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Mesotunnels on the Silica Wall of Ordered SBA-15 to Generate Three-Dimensional Large-Pore Mesoporous Networks

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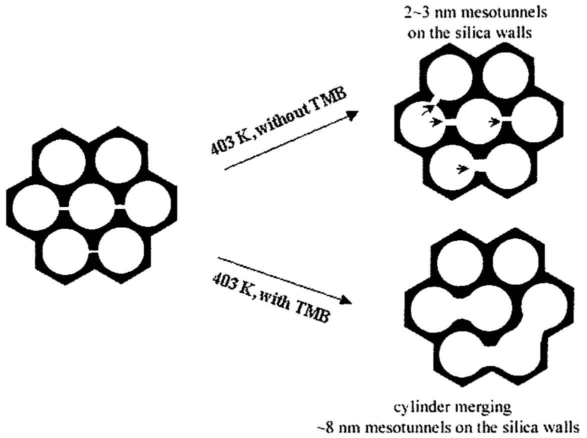
The synthesis of molecular sieves with large pores is of great importance for many applications such as catalysis, separation, adsorption.[1−5] With the recent discovery of hexagonal and cubic large-pore mesoporous materials (SBA-15, SBA-16, FDU-1),[6,7] block copolymers have turned out to be valuable supramolecular templates for the synthesis of ordered large-pore mesoporous materials because of their facile structure-directing ability, low-cost commercial availability, and biodegradability. Compared to three-dimensional (3D) cubic mesoporous materials, 1D pore channels for SBA-15 have the disadvantage in the diffusion and transport of large molecules, which limits their extensive applications in catalysis and separation. As previously reported, when 1,3,5-trimethylbenzene (TMB) is used as an organic cosolvent, only a disordered mesofoam structure (MCF) can be formed.[8] Recently, transmission electron microscopy (TEM) technology has revealed that cubic mesoporous materials such as SBA-6 and SBA-16 have large caged mesostructures, in which small-size windows block the large-pore channels.[9] Therefore, it is challenging to synthesize ordered large-pore mesoporous material structures with 3D mesoporous networks. A great deal of attention has been focused on the complementary micropores on the wall of SBA-15, which is generated from partial occlusion of poly(ethylene oxide) (EO) chains of the copolymers into the silica walls.[10] This type of pore−pore communication may be useful on catalysis and microreactors.[11]

Scheme 1. Schematic Illustration for the Pore Structure of 3D Mesoporous SBA-15.



Here, we report the synthesis of a 3D-modified mesoporous silica SBA-15 with the average mesostructure of hexagonal plane group symmetry *p6mm*. The 3D SBA-15 has many nanosized (2−8 nm) connections/tunnels, which are randomly distributed between the 1D channels. The pore structure is described in Scheme 1. The 3D SBA-15 is produced by a high-temperature hydrothermal process, even involving the introduction of TMB into embryo mesostructured materials.[12]

The ordered hexagonal arrangements with interconnected channels for 3D SBA-15 materials prepared at high hydrothermal temperature (403 K) show well-resolved XRD patterns (Figure 1a, b). The four well-resolved diffraction peaks can be clearly observed and assigned to 100, 110, 200, and 210 reflections similar to those conventional SBA-15 with 2D hexagonal space group (*p6mm*) prepared at low temperature ($\leq$373 K) (Figure 1c). The cell parameter (a = 13.0 nm) for calcined 3D SBA-15 prepared with TMB is much larger than that for calcined conventional SBA-15 (a = 10.4 nm) (Table 1). Scanning electron microscopy (SEM) images (Supporting Information 1) of 3D SBA-15 with TMB show a morphology similar to that of conventional SBA-15, further suggesting that hexagonal ordered mesoscopical packing of the 3D SBA-15 remains. It should be noted that 3D SBA-15 can also be synthesized by a high-temperature process (403 K) without addition of TMB; the cell parameter (10.4 nm) is the same as that for calcined conventional SBA-15 (Table 1).

