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Triblock Copolymer Synthesis of Highly Ordered Large-Pore Periodic Mesoporous Organosilicas with the Aid of Inorganic Salts

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Much progress has been made recently in the preparation of a new class of organic−inorganic hybrid materials called periodic mesoporous organosilicas (PMOs) through surfactant-templated condensation of organosilanes with two trialkoxysilyl groups bridged by an organic group.[1−14] Not only were a number of new synthesis strategies developed for the preparation of PMOs under a wide range of pHs from highly basic to strongly acidic conditions using cationic,[1−5] anionic,[6a] and neutral[9] surfactants and a variety of commercially available block copolymers,[8,13] but also several new mesostructures such as HMM-2,[1] HMM-3,[4] and mesoporous benzene-silica[14] with crystal-like pore walls were synthesized. Furthermore, PMOs have already found use as novel catalysts,[15] adsorbents,[16] and hosts for nanocluster synthesis[17] as the porous structures, surface, and framework properties of PMO materials can be finely tuned by changing the bridging organic groups incorporated and the synthesis conditions employed.[18] It is apparent that the structural order of porous materials is directly related to their ability to perform the desired function in a particular application.[19] Well-ordered mesoporous materials with large pores (>4.5 nm) have recently attracted particular interest from the viewpoint of the immobilization and encapsulation of large molecules.[20] Unfortunately, PMO materials prepared under acidic media usually exhibit poorly ordered mesostructures compared to those obtained from basic media.[11] Up to now, the synthesis of large-pore PMOs with long-range structural order templated by triblock copolymers under strongly acidic conditions via the $(S^\circ H^+)(X^-I^+)$ pathway has been a challenging objective.[8,10] On the other hand, inorganic salts have been used to improve the hydrothermal stability,[21] control the morphology,[22] extend the synthesis domain,[23] and tailor the framework porosity[24] during the formation of mesoporous materials, results that can be attributed to the specific effect of inorganic salts on the self-assembly interaction between surfactant headgroups and inorganic species.[23] Here, we report the synthesis of highly ordered hexagonal PMOs with the aid of inorganic salts under strongly acidic conditions using the nonionic triblock copolymer Pluronic P123 as the template and 1,2-bis(trimethoxysilyl)ethane (BTME) as the organically bridged silica source.

In a typical synthesis, 1.2 g of P123 and 3.5 g of NaCl were dissolved in 10 g of water and 30 g of 2.0 M HCl solution with stirring at 40 °C. To this homogeneous solution was added 1.6 g of BTME, and then the mixture

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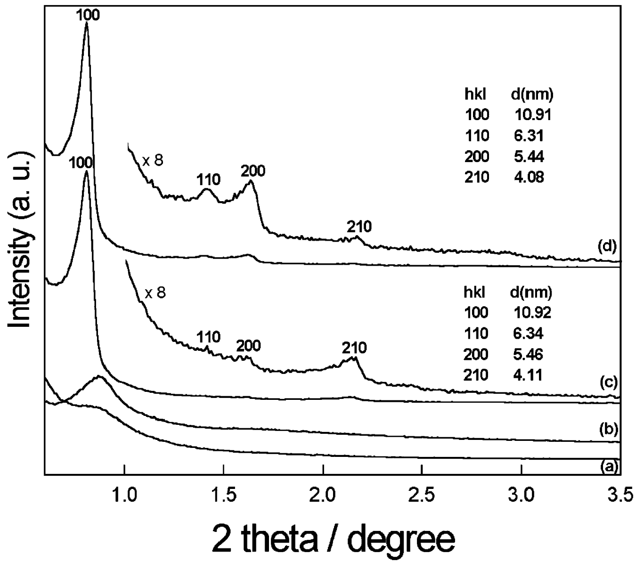

Figure 1. XRD patterns of (a) as-synthesized and (b) solvent-extracted PMOs in the absence of inorganic salts; (c) as-synthesized and (d) solvent-extracted PMOs synthesized with the aid of inorganic salts. The XRD patterns were recorded on a Rigaku D/MAX-III diffractometer using Cu Kα radiation.

was stirred for 24 h at the same temperature. Subsequently, the resulting mixture was transferred into a Teflon-lined autoclave and heated at 80 °C for an additional 24 h under static conditions. The final reactant molar composition was 0.5 BTME/0.017 P123/5.07 HCl/5.07 NaCl/178 H_2O. The solid products were collected by filtration, washed thoroughly with water, and air-dried at room temperature. The surfactant was removed by stirring 1.0 g of as-synthesized sample in 150 mL of ethanol with 3.8 g of 36% HCl aqueous solution at 50 °C for 6 h. The resulting solid was recovered by filtration, washed with ethanol, and dried in air. This extraction procedure was repeated to remove the surfactant completely. A control sample was prepared according to the protocol described above, without the addition of the NaCl component.

