Biphenylene Bridged Bifunctional Hybrid Mesoporous Silsesquioxanes with Sulfonic Acid Functionalities and Crystalline Pore Walls

Mahendra P. Kapoor, Qihua Yang,[†] Yasutomo Goto, and Shinji Inagaki*
Toyota Central R&D Labs. Inc., 41-1 Yokomichi, Nagakute, Aichi 480-1192
[†]*CREST, Japan Science and Technology (JST)*

(Received June 30, 2003; CL-030580)

The first synthesis of highly hydrophobic bifunctional biphenylene bridged hybrid mesoporous silsesquioxane with sulfonic acid functionalities and crystalline pore walls is reported.

Hybrid organic-inorganic mesoporous silsequioxanes with homogeneously distributed organic molecule as an integral part of the chemical connectivity was first reported in 1999.[1–3] Since its discovery, several approaches and strategies for the synthesis of hybrid mesoporous materials with unique surface adsorption properties for their great potential in separation technology and catalysis are reported.[4–7] Earlier, we have reported the synthesis of the periodic mesoporous benzene-silica with lamellar pore wall structure.[8] In the subsequent report, we have also described the synthesis of biphenylene bridged silsesquioxanes with molecular scale periodicity in the pore wall.[9] The alternately arranged organic moieties and SiO_2 layer will be of great advantages for the enhanced activity for selective catalysis. Additionally, it is very interesting to synthesize sulfuric acid-functionalized mesoporous organosilicas having both hydrophobic and acidic functionalities because it would facilitate diffusion of reactants and products during acid-functionalized catalytic reactions. Thus, later we described the synthesis of sulfuric acid-functionalized benzene-silica[10] by co-condensation of 1,4-bis(triethoxysilyl) benzene and 3-mercaptopropyl trimethoxysilane using a cationic surfactant template in basic medium followed by oxidation using HNO_3. The biphenylene bridged mesoporous silsesquioxane system is rather interesting because it has an equimolar ratio of phenylene to silica, which provides a possibility to exert an enhanced hydrophobic character in the resulted mesoporous silsesquioxane. In the present communication, we describe the first synthesis of highly hydrophobic biphenylene bridged bifunctional hybrid mesoporous silsesquioxane with sulfonic acid functionalities and crystalline pore walls.

Materials were synthesized by co-condensation of 4,4′-bis(triethoxysilyl)biphenyl [BTEBP; $(EtO)_3Si\text{-}(C_6H_4)_2\text{-}Si(EtO)_3$] precursor and 3-mercaptopropyltrimethoxysilane [MPTMS; $(MeO)_3Si\text{-}CH_2CH_2CH_2SH$] in a basic medium and cationic surfactant followed by an oxidation treatment as described in Ref. 10. Typically, the BTEBP plus MPTMS (5.6 mmol) was slowly added to a mixture of octadecyltrimethylammonium chloride ($C_{18}TMACl$) surfactant (6.43 mmol), 6 M sodium hydroxide (36 mmol) and distilled water (4.44 mol) under vigorous stirring at ambient temperature. The suspension was stirred for 18 h and aged under reflux at 95 °C for another 20 h. The powder materials were recovered after filtration, repeated washing with distilled water and drying under vacuum. Materials were prepared with varying ratio of BTEBP and MPTMS. The molar composition of initial gel was adjusted corresponding to MPTMS molar concentrations of 15, 30, 50, and 70% and materials are denoted as M15, M30, M50, and M70, respectively. Surfactant free mesoporous materials were obtained after extraction with HCl/EtOH for 8 h at ambient temperature as described elsewhere.[9] The oxidation of –SH group in the bifunctional mesoporous silica was performed with concentrated nitric acid under ambient conditions for 24 h.[10]

The powder X-ray diffraction profiles of as synthesized and surfactant free bifunctional mesoporous silsesquioxanes incorporating varied amount of MPTMS before and after oxidation are shown in Figure 1. Similar to biphenylene bridged hybrid silsesquioxane reported earlier[9] the bifunctional materials exhibit a strong d_{100} reflection with 2D hexagonal structure. Additionally the PXRD profiles at medium scattering angles ($2\theta = 6$–$40°$) also showed another five peaks at d spacing of 11.9, 5.9, 3.9, 2.9, and 2.4 Å. The d-spacings were the same for as synthesized and surfactant free materials before and after oxidation. These diffractions are assigned as a molecular scale periodicity with a spacing of 11.9 Å and higher order reflections.[9] Although the intensity of the d_{100} reflection gradually decreases with an increase in MPTMS content, the molecular scale periodicity in the pore wall remains intact for the materials containing even 70 mol% MPTMS content in the initial reaction mixture.