N_2 sorption measurements for calcined 3D SBA-15 prepared at high temperature (403 K) without and with addition of TMB (Supporting Information 2) show typical IV isotherms with large type H_1 hysteresis loops and relative narrow mesopore distributions at mean size of 10.7 and 17.6 nm, respectively. It is interesting that the mean pore size calculated from the adsorption branch for 3D SBA-15 is much larger than that from desorption branch. However, the mean pore size for conventional SBA-15 (<373 K) has almost the same values calculated from both adsorption and desorption branches (Supporting Information 2),

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(12) In a typical synthesis, 2.0 g (0.4 mmol) of triblock copolymer Pluronic P123 ($EO_{20}PO_{70}EO_{20}$, BASF, MW 5800) was dissolved in 75 mL of 1.6 M HCl at 313 K. Then 4.3 g (21 mmol) of tetraethyl orthosilicate was added into that solution under stirring. After the mixture was stirred for 65 min at 313 K, a cloudy solution was obtained, implying that an embryo mesostructured SBA-15 was formed. The solution was immediately filtered. The obtained precipitate was dispersed in a solution of 1 g of P123 and 75 mL of 1.6 M HCl. To this mixture 2 g of TMB was added. To avoid the leaching out of the copolymer and to emulsify TMB, the solution contaning P123 is necessary. After stirring for 24 h at 313 K, the mixture was transferred into an autoclave and heated at 403 K for 24 h. Solid products were collected by filtration and dried at room temperature in air. The resulted powders were calcined at 823 K for 6 h to obtain mesoporous silica materials.

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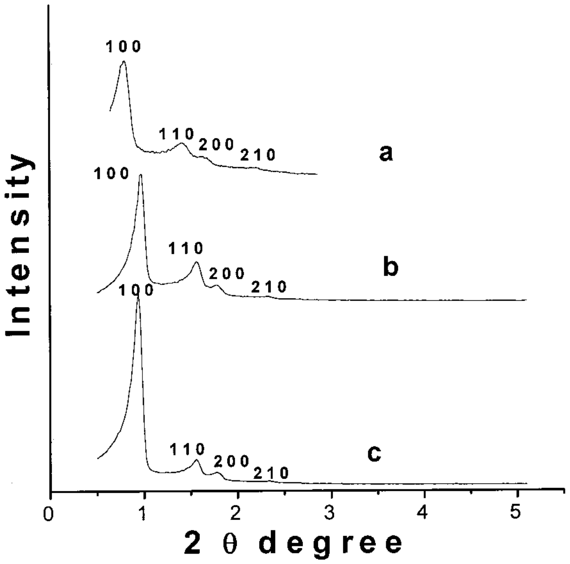

Figure 1. XRD patterns of calcined 3D mesoporous SBA-15 prepared at 403 K (a) with TMB, (b) without TMB, and (c) conventional SBA-15 prepared at 373 K.

Table 1. Physicochemical Data for Mesoporous Silica SBA-15 Samples Prepared under Different Conditions[a]

	hydrothermal temperature (K)	Pa (nm)	Pd (nm)	unit cell parameter (nm)	pore volume (cm^3/g)	BET surface area (m^2/g)
			Without TMB			
S1	313	4.0	4.0	9.5	0.47	448
S2	333	4.9	4.9	9.7	0.51	459
S3	353	8.0	7.6	10.1	1.08	789
S4	373	9.6	8.0	10.4	1.04	521
S5	403	10.7	7.6	10.4	1.11	417
			With TMB			
ST1	373	10.7	9.0	12.0	1.52	767
ST2	393	12.7	9.2	12.5	1.40	538
ST3	403	17.6	12.7	13.0	1.43	324
ST4	413	22.3	12.6	13.0	1.25	254

[a] Pore size Pa and Pd were calculated from nitrogen sorption isotherm based on BJH model from adsorption and desorption branches, respectively.

indicating that the latter has a perfect cylindrical channel while the former does not. Furthermore, the cell parameters for 3D SBA-15 products with or without TMB (13.0 or 10.4 nm, respectively) are smaller than the pore sizes (17.6 or 10.7 nm, respectively). These results imply that 3D SBA-15 products have interconnections of channels.

