Preparation of a Hollow Microsphere Composed of Porous Organic-Inorganic Hybrid Wall in a W/O Microemulsion System

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Hollow microspheres composed of organic-inorganic hybrid wall (polyorganosiloxane) have been synthesized as a new material in a W/O emulsion system from organosilanes. The average diameter of spheres for a typical run is 1.8 μm (standard deviation = 0.84) with a large spherical cavity in them and thermally stable at least up to 400 °C in air. The polyorganosiloxane wall is amorphous and becomes porous by treating at around 400 °C in air.

Vast numbers of works have already been accumulated for the preparation, characterization and application of various kinds of silica as described by Iler.[1] Among these studies, monodispersed silica particles[2] and silica with ordered mesostructures such as MCM-41[3] and FSM-16[4] have had considerable attention as new materials. In recent years, a lot of efforts have been made for the preparation of spherical mesoporous silica[5] and hollow silica particles[6–10] because of their potential uses as confined-space catalysts, microcapsules, slow drug-release systems, chromatographic adsorbents and so on. Recently, Yu et al.[10] prepared siliceous hollow spheres with ultra large mesopores.

Organic-inorganic hybrid materials such as organosilica are very interesting as a new material possessing both organic and inorganic properties and relatively high thermal stability. We[11] showed that aluminum-containing organosilica acts as a solid acid catalyst. Choi et al.[12] prepared spherical organosilica powders from a organoalkoxysilane-water system. However, there have been few studies for the preparation of hollow and/or porous organosilica particles. In the present study, a hollow microsphere composed of porous organic-silica wall has been prepared as a new material from organosilanes in a W/O microemulsion system.

The silanes used here were methyltrichlorosilane (MTCS), methyltriethoxysilane (MTEOS), and octyltrichlorosilane (OTCS) purchased from Shin-Etsu Chemical. A typical synthesis was carried out as follows: A W/O emulsion was prepared by mixing toluene (100 ml), distilled water (1.5 ml), and OTCS (24 mmol) followed by ultrasonic agitation. Then MTCS, MTEOS or the mixture of them (see Table 1 for the composition of the mixtures) dissolved in toluene (ca. 20 ml) was poured into the emulsion under magnetic stirring. The mixture was stirred at room temperature for more than 24 h. During the reaction, a large amount of air (ca. 3 l min^{-1}, relative humidity is ca. 40%) was supplied continuously at least for 6 h to remove hydrogen chloride gas evolved from the silanes. The produced solid was separated, washed thoroughly with toluene and ethanol, and dried at 120 °C.

Thermal treatment of the samples was carried out at 400 or 600 °C for 3 h in an electric furnace. The samples were characterized by using FE-SEM (Hitachi, S-4100), N_2 adsorption isotherm (Micromeritics, ASAP-2000), XRD (Rigaku, RINT-2200V), and thermal analysis (Shimadzu, DTG-50HS).

As shown in Figure 1(a), FE-SEM observation revealed that most of the products are microspheres. The average diameter of the spheres is 1.8 μm (standard deviation = 0.84) for a typical run. In Figure 1(b) is the inside shape of a microsphere. The

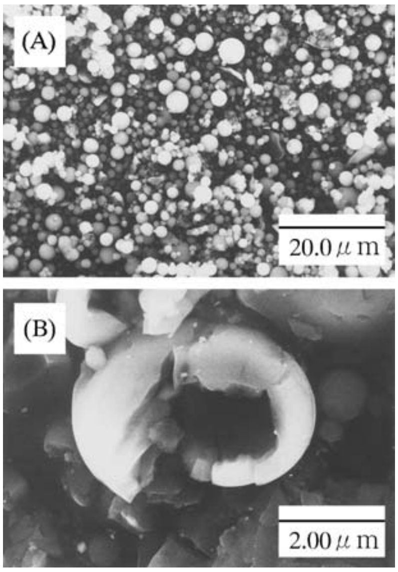


Figure 1. FE-SEM micrograph of a) the outside and b) the inside of Mix-1 (prepared from 1 : 1 mixture of MTCS and MTEOS).

Table 1. The amount of starting materials, yield, and shape of prepared particles

Sample	Water/ml	Starting materials/mmol OTCS	MTEOS	MTCS	Yield/%[a]	Shape	Diameter/μm
MTEOS-1	1.5	24	17	0	10–11	sphere, hollow	1.5–4
MTCS-1	1.5	24	0	17	16–18	sphere, packed	0.5–6
Mix-1	1.5	24	3	3	16–20	sphere, hollow	1–4
Mix-2	1.5	24	6	6	16–17	sphere, hollow	1–3.5

[a]The values of yield were calculated based on the amount of MTCS, MTEOS, and OTCS used for each run.

particle has a cavity (ca. 1 μm in diameter). Similar cavity is observed for the particles prepared from MTEOS or mixtures of MTCS and MTEOS (see Table 1 for the composition of the mixtures). On the other hand, the particles prepared from MTCS tend to form spheres without cavity. The shape and yield of the particles prepared under several conditions are summarized in Table 1. The spheres still kept the shape after calcination at 400 or 600 °C for 3 h. The low yields suggest that a part of the silanes added to the system exists as monomer or oligomer.

It was found at the preparation of hollow particles that supply of dry air passing through a silica gel column, instead of humid air, caused deformation of particles to the shape of air-removed rubber ball. The result implies that the water vapor supplied during reaction plays an important role to avoid deformation of microspheres.