In the porosity measurement (Table 1) all bifunctional hybrid mesoporous materials exhibited clear capillary condensation step with type IV characteristic, qualitatively consistent with those previously obtained for the corresponding biphenylene bridged hybrid mesoporous materials. A variation was also observed with increasing MPTMS content.

The ^{29}Si MAS-NMR spectra of surfactant free materials before and after oxidation showed the two set of T_n resonances (T_2 and T_3, T_2' and T_3') assignable to two different silicon moieties covalently bonded to carbon atoms derived from bridged and terminally bonded silicon atoms (Figure 2). The resonances

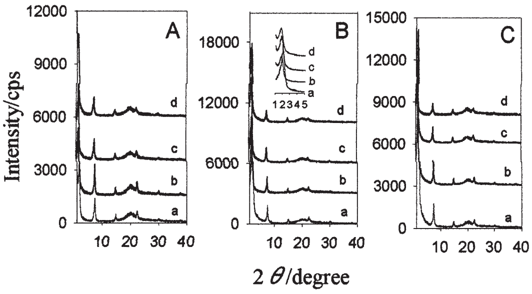

Figure 1. PXRD patterns of A) as synthesized, B) surfactant free, and C) oxidized bifunctional hybrid mesoporous materials. a) M15, b) M30, c) M50, and d) M70.

Table 1. Textural properties of bifunctional hybrid materials

Material	S_{BET} m^2/g	PD$_{BJH}$ Å	PV cc/g	^{a}Lattice Spacing, Å
M15-Ext	862	24.5	0.56	43.5
M30-Ext	832	22.6	0.48	48.8
M50-Ext	848	21.3	0.46	48.5
M70-Ext	775	19.4	0.45	50.2

^{a}Lattice spacings $(a_o) = 2d_{100}/\sqrt{3}$.

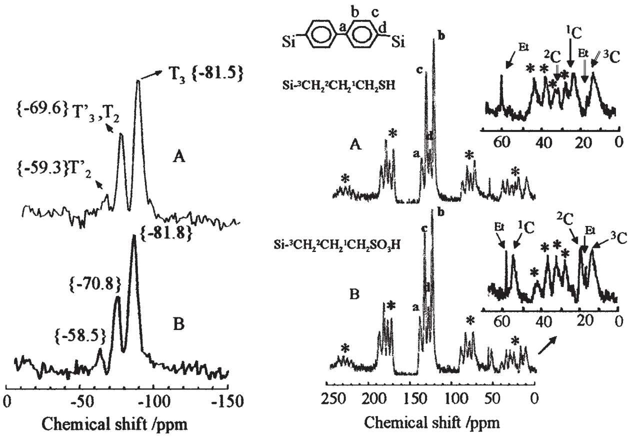

Figure 2. ^{29}Si-NMR spectra (Left) and ^{13}C CP-NMR spectra (Right) of hybrid bifunctional mesoporous materials (A) after solvent extraction (B) after oxidation.

are due to SiC(OH)(OSi)$_2$ and SiC(OSi)$_3$ of the silica attached with terminal mercaptopropyl and bridging biphenylene groups.[8–10] No resonances for the Q$_n$ sites were observed. This clearly indicated that all the Si–C bonds of the material remain uncleaved under the conditions employed. Also, the chemical shifts were almost the same for before and after oxidation.

The ^{13}C CP-MAS-NMR spectrum (Figure 2) of surfactant free M50 material revealed that all organic moieties were indeed intact in the materials. The four aromatic resonances with two intense signals at 125.7 and 134.9 ppm are assigned to unsubstituted carbons i.e carbon bonded to hydrogen. The other two resonances at 130.4 and 141.1 ppm are of the substituted carbons on the biphenyl ring. In addition, the resonance of mercaptopropyl group was also observed. The signal at 12.3 ppm is due to the ^{3}CH$_2$ group (C3 carbon) directly bonded to Si atom. The clear signals at 29.5 (slightly overlapped with side band of the biphenylene signal) and 21.9 are assigned to –^{2}CH$_2$ group (C2 carbon) and –^{1}CH$_2$ group (C1 carbon bonded to –SH moieties).[11,12] The two weak signals appearing at 57.5 and 15.3 ppm are due to irreversibly adsorbed ethanol.[8] The remaining signals are the group side bands of biphenylene as reported in earlier reports.[9] The ^{13}C NMR spectrum of oxidized M50 sample revealed the presence of –SO$_3$H moieties. An additional resonance at 53.8 ppm is assignable to ^{1}C carbon directly bonded to –SO$_3$H group while the signals for the –^{2}CH$_2$ and –^{3}CH$_2$ carbons appeared at 18.0 and 11.9 ppm, respectively.[10] No signal at 29.5 ppm due to resonance of –SH was observed indicating the complete oxidation of the material under the given conditions. The molecular scale periodicity and ordered mesoporosity survived the oxidation process as evidenced by characterization results.

