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Organization of Phenylene-Bridged Hybrid Mesoporous Silisesquioxane with a Crystal-like Pore Wall from a Precursor with Nonlinear Symmetry

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Synthesis of a highly ordered, two-dimensional hexagonal ($P6mm$) mesoporous benzene−silica composite having molecular-scale periodicity in the pore wall from the self-assembly of nonlinear symmetric 1,3-bis(triethoxysilyl)benzene and octadecyltrimethylammonium surfactant is described. The synthesis of hybrid organosilicas with mesoscopically ordered pores and molecularly ordered pore walls is not confined only to the symmetrically linear bridged organosilane precursors such as 1,4-bis(triethoxysilyl)benzene but a similar arrangement can also be formed by using nonlinear symmetric bridged organosilane precursors.

Introduction

Periodic mesoporous silsesquioxanes with integral organic functionality derived from bridged organosilanes [$(R'O)_3Si-R-Si(OR')_3$] in the presence of surfactant have a homogeneous distribution of organic fragments and silica moieties within the framework.[1−5] The materials have uniform pores, higher stability, and control on morphologies and potential application in a variety of areas, including optoelectronics, sensing, enantioselective separation, catalysis, and probably data storage.[6−8] The main objective of contemporary hybrid mesoporous material synthesis is to control the geometry of a material at the molecular level of design. Changing the nature of the organic molecule in the hybrid mesoporous silsesquioxanes are widely published[1−8] and offer a wide range of opportunities to control the surface properties. Although a number of bridged organosilane precursors have already been successfully used, thus far reports on the synthesis of hybrid mesoporous silsesquioxanes using more complex molecular building block monomers are very limited.[9−20]

Recently, we have described the surfactant-mediated synthesis of phenylene-silica hybrid mesoporous materials with precise control of the nanoarchitecture possessing well-oriented phenylene and silica fragments from 1,4-bis(triethoxysilyl)benzene.[21] The material has a hexagonal array of mesopores as well as crystal-like pore walls exhibiting structural periodicity along the channel direction. This was the first synthesis of an ordered mesoporous material possessing a *crystal-like periodic pore wall structure.* The addition of *crystallinity* to the pore wall of mesoporous materials has long been sought after and is a most important development in this research field. Very recently, we have also reported a synthesis of an ordered mesoporous 4,4′ biphenylene-bridged silsesquioxane with a crystal-like pore wall[22] similar to those reported for 1,4-phenylene-bridged mesoporous organosilica.[21] These organic bridged mesoporous materials with crystal-like periodic pore walls structures have a great advantage to be used for highly selective and active catalysis. The sulfonated mesoporous hybrid material[21] and sulfonic acid-functionalized mesoporous benzene−silica hybrid material[23] could be

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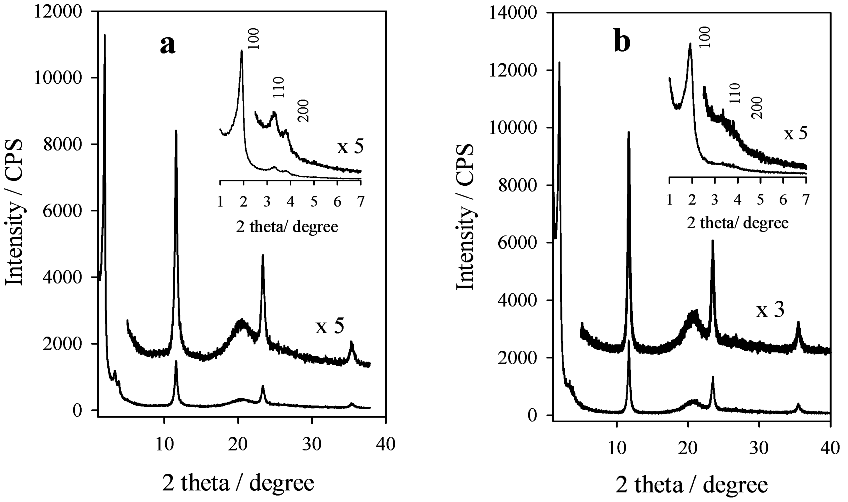
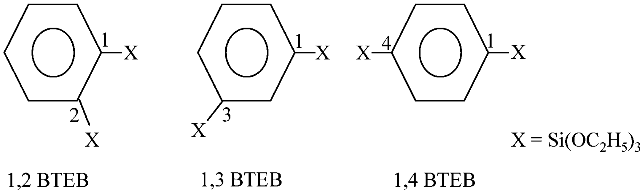


Figure 1. Powder X-ray diffraction patterns of 1,3-benzene-bridged hybrid mesoporous materials: (a) surfactant-free; (b) as-synthesized.

