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An Alternate Route for the Synthesis of Hybrid Mesoporous Organosilica with Crystal-Like Pore Walls from Allylorganosilane Precursors

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Abstract: The bridged allylorganosilanes 1,4-bis(diallylethoxysilyl)benzene and 1,4-bis(triallylsilyl)benzene are presented as new precursors for the surfactant-assisted synthesis of ordered mesoporous organosilica with pore walls having crystal-like molecular-scale periodicity. This approach provides a new route to the formation of periodic mesostructures with crystal-like pore walls. The synthesis method presented is applicable to the preparation of mesoporous organosilica with bulky organic groups, the precursors of which are typically impossible to obtain in high purity.

Introduction

Hybrid mesoporous organosilica is a periodic solid that can be designed to carry organic, inorganic or even biological functionalities.[1] The unique structural properties of this materials make it potentially applicable in a wide range of advanced applications, including separation technology, filtration, sensing, environmental cleanup, catalysis, and optoelectronics.[2] Crystallization of the pore walls of originally amorphous mesoporous material is an important improvement required to achieve greater functionality. The present authors have attempted crystallization through the surfactant-mediated synthesis of benzene- and biphenylene-bridged silica under precise control of the nanoarchitecture.[3,4] The materials synthesized by this route display a hexagonal arrangement of mesopores and pore walls with crystal-like domains exhibiting a structural periodicity with a spacing of 7.6 and 11.6 Å for the benzene- and biphenylene-bridged silica, respectively. This periodicity has been attributed to $\pi-\pi$ stacking of the bridging functional groups.

A wide range of synthetic routes to mesoporous organosilica with different mesophases and morphologies have been reported, including the use of cationic, neutral and nonionic surfactants and even surfactant mixtures under basic, acidic and neutral conditions.[1−5] The most commonly used organosilicon precursors contain a trialkoxy leaving group [$(OR')_3$], such as the trialkoxy derivatives of bridged organosilicon molecules $(R'O)_3Si-R-Si(OR')_3$. However, the range of suitable alkoxysilane precursors is limited because alkoxysilane precursors containing relatively large organic groups are difficult to obtain in high purity due to the limitations of distillation and chromatographic separation for such nonvolatile compounds. It is therefore vital to discover a alternative precursors for the synthesis of novel mesoporous organosilicas. Alkoxy, halide, acyloxy, and amino groups on silicon atoms have also been used for Si−O−Si bond formation.[6] However, these functional groups are highly reactive toward hydrolysis, rendering the silicon compounds difficult to handle under hydrolytic conditions and during purification by silica gel chromatography. Our group has also developed a new method for functionalizing the surface of FSM-16 silica using allylorganosilanes at toluene reflux temperatures.[7]

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(1) (a) Inagaki, S.; Guan, S.; Fukushima, Y.; Ohsuna, T.; Terasaki, O. *J. Am. Chem. Soc.* **1999**, *121*, 9611. (b) Melde, B. J.; Holland, B. T.; Blanford, C. F.; Stein, A. *Chem. Mater.* **1999**, *11*, 3302. (c) Asefa, T.; MacLachlan, M. J.; Coombs, N.; Ozin, G. A. *Nature* **1999**, *402*, 867 (d) Yoshina-Ishii, C.; Asefa, T.; Coombs, N.; MacLachlan M. J.; Ozin, G. A. *Chem. Commun.* **1999**, 2539.

(2) (a) Fan, H.; Lu, Y.; Stump, A.; Reed, S. T.; Bear, T.; Schunk, R.; Perez-Luna, V.; Lopez, G. P.; Brinker, C. J. *Nature* **2000**, *405*, 56. (b) Sayari, A.; Hamoudi, S. *Chem. Mater.* **2001**, *13*, 3151. (c) Lu, Y.; Fan, H.; Doke, N.; Loy, D. A.; Assinik, R. A.; LaVan D. A.; Brinker, C. J. *J. Am. Chem. Soc.* **2000**, *122*, 5258. (d) McInal, M. D.; Scott, J.; Mercier, L.; Kooyman, P. J. *Chem. Commun.* **2001**, 2282. (e) Rogers, J. A.; Bao, Z.; Makhija, A.; Braum, P. *Adv. Mater.* **1999**, *11*, 741.

