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Self-Assembly of Biphenylene-Bridged Hybrid Mesoporous Solid with Molecular-Scale Periodicity in the Pore Walls

Mahendra P. Kapoor,† Qihua Yang,‡ and Shinji Inagaki*,†

Contribution from Toyota Central R&D Laboratories Inc., Nagakute, Aichi 480−1192 and CREST, JST, Japan

Received October 24, 2002

The chemistry of hybrid materials obtained from organic-bridged silane precursors is very successful in opening new routes for synthesis of hybrid mesoporous materials. Several reports are available on $-CH_2-$, $-CH_2-CH_2-$, $-CH{=}CH-$, $-C_6H_4-$, and thiophene-bridged mesoporous polysilsesquioxanes of different morphologies.[1−3] Remarkable advances have already been achieved in the fabrication of templated sol−gel materials (so-called hybrid mesoporous polysilsesquioxanes) with desirable morphology. This includes thin films, particulate materials, and patterns printed on solid substrates by employing pen lithography and ink-jet printing.[4] However, the amorphous pore walls of these materials could hinder their utility for various potential applications. Recently, we reported the surfactant-mediated synthesis of benzene−silica hybrid materials with precise control of the nanoarchitecture possessing well-oriented building blocks of organic and inorganic fragments.[5] The material showed the hexagonal array of mesopores and crystal-like pore walls exhibiting structural periodicity in the wall along the channel direction with a spacing of 7.6 Å. The sulfonated derivatives of mesoporous phenylene-bridged silsesquioxane can be use as solid acid catalysts in several liquid and gas-phase reactions as well as solid electrolytes for fuel cells.[5,6] It will be interesting to see whether this unique rearrangement in the wall can be generalized for hybrid materials made of other combinations of organic and inorganic units. The work by Shea et al. describes the detailed synthesis of biphenyl containing organic−inorganic silica gel polymers by hydrolysis and polycondensation of organosilane precursors.[7] However, the gels were frequently considered as amorphous material with no preferential orientation of the molecular units (isotropic orientation), but the materials have considerably high surface areas. Later, the controlled anisotropic organization of nanostructured biphenyl−silica hybrid materials using 4,4′bis(trimethoxysilyl)biphenyl precursor was demonstrated by its bifringence properties.[8,9] Here we report the successful synthesis of an ordered mesoporous biphenylene-bridged silsesquioxane with crystal-like pore wall similar to those recently reported for phenylene-bridged silsesquioxane.

The synthesis of mesoporous biphenylene-bridged polysilsesquioxane was accomplished using 4,4′bis(triethoxysilyl)biphenyl $[(C_2H_5O)_3Si-(C_6H_4)_2-Si(OC_2H_5)_3]$ precursor in the basic medium in the presence of octadecyltrimethylammonium chloride (C_{18}-TMACl) surfactant. To obtain a highly ordered material it is important to control both the reaction conditions and the initial reactant ratio. In a typical procedure, the 4,4′bis(triethoxysilyl)-biphenyl (2.5 mmol) was added to a mixture of C_{18}TMACl surfactant (3.2 mmol), 6 N sodium hydroxide (30.4 mmol), and distilled water (3.3 mol) under vigorous stirring at ambient temperature. The suspension was stirred for another 20 h. Heating the suspension at ~95 °C for 22 h under static conditions resulted in a precipitate that was filtered and washed with deionized water, thus affording synthesized biphenylene-bridged hybrid mesoporous materials. The surfactant was removed by extracting the 0.75 g of as-made material in 150 mL of ethanol with 3.1 g of 2 M HCl aqueous solutions at ambient temperature for 8 h.

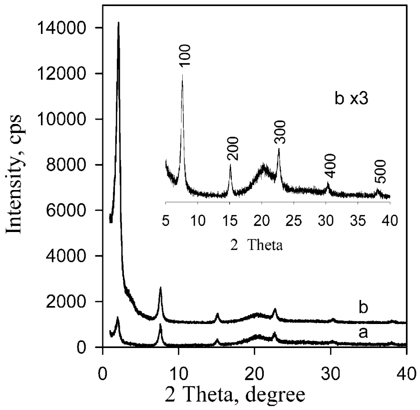

Figure 1. Powder X-ray diffraction profiles of mesoporous biphenylene-bridged polysilsesquioxane. (a) As-made material containing surfactants, (b) surfactant-free material by solvent extraction.