Scheme 1. Description of the Different Geometries of the Benzene-Bridged Silane Precursors



a potential solid acid catalyst in liquid- and gas-phase reactions as well as an electrolyte for fuel cells.

However, for further advancements in the research concerning the synthesis of hybrid organic–inorganic mesoporous materials with crystal-like pore walls, exploration of possible approaches to designing new bridged organosilane precursors by inserting organic molecules of different geometry as an integral part of the chemical connectivity of the material is still needed. Also, altering the symmetry of the rigid organosilane precursor could be useful from the standpoint of a possible alteration of certain fundamental properties of the resulting mesoporous silsesquioxane materials such as controlled extensive cross-linking. For example, the 1,4-bis(triethoxysilyl)benzene (1,4 BTEB) has a linear rigid rodlike geometry whereas the other derivatives, 1,3-bis(triethoxysilyl)benzene (1,3 BTEB) and 1,2-bis-(triethoxysilyl)benzene (1,2 BTEB) organosilica precursors were the nonlinear symmetric structures, that is, bent geometry and nonlinear asymmetric structures, respectively (Scheme 1). Recently, Kuroki et al. reported the synthesis of mesoporous materials from 1,3 BTEB in addition to 1,3,5-tris(triethoxysilyl)benzene under acidic conditions. However, the materials had no molecular-scale periodicity in the pore walls because the acidic conditions would not be appropriate to orient phenylene groups.[24] The purpose of this communication is to demonstrate that the synthesis of hybrid organosilicas with mesoscopically ordered pores and molecularly ordered pore walls is not confined only to the symmetrically linear bridged organosilica precursors but that a similar arrangement can also be formed by using nonlinear symmetric bridged organosilica precursors. Therefore, we describe here a totally new synthesis and characterization of a highly ordered, two-dimensional hexagonal (*P*6*mm*) mesoporous benzene–silica composite with molecular-scale periodicity derived from the self-assembly of 1,3 BTEB and octadecyltrimethylammonium (C$_{18}$TMACl) surfactant under basic conditions.

Preparation of Mesoporous 1,3-Phenylene–Silica Material

In a typical synthesis, in a round-bottom flask the C$_{18}$TMACl surfactant (1.7 g, 4.9 mmol) was first dissolved in 60 g of distilled water and mixed with 5.6 mL of 3 N aqueous sodium hydroxide (NaOH, 16.8 mmol). Then 2.1 g of 1,3 BTEB (5.2 mmol, supplied by Azmax, Japan) was slowly added (about 5 min) to the resulting solution under continuous stirring at ambient temperature (~25 °C) and stirred vigorously until the precursor was completely dispersed in the aqueous medium. The stirring of the solution was continued for another 24 h and then it was finally refluxed at 92 ± 3 °C for 24 h under static conditions. The precipitate obtained was filtered and washed thoroughly with a copious amount (>500 mL) of deionized water and dried under evacuation at ambient temperature. The surfactant was removed by extracting 1.0 g of an as-synthesized material in 200 mL of ethanol with 3.0 g of 36% HCl aqueous solution at 60 °C for 6 h and then the solvent extraction process was repeated again for complete removal of the surfactant.

Results and Discussion

The powder X-ray diffraction (PXRD) profiles of a surfactant-free sample exhibited three clear diffraction peaks in the lower angle region ($2\theta < 5°$), indicating a high degree of mesostructural ordering (Figure 1). The material had a two-dimensional hexagonal (*P*6*mm*) phase characterized by (100), (110), and (200) reflections with d spacings of 46.0, 26.6, and 23.1 Å, respectively.

In addition to the PXRD results, both the transmission electron microscope (TEM) images and the related electron diffraction pattern (EDP) confirm the clear hexagonal arrangement of the well-defined mesoporous arrays with uniform pore dimensions. The TEM picture given in Figure 2 is more than 99% representative of the materials. The lattice constants ($a_o = 2d_{100}/\sqrt{3}$) of the as-synthesized and surfactant-free materials were 54.0 and 53.1 Å, respectively. The reduction in the unit

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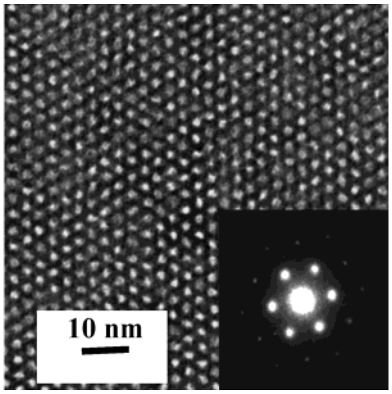

Figure 2. Transmission electron microscope image and electron diffraction pattern (inset) of surfactant-free 1,3-benzene-bridged hybrid mesoporous material.