Small-angle X-ray diffraction (XRD) patterns of as-synthesized and solvent-extracted PMO materials are shown in Figure 1. The as-synthesized PMO sample using NaCl as the auxiliary agent exhibits four well-resolved peaks (Figure 1c) that can be indexed as the (100), (110), (200), and (210) reflections of *p*6*mm* hexagonal symmetry with lattice *d* spacings of 10.92, 6.34, 5.46, and 4.11 nm, respectively. The corresponding unit cell parameter, a_0, is 12.61 nm. After solvent extraction, the XRD pattern (Figure 1d) shows that the ordered hexagonal (*p*6*mm*) pore structures are well preserved, as the lattice *d* spacings for the solvent-extracted sample are almost identical to those for the as-synthesized sample. The unit cell parameter derived from the first strong diffraction peak (100) of the solvent-extracted PMO sample is 12.60 nm. The well-resolved XRD data demonstrate that highly ordered hexagonal PMOs with large pores have been obtained using inorganic salts as the auxiliary agents. By contrast, the XRD patterns of PMO materials in the absence of inorganic salts show that only disordered mesoporous structures with a single broad diffraction peak were formed, which is consistent with the results from previous reports.[8,10]

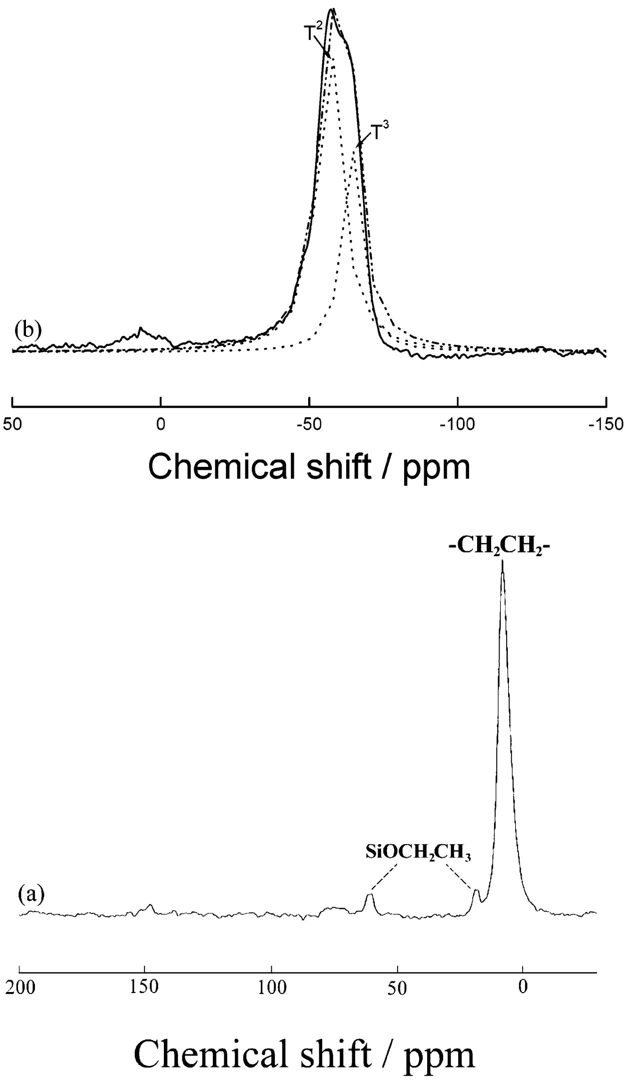

Figure 2. (a) ^{13}C CP MAS NMR and (b) ^{29}Si MAS NMR spectra of solvent-extracted PMO material synthesized with the aid of inorganic salts. The spectra were obtained with a Bruker DSX400 spectrometer.

The incorporation of ethane groups inside the framework was confirmed by solid-state NMR spectroscopy. The ^{13}C cross-polarization (CP) MAS NMR spectrum (Figure 2a) displays a strong resonance at 6.8 ppm that is attributed to ethane carbon atoms ($-CH_2CH_2-$) in the framework. The two weak signals at 18.8 and 59.9 ppm assigned to the carbons of surface ethoxy groups ($Si-OCH_2CH_3$) were formed in the course of solvent extraction using HCl/EtOH solution.[4,5b] No carbon signal due to P123 surfactant was observed, suggesting complete removal of the surfactant from the PMO materials by the solvent extraction process. The ^{29}Si MAS NMR spectrum (Figure 2b) of the solvent-extracted PMO material shows two signals at −56.8 and −64.2 ppm corresponding to T^2 [$RSi(OSi)_2OH$] and T^3 [$RSi(OSi)_3$] resonances, respectively. The absence of signals due to Q^n [$Si(OSi)_n(OH)_{4-n}$] species between −90 and −120 ppm indicate that all silicon atoms are covalently connected to carbon atoms, and that no carbon−silicon bond cleavage occurred under the strongly acidic synthesis conditions used herein.

