Facile Route for the Preparation of Hollow Silica Using Aromatic Desilylation in Phenylsilsesquioxane Particles

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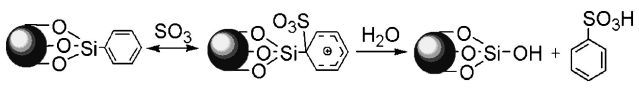
Using aromatic desilylation reaction, monodispersed porous hollow silica particles with spherical shape could be prepared from hollow PPSQ particles via simple treatment with fuming sulfuric acid.

Recently, many researchers have their interest in the preparation of hollow particles because of their potential applicability in various fields such as drug delivery, catalysis, coatings, composite materials, and other industrial fields.[1] Especially, hollow silica has been the most intensively studied one among the inorganic hollow particles.[2] For the preparation of hollow silica particles, templating method usually includes the procedure of removing a sacrificial core, such as latex, via a thermal decomposition or a chemical dissolution. However, thermal removal of the core generally requires high temperature that may give adverse effects on the structure.

In the previous paper, we reported the preparation of monodisperse hollow particles without using templates via a simple two-step process in an aqueous solution, where the particle size and the hollow diameter could be controlled by varying experimental conditions.[3] These particles have polyphenylsilsesquioxane (PPSQ; $PhSiO_{3/2}$) structure, which contains Si–C bond that can be cleaved by treatment with a strong acid. In this study, we investigated the reaction of PPSQ particles with strong acid in order to prepare hollow silica (SiO_2) particles by low-temperature process.

The Si–C bond cleavage comes from aromatic desilylation, which results from competitive substitution in aromatic rings attached to silicon. Electrophilic aromatic substitution generally proceeds via a σ-complex intermediate, and the cleavage of the Si–C bond is in the direction $C^-SiR_3^+$ in the same sense as aryl–H bonds are broken C^-H^+.[4] In spite of aryl–SiX_3 bonds could be cleaved much less readily than aryl–$SiMe_3$ bond when X is a more electronegative group than carbon, there are some reports wherein the desilylation in aryl–$Si(OSi)_3$ compounds under acidic condition is mentioned.[5]

Whereas the aromatic desilylation has been used as a versatile method for the introduction of various groups into aromatic compounds, this reaction has been generally regarded as an undesirable reaction in the modification of particle surfaces, such as the introduction of arene sulfonic acid functionality into particles. However, we report here that this reaction can be used as a facile method for preparing hollow silica particles.



Scheme 1. Schematic representation of the desilylation in PPSQ particles.

The general experimental procedure of the preparation of hollow silica particles is as follows: To a 3-neck flask with a magnetic stirrer were placed 1.3 g of hollow PPSQ particles[3] and ca. 6 mL of sulfuric acid in an ice bath. After particles were completely dispersed, 1.39 mL of fuming sulfuric acid (30% oleum) was added slowly by a dropping funnel. The reaction mixture was stirred at 0 °C for 30 min. The reaction mixture was heated to 50 °C and stirred for additional 2 h. After cooling to room temperature, the slurry solution mixture was carefully poured into crushed ice. The resulting white (or faint yellow) precipitate was collected by filtration and washed with water and methanol thoroughly. The final product, designated S-PPSQ (it denotes PPSQ particles treated with sulfuric acid) hereinafter in this paper, was dried at 80 °C in a vacuum oven. The amount of fuming sulfuric acid, heating temperature, and reaction time were varied for the examination on the results depending on experimental conditions.

Scheme 1 shows the mechanism of aromatic desilylation in PPSQ particles. The *ipso* substitution is occurred at the carbon attached to silicon, and the intermediate is attacked by a water molecule, then a silanol and a benzenesulfonic acid are formed.[6] With the assumption that the decomposed product was benzenesulfonic acid and it could readily be dissolved in water, the filtrant (aqueous acidic solution) after the reaction was analyzed by ^1H and ^{13}C liquid nuclear magnetic resonance (NMR) spectroscopy. Then, it is confirmed that the decomposed product was benzenesulfonic acid.

Electron micrograph images of the S-PPSQ particles were given in Figure 1. It is worth noting that the monodisperse spherical structure and the hollow morphology of particles were retained after the reaction; however, the diameter of S-PPSQ particles is somewhat reduced (50–100 nm), and this might be due to the condensation of silanol groups. In addition, the surface roughness of the particles increased slightly. The morphology of the hollow silica particles maintained after the calcination at 1000 °C for 3 h.