Table 2. Textural properties of oxidized bifunctional materials

Material	S_{BET} m^2/g	PD$_{BJH}$ Å	PV cc/g	^{a}Lattice Spacing, Å	H$^+$ mmol/g
M15-Oxd	816	23.5	0.55	43.0	0.28
M30-Oxd	744	22.4	0.45	47.7	0.47
M50-Oxd	752	21.5	0.44	48.2	0.71
M70-Oxd	443	17.7	0.24	50.9	0.99

^{a}Lattice spacings $(a_o) = 2d_{100}/\sqrt{3}$.

The presence of –SO$_3$H groups were confirmed by acid–base titrations. The concentration of –SO$_3$H moieties in the oxidized samples was quantitatively determined. The acidity of the materials was found to be increased with increasing MPTMS content. The higher acidity observed was 0.99 mmol H$^+$/g, which is comparatively higher to the value (0.70 mmol H$^+$/g) reported for benzene-bridged hybrid mesoporous silica[10] and comparable to previously reported post-synthesis oxidation of the TEOS–MPTMS system.[13] The BET surface area, pore diameter and pore volume were decreased after oxidation (Table 2). The oxidized mesoporous materials also exhibited the type IV isotherms, however, the step was lowered with an increase in MPTMS content. Further, for the M70 material, after oxidation the isotherm fell between type IV and type I. The amount of porosity also gradually decreased with increasing MPTMS content. Overall, the results indicate that the incorporation of terminal bonded MPTMS in the mesoporous network does not affect the stability of the mesophases for further chemical reactions.

In summary, the sulfonic acid functionalized bihenylene bridged mesoporous silsesquioxanes are successfully synthesized by co-condensation of BTEBP and MPTMS using a cationic surfactant followed by oxidative transformation of –SH group to –SO$_3$H. The materials afford a far better 0.99 m-equiv/g of acid functionality. This can be regarded as an excellent methodology for creating functional active sites for potential applications.

References

1 S. Inagaki, S. Guan, Y. Fukushima, T. Ohsuna, and O. Terasaki, *J. Am. Chem. Soc.*, **121**, 9611 (1999).
2 T. Asefa, M. J. MacLachlan, N. Coombs, and G. A. Ozin, *Nature*, **402**, 867 (1999).
3 B. J. Melde, B. T. Holland, C. F. Blanford, and A. Stein, *Chem. Mater.*, **11**, 3302 (1999).
4 C. Y. Ishii, T. Asefa, N. Coombs, M. J. MacLachlan, and G. A. Ozin, *Chem. Commun.*, **1999**, 2235.
5 M. P. Kapoor, A. Bhaumik, S. Inagaki, K. Kuraoka, and T. Yazawa, *J. Mater. Chem.*, **12**, 3078 (2002).
6 M. P. Kapoor, A. K. Sinha, S. Seelan, S. Inagaki, S. Tsubota, H. Yoshida, and M. Haruta, *Chem. Commun.*, **2002**, 2902.
7 A. Bhaumik, M. P. Kapoor, and S. Inagaki, *Chem. Commun.*, **2003**, 471.
8 S. Inagaki, S. Guan, T. Ohsuna, and O. Terasaki, *Nature*, **416**, 304 (2002).
9 M. P. Kapoor, Q. Yang, and S. Inagaki, *J. Am. Chem. Soc.*, **124**, 15176 (2002).
10 Q. Yang, M. P. Kapoor, and S. Inagaki, *J. Am. Chem. Soc.*, **124**, 9694 (2002).
11 A. J. Aznar and E. Ruiz-Hitzky, *Colloid Polym. Sci.*, **270**, 165 (1992).
12 D. Margolese, J. A. Melero, S. C. Christiansen, B. F. Chmelka, and G. D. Stucky, *Chem. Mater.*, **12**, 2448 (2000).
13 X. Feng, G. E. Fryxell, L. Q. Wang, A. Y. Kim, J. Liu, and K. M. Kemner, *Science*, **276**, 923 (1997).

Published on the web (Advance View) September 8, 2003; DOI 10.1246/cl.2003.914