

Preparation and Formation Mechanism of Silica Microcapsules (Hollow Sphere) by Water/Oil/Water Interfacial Reaction

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Silica microcapsules (hollow spheres) were readily prepared by an interfacial reaction using a water/oil/water (W/O/W) emulsion system. A W/O emulsion consisting of an aqueous solution of sodium silicate (WP-1) and an *n*-hexane solution of Tween 80 and Span 80 (OP) was added to another aqueous solution of a precipitant (WP-2). The reaction of sodium silicate with a precipitant to form silica on this W/O/W emulsion system (WP-1/OP/WP-2) forms the hollow structure spontaneously. Therefore, no core material often utilized in silica hollow sphere fabrication was required in this process. The formation and the particle size of the silica microcapsule depended on the precipitant employed. When NH_4HCO_3 was used as precipitant, the particle size of the silica microcapsule was successfully controlled by the volume ratio of WP-1/OP/WP-2, the rotation number of the homogenizer, and the concentration of sodium silicate in WP-1. However, this control of the particle size was not achieved when other precipitants such as NH_4Cl were used. In the case of NH_4HCO_3 , silica formation takes place at the outer interface between OP and WP-2 on the W/O/W emulsion system. On the other hand, when NH_4Cl is utilized, silica is yielded at the inner interface between WP-1 and OP. These differences of reaction mechanisms of sodium silicate among precipitants were important factors in the preparation and properties of microcapsules.

Introduction

Fabrication of silica materials with designed structures is an active subject in modern material chemistry.^{1,2} The preparation of dense silica micro- and nanospheres, whose insides are filled with silica matrix, is a representative example.^{3–5} One of the recent research interests in silicas with controlled structures is the preparation of hollow materials such as hollow spheres and hollow fibers (tubes).^{6,7} A typical strategy to produce silica hollow spheres is the utilization of core–shell-type materials.^{8–18} In these cases, polymer latexes, inorganic spheres, oil droplets, and aggregates of polymers or

surfactants are used as cores, and silica matrixes or silica microparticles are formed on the core templates. Another representative approach to create silica hollow spheres is the vehicle template mechanism, where various kinds of surfactant vehicles are applied.^{19–24} A multistep preparation method is also claimed to be effective for silica hollow sphere synthesis.²⁵ However, most of these processes using core templates require the removal of templates inside by calcination or solvent treatments for creating vacant inner spaces. These treatments often result in fractures of the silica shells. The preparation of silica hollow spheres without a template was also examined recently. In the cases of

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Table 1. Profiles of Silica Microcapsules Obtained with Various Precipitants^a

sample no.	precipitant	volume ratio ^b	SSA ^c (m ² /g)	PV ^d (mm ³ /g)	PPD ^d (nm)	peak particle size ^e (μm)
1	NH ₄ Cl	1/2/7	337 (481) ^f	245 (189) ^f	2.11	7.96
2	(NH ₄) ₂ SO ₄	1/2/7	473	406	6.59	6.63
3	NH ₄ NO ₃	1/2/7	38	106	21.34	8.68
4	NH ₄ HCO ₃	1/2/7	757 (414) ^f	1023 (1660) ^f	8.21	12.51
5	NaHCO ₃	1/2/7	185	786	23.81	10.42
6	KHCO ₃	1/2/7	480	846	6.59	11.47
7	NH ₄ HCO ₃	2/1/14	309	716	12.09	7.23
8	NH ₄ HCO ₃	1/1/7	530	875	8.93	8.68
9	NH ₄ HCO ₃	1/4/7	560	991	8.93	15.02
10	NH ₄ HCO ₃	1/8/7	479	649	6.17	18.04
11 ^g	NH ₄ HCO ₃	1/2/7	413	965	10.83	7.23
12 ^h	NH ₄ HCO ₃	1/2/7	391	859	13.69	4.60
13 ⁱ	NH ₄ HCO ₃	1/2/7	426	867	13.69	4.60
17 ^j	NH ₄ HCO ₃	1/2/7	523	1814	11.90	7.23
18 ^k	NH ₄ HCO ₃	1/2/7	467	744	8.21	18.04

^a Concentrations of sodium silicate in WP-1 and precipitant in WP-2 were 4 and 2 M, respectively, and the contents of Tween 80 and Span 80 in OP were 13.9 and 6.9 g/L, respectively. The rotation number of the homogenizer for the W/O emulsion was 8200 rpm. ^b Volume ratio of WP-1 to OP to WP-2. ^c A BET plot was used for the determination of specific surface area (SSA). ^d The BJH method was applied to the estimation of pore volume (PV) and peak pore diameter (PPD). ^e Measured by laser diffraction analysis. ^f Sample obtained from direct mixing of two aqueous solutions (WP-1 and WP-2). ^g The rotation number of the homogenizer for the W/O emulsion was 10200 rpm. ^h The rotation number of the homogenizer was 15800 rpm. ⁱ The rotation number of the homogenizer was 19900 rpm. ^j The concentration of sodium silicate in WP-1 was 2 M. ^k The concentration of sodium silicate in WP-1 was 6 M.

hydrothermal syntheses of a silicate-type shell,^{26–29} the starting particles become hollow structures spontaneously. The use of air–water interfaces produces silica hollow spheres in some cases.^{30–32} Furthermore, two-step processes of hydrolysis of alkoxysilane with a phenyl group fabricate a hollow sphere without the utilization of a core template.³³

It is well-known that interfacial “polymerization” is a representative method to produce hollow organic polymers.^{34,35} We originally found that inorganic reactions of two aqueous solutions to form precipitates can be carried out on the interface of a water/oil/water (W/O/W) emulsion system. Precipitate formation from a precipitate source and a precipitant (reagent for precipitation formation) occurs along the interface of the W/O/W emulsion. When the reaction systems and conditions are properly chosen, inorganic hollow sphere particles are successfully formed.^{36–44} We call this reaction procedure “interfacial reaction” and these unique inorganic materials “microcapsules”. Microcapsules of calcium carbonate,^{36,37} metal silicates,³⁸ iron oxide,³⁹ manganese carbonate,⁴⁰ and amorphous silica^{41,42} are successfully produced by this preparation system. An amorphous silica microcapsule is readily prepared from sodium silicate with suitable salts as precipitants. Furthermore, various compounds can be included in