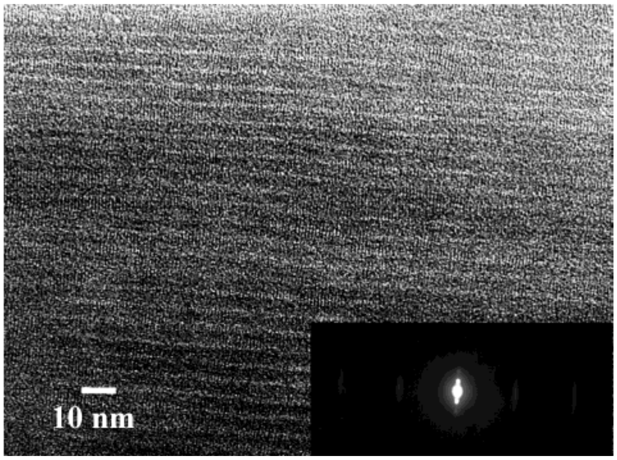

Figure 3. Transmission electron microscope image and electron diffraction pattern (inset) perpendicular to channels showing many lattice fringes in the pore walls with a spacing of 7.6 Å.

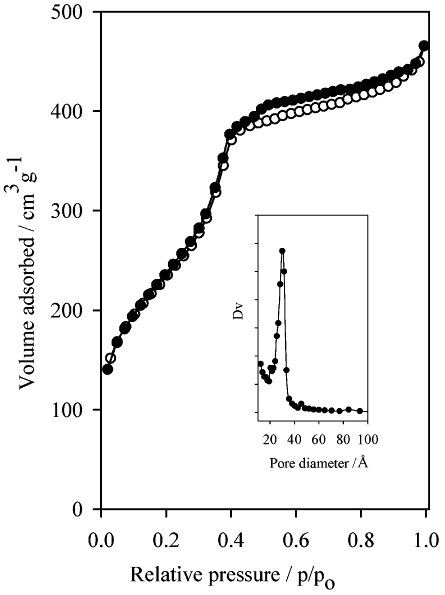

Figure 4. Nitrogen adsorption (○)−desorption (●) isotherm and BJH pore size distribution plot (inset) for the surfactant-free 1,3-benzene-bridged hybrid mesoporous material.

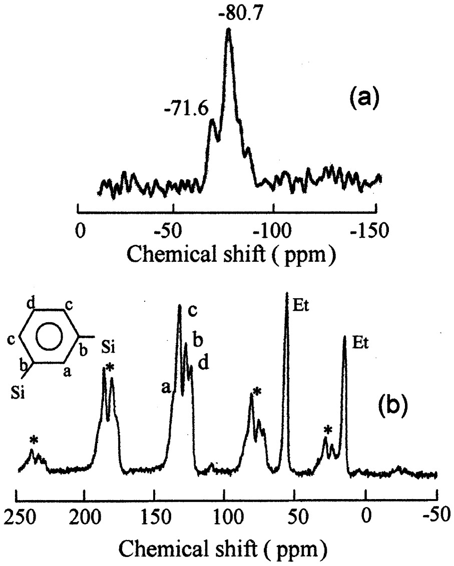

Figure 5. (a) ^{29}Si MAS NMR and (b) ^{13}C CP MAS NMR spectra of the surfactant-free 1,3-benzene-bridged hybrid mesoporous material.

cell dimensions upon surfactant removal was less than 2%. The PXRD patterns also displayed additional diffraction peaks in the range of 2θ =10−40° at the d spacings of 7.6, 3.7, and 2.5 Å, confirming the periodic structure with a molecular scale of 7.6 Å.

Further, the existence of molecular-scale periodicity in the pore wall was confirmed clearly by the many lattice fringes stacked along the channel axes in the TEM image shown in Figure 3. An electron diffraction spot related to the observed periodicity (7.6 Å) as well as its higher order diffractions was noticed perpendicular to the diffraction spot corresponding to the mesoscopic order.