(3) (a) Inagaki, S.; Guan, S.; Ohsuna, T.; Terasaki, O. *Nature* **2002**, *416*, 304. (b) Kapoor, M. P.; Yang, Q.; Inagaki, S. *Chem. Mater.* **2004**, *16*, 1209. (c) Kapoor, M. P.; Inagaki, S. *Chem. Lett.* **2004**, *33*, 88.

(4) (a) Kapoor, M. P.; Yang, Q.; Inagaki, S. *J. Am. Chem. Soc.* **2002**, *124*, 15176. (b) Kapoor, M. P.; Yang, Q.; Goto, Y.; Inagaki, S. *Chem. Lett.* **2003**, *32*, 914.

(5) (a) Yang, Q.; Kapoor, M. P.; Inagaki, S. *J. Am. Chem. Soc.* **2002**, *124*, 9694. (b) Goto, Y.; Inagaki, S. *Chem. Commun.* **2002**, 2410. (c) Hamoudi, S.; Kaliaguine, S. *Chem. Commun.* **2002**, 2118. (d) Sayari A.; Yang, Y. *Chem. Commun.* **2001**, 2582. (e) M. P. Kapoor, Setoyama, N.; Yang, Q.; Ohashi, M.; Inagaki, S. *Langmuir* **2005**, *21*, 443. (f) Kapoor, M. P.; Inagaki, S. *Chem. Mater.* **2002**, *14*, 3509. (g) Okamoto, K.; Kapoor, M. P.; Inagaki, S. *Chem. Commun.* **2005**, 1423.

(6) Vansant, E. F.; Vrancken, C. *Stud. Surf. Sci. Catal.* **1995**, 93.

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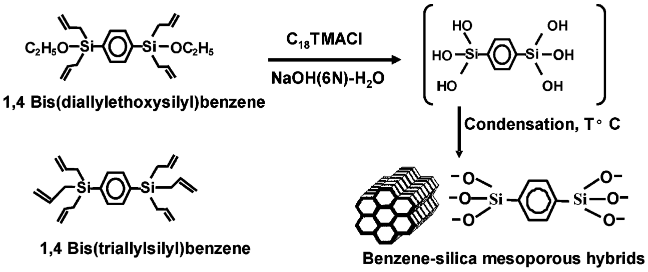
Scheme 1. Synthesis of Benzene-Silica Mesoporous Hybrids from Allylorganosilane Precursors



The present paper deals with the preparation and of a new family of bridged allylorganosilane precursors that upon surfactant-assisted assembly afford ordered mesoporous organosilica having pore walls with molecular-scale periodicity (Scheme 1). The approach provides important insights into the development of molecular-scale periodicity, spurring new debate on the formation of periodic mesostructures with crystal-like pore walls.

Experimental Section

General. Two stable allylorganosilane precursors, 1,4-bis(diallylethoxysilyl)benzene and 1,4-bis(triallylsilyl)benzene, were synthesized and purified by silica gel column chromatography under ambient conditions. All reactions were carried out in a nitrogen atmosphere with dry, freshly distilled solvents under anhydrous conditions unless otherwise noted. Tetrahydrofuran (THF) and diethyl ether were distilled from sodium benzophenone. All reagents were of highest commercial quality and used without further purification unless otherwise noted.

^{1}H nuclear magnetic resonance (NMR) spectra were recorded on a JEOL JNM ECP-500 (500 MHz) spectrometer. The chemical shifts are reported with respect to either tetramethylsilane (0.00 ppm) or $CHCl_3$ (7.26 ppm) as an internal standard, using the following for multiplicities: s, singlet; d, doublet; t, triplet; q, quartet; m, multiplet; b, broad. ^{13}C NMR spectra were recorded on a JEOL JNM-500 (125 MHz) spectrometer with $CDCl_3$ (77.0 ppm) as an internal standard.^{29}Si NMR spectra were acquired on a JEOL JNM-500 (99 MHz) spectrometer. Infrared spectra (IR) were recorded on a JASCO Fourier transform IR (FT-IR) spectrometer, and elemental analyses were performed on a Perkin-Elmer 2400 analyzer.