Figure 3 shows a representative N_2 adsorption−desorption isotherm and the corresponding pore size

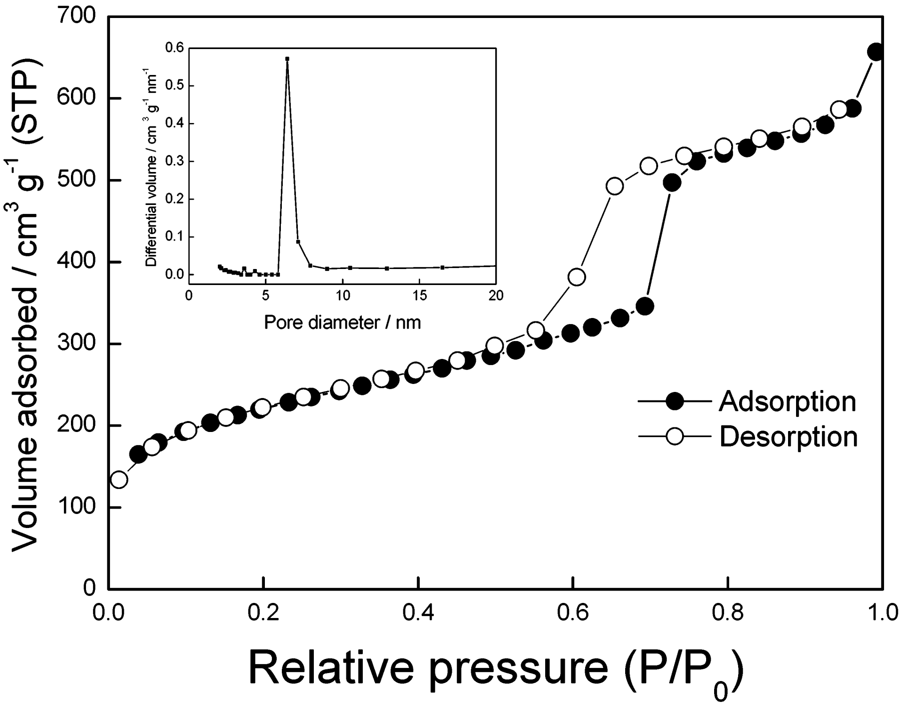

Figure 3. Nitrogen adsorption–desorption isotherm for solvent-extracted PMO material synthesized with the aid of inorganic salts. The inset shows the pore size distribution calculated by the BdB method. The isotherm was measured at the temperature of liquid nitrogen using a Quantachrome Autosorb-1 system.

