# Fabrication of Mesoporous Polycarbosilane from SBA-15 Templated Polymethylsilane

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Mesoporous silica materials have been used as templates for syntheses of carbon,[1,2] metal[3] and polymer-based[4] mesoporous replicas *via* nanocasting process. Since mesoporous silica templates have a narrow pore size distribution and uniform wall thickness,[5,6] the replicas obtained by synthesis using mesoporous silica templates also have nanometer-sized pores with a narrow pore size distribution. Incorporation of hydrocarbon polymer through polymerization of monomer such as aniline,[7] acrylonitrile,[8] ethylene,[9] methyl methacrylate[10] and phenolformaldehyde[11] within mesoporous MCM-41 could lead to the fabrication of organic nanofibers. Syntheses of mesoporous polymer networks with three dimensional continuity by the replication of mesoporous materials were reported. The preparation of highly ordered macroscopic silicon carbide,[12] mesoporous silicon imido nitride[13] and bimodal porous silicon oxycarbide[14] from liquid preceramic polymer were also reported. In this communication, we report for the first time the preparation of mesoporous polycarbosilane from liquid polymethylsilane as a polymer precursor and SBA-15 as a template.

The silica mesoporous material SBA-15 used as a template for synthesis of mesoporous polycarbosilane have been synthesized, following the procedure in the literature.[6] The XRD (Rigaku D/Max 2200 diffractometer) pattern of calcined SBA-15 reflected the formation of high quality SBA-15 with hexagonal symmetry (not shown here). Figure 1(a) shows transmission electron micrograph (TEM, JEOL JEM-2010) image of rod-shaped calcined SBA-15 with the regular channel array in parallel along the crystallographic c-axis. The external morphology of SBA-15 is rod shape with the length of *ca.* 1 $\mu$m and the diameter of *ca.* 400 nm, as shown in Figure 1(a). $N_2$ adsorption-desorption isotherm of calcined SBA-15 was measured using Micromeritics ASAP2010 instrument (Figure 2(a)). Brunauer-Emmett-Teller (BET) surface area was 849 $m^2/g$, the average pore diameter, 5.1 nm, total pore volume, 1.073 cc/g, and micropore volume, 0.058 cc/g. The $d_{100}$ spacing calculated from (100) peak at 1.03° of XRD pattern was 8.6 nm, the unit cell parameter ($a_0=2d_{100}/\sqrt{3}$), 9.9 nm and the wall thickness, 4.8 nm.

The agent impregnated to the pore of SBA-15 for the synthesis of polycarbosilane-based mesoporous material was polymethylsilane prepared by polymerization *via* dehalocoupling of dichloromethylsilane using Na catalyst as following procedure in the literature.[15] The number average molecular weight and the weight average molecular weight of polymethylsilane determined by gel permeation chromatography were 927 and 4120, respectively.

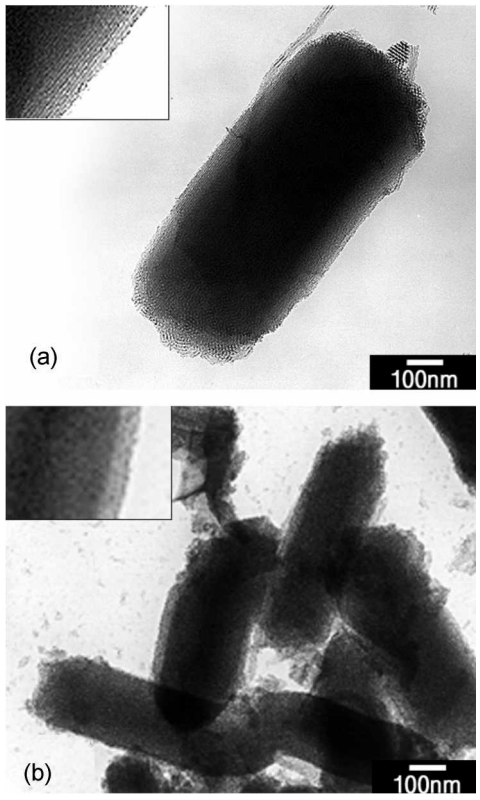


**Figure 1.** Transmission electron micrographs for (a) template-extracted SBA-15 and (b) silica-extracted mesoporous polycarbosilane after treated at 600 °C.

The synthesis of mesoporous polycarbosilane was performed using SBA-15 as a host material and polymethylsilane as a guest material. 0.32 g of calcined SBA-15 was dried under vacuum of $10^{-3}$ torr, and impregnated with 0.28 g of polymethylsilane dissolved in 0.5 mL of toluene in the glove box filled with nitrogen atmosphere. The resultant composite was put into a fused quartz tube equipped with fritted disk. After removal of toluene under vacuum for 24 h at 160 °C, the composite was heated to 250 °C at a heating rate of 5 °C$min^{-1}$, cured at 250 °C for 4 h and heated at 600 °C for 2 h in Ar atmosphere. The heat-treated composite was dissolved with stirring for 2 h in 48% HF solution to remove SBA-15 template. The resulting mesoporous polycarbosilane was washed with ethanol/$H_2O$ solution and dried at 60 °C for 12 h. The yield percentage based on the impregnated weight