1,4-Bis(triethoxysilyl)benzene was prepared according to the literature procedure.[8] To a solution of magnesium turnings (15 g, 0.61 mol) and tetraethoxysilane (450 mL, 2.0 mol) in THF (300 mL) under nitrogen was added a small crystal of iodine, and the mixture was brought to reflux. A solution of 1,4-dibromobenzene (48 g, 0.20 mol) in 100 mL of THF was then added dropwise over 5 h. Within 30 min of initiating the addition, the reaction became mildly exothermic. The reaction mixture was refluxed for 1 h after completion of dibromide addition. The resultant gray mixture was then allowed to cool to room temperature. Hexane (500 mL) was added to precipitate any remaining magnesium salt, and the mixture was quickly filtered under nitrogen to afford a clear light-yellow solution. The solvent was removed by rotary evaporation, and the residue was distilled under vacuum (0.2 mmHg, 140 °C) to give a clear oil (41.1 g, 50%). ^{1}H NMR (500 MHz, $CDCl_3$) δ 1.16 (t, $J = 7.0$ Hz, 18H), 3.79 (q, $J = 7.0$ Hz, 12H), 7.60 (s, 4H). ^{13}C NMR (125 MHz, $CDCl_3$) δ 18.1, 58.6, 133.0, 134.0. ^{29}Si NMR (99 MHz, $CDCl_3$) δ −57.5. Elemental Anal. Calcd for $C_{18}H_{34}O_6Si_2$: C, 53.70; H, 8.51. Found: C, 53.67; H, 8.56.

Synthesis of 1,4-Bis(triallylsilyl)benzene. To a 500 mL, three-necked round-bottom flask equipped with a reflux condenser was added lithium chips (8.4 g, 1.20 mol) in THF (100 mL) along with a pressure-equalizing dropping funnel and magnetic stirrer. The reaction flask was cooled to −10 °C in a NaCl-ice water bath. Under vigorous stirring, a solution of allyl phenyl ether (13.7 mL, 0.10 mol) in THF (50 mL) was then added dropwise to the mixture over 2 h through the dropping funnel. After further stirring for 1 h, the supernatant was transferred to a solution of 1,4-bis(triethoxysilyl)benzene (3.2 g, 8.0 mmol) in THF (100 mL) via a cannula and stirred for 1 h at 0 °C. The resultant mixture was then poured into water and extracted with ether. The organic extracts were dried over $MgSO_4$ and filtered. Evaporation of solvents and purification of the residual oil by column chromatography on silica gel (hexane/AcOEt = 40:1 as eluent) gave a colorless oil (2.29 g, 76%). ^{1}H NMR (500 MHz, $CDCl_3$) δ 1.78−1.79 (m, 12H), 4.80−4.86 (m, 12H), 5.69−5.74 (m, 6H), 7.41 (s, 4H). ^{13}C NMR (125 MHz, $CDCl_3$) δ 19.4, 114.3, 133.3, 133.7, 136.4. ^{29}Si NMR ($CDCl_3$) δ −7.60. Elemental Anal. Calcd for $C_{24}H_{34}Si_2$: C, 76.12; H, 9.05. Found: C, 76.05; H, 9.09.