The results of the analyses on the chemical composition of

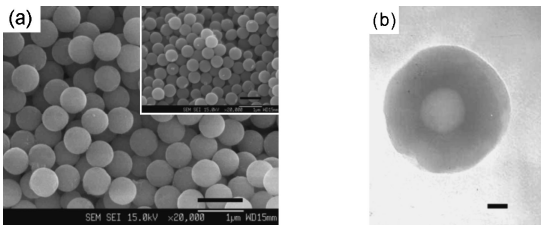


Figure 1. EM micrographs of the S-PPSQ particles: (a) FE-SEM (×20 K, bar = 1 μm (inset: after calcination); (b) TEM (×100 K, bar = 50 nm).

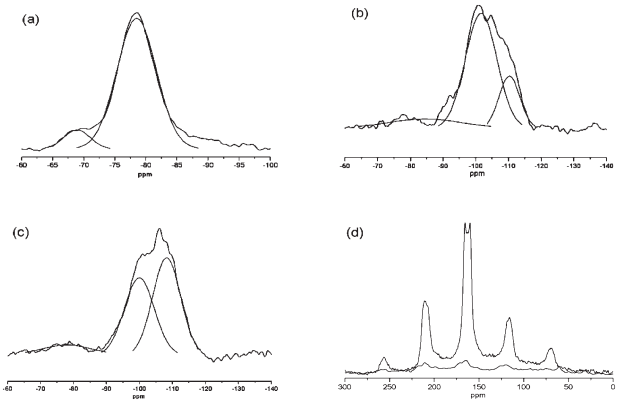


Figure 2. Solid-state ^{29}Si MAS NMR spectra of (a) PPSQ, (b) S-PPSQ (0.25 mol SO_3/mol phenyl) and (c) S-PPSQ (1.5 mol SO_3/mol phenyl) particles; (d) Solid-state ^{13}C CP–MAS NMR Spectra of PPSQ (upper line) and S-PPSQ (lower line) particles.

the particles showed that the S-PPSQ particles had silica structure. In the comparison of FT-IR spectra of S-PPSQ particles with that of PPSQ particles, the intensities of the peaks assigned to aromatic C=C stretching bonds at 1430 & 1590 cm^{-1} was much reduced, and the bands around 1100 cm^{-1} assigned to Si–O–Si stretching bonds were comparatively broadened. In addition, silanol absorption bands at 3000–3500 cm^{-1} broadened with an additional peak at 1640 cm^{-1} due to physically adsorbed water molecules. This implies increased hydrophilicity of S-PPSQ particles resulting from the conversion of phenyl groups into hydroxy groups.

As shown in the solid-state ^{29}Si magic angle spinning (MAS) NMR spectra (Figure 2), the peaks at -78.1 and -69.4 ppm disappeared, which corresponded to T_3 and T_2 silicon sites respectively, and new peaks at -108 and -99 ppm corresponding to Q_4 and Q_3 silicon units were observed. This means that the desilylation occurred in the particles, and thus Si–C bonds were converted to Si–O bonds. The occurrence of Q_4 units indicates that the further condensation of the Q_3 silanol groups generated from T_3 units was occurred under an acidic condition. The extent of condensation was dependent on the amount of SO_3 in the reaction as shown in Figures 2b and 2c, and this might be due to the difference in condensation rate of silanol groups on the acidity. This fact gives an opportunity in preparing silanol-abundant hollow silica particles by adjusting experimental conditions, which can rarely be made through the core-removal process in high temperature. ^{13}C MAS NMR spectra (Figure 2d) also show the disappearance of phenyl groups in PPSQ particles.

The removal of phenyl groups in PPSQ particles was also confirmed by elemental analyses.[7] On the basis of the assumption that the unit structure of PPSQ particles is $C_6H_5SiO_{1.5}$, the observed values for PPSQ agree well with the theoretical values (55.77% for carbon and 3.91% for hydrogen). On the contrary, carbon content of S-PPSQ was less than one-fifth of those of PPSQ particles.

