(Original article)

Preparation of Porous Thin-film Polymethylsiloxane Microparticles in a W/O Emulsion System

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Running head: Thin-film polymethylsiloxane microparticles

(Abstract)

Porous thin-film polymethylsiloxane microparticles have been prepared successfully from octyltrichlorosilane and methyltrichlorosilane in W/O emulsion system by using several oil phase and changing the amount of the silanes or a surfactant Span 60. Hollow microspheres of various shell thickness (120-180 nm) with high surface area were prepared by using four kinds of nonpolar solvents as oil phase of the W/O emulsion. Diameter of the spheres can also be controlled (1-1.6 μm) by using different oil phase. Results of thermal analysis, nitrogen adsorption isotherm, IR spectra and XRD data showed that hollow microspheres of amorphous polymethylsiloxane with high surface area (360-385 m^2g^{-1}) can be obtained by heat treatment in the air at 673K and the microspheres turn to nonporous silica particles after calcination at 873K for 3 h. Cup shape microparticles of polymethylsiloxane with nano-order thickness (20-120 nm) was prepared by using smaller amounts of silanes. Small hollow particles were prepared by replacing small amounts of octyltrichlorosilane with Span 60.

INTRODUCTION

Silica gel a representative inorganic porous material of high surface area has frequently been applied as desiccant, catalyst support, etc. In recent years, there have been various attempts for the preparation of new silica of special morphology and function such as monodispersed spheres,[1-5] films,[6-8] monoliths,[9-13] nanofibers,[14-17] hollow spheres[18-28] because of their potential importance as new functional material. Similar studies have also been reported for other metal oxides such as zeolite[29-33] and titania.[34-36]

Among metal oxides of special morphology, porous thin-film microparticles of 1-10 μm in diameter and 1-100 nm in thickness are also interesting as a functional material. Notable characteristic of porous thin-film particles is its wide outer surface due to the thin-film structure. When porous thin-film particles are applied as catalyst support, for example, major parts of catalytic site are mounted on the outer surface of the particle. As a result, adsorption of reactants and desorption of products during catalytic reaction become easy because the migration length of reactants and products between gas phase or liquid phase and catalytic site is less than the thickness (*e.g.,*

1-100 nm) of the thin-film. On the other hand, in the case of high surface catalysts prepared using usual porous particles, the migration length of reactants and products through micropore of the catalyst would often larger than the diameter of catalyst particles (*e.g.*, > 1 μm). Thus it is expected for some catalytic reaction that catalysts prepared using porous thin-film particle result in excellent activity and/or selectivity compared with conventional porous catalysts.

Hollow microspheres formed by thin-film shell can be regarded as a porous thin-film particle. There are several studies[22,23,28] for the fabrication of hollow silica microparticles formed by thin-film shell. Zoldesi *et al.*,[22,23] for example, made silica of hollow microspheres, cup shape microcapsules and microballoons from TEOS in an emulsion systems. Although there are few studies for the application of thin-film silica particles as a functional material such as catalyst and adsorbent, such particles are of importance as a new functional material.

We[37] reported that hollow microspheres composed of polymethylsiloxane prepared by applying a W/O emulsion system show relatively high surface area (>300 m^2/g) and high thermal stability (>673K). Since polymethylsiloxane is an

organic-inorganic hybrid material including large amount of methyl group bonding to silicon atom, thin-film particles of polymethylsiloxane are very interesting as a new functional material different from thin-film silica. However, there are few studies for the preparation of thin-film polymethylsiloxane microparticles. In the present study, we applied the method reported in our preceding paper[37] for the preparation of porous thin-film particle of polymethylsiloxane.

EXPERIMENTAL PROCEDURE

Materials

Octyltrichlorosilane (OTCS) and methyltrichlorosilane (MTCS) were purchased from Aldrich Chemical Co., Ltd., and Shin-Etsu Chemical Co., Ltd., respectively. Toluene, isooctane (2,2,4-trimethylpentane), trichloroethylene and *n*-hexane were GR grade purchased from Wako Chemical Co., Ltd. Sorbitan monostearate (Span 60) was obtained from Wako Chemical Co., Ltd. All of the materials were used as received.

