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Sulfuric Acid-Functionalized Mesoporous Benzene−Silica with a Molecular-Scale Periodicity in the Walls

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

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

Received May 6, 2002

Periodic mesoporous organosilicas synthesized from organosilanes, $(R'O)_3Si-R-Si(R'O)_3$, in the presence of surfactant gained much attention because various organic functionalities can be designed in the stable inorganic framework.[1−6] Recently, we reported the synthesis of periodic mesoporous benzene−silica with crystal-like pore walls.[7] The ordered mesoporous materials have surface structure with alternatively arranged hydrophobic benzene and hydrophilic silica layers with a periodicity of 7.6 Å. The periodic surface structure is a great advantage to enable structural orientation of guest molecules enclosed in the pores, which would result in the enhancement of selectivity and activity in catalysis.[8] We have reported the direct sulfonation of phenylene group in the pore walls of mesoporous benzene−silica and the possibility of its use as solid acid catalysts.[7] The sulfuric acid groups were located on the hydrophobic benzene layers in the mesoporous benzene−silica. Here we reported the synthesis of alternative sulfuric acid-functionalized benzene−silica with a propyl sulfuric acid group ($-C_3H_6SO_3H$) attached on the hydrophilic silica layers (Figure 1A). In this material, catalytic acid sites and hydrophobic benzene sites are separately designed and apart from each other on the mesoporous surface. Thus, the dimensionally designed surface structure is a better catalytic environment. We derived the novel sulfuric acid-functionalized mesoporous material from the mesoporous benzene−silica possessing mercaptopropyl ($-C_3H_6SH$) groups by the oxidative transformation of the thiol ($-SH$) into sulfonic ($-SO_3H$) groups. The thiol-functionalized benzene−silicas were synthesized by co-condensation of 1,4-bis(triethoxysilyl)benzene (BTEB) and 3-mercaptopropyltrimethoxysilane (MPTMS) using a surfactant template in basic conditions with the different mixture ratio of BTEB and MPTMS.[9]

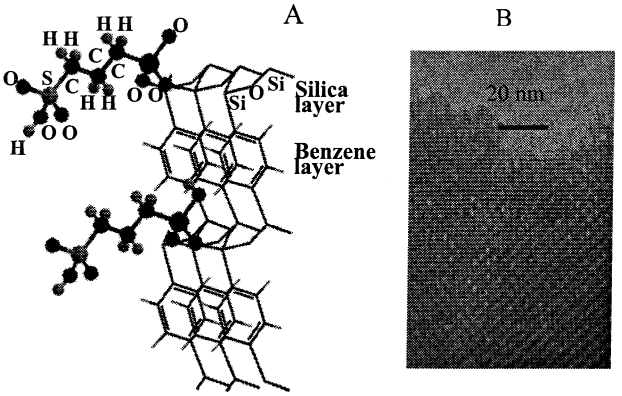

Figure 1. (A) Structural model of periodic pore surface attached with propylsulfuric acid groups. (B) TEM image of surfactant-free Ph-MP$_{40}$.

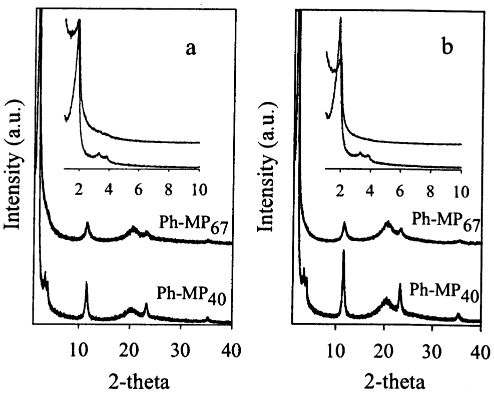

Figure 2. PXRD patterns of surfactant-free mesoporous bifunctional materials (a) before and (b) after oxidation with HNO_3.