The powder X-ray diffraction (PXRD) profile of the as-synthesized sample (Figure 1) exhibited a peak at $2\theta =$ ca.2.0° (d spacing of 43.9 Å), whose intensity increased significantly upon surfactant extraction (d spacing of 41.8 Å). This suggests that the biphenylene-bridged silsesquioxane has a mesoscopically ordered structure. In addition to the lower angle of diffraction, the PXRD profiles at medium scattering angles ($2\theta = 6-40°$) also showed another five peaks at d spacings of 11.6, 5.9, 3.9, 2.9, and 2.4 Å. The d spacings were the same for as-synthesized and surfactant-free materials. The peaks are assigned as a periodicity with a spacing of 11.6 Å and higher-order reflections (Figure 1). A transmission electron microscope image (Figure 2a) reveals many lattice fringes with a spacing of 11.6 Å on the pore walls of mesoporous material with a 2D hexagonal structure. The results indicate that the biphenylene-bridged silsesquioxane has a lamellar structure in the pore walls in addition to meso-scale periodicity similar to the phenylene-bridged mesoporous material.[5] The periodicity 11.6 Å is larger than the periodicity 7.6 Å observed in phenylene-bridged mesoporous material. This is due to the larger length of biphenylene compared to that of the phenylene group. The BET (Brunauer−Emmett−Teller) surface area, pore diameter (DFT), and pore volume, determined from adsorption branch of nitrogen isotherms, were 869 $m^2\ g^{-1}$, 35.4 Å, and 1.15 $cm^3\ g^{-1}$, respectively (Figure 2b).

Solid-state ^{29}Si and ^{13}C magic angle spinning nuclear magnetic resonance (MAS NMR) spectra of biphenylene-bridged mesoporous

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* To whom correspondence should be addressed. E-mail: inagaki@mosk.tytlabs.co.jp.

† Toyota Central R&D Laboratories Inc.

‡ CREST, JST.

10.1021/ja0290678 CCC: $22.00

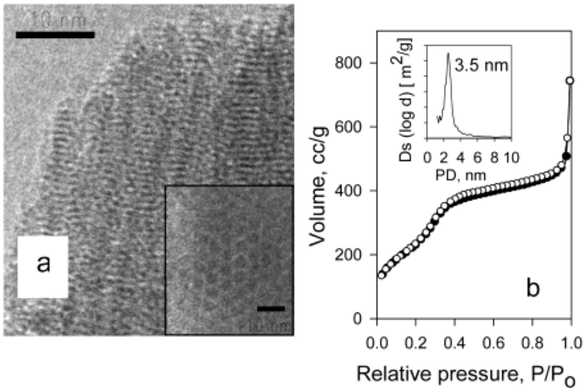

Figure 2. (a) Transmission electron microscope image of surfactant-free mesoporous biphenylene-bridged silsesquioxane. Lattice fringes with a spacing of 11.6 Å on the pore walls and hexagonal arrangement of uniform mesopores (inset) are observed. (b) Nitrogen adsorption (●) -desorption (○) isotherms and pore size distribution plots (inset) for surfactant-free mesoporous biphenylene-bridged silsesquioxane.