Sample preparation

Following method is the representative procedure (called as the standard method, hereinafter) for preparing microparticles: a W/O emulsion was prepared by mixing 0.75 mL of water and 2.97 g (12 mmol) of OTCS dissolved in 50 mL of a solvent (toluene, trichloroethylene, *n*-heptane or isooctane) as oil phase followed by ultrasonic agitation (45kHz) for 5 min; then 1.35 g (9.0 mmol) of MTCS dissolved in 10 mL of the same solvent was poured into the W/O emulsion under magnetic stirring; the mixture was stirred at room temperature for more than 3 h for the completion of the reaction. During the reaction, water-saturated air was continuously supplied (0.1 L min^{-1}) to remove evolved hydrogen chloride and to accelerate hydrolysis and polymerization of OTCS and MTCS by supplying water vapor. Obtained solid was separated by centrifugation, washed thoroughly with the same solvent and dried at 323K for 24 h, then washed with ethanol aqueous solution (50 % in volume) and dried at 393 K for more than 3 h. Finally, obtained solid samples were calcined at 673 or 873 K in an electronic furnace.

To prepare further thin particles, the amount of OTCS and MTCS added to the system

were reduced to 50, 20, and 10%, simultaneously, of the amounts used for the standard

method by using isooctane as the oil phase.

   To examine effects of the emulsifier on the shape of product, a part of OTCS used in

the standard method was replaced with Span 60. Namely, sum of the amount of OTCS

and Span 60 is always equal to 12 mmol.

Characterization

       Thermogravimetric-differential thermal analyses were carried out by using

Shimadzu DTG-50 at the heating rate 10 K /min.   Fourier transform infrared spectra

were recorded on Shimadzu FT-IR 4200A by applying KBr pelletizing method.

Scanning electron micrographs were obtained on Hitachi S-4200 field-emission

scanning electron microscope. X-ray diffraction patterns were obtained by using Rigaku

RINT 2200V/PC (monochromatic Cu K_{α}) operated at 20 mA, 40 kV.   Nitrogen

adsorption-desorption isotherms at 77 K were obtained by using Micromeritix

ASAP2000. Solid-state ^{13}C MAS NMR spectra were recorded on Bruker ASCEND 500

spectrometer on the resonance frequency of 125.77 MHz and the spinning frequency of

10 kHz.

RESULTS AND DISCUSSION

Effect of the kind of oil phase on the shape of products

The SEM images of particles prepared by applying the standard method using

toluene as the oil phase are shown in Figure 1. As shown in Figure 1 (a), prepared

particles calcined at 673 K for 3 h were microspheres of 1-5 μm in diameter, and as

shown in Fig. 1 (b), microspheres cleaved in a mortar suggested that the particles are

hollow with a large void core and a relatively thick shell (*c.a.*, 180 nm). Similar hollow

spheres were obtained by using isooctane, trichloroethylene, and *n*-heptane as oil phase.

From these results, it has been revealed that hollow microsphares can be prepared from

OTCS and MTCS in W/O emulsion system using nonpolar solvents as oil phase.

In the W/O emulsion produced by ultrasonic agitation, water microdroplets are

stabilized by OTCS which operates as an emulsifier due to hydrophobic octyl group and hydrophilic Si-Cl group of OTCS. Since MTCS with hydrophobic methyl group may also be apt to aggregate at the water-oil interface, hydrolysis and polymerization of MTCS and OTCS would proceed at the water-oil interface. As a result, hollow microspheres are formed by using water droplets as template.

(Insert Figure 1)

Values of yield, surface area, particle size and shell thickness of samples prepared by using four kinds of solvent as the oil phase are summarized in Table 1 together with the dielectric constant ε_r of the solvents. The same yields (28%) were observed independent of the kind of oil phase. The low yields suggests that a large amount of OTCS and MTCS added to the system still exists in the oil phase as monomer or oligomer even after particle formation. Specific surface areas shown in the table suggest that the shell of all hollow particles after calcined at 673 K for 3 h are porous (360-385 m^2g^{-1}) independent of the kind of oil phase.