The thermogravimetric analyses showed a slight difference in weight loss about 300 °C in S-PPSQ particles as compared to PPSQ particles. This might be due to the condensation of silanol groups in the presence of physisorbed water molecules as mentioned for FT-IR analyses. The transformation of organic groups into volatile species should be responsible for the abrupt mass loss for PPSQ at 600 °C.[8] Elemental analyses indicated that almost all carbon was removed at 600 °C in oxygen atmosphere (carbon : < 0.04%, hydrogen: < 0.05%).

Table 1. Results of BET analyses of the particles

Specimen	Amount of Added SO_3[a]	Surface Area /m^2/g	Pore Volume /cm^3/g	Average Pore Diameter/Å
PPSQ	0	19.03	0.032	67.9
S-PPSQ	0.25	270.52	0.16	24.2
	1.0	389.7	0.21	21.3
	1.5	537.0	0.30	22.6

[a]This values mean the molar ratio of SO_3 to phenyl units calculated under an assumption that the structural unit of PPSQ particles is $[C_6H_5SiO_{1.5}-]$.

The surface area of the resultant particles was determined using Brunauer–Emmett–Teller (BET) measurement from N_2 isothermal adsorption at 77.35 K, and the results of BET analyses were summarized in Table 1. The nitrogen adsorption isotherm of S-PPSQ was of type I rather than type IV and this implies that the pore size of the particles is close to micropore range. The great increase in low-pressure nitrogen adsorption for S-PPSQ particles compared to PPSQ can be related to the change in surface groups in the particles from organic groups which interact weakly with nitrogen atoms into hydroxy groups.[9] The surface area of the resultant particles was much increased as compared to that of PPSQ particles, and the average pore diameter was reduced. This might result from the small pore formation during the removal of phenyl groups and the structural rearrangement on condensation.

In summary, we have shown that the monodispersed porous hollow silica can be prepared from hollow PPSQ particles through treatment with sulfuric acid using simple aromatic desilylation reaction. The hollow and particle size of the silica can be controlled using appropriate PPSQ particles as precursors. Since this process does not require high temperature in a thermal template-removal process, it may be used as a facile route for preparing porous silica particles.

References

1 F. Caruso, R. A. Caruso, and H. Möhwald, *Science*, **282**, 1111 (1998); F. Caruso, *Chem.—Eur. J.*, **6**, 413 (2000); A. Imhof and D. J. Pine, *Nature*, **389**, 948 (1997); A. Dong, Y. Wang, Y. Tang, N. Ren, Y. Zhang, and Z. Gao, *Chem. Mater.*, **14**, 3217 (2002).
2 S. Schacht, Q. Huo, I. G. Voigt-Martin, G. D. Stucky, and F. Schüth, *Science*, **273**, 768 (1996); C. E. Fowler, D. Khushalani, and S. Mann, *J. Mater. Chem.*, **11**, 1968 (2001); I. Tissot, J. P. Reymond, F. Lefebvre, and E. Bourgeat-Lami, *Chem. Mater.*, **14**, 1325 (2002).
3 H. J. Hah, J. S. Kim, B. J. Jeon, S. M. Koo, and Y. E. Lee, *Chem. Commun.*, **2003**, 1712.
4 A. R. Bassindale and P. G. Taylor, in "The Chemistry of Organic Silicon Compounds," ed. by S. Patai and Z. Rappoport, John Wiley & Sons, Avon (1989), Vol. 1, Chap. 14.
5 R. D. Badley and W. D. Ford, *J. Org. Chem.*, **54**, 5437 (1989); J. M. J. Fréchet, G. D. Darling, S. Itsuno, P. Z. Lu, M. V. de Meftahi, and W. A. Rolls, Jr., *Pure Appl. Chem.*, **60**, 353 (1988).
6 R. W. Bott, C. Eaborn, and T. Hashimoto, *J. Organomet. Chem.*, **3**, 442 (1965).
7 Elemental analysis (mass %) for PPSQ: C, 55.47; H, 4.11. For S-PPSQ: C, 10.81; H, 2.37; S, 2.45.
8 R. Kalfat, F. Babonneau, N. Gharbi, and H. Zarrouk, *J. Mater. Chem.*, **11**, 1673 (1996).
9 M. Kuroki, T. Asefa, W. Whitnal, M. Kruk, C. Y.-Ishii, M. Janoniec, and G. A. Ozin, *J. Am. Chem. Soc.*, **124**, 13886 (2002); M. Kruk and M. Jaroniec, *Chem. Mater.*, **13**, 3169 (2001).

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