The nitrogen adsorption isotherm (Figure 4) exhibits clear features of the pronounced capillary condensation steps as reported earlier.[25] However, a small adsorption−desorption hysteresis related to capillary condensation in large mesopores existing in the interparticle space was observed at relative pressures above ~0.45. The pore diameter (PD) calculated from the adsorption branch by the BJH (Barrett−Joyner−Halenda) and NLDFT (nonlocal density functional theory) method were 30 and 41 Å, respectively. The NLDFT method for pore size distribution analysis was shown to provide reliable results for mesoporous systems.[25] The BET (Brunauer−Emmett−Teller) surface area and the primary mesopore volume were 861 m^2 g^{-1} and 0.72 cm^3 g^{-1}, respectively. The pore wall thickness (a_o-PD$_{DFT}$) was found to be 12 Å. These results revealed that 1,3 BTEB precursor can also form a highly ordered mesoporous structure with crystal-like pore walls after interacting with a surfactant and such behavior is not confined only to the symmetrically linear bridged organosilane precursors.[21,22]

The ^{29}Si MAS NMR spectra of surfactant-free 1,3-benzene-bridged polysilsesquioxane exhibited two resonances (Figure 5a). The first resonance (−80.7 ppm) was assigned to T^3[SiC(OSi)$_3$], a fully condensed silicon with three siloxane bonds and the other (−71.6 ppm) was attributed to T^2[SiC(OH)(OSi)$_2$], a partially condensed silica species with one hydroxyl group.[16] Virtually, no signals due to SiO$_4$ species (Si sites attached to four

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oxygen atom Q^n, $n = 1-4$) between −98 and −111 ppm were detected, indicating essentially no evidence for Si−C bond cleavage during the sol−gel processing and during synthesis. The T^3/T^2 intensity ratio of 2.42 suggests a high degree of framework cross-linking.[27] The ^{13}C CP-MAS NMR spectrum (Figure 5b) displays four aromatic resonances in accordance with the four different kinds of carbons of the 1,3-substituted benzene. The signal at 130.8 ppm is assignable to the substituted carbons on the benzene ring (carbons **b**), while the other resonances at 139.7, 135.6, and 126.3 ppm are due to the carbons attached to hydrogen, that is, unsubstituted carbons, (carbon **a**, carbon **c**, and carbon **d**, respectively), whereas similar groups of the resonances marked by an asterisk (*) are the spinning sidebands. The two sharp resonances observed at ~58 and ~16 ppm are due to ethoxy groups bonded to silicon ($Si-O-C_2H_5$), which are formed by ethanolysis of the surface silanols (Si−OH) during the extraction of surfactant with ethanol solution. In addition, virtually no signal was observed at ~30 ppm, indicating that the surfactant was completely removed from the material during the extraction process. The results evidently indicate that the pore wall of the mesoporous 1,3-benzene-bridged polysilsesquioxanes are composed of a covalently bonded network comprised of 1,3-substituted $O_{1.5}Si-C_6H_4-SiO_{1.5}$ units.

The thermo-gravimetric analysis performed in air as well as under a nitrogen stream indicates that the material has high thermal stability and the phenylene species stay in the mesoporous network up to 500 °C, similar to the benzene−silica mesoporous material derived from 1,4 BTEB precursor.[21] The lack of any substantial weight loss in the 200−400 °C range indicated that the surfactant was successfully removed via solvent extraction (Figure 6).

Figure 7 displays a structural model of the pore wall region of the mesoporous 1,3-benzene−silica that is constructed on the basis of a well-defined structure of crystalline 1,4-bis(trihydroxysilyl)benzene[28] as well as a lamellar arrangement of 1,4-phenylene-bridged mesoporous materials.[21] The framework energy of the covalently bonded periodic lattice was minimized using a molecular mechanism simulation, which resulted in an interlayer spacing of 7.6 Å. This value is in good agreement with the 7.6-Å periodicity observed by PXRD and TEM. This clearly supports the validity of the proposed lamellar structure model in the wall, where the hydrophobic and hydrophilic interactions direct the self-assembly of the 1,3 BTEB precursor with a lamellar arrangement in the wall. For comparison a simulated structural model of the pore wall region of the mesoporous 1,4-benzene−silica is also shown in Figure 7.

Interestingly, both experimental and simulation results show that there is very little difference in the molecular-scale periodicities of the mesoporous materials synthesized using the 1,4 BTEB[21] and the 1,3 BTEB precursors, although they have different molecular geometry. The benzene moieties in the framework are tilted to a certain angle for mesoporous benzene−silicas. This in part reduces the difference in the interlayer distance for the 1,3 and 1,4 system. Further, the simulation results also reveal that the Si−O−Si bond angles of the silica layers and the C−C bond length of the phenylene groups are somewhat different for each system, which also contribute to the matching of the molecular-scale periodicity of each material.