The powder X-ray diffractions (PXRD) of most thiol-functionalized mesoporous materials (surfactant free) showed three peaks in the lower-angle diffraction regime ($2\theta < 10°$), which are assigned to two-dimensional hexagonal (*P*6*mm*) symmetry (Figure 2). The nitrogen adsorption isotherms of all synthesized materials showed type IV isotherms with uniform pore size distribution (Table 1 and Supporting Information).[10] Transmission electron microscopy (TEM) clearly showed the formation of ordered mesostructures with a hexagonal arrangement of mesoporous channels (Figure 1B). The PXRD patterns at 2θ between 10 and 50° display three additional peaks at d spacing of 7.6, 3.8, and 2.5 Å that could be assigned to a periodic structure (molecular-scale periodicity) with a spacing of 7.6 Å existing in the pore walls.[7] The mesoporous materials have essentially the same periodic structure in the pore walls as to the mesoporous benzene−silica reported previously because of their similar XRD patterns and quite the same molecular-scale periodicity. Although the intensity of d_{100} reflection gradually decreases with an increase in MPTMS content, the molecular periodicity in the pore walls remains intact even up to 67 mol % of MPTMS content in the initial reaction mixture. Mercaptopropyl groups are attached on the silica layers. The actual incorporated number of mercaptopropyl groups is lower than in the initial reaction mixtures, which was confirmed by elemental analysis of the products (Table 1).

The connectivity of phenylene, silicate, and mercaptopropyl groups was confirmed by ^{29}Si and ^{13}C NMR spectroscopy (Figure 3). ^{29}Si NMR spectra showed three signals at −81.5, −71.6, and −63.8 ppm. They can be assigned as ^2T and ^3T for Si attached with phenylene (−71.6 and −81.5 ppm) and mercaptopropyl (−63.8, −71.6 ppm), respectively. The broad signal centered at −71.6 ppm is the mixture of ^3T and ^2T for Si connected with mercaptopropyl and phenylene groups, respectively. The absence of Q sites indicates that carbon−silicon bond is stable during the

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* To whom correspondence should be addressed. E-mail: inagaki@mosk.tytlabs.co.jp.
[†] CREST, JST.
[‡] Toyota Central R&D Laboratories, Inc.

10.1021/ja026799r CCC: $22.00

Table 1. Structural and Textural Properties of the Thiol- and Sulfuric Acid-Functionalized Mesoporous Benzene−Silicas

sample description	MPTMS content (mol %) solution	framework	BET[a] (m^2/g)	pore diameter (Å)	a_0[b] (Å)	H$^+$ (mmol/g)[c]	degree of oxidation (%)
Ph-MP$_{25}$	25	8.5	921 (834)	28.0 (26.0)	52.0 (51.7)	0.14	35.0
Ph-MP$_{40}$	40	11.8	747 (722)	28.0 (26.0)	53.6 (53.3)	0.30	40.0
Ph-MP$_{60}$	60	17.0	768 (779)	28.0 (28.0)	54.2 (54.5)	0.66	57.4
Ph-MP$_{67}$	67	24.3	643 (481)	22.6 (21.8)	54.7 (53.5)	0.70	41.7

[a] The values in parentheses are for the sulfuric acid-functionalized benzene−silicas. [b] Calculated from $a_0 = 2d_{100}/\sqrt{3}$. [c] To 20 g of aqueous solution containing NaCl (2 M) was added 0.1 g of oxidized organic silica. The solution was stirred at room temperature for 24 h and then titrated with 0.1 M NaOH to produce the titration curve.

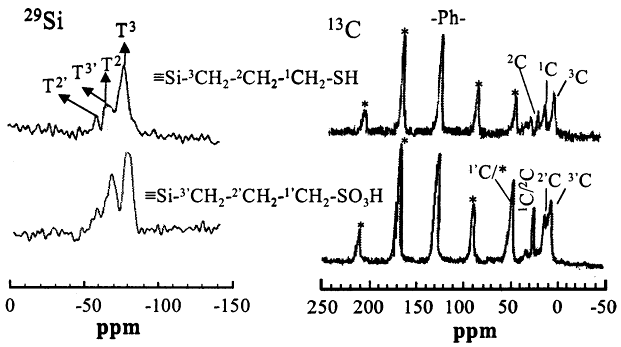

Figure 3. ^{29}Si and ^{13}C NMR spectra of Ph-MP$_{67}$ (T′ and T refer to Si connected with mercaptopropyl and phenylene group, respectively; ∗ refers to sidebands).

