks in the spectra for the pyrolyzed samples easier. In a few cases, however, the overlapping of the broad signals in the solid-state NMR spectra made clear assignments impossible for a number of other peaks.

Pyrolysis Mass Spectra. The thermal decomposition mass spectra (540 °C, under vacuum) of solid samples **1**, **2**, and **3**

(Supplementary Figure 14S) showed H_2O , CO_2 , CH_2 , and CO as major decomposition products in all cases. However, there exist some striking differences in the spectra. For instance, a peak at $m/z = 78$ corresponding to benzene appeared much higher in intensity for sample **3** than those for samples **1** and **2**. It is reasonable, therefore, to suggest again that the thermodesorption of benzene groups at 540 °C in sample **3** whose benzene group is attached only to one silicon atom took place more easily than those in samples **1** and **2** in which the benzene groups are attached to two or more than two silicon atoms and are more thermally stable.

Conclusion

The synthesis of 1,3,5-benzene PMO, the first PMO material with organic functional group bonded via three Si–C linkages within the framework, is reported. When cetylpyridinium surfactant was used as a template, the resulting PMO exhibited a moderate adsorption capacity and pore diameter close to the micropore range, but a PMO with a larger pore diameter and a very high specific surface area can be synthesized using CTABr template. Detailed thermal studies indicated that 1,3,5-benzene PMO undergoes thermally induced sequential channel metamorphosis resulting in the formation of disiloxylbenzene PMO and monosiloxylbenzene materials before losing the benzene groups completely. The benzene rings in aromatic PMOs in general and in 1,3,5-benzene PMO in particular were also found to be more stable due to their linkages to two and three siloxanes respectively, compared to alkene containing PMOs. The presence of benzene rings uniformly bound in the framework of a mesoporous structure with such enhanced thermal stability and large specific surface area can make the material useful in various applications. Moreover, the successful synthesis of PMO with three-point attachment of the organic group that exhibits strictly defined angles between the attachment points provides a strong indication that it is possible to synthesize a variety of PMOs with three-point or multi-point bonding of organic groups in the framework and with strictly defined bonding geometry. On the basis of earlier studies,^{6i,j,7c} such novel aromatic PMO compositions may exhibit ordering of the aromatic groups in the framework to give crystalline-type frameworks, and therefore may be ordered on both molecular and nanoscopic levels.

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Supporting Information Available: PXRD patterns, TEM images, TGA plots, adsorption isotherms, thermal property, and mass spectroscopy data for various 1,3,5-benzene PMO gel samples templated by CTABr and CPCI (14 figures and one table) are available. This material is available free of charge via Internet at <http://www.pubs.acs.org>.

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