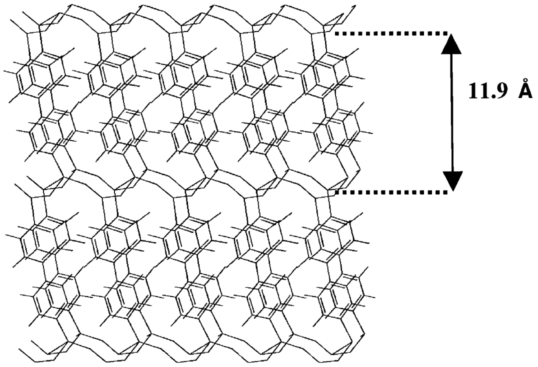

Figure 3. Structural model for mesoporous biphenylene-bridged hybrid mesoporous solid. Image of layered arrangement of $O_{1.5}Si-(C_6H_4)_2-SiO_{1.5}$ units in the pore wall. The structure was optimized by minimizing the three-dimensional periodic lattice using the force field COMPASS.

material clearly showed that covalently bonded network-comprised $O_{1.5}Si-(C_6H_4)_2-SiO_{1.5}$ units exist in the material and that the carbon−silica bond of the biphenylene organosilane precursor remained intact during synthesis and surfactant removal. The intense signals at −65, −72, and −91 ppm observed in the ^{29}Si MAS NMR spectrum (Figure S-1a, see Supporting Information) are of polysilsesquioxane with one siloxane bond and are denoted as T^1, those with two siloxane bonds are denoted as T^2, and those with three siloxane bond are denoted as T^3.[7] The ^{13}C MAS NMR spectrum (Figure S-1b; Supporting Information) displays the four aromatic resonances with two intense signals at 125.6 and 135.1 ppm, which can be assigned to carbons (positions 2 and 3 in Figure S-1b) bonded to hydrogen that is, unsubstituted carbons. The remaining two weak signals at 130.3 and 140.6 ppm are of the substituted carbons (positions 4 and 1 in Figure S-1b) on the biphenyl. The similar classification of ^{29}Si and ^{13}C MAS NMR signals were reported earlier for the amorphous biphenylene-bridged polycondensed silica gels with somewhat different chemical shifts.[7]

Figure 3 displays a structural model of the pore wall region of the mesoporous biphenyl−silica, which is constructed on the basis of the lamellar structure of the phenylene-bridged mesoporous materials.[5] Minimizing the framework energy of the covalently bonded periodic lattice using a molecular mechanism simulation resulted in the interlayer spacings of 11.9 Å. The periodicity 11.9 Å is in good agreement with the 11.6 Å periodicity observed by PXRD, indicating the validity of the lamellar structure model in the wall. The organization of lamellar structure for biphenylene-bridged silane precursor is also suggested in previous work on the structural analysis of a molecular crystal of 4,4′bis (trihydroxysilyl)-biphenyl.[10] The trihydroxysilyl molecules, a triol analogue of the biphenylene-bridged precursor, are arranged in a head-to-tail manner to form a lamellar structure in the molecular crystal.[10] Thus, it is reasonable that the biphenylene-bridged precursor molecules are organized as a lamellar structure in the pore wall region of mesoporous material. Hydrophobic and hydrophilic interactions direct the self-assembly of the biphenylene-bridged precursor with a lamellar arrangement in the wall. The thermogravimetric analysis, performed in air as well as in a nitrogen environment, indicate that the biphenyl species stays in the mesoporous network up to 500 °C (Figure S-2).

In summary, these results clearly indicate that in the mesoporous biphenylene-bridged polysilsesquioxanes molecular-scale periodicity exists in the whole region of the pore wall that is composed of a hydrophilic silicate layer and a hydrophobic biphenylene layer arrayed alternatively. We have demonstrated that the novel hierarchically ordered structure with both meso- and molecular-scale periodicity could be observed for not only phenylene but also for the biphenylene-bridged mesoporous systems. As better and more diverse preparation of the hierarchical porous structures becomes available, an increasing number of applications are highly anticipated. Biphenylene-bridged mesoporous polysilsesquioxane is more interesting because it has an equimolar ratio of phenylene to silica. This provides the possibility for a relatively large number of functional groups to be incorporated on the material surface, which imparts better catalytic applications compared to benzene−silica hybrid material.

Acknowledgment. We thank N. Suzuki of Toyota CRDL Inc. for TEM observation.

Supporting Information Available: Figures of ^{29}Si and ^{13}C NMR and thermogravimetrical analyses of the biphenylene-bridged mesoporous materials (PDF). This material is available free of charge via the Internet at http://pubs.acs.org.

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JA0290678