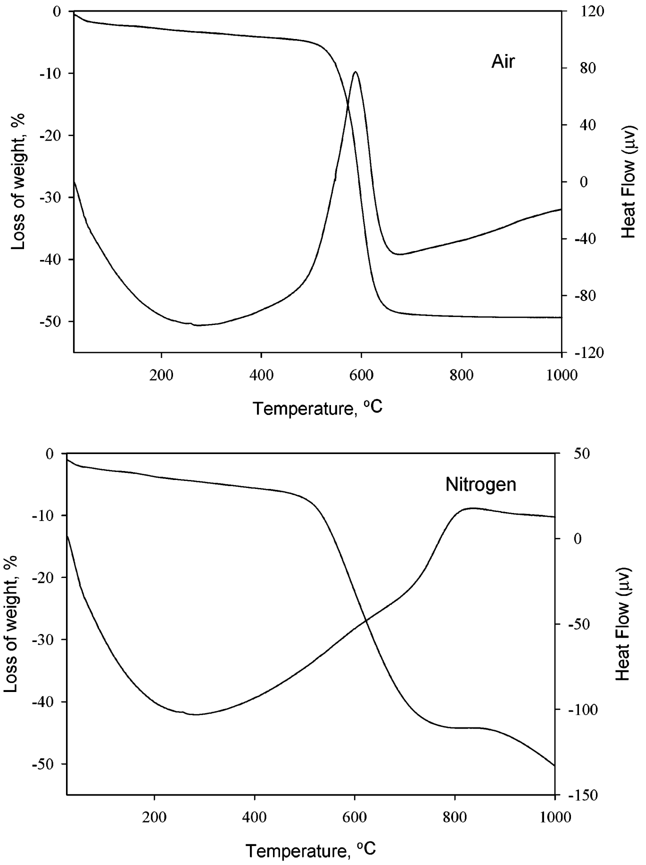

Figure 6. Thermogravimetric analysis of the surfactant-free 1,3-benzene-bridged hybrid mesoporous material under an air and nitrogen atmosphere.

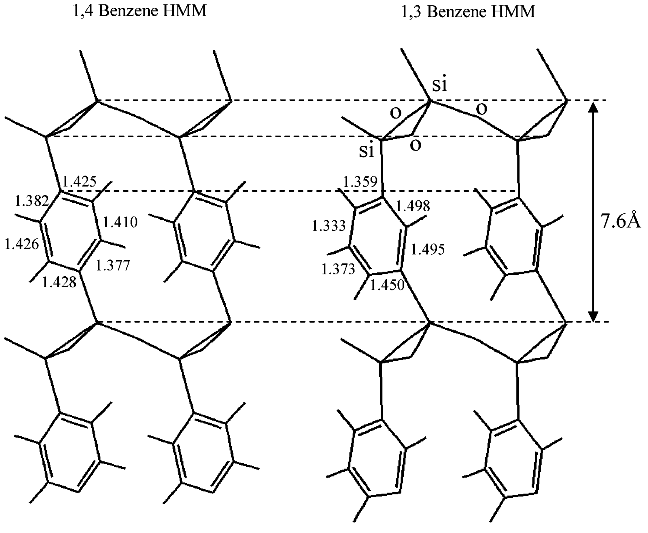

Figure 7. Simulated structure models of benzene-bridged mesoporous material derived from precursors of different geometries.

The 1,3-substituted benzene−silica has the advantage to be modified with functional groups easier than the 1,4-substituted benzene−silica system due to the high

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activity of the 4,6 carbons (carbons **c**) of benzene and low steric hindrance. Especially, electrophilic reactions such as the sulfonation of benzene are favored for the 1,3-substituted benzene bridged mesoporous silsesquioxanes.

Conclusions

In summary, we have successfully demonstrated that benzene-bridged hybrid mesoporous materials can also be formed with a bridging group having a nonlinear geometry. The results also revealed that the resultant material is a highly ordered mesophase with a hexagonal array and crystal-like pore walls that exhibit structural periodicity along the channel direction and demonstrate that such a crystalline-type framework that is ordered on both the molecular and nanoscopic levels is not limited only to the symmetrically linear organosilane precursors. The concept of using nonlinear symmetric organic groups in the framework provides flexibility to incorporate other novel functionalities such as sulfonic acid groups in the matrix for advanced applications in catalysis and particularly can serve as a proton carrier in an electrolyte for the fuel cells. Experiments are underway to completely describe and compare the formation path of mesophases from the symmetrically linear and nonlinear symmetric bridged organosilane precursors and their promising applications in mentioned selective fields.

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