HREM images (Figure 2) reveal that calcined 3D SBA-15 samples prepared with and without TMB at 403 K have ordered hexagonal pore arrangements and that the center-to-center distances of adjacent channels are 13.0 and 10.2 nm, respectively, in accordance with XRD results. Figure 2a clearly shows some mesotunnels with the size of 2−3 nm randomly distributed on the silica wall of 3D SBA-15. After addition of TMB, the size of the tunnels is approximately equal to the cylindrical channel size (∼8 nm), implying that the hexagonal channels for 3D SBA-15 can be completely interconnected. HREM images along [110] direction (Figure 2, b,d) also show that 3D SBA-15 has modulated gourd-like channels, and some randomly distributed mesotunnels between the main channels are clearly observed.

The formation of disordered mesotunnels may be related to the change of the hydrophobic/hydrophilic property of the block copolymer with temperature. When the hexagonal mesostructure is formed at low temperature, the hydrophilic PEO chains have strong interaction with the silica species and are partially occluded into the silica wall.[10] The PEO chains become hydrophobic and leave the wall at high temperature, and therefore microporous voids are formed. Furthermore, the high-temperature process would result in volume expansion of the block copolymer. The void space would be attacked by the copolymer and become expanded, resulting in formation of the mesotunnels. It is also expected that by addition of TMB the number and size of the mesotunnels increase because of larger volume expansion of the block copolymer caused from TMB.

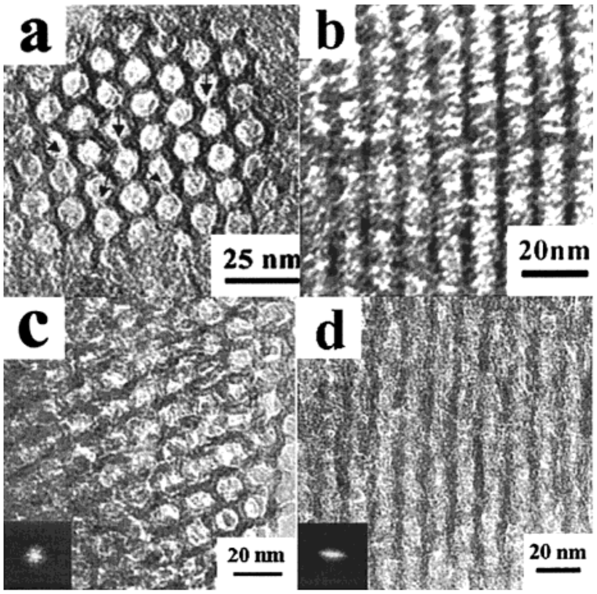

Figure 2. HREM images and electron diffraction patterns of calcined 3D mesoporous SBA-15 prepared at 403 K (a, b) without TMB and (c, d) with TMB. Viewed along the (a, c) [100] and (b, d) [110] directions. The images were taken by a JEM-3010 microscope (JEOL), operated at 300 kV.

The time to add organic cosolvent is a key factor for the formation of 3D SBA-15. To avoid the formation of disordered MCFs, TMB should be added after the "embryo" mesostructure is formed. When SBA-15 mesostructure is completely formed after a long reaction time, the addition of TMB has no effect on the size of the mesotunnels. The best time for the addition of TMB is 65 min after the reaction starts. The hydrothermal temperature also has a great effect on the size of the mesopores and mesotunnels (Table 1). The mesotunnel size increases with the temperature. Other organic cosolvents, such as *n*-butanol and *n*-hexane can also be used as the cosolvents for formation of 3D SBA-15. When the same amount of *n*-butanol or *n*-hexane cosolvent (in molarity) as TMB is used, the size of the mesotunnels is smaller than that for mesotunnels from TMB.

In summary, a modified mesoporous SBA-15 with interconnecting 3D large-pore networks has been synthesized by high-temperature hydrothermal treatment even introducing TMB into embryo mesostructures. Although full control of the mesotunnel size maybe difficult which may limit the use of the described approach, improved pore−pore communication through the mesotunnels on the silica wall in the 3D SBA-15 would facilitate diffusion and transport of molecules between the channels.

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Supporting Information Available: Nitrogen sorption isotherm and pore size distribution curves of 3D SBA-15 samples; SEM images of conventional and 3D SBA-15 (PDF). This material is available free of charge via the Internet at http://pubs.acs.org.

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