In Table 1, particles obtained by using toluene and trichloroethylene give similar average particle diameter (1.5-1.6 µm) and shell thickness (160-180 nm). On the other hand, particles obtained by using n-heptane and isooctane are smaller (1.0 µm) with thinner shell (120 nm) compared with those obtained by using toluene and trichloroethylene. Since the size of hollow particles depend on the size of water droplets acting as the template in the emulsion, it is suggested that solvent of low dielectric constant ($\varepsilon_r = 1.9$) such as n-heptane and isooctane stabilize smaller water droplets than solvents of higher dielectric constant such as toluene ($\varepsilon_r = 2.4$) and trichloroethylene ($\varepsilon_r = 3.3$). From the results described above, it is concluded that the average size and shell thickness can be controlled in the range 1.0-1.6 µm and 120-180 nm, respectively, by using solvents of different dielectric constant as oil phase.

(Insert Table 1)

Thermal analysis

Results of thermal analyses of samples obtained by using toluene as the oil phase

are shown in Figure 2. Two exothermic peaks accompanying weight loss are observed

around 500-600 K and around 800 K. Considering that the particles obtained here can

be regarded as a copolymer of polyoctylsiloxane and polymethylsiloxane, the

exothermic peak around 500-600 K with weight loss can be attributed to oxidation of

octyl group which is thermally unstable compared with methyl group. Similarly, the

peak around 800 K with weight loss can be ascribed to oxidation of methyl group.

These results suggest that as made particles are copolymer of polyoctylsiloxane and

polymethylsiloxane. After treatment around 500-600 K, the particles turn

polymethylsiloxane which turns polysiloxane (silica) after treatment around 800 K.

Similar results were obtained for particles obtained using other oil phase, so that it is

suggested that as made particles obtained using other oil phase are also copolymer of

polyoctylsiloxane and polymethylsiloxane.

(Insert Figure 2)

IR spectra

FT-IR spectra of hollow microspheres prepared using toluene as oil phase are shown in Figure 3. Curve (a) shows IR spectrum of as made sample dried at 393 K. Since the results of thermal analysis suggested that this sample can be regarded as copolymer of polyoctylsiloxane and polymethylsiloxane, observed bands around 2900 cm^{-1} can be assigned to C-H stretching vibration of octyl and methyl group. Similarly, bands around 1500-1800 cm^{-1} can be assigned to C-H deformation vibration of octyl and methyl group. Spectrum (b) of the sample heat treated at 673 K also gives C-H stretching and deformation bands. As described above, this sample is regarded as polymethylsiloxane, so that the observed stretching and deformation bands can be assigned to methyl group. Curve (c) shows the spectrum of sample calcined at 873 K for 3h. As described above, thermal analysis suggested that this sample can be regarded as silica. Actually there is no absorption bands correspond to octyl and methyl group and the spectrum is qualitatively agree with that of silica gel. it is concluded from IR spectra that hollow spheres dried at 393 K, calcined at 673 and 873 K for 3 h are a copolymer, polymethylsiloxane and silica, respectively, in accordance with results of thermal analysis. Similar IR spectra were obtained for particles obtained by using other oil

phase.

(Insert Fig. 3)

XRD analysis

XRD patterns of particles obtained using toluene as the oil phase are shown in Figure 4. Curve (a), (b) and (c) are patterns of samples dried at 393 K, calcined at 673 and 873 K for 3 h, respectively. All samples give no sharp diffraction peak, they can be regarded as amorphous independent of treating temperature. Considering the results of IR spectra described above, broad diffraction peak around $2\theta = 20\text{-}25°$ observed in Curve (a)-(c) is ascribed to amorphous silica, broad peak around $2\theta = 10°$ observed in Curve (a) and (b) may be ascribed to polymethylsiloxane, broad peak around $2\theta = 5°$ observed in Curve (a) may be ascribed to polyoctylsiloxane. However, detailed structures corresponding to diffraction peaks at $2\theta = 5°$ and $10°$ are not clear at the present stage. Similar diffraction patterns were obtained for samples prepared using other oil phase.