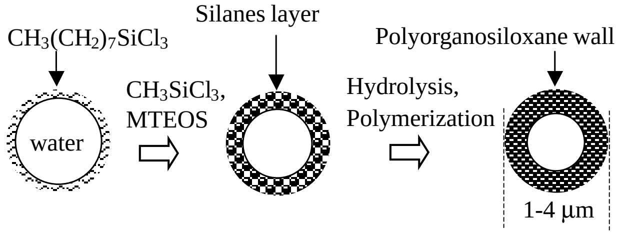
The specific surface area of the samples estimated by BET method is shown in Table 2. The surface area of samples dried at 120 °C is extremely small. On the other hand, samples calcined at 400 °C for 3 h show relatively large surface area (313–349 m^2g^{-1}). Surface area of the samples calcined at 600 °C is quite small compared with that of samples calcined at 400 °C. These results suggest that the wall of the microspheres is porous only when the samples are calcined at around 400 °C. Analysis based on XRD suggested that the samples are amorphous independent of calcination temperature.

Table 2. Treating temperatures and surface area of samples

	specific surface area/m^2g^{-1}		
Temperature/°C	MTEOS-1	MTCS-1	Mix-1
120	≈0	≈0	≈0
400	348	331	313
600	≈0	7	10

Thermal analysis of the samples revealed that exothermic peaks with decrease in mass are observed at around 250 and 500–600 °C. On the other hand, IR-spectra of the samples suggested that both octyl and methyl group exist in as-made samples. Absorption peaks of octyl and methyl group disappear essentially by treating the samples at 400 and 600 °C, respectively. These results show that the wall of as-made samples are composed of polyorganosiloxane including octyl and methyl group and that the wall turns to polymethylsiloxane by treating at 400 °C. Thus it is concluded that the hollow microspheres prepared here is composed of organic-inorganic hybrid material stable up to 400 °C.

Formation of the hollow spheres may be explained as the mechanism shown in Scheme 1. In the W/O emulsion system, OTCS aggregates at the water-oil interface and contributes to stabilize water-microdroplets as a surfactant. The silane molecules (MTCS, MTEOS, or mixture of them) poured into the emulsion diffuse through oil phase to the interface. Since MTCS and MTEOS have a methyl group with hydrophobic nature, they also tend to aggregate at the water-toluene interface and are hydrolyzed under strong acidic conditions made by a large amount of hydrogen chloride evolved from the silanes. Then the hydrolyzed silanes are polymerized to form hollow microsphere by using water-microdroplets as template.



Scheme 1.

Consumption of water due to hydrolysis would result shrinkage of water-microdroplets. According to the shrinkage, polyorganosiloxane spheres covering water-microdroplets would transform into the shape of air-removed rubber ball which is observed for the samples prepared by supplying dry air. Thus a part of water for the hydrolysis should be supplied as vapor from outside of the system to avoid deformation of hollow microspheres.

As described above, particles prepared from MTCS tend to form spheres without cavity. It is implied from the result that hydrolysis and polymerization of MTCS would proceed rapidly not only at the interface but also in water-microdroplets due to the violent reaction of MTCS and water in the absence of MTEOS.

In conclusion, hollow porous microspheres composed of organic-inorganic hybrid wall were prepared as a new material in a W/O microemulsion system.

References

1 R. K. Iler, ''The Chemistry of Silica,'' John Wiley, New York (1979).
2 W. Stöber, A. Fink, and E. Bohn, *J. Colloid Interface Sci.*, **26**, 62 (1968); K. Osseo-Asare and F. J. Arriagada, *Colloids Surf.*, **50**, 321 (1990); W. Wang, X.-a. Fu, J.-a. Tang, and L. Jiang, *Colloids Surf., A*, **81**, 177 (1993); F. J. Arriagada and K. Osseo-Asare, *J. Colloid Interface Sci.*, **170**, 8 (1995); G. H. Bogush, M. A. Tracy, and C. F. Zukoski, IV, *J. Non-Cryst. Solids*, **104**, 95 (1998).
3 C. T. Kresge, M. E. Leonowicz, W. J. Roth, J. C. Vartuli, and J. S. Beck, *Nature*, **359**, 710 (1992).
4 S. Inagaki, Y. Fukushima, and K. Kuroda, *J. Chem. Soc., Chem. Commun.*, **1993**, 680; M. Grün, I. Lauer, and K. K. Unger, *Adv. Mater.*, **9**, 245 (1997).
5 Q. Huo, J. Feng, F. Schüth, and G. D. Stucky, *Chem. Mater.*, **9**, 14 (1997); H. Yang, G. Vovk, N. Coombs, I. Sokolov, and G. A. Ozin, *J. Mater. Chem.*, **8**, 743 (1998); J. Esquena, R. Pons, N. Azemar, J. Caelles, and C. Solans, *Colloids Surf., A*, **123–124**, 575 (1997).
6 S. Schacht, Q. Huo, I. G. Voigt-Martin, G. D. Stucky, and F. Schüth, *Science*, **273**, 768 (1996).
7 H. Ono and K. Takahashi, *J. Chem. Eng. Jpn.*, **31**, 808 (1998).
8 P. S. Singh and K. Kosuge, *Chem. Lett.*, **1998**, 101.
9 M. Jafelicci, Jr., M. R. Davolos, F. J. dos Santos, and S. J. de Andrade, *J. Non-Cryst. Solids*, **247**, 98 (1999).
10 C. Yu, B. Tian, J. Fan, G. D. Stucky, and D. Zhao, *Chem. Lett.*, **2002**, 62.
11 S. Mishima, T. Nakajima, and T. Hiki, *Bull. Chem. Soc. Jpn.*, **63**, 126 (1990).
12 J. Y. Choi, C. H. Kim, and D. K. Kim, *J. Am. Ceram. Soc.*, **81**, 1184 (1998).