Synthesis of 1,4-Bis(diallylethoxysilyl)benzene. To a 500 mL, three-necked round-bottom flask fitted with an N_2 inlet adapter was added 1,4-bis(triethoxysilyl)benzene (13.4 g, 33.3 mmol) at 0 °C along with a magnet stirrer and rubber septum. A solution of allylmagnesium bromide (1.0 M in ether, 200 mL, 0.20 mol) was slowly added dropwise. After complete addition of the Grignard reagent, the mixture was allowed to warm to room temperature and stirred for a further 9 h. The mixture was poured into aqueous 5% HCl solution (150 mL) and extracted with ether. The organic extracts were neutralized with saturated aqueous $NaHCO_3$ solution, washed with brine, dried over $MgSO_4$, and filtered. Evaporation of solvents and purification of the residual oil by column chromatography on silica gel (hexane/AcOEt = 40:1 as eluent) gave a colorless oil (11.8 g, 92%). ^{1}H NMR (500 MHz, $CDCl_3$) δ 1.12 (t, $J = 7.0$ Hz, 6H), 1.83−1.89 (m, 8H), 3.69 (q, $J = 7.0$ Hz, 4H), 4.81−4.89 (m, 8H), 5.70−5.79 (m, 4H), 7.50 (s, 4H). ^{13}C NMR (125 MHz, $CDCl_3$) δ 18.3, 21.1, 59.2, 114.7, 132.8, 133.1, 136.8. ^{29}Si NMR (99 MHz, $CDCl_3$) δ −1.78. Elemental Anal. Calcd for $C_{22}H_{34}O_2Si_2$: C, 68.34; H, 8.86. Found: C, 68.61; H, 8.99.

Table 1. Parameters for Mesoporous Benzene-silica Hybrid Synthesis Using 1,4-bis(diallylethoxysilyl)benzene

preparation	surfactant (g)	precursor (g)	NaOH (6N) (g)	H_2O (g)	synthesis temp.
1	0.57	0.42	0.24	23	35 ± 3
2	0.56	0.40	0.40	20	50
3	0.46	0.50	0.20	22	70
4	0.56	0.41	0.38	20	92 ± 3
5	0.72	0.75	0.50	33	92 ± 3
6[a]	1.22	1.0	0.7	22	92 ± 3
7[b]	1.67	2.0	4.0	50	92 ± 3

[a] Equimolar ratio of precursor and TEOS. [b] 1,4-bis(triethoxysilyl)benzene[3].

Synthesis of Mesoporous Benzene-Silica Solid. Refer to the synthesis parameters presented in Table 1. For the best synthesis (preparation 5), 1,4-bis(diallylethoxysilyl)benzene (0.75 g) was suspended in an aqueous solution of octadecyltrimethylammonium chloride (C_{18}TMACl) surfactant (0.72 g in 33 g ion-exchanged water) containing 6N sodium hydroxide (0.5 g) and stirred to promote hydrolysis at ambient temperature for 20 h followed by aging at 95 °C for a further 20 h. The resultant white precipitate was then recovered by filtration and washed repeatedly with distilled water. The benzene-silica mesoporous solid was finally collected after removal of the surfactant by solvent extraction.[3] The yield of the final product was approximately 34%.

One-pot co-condensation of 1,4-bis(diallylethoxysilyl)benzene and tertaethyl orthosilicate (TEOS) was also attempted using an equimolar ratio of both silica precursors under similar reaction conditions (preparation 6; Table 1). The synthesis parameters for mesoporous materials derived from 1,4-bis(triethoxysilyl)benzene[3] are also presented in Table 1 for comparison (preparation 7).

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(7) (a) Shimada, T.; Aoki, K.; Shinoda, Y.; Nakamura, T.; Tokunaga, N.; Inagaki, S.; Hayashi, T. *J. Am. Chem. Soc.* **2003**, *125*, 4688. (b) Aoki, K.; Shimada, T.; Hayashi, T. *Tetrahedron Asymmetry* **2004**, *15*, 1771.

(8) Shea, K. J.; Loy, D. A.; Webster, O. *J. Am. Chem. Soc.* **1992**, *114*, 6700.