(Insert Figure 4)

Effects of the amount of OTCS and MTCS used for preparing particles

To examine the effect of the amount of OTCS and MTCS on the shape of particles, samples are prepared using isooctane as oil phase and different amounts of OTCS and MTCS. Samples prepared by using 50, 20 and 10 % of OTCS and MTCS compared with those of the standard method are denoted as S-1, S-2 and S-3, respectively, and samples obtained by the standard method is denoted as S-0, hereinafter. The SEM image of the particles after calcination at 673 K for 3 h are shown in Figure 5. Although particles prepared by the standard method (S-0) are spherical, major parts of S-1, S-2, and S-3 are cup shape and become thinner and larger when smaller amounts of MTCS and OTCS were used. These TEM images suggest that shell of hollow sphere become thinner when smaller amounts of MTCS and OTCS were used, and the spheres are apt to deform from hollow spheres to cup shape during preparation process.

(Insert Figure 5)

Yield and physical characteristics of S-0, S-1, S-2 and S-3 are summarized in

Table 3. The yield of particles decreases when smaller amounts of OTCS and MTCS are

used. As described, it was suggested that a portion of OTCS and MTCS added to a W/O

emulsion exists as monomer or oligomer in the oil phase. Thus the lower yields of

particles obtained by using smaller amount of OTCS and MTCS may be ascribed to

increase in the ratio of organosiloxanes dissolving in the oil phase.

The size of major parts of particles of S-0 are 0.5-1 μm as shown in Figure 5. The

size of major parts of particles become larger for S-1 (1-1.5 μm), S-2 (3-4 μm) and S-3

(> 4 μm). When degreasing amounts of OTCS and MTCS are used for sample

preparation, the amounts of water consumed for hydrolysis are also degreased, so that

degree of shrinkage of water droplets during reaction becomes smaller when smaller

amount of OTCS and MTCS are used. Thus the difference of particle size observed here

may be ascribed to the degree of shrinkage of water droplets acting as template during

the reaction.

As shown in the table, S-0 is sphere and the average shell thickness is 120 nm. On the other hand, S-1, S-2 and S-3 are cup shape and the average shell thickness decreases. Especially, it is noteworthy that the shell thickness of S-3 is only *c.a.* 20 nm. These results suggest that the shell thickness of the particles can be easily and widely (20-200 nm) controlled by using different amount of OTCS and MTCS. As shown in the table, all of the samples give large specific surface area (315-382 m^2g^{-1}) independent of the thickness of shell. These results show that the shell of them are porous. The cup shape microparticles with nano-wall obtained here are very interesting as a new material rich in outer surface area.

(Insert Table 2)

Solid-state ^{13}C MAS NMR spectra of S-2 are shown in Figure 6, where spectra (a), (b) and (c) are correspond to S-2 dried at 393 K, heat treated at 673 K for 3 h in the air and calcined at 873 K, respectively. By comparing these results with those reported in an literature,[38] peaks 1-8 of spectrum (a) can be attributed to octyl group bonding to

silicon atom. Since dried S-2 is considered to be a copolymer of polyoctylsiloxane and polymethylsiloxane, the peak observed around 0 ppm in spectra (a) and (b) can be assigned to methyl group bonding to silicon atom. Thus disappearance of peaks of octyl group from spectrum (b) suggest that the as made copolymer turn polymethylsiloxane after heat treatment at 673 K accompanying enhancement of complete combustion of octyl group. On the other hand, the peak attributable to methyl group of spectrum (b) disappears from spectrum (c) of the sample calcined at 873 K. This result show that polymethylsiloxane particles obtained by heat treatment at 673 K turn silica after calcination at 873K. From the results described above, it is concluded that polymethylsiloxane particles with very thin film (c.a. 40 nm) obtained as S-2 after heat treatment at 673 K is also shows the same thermal

stability as polymethylsiloxane particles prepared by the standard method.