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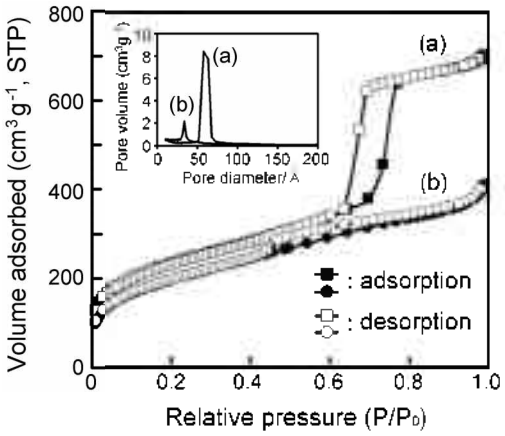


**Figure 2**. $N_2$ adsorption-desorption isotherm for (a) calcined SBA-15 and (b) silica-extracted polycarbosilane after treated at 600 °C. Inset shows the pore size distribution of (a) calcined SBA-15 and (b) mesoporous polycarbosilane.

of polymethylsilane was 68%. The transformation of polymethylsilane to polycarbosilane within mesopore in SBA-15 was confirmed by infrared spectroscopy (Shimadzu Corp. FT-IR-8201PC) (not shown here). The appearance of band at 1023 $cm^{-1}$ (Si-C-Si) and the decrease of 1239 $cm^{-1}$ (Si-$CH_3$) can be assigned to the formation of Si-C-Si bond with the breaking of Si-$CH_3$ bond via Kumada rearrangement.[16]

Figure 1(b) shows the TEM image of silica-extracted mesoporous polycarbosilane after treated at 600 °C. While the particle size of mesoporous polycarbosilane is smaller than that of SBA-15, as shown in Figure 1(a), the morphology of polycarbosilane bears a resemblance in shape to that of SBA-15. It indicates that most of polymethysilane incorporated into SBA-15 channel and transformed to polycarbosilane within the channels of SBA-15. That is, it seems that the mesoporous polycarbosilane generated through the replication of SBA-15 template. The contraction of particle size may be due to the shrinkage of polycarbosilane framework during the removal of silica. This shrinkage is attributable to the incomplete filling of polymethylsilane in micropore and mesopore of SBA-15 template and weight loss during heat treatment for Kumada rearrangement. These lead to the irregularity of pore array of mesoporous polycarbosilane as well as the contraction of particle size.

On the comparison with that of SBA-15 as shown in Figure 1(a), the pore array of polycarbosilane was disordered, indicating that this material does not completely replicate. $N_2$ adsorption-desorption isotherm of polycarbosilane reflects the formation of mesopore, as shown in Figure 2(b). The BET surface area was 703 $m^2/g$, the total pore volume at 0.9904 of $P/P_0$, 0.64 cc/g and micropore volume, 0.015 cc/g. The curve (b) in inset of Figure 2 shows the pore size distribution of mesoporous polycarbosilane. The average pore diameter calculated by BJH method from the desorption branch of isotherm was 3.6 nm.

As shown in Figure 3, $^{29}$Si-MAS (magic angle spinning) NMR (Bruker DSX 400 MHz, 4 mm ZrO rotor) spectrum of mesoporous polycarbosilane has two broad peaks at -4.8 and

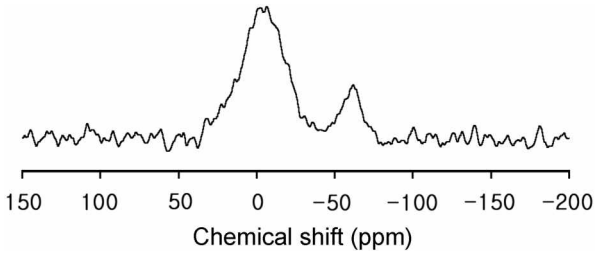


**Figure 3**. $^{29}$Si-MAS NMR of silica-extracted mesoporous polycarbosilane after treated at 600 °C.

-62.0 ppm. The peak at -4.8 ppm can be assigned to Si (83 atomic % from NMR peak area) of polycarbosilane framework, another peak at -62.0 ppm to Si (17 atomic %) of polycarbosilane bonded to oxygen, which comes from the silica surface of SBA-15 during thermal treatment. That is, the hydroxy group of the surface silanol of SBA-15 combined to polycarbosilane during thermal treatment may be resided after HF treatment, while most of silica framework of SBA-15 were removed by HF treatment. The removal of silica framework as a template is confirmed by the absence of the peak at *ca.* -110 ppm in $^{29}$Si-MAS NMR. The presence of oxygen in mesoporous polycarbosilane is evidenced by the results of EDX (energy dispersive X-ray spectroscopy, KEVEX Corp. KEVEX superdry detector) measurement showing 54 at. % of Si, 42 at. % of C and 4 at. % of O.

It is expected that the regularity of polycarbosilane mesopore can be improved by the control of the average molecular weight of polymer precursor and the condition for thermal treatment.

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