synthesis condition. ^{13}C NMR spectra also showed both signals of phenylene (133.4 ppm) and mercaptopropyl (40−10 ppm) groups. The signal at 13.4 ppm is due to the $-^3CH_2$ group (C3 carbon) directly bonded to Si atom. Another resonance at 29.3 and 22.4 ppm are assigned to $-^2CH_2$ (C2 carbon) and $-^1CH_2$ (C1 carbon bonded to −SH group), respectively.[11] Such clear splitting of $^2CH_2$ and $^1CH_2$ carbon was only observed earlier for the MCM-41 with 76% surface coverage of MPTMS, which was attributed to the homogeneous conformation of the grafted MPTMS.[12] The good resolution of all three carbons observed in our material indicates that 3-mercaptopropyl groups are aligned in similar orientation because of the highly ordered mesostructure. The weak signal appearing at 37.2 ppm could be tentatively assigned to an additional oxidation product such as sulfide during the synthesis at high temperature.[13]

The oxidation of −SH group in the mesoporous benzene−silicas was carried out by treatment with concentrated HNO_3 at room temperature for 24 h.[13] The ^{13}C NMR spectra of the samples after oxidation revealed the presence of $-SO_3H$ surface moieties. The resonance at 53.4 ppm can be assigned to the ^{1}C carbon attached to $-SO_3H$ moieties while the resonance for the $-^2CH_2$ and $-^3CH_2$ carbons appeared at 18.4 and 13.2 ppm, respectively (the signal at 53.4 ppm overlapped with the sideband signal of phenylene). The resonance of −SH at 29.6 ppm (mixture of C1 and C2 due to the decreasing of order of the surface thiol group after oxidation) evidenced an incomplete oxidation because of inaccessible of SH group. The mesoporous crystal-like pore walls and carbon−silicon bond survived the oxidation process, as evidenced by PXRD and ^{29}Si NMR. However, the shape and textural properties of oxidized materials do not appear different from before oxidation except a decrease in BET surface area of Ph-MP$_{67}$ sample (Table 1). The densities of $-SO_3H$ groups in the oxidized samples were measured by acid−base titration (Table 1).[14] The highest acidity observed was 0.70 mmol H$^+$/g, indicating 41.7% oxidation of thiol groups (1.68 mmol/g) in the framework. The further investigations are underway for the enhancement of the acid−base properties of the materials.

In summary, the highly ordered bifunctional organic−inorganic hybrid mesoporous structures with crystal-like pore walls can be synthesized with higher degree incorporation of MPTMS, and the transformation of −SH to $-SO_3H$ group provides a good methodology for creating functional active sites for advanced potential applications.

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

Supporting Information Available: N_2 sorption isotherm and BJH pore size distribution of materials before and after oxidation; XRD patterns of Ph-MP$_{25}$ and Ph-MP$_{60}$ before and after oxidation; FTIR spectra; thermal gravimetrical analyses of the materials before and after oxidation and the titration curve of oxidized materials with NaOH (PDF). This material is available free of charge via the Internet at http://pubs.acs.org

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(9) C_{18}TMAC was dissolved in a mixture of ion-exchange water and sodium hydroxide aqueous solution. The mixture of BTEB and MPTMS was added to the above solution, and the suspension was stirred at room temperature for 12 h and aged at 90 °C for 24 h. The resulting white precipitate was recovered by filtration to yield the as-synthesized sample. The initial molar ratios were Si:CTAC:NaOH:H_2O = 1:0.96:2.67:559 and 1:0.96:1.78:559 for Ph-MP$_n$ (n = 25, 40, 60) and Ph-MP$_{67}$ (n represent the mol percentage of MTPMS in the starting materials). Surfactant was removed by stirring 1.0 g of as-synthesized sample in 200 mL of ethanol with 3.0 g of HCl (36%) at 55 °C for 6 h before filtration.
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JA026799R