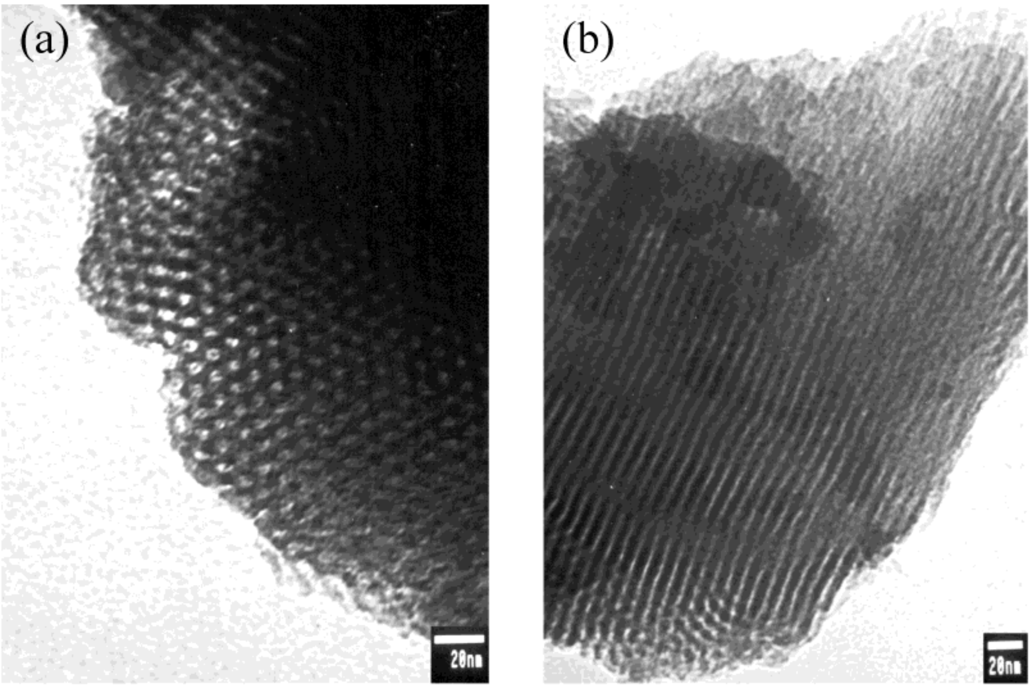

Figure 4. TEM images of solvent-extracted PMO material synthesized with the aid of inorganic salts: (a) in the direction of the pore axis and (b) in the direction perpendicular to the pore axis. The TEM images were acquired on a JEOL JEM-2010 microscope operating at 200 kV.

distribution calculated by the BdB (Broekhoff and de Boer) method[25] for the solvent-extracted PMO sample. The isotherm is of type IV, with a clear H_1-type hysteresis loop at high relative pressure, which is characteristic of large-pore mesoporous materials with 1D cylindrical channels.[20] The narrow BdB pore size distribution reveals uniform mesopores with a maximum at 6.42 nm. The PMO material has a BET surface area of 737 m^2 g^{-1} and a pore volume of 0.88 cm^3 g^{-1}. These data are similar to those of previously reported silica-based SBA-15.[20] The combination of XRD (unit cell parameter) and N_2 adsorption (pore diameter) data gives a pore wall thickness of 6.18 nm in the PMO material. The sharp nitrogen condensation step and the narrow pore size distribution, together with the well-

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resolved XRD peaks, provide strong evidence of the high quality of the PMO material whose structural order is analogous to that observed in silica-based SBA-15.[20] Moreover, the PMO material is very stable in boiling water. For example, when the PMO material with a pore size of 6.42 nm, a BET surface area of 737 $m^2\ g^{-1}$, and a pore volume of 0.88 $cm^3\ g^{-1}$ was treated in boiling water for 6 days, it then showed a pore size of 6.73 nm, a BET surface area of 772 $m^2\ g^{-1}$, and a pore volume of 0.92 $cm^3\ g^{-1}$. The XRD pattern of the solvent-extracted PMO sample was essentially unchanged after hydrothermal treatment (Supplementary Figure 1, see Supporting Information). The high hydrothermal stability of the PMO material can be attributed to the contribution of thick pore walls and hydrophobicity imparted by the organic components in the PMO framework.[2]

Transmission electron microscopy (TEM) analysis confirms the well-ordered hexagonal arrays of 1D mesoporous channels in the PMO material (Figure 4). The distance between two consecutive centers of hexagonal pores is estimated to be 12 ± 0.5 nm. The pore diameter shown in the TEM image is around 6.5 nm, in good agreement with the value determined from the N_2 adsorption measurement.

Other neutral inorganic salts such as KCl, Na_2SO_4, and K_2SO_4 can also be used as auxiliary agents in the synthesis of large-pore hexagonal PMOs with long-range structural order. Thus, inorganic salts might play an important role in the formation of highly ordered PMO materials. PEO/PPO/PEO triblock copolymers form micelles in water with the core of the PPO block surrounded by a shell of hydrated PEO end blocks.[26] The addition of inorganic salts causes dehydration of ethylene oxide units from the hydrated PEO shell remaining adjacent to the PPO core, leading to an increase in the hydrophobicity of the PPO moieties and a reduction in the hydrophilicity of the PEO moieties.[24a] By the counterion-mediated $(S^\circ H^+)(X^-I^+)$ pathway, the low-hydrophilic PEO headgroups in the positively charged surfactant are expected to have increased interactions with the positively charged organosilane species with low hydrophilicity because of the organic components. This enhanced self-assembly interaction can result in long-range-ordered domain of organosilica−surfactant mesostructures.

In conclusion, we have presented a novel route for the first preparation of large-pore hexagonal PMO materials with long-range structural order using triblock copolymer P123 as the template under strongly acidic conditions with the aid of inorganic salts. By this route, other highly ordered PMO materials have been obtained using F127, F68, and L64 as templates. Detailed work will be reported in the future.

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Supporting Information Available: XRD patterns of PMO materials before and after hydrothermal treatment (PDF). This material is available free of charge via the Internet at http://pubs.acs.org.

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