(Insert Figure 6)

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Effect of surfactant on the shape of prepared particles

To examine the effect of surfactant on the shape of prepared particles, a portion of

OTCS in the standard method (12 mol) was replaced by the same mole of a surfactant

Span 60. Toluene a good solvent of Span 60 was used as oil phase. SEM images of

obtained product are shown in Figure 7. Samples prepared by replacing 1% and 5% of

OTCS with Span 60 (denoted as S-4 and S-5, respectively) are small spherical hollow

particles. Samples prepared by replacing 10%, and 50% of OTCS with Span 60

(denoted as S-6 and S-7, respectively) were deformed or unshaped products. It is

obvious that obtained particles becomes smaller when larger amounts of Span 60 was

used instead of OTCS. Since the size of obtained particles should be depending on the

size of water droplets in the W/O emulsion, it is suggested that existence of larger

amount of Span 60 makes smaller the water droplets.

Numerical results and morphology of particles are summarized in Table 3. In the

table, yield of product become smaller when larger amounts of Span 60 are used.

Especially, yields are very small (0.1-1%) for samples prepared by replacing 50% of

OTCS (S-7) and 100% of OTCS (S-8). These results suggest that existence of large

amount of Span 60 prevents polymerization of OTCS and MTCS. It is known from the

particle distribution in the table that obtained particles becomes smaller when larger

amounts of Span 60 are used; namely, particle sizes are 0.5-6, 0.5-4, 0.1-2 and 0.5-1 μm

for S-0, S-4, S-5 and S-6, respectively. As shown in Table 3, specific face area of

samples S-4, 5 and 6 calcined at 673 K for 3 h were relatively large (331-576 m^2g^{-1}), so

that these particles are regarded as porous material.

It is revealed that size of hollow particles obtained here can be controlled by

replacing a portion of OTCS by Span 60 and that particles obtained by using Span 60

are also porous material.

(Insert Figure 6 and Table 3)

CONCLUSIONS

As described above, it has been demonstrated that porous thin-film

polymethylsiloxane microparticles can be prepared by using W/O emulsion system.

These particles are porous (360-385 m^2g^{-1}) and stable up to 673K. The mean diameter

of the micropaticles can be controlled in a range 1-1.6 µm by using various nonpolar solvents with different dielectric constant and the mean diameter can be diminished drastically (e.g., 0.5-1 µm) by adding small amount of Span 60 in the W/O emulsion. The thickness of the polymethylsiloxane microparticles can be controlled easily and widely (2-200 nm) by reducing the amount of OTCS and MTCS (1-10%) compared with the standard method.

As described in the introduction part, thin-film particles can be regarded a new functional material with very wide outer surface area and have potential application as excellent catalysts and adsorbents.

CONFLICT OF INTEREST

The authors declare no conflict of interest

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Figure captions

Figure 1. SEM images of (a) microspheres obtained by using toluene as oil phase and

calcined at 673 K for 3h, and (b) a cleaved microsphere.

Figure 2. Results of thermal analysis of hollow microspheres prepared from OTCS and

MTCS in a W/O emulsion system using toluene as oil phase.

Figure 3. FT-IR spectra of hollow microspheres prepared from OTCS and MTCS using

toluene as oil phase. Samples are (a) dried at 393 K, (b) heat treated at 673 K

and (c) 873 K for 3 h in the air.

Figure 4. XRD patterns of hollow spheres prepared using toluene as oil phase. Samples

are (a) dried at 393 K, (b) heat treated at 673 K and (c) 873 K for 3h in the air.

Figure 5. The effect of the amount of OTCS and MTCS on the shape of prepared

particles. Sample S-0 is particles obtained by the standard method. Samples

S-1, S-2 and S-3 are particles obtained by using 50, 20 and 10 % of OTCS

and MTCS, respectively, compared with the standard method.

Figure 6. Solid-state ^{13}C MAS NMR spectra of S-2. (a) as made, heat treated (b) at 673

K, and (c) at 873 K for 3 h in the air.

Figure 7. SEM images of products obtained by adding different amounts of Span 60

using isooctane as oil phase. For samples S-4, S-5, S-6 and S-7, OTCS is

replaced with 1.0, 5.0, 10.0 and 50% of Span 60, respectively. The inset of

photographs of S-4, S-5 and S-6 shows SEM image of a particle cleaved in a

mortar.