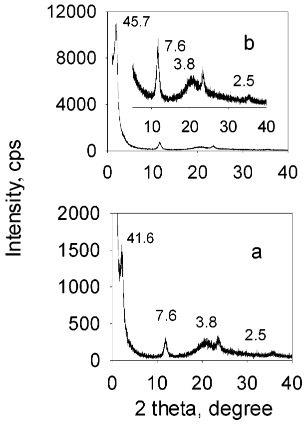

Figure 1. PXRD diffraction patterns of hybrid mesoporous benzene-silica prepared from 1,4-bis(diallylethoxysilyl)benzene: (a) as-synthesized, (b) solvent extracted (preparation 5, Table 1).

In other typical syntheses, 0.22 g of 1,4-bis(triallylsilyl)benzene precursor was mixed in an alkaline aqueous solution (6N NaOH, 0.17 g; H_2O, 15 g) of C_{18}TMACl surfactant (0.24 g) and hydrolyzed at ambient temperature for 48 h followed by aging at 92 ± 3 °C for a further 24 h. The material was recovered by filtration, drying and surfactant removal by solvent extraction as described in ref 3.

Characterization. Powder X-ray diffraction (PXRD) patterns were measured on a Rigaku RINT-2200 diffractometer with CuKα radiation (40 kV, 30 mA) from 1° to 40° (2θ) in 0.01° steps at a scan speed of $1°(2\theta)\ \mathrm{min}^{-1}$. Porosimetry measurements (N_2 isotherms) were obtained on a Quantachrome Autosorb-1 sorptometer at −196 °C. Prior to measurement, all samples were outgassed at 80 °C and 10^{-4} Torr. Brunauer−Emmett−Teller (BET) surface areas were calculated from the linear section of the BET plot ($P/P_0 = 0.05-0.3$). Pore-size distributions were determined using the Barrett−Joyner−Halenda (BJH) method from the adsorption branch of the isotherms. ^{13}C cross-polarization (CP) and ^{29}Si magic-angle spinning (MAS) NMR spectra were recorded on a Bruker-300 spectrometer at 75.47 and 59.62 MHz using 4 mm zirconia rotors and a sample spinning frequency of 3 kHz, respectively. The chemical shifts for all spectra were referenced to tetramethylsilane at 0 ppm.

Results and Discussion

Mesoporous Hybrids from 1,4-Bis(diallylethoxysilyl)benzene Precursor. The PXRD patterns (Figure 1a) of the as-synthesized benzene-silica hybrid mesoporous material derived from 1,4-bis(diallylethoxysilyl)benzene display a d_{100} reflection peak at 41.6 Å and sharp peaks at $d = 7.6$, 3.8 and 2.5 Å at intermediate scattering angles ($2\theta = 10-40°$), indicating that the pore walls are formed of crystal-like domains with a spacing of 7.6 Å in the channel direction. The surfactant-free material (Figure 1b) also exhibited a well-defined pattern with diffraction peaks in the low-angle region (d_{100} spacing of 45.7 Å). The PXRD peak (d_{100}) was strengthened significantly upon solvent extraction due to the enhancement of contrast of density between framework and pore channels. The as-synthesized material displayed a slightly smaller lattice constant of $a = 48.1$ Å. The molecular-scale periodicity was fully retained upon surfactant removal, indicating substantial framework ordering with crystalline pore walls. The final material was identical to the materials synthesized from the alkoxy derivative of the benzene-bridged precursor [1,4-bis(triethoxysilyl)benzene],[3] which exhibited weaker peaks related to molecular-scale periodicity.

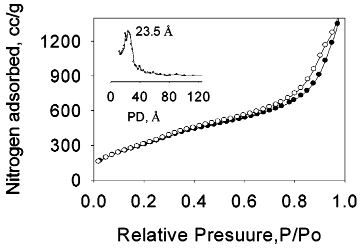

Figure 2. Nitrogen adsorption (●) and desorption (○) isotherms and pore-size distribution (inset) for hybrid mesoporous benzene-silica prepared from 1,4-bis(diallylethoxysilyl)benzene.

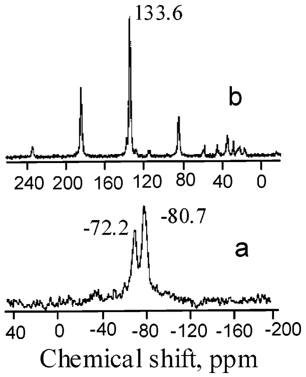

Figure 3. (a) ^{29}Si and (b) ^{13}C NMR spectra of hybrid mesoporous benzene-silica prepared from 1,4-bis(diallylethoxysilyl)benzene.

The nitrogen adsorption isotherm indicates a type-IV isotherm based on the International Union of Pure and Applied Chemistry (IUPAC) classification, confirming the existence of uniform mesopores (Figure 2). However, a small hysteresis related to capillary condensation in the interparticle mesopores was observed at relative pressure above $P/P_0 = 0.8$. The BJH pore diameter, BET surface area, and mesopore volume were 23.5 Å, 744 $m^2\ g^{-1}$, and 0.53 $cm^3\ g^{-1}$, respectively.

The ^{29}Si and ^{13}C MAS NMR results also confirmed that the pore walls of the mesoporous benzene-silica are composed of a covalently bonded network of $O_{1.5}Si-C_6H_4-SiO_{1.5}$ units. The two sharp resonance at −72.2 and −80.7 ppm in the ^{29}Si NMR spectrum are assigned to T^n silica species $T^2[\mathit{Si}C(OH)(OSi)_2]$ and $T^3[\mathit{Si}C(OSi)_3]$, respectively, indicating the complete removal of the allyl leaving group (i.e., complete deallylation during hydrolysis). No signals due to SiO_4 species (Si sites attached to four oxygen atoms Q^n, $n = 1-4$) were detected between −98 and −110 ppm, indicating essentially no evidence for Si−C bond cleavage during the sol−gel process or synthesis (Figure 3a). The ^{13}C NMR spectrum displays a resonance at 133.6 ppm due to carbons on the benzene ring, and another resonance (*) due to the spinning sidebands. The absence of signals due to allyl carbons,[7] which would appear at around 135, 113 and 23 ppm in the ^{13}C NMR spectra, also confirms the complete elimination of allyl groups during synthesis (Figure 3b). The signals below 50 ppm are probably due to partial ethanolysis of surface silanols (Si−OH) during template removal by HCl/ethanol extraction and possible traces of the surfactant.[3−7]

Structural Evolution. Figure 4 shows the PXRD patterns obtained during development of the mesoporous materials prepared from 1,4-bis(diallylethoxysilyl)benzene. The peak intensities and sharpness of the patterns, which indicate the degree of structural ordering, depend heavily on the synthesis parameters. No precipitate appeared when condensation was

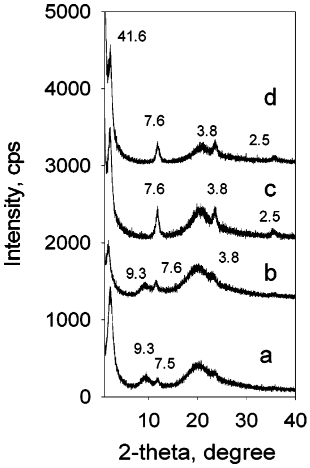

Figure 4. PXRD patterns showing the evolution of hybrid mesoporous benzene-silica prepared from 1,4-bis(diallylethoxysilyl)benzene: (a) preparation 2 (50 °C), (b) preparation 3 (70 °C), (c) preparation 4 (92 ± 3 °C), and (d) preparation 5 (92 ± 3 °C).

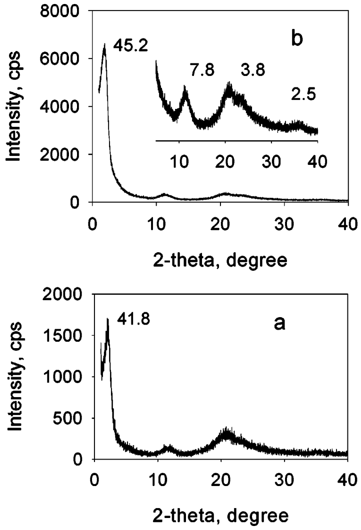

Figure 5. PXRD patterns of hybrid mesoporous benzene-silica prepared from a mixture of 1,4-bis(diallylethoxysilyl)benzene and TEOS: (a) as-synthesized, (b) solvent extracted (preparation 6, Table 1)

performed at below 40 °C (preparation 1). The mesostructured materials could be formed after 4 days' aging of the initial gel at 50 °C, although the resultant material displayed poor molecular-scale periodicity and the apparent collapse of structural order following surfactant removal by solvent extraction (preparation 2; Figure 4a). The material synthesized at 70 °C was also poorly ordered, with relatively lower molecular-scale periodicity (preparation 3; Figure 4b). An additional hump centered around a *d* spacing of 9.3 Å was observed for the materials prepared at both 50 and 70 °C, indicating incomplete condensation. The ^{29}Si NMR spectra of these materials revealed the presence of T^n silicon sites and some U^n species, suggesting that some allyl groups remained. The stable, structurally ordered mesoporous benzene-silica materials were obtained when the gel was aged at 92 ± 3 °C. The structural ordering and molecular-scale periodicity could be clearly in this preparation (preparation 4; Figure 4c). The modified initial gel composition also yields a highly ordered mesoporous material, as described above (preparation 5, Figure 4d). These results indicate that the basicity of the reaction mixture is an important factor determining the structural order and crystallinity of the products.

Ordered Hybrids from Mixed Precursors. Materials were also prepared via the co-condensation of equimolar ratios of 1,4-bis(diallylethoxysilyl)benzene and TEOS under basic conditions (preparation 6; Table 1). The ordered mesoporous material obtained exhibited molecular-scale periodicity in the pore walls (Figure 5). The d_{100} reflection peak (d_{100} spacing of 45.2 Å) for the surfactant-free materials was weaker than that for the benzene-silica hybrid material prepared from 1,4-bis(diallylethoxysilyl)benzene. This material also displayed relatively broad peaks at *d* spacings of 7.8, 3.8, and 2.5 Å at intermediate scattering angles, indicating relatively poor crystallinity compared to the parent material. A significantly strengthening of the d_{100} peak was also observed for this material upon solvent extraction.

The ^{29}Si and ^{13}C MAS NMR results confirmed the presence of both T^n (−71.6 and −81.9 ppm) and Q^n (−92.3, −100.9, −108.4 and −111.8 ppm) silicon species in the materials and the presence of a covalently bonded network of $O_{1.5}Si-C_6H_4-SiO_{1.5}$ units (Figure 6). The nitrogen adsorption isotherms had type-IV character with a small hysteresis loop, and the pore-size distribution curve indicated that the pore size was highly uniform (Figure 7). The BJH pore diameter, BET surface area and mesopore volume were 26.1 Å, 1014 m^2 g^{-1}, and 0.73 cm^3 g^{-1}, respectively

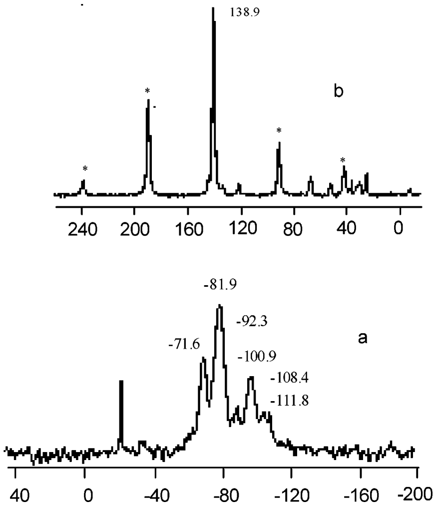

Figure 6. (a) ^{29}Si and (b) ^{13}C NMR spectra of hybrid mesoporous benzene-silica prepared from a mixture of 1,4-bis(diallylethoxysilyl)benzene and TEOS.

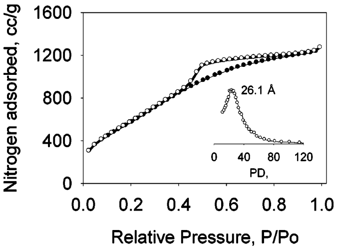

Figure 7. Nitrogen adsorption (●) and desorption (○) isotherms and pore-size distribution (inset) of hybrid mesoporous benzene-silica prepared from a mixture of 1,4-bis(diallylethoxysilyl)benzene and TEOS.

Mesoporous Hybrids from 1,4-Bis(triallylsilyl)benzene Precursor. In another approach, a stable 1,4-bis(triallylsilyl)-benzene precursor without a alkoxy group was synthesized and the formation of mesostructures under basic conditions was

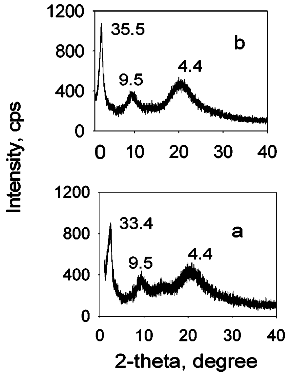

Figure 8. PXRD patterns of hybrid mesoporous benzene-silica prepared from 1,4-bis(triallylsilyl)benzene: (a) as-synthesized, (b) solvent extracted.

attempted. The PXRD pattern of the surfactant-free material clearly shows the successful formation of a mesostructure with a d_{100} spacing of 35.5 Å (Figure 8). The other two broad reflections at $d = 9.5$ and 4.4 Å are due to the molecular-scale periodicity of the pore walls. However, the peaks are not as sharp as observed for the benzene-silica mesoporous materials prepared from 1,4-bis(triethoxysilyl)benzene[3] and 1,4-bis(diallylethoxysilyl)benzene. This material exhibits structural ordering, with a BET surface area of 968 $m^2\ g^{-1}$ and a BJH pore diameter of 23.2 Å.

The 1,4-bis(diallylethoxysilyl)benzene precursor is preferable to 1,4-bis(triethoxysilyl)benzene in terms of cost and the ease of handling and purification during synthesis. However, the final yield of the allylorganosilanes precursor is slightly lower (ca. 34.1%) than that for the trialkoxyorganosilane precursor[3] (36.7%). The triethoxy derivative of the benzene precursor releases ethanol during the hydrolysis reaction, whereas propane is the main leaving species in the hydrolysis of 1,4-bis(diallylethoxysilyl)benzene or 1,4-bis(triallylsilyl)benzene.[7] Propane is unreactive toward silica and readily leaves the reaction mixture. The reaction pathway for the deallylation of allylorganosilane precursors under acidic conditions has been reported for the protodesilylation of allylic silanes.[7,9] However, under basic conditions, it is likely that deallylation starts with nucleophilic attack by hydroxide ions toward the silicon atom of the precursors. Detailed study of this mechanism is currently in progress.

Conclusion

Hybrid mesoporous benzene-silica with crystal-like pore walls was synthesized for the first time using new allylorganosilane precursors. The formation of hybrid organosilica with mesoscopic pore ordering and molecular-scale periodicity of the pore walls can be achieved using both the alkoxy derivative of the precursors and the allylorganosilane precursors themselves. This achievement represents a small step toward the discovery of alternative organosilane precursors and syntheses for the preparation of mesoporous organosilica with bulky organic groups, the existing precursors of which are difficult to obtain in high purity. Our group is currently involved in extensive research in this area, and the findings will be presented soon.

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(9) (a) Chan, T. H.; Fleming, I. *Synthesis* **1979**, 761. (b) Sommer, L. H.; Tyler, L. J.; Whitmore, F. C. *J. Am. Chem. Soc.* **1948**, *70*, 2872. (c) Morita, T. Okamoto Y.; Sakurai, H. *Tetrahedron Lett.* **1980**, *21*, 835. (d) Schenk, U.; Hunger M.; Weitkamp, *J. Magn. Reson. Chem.* **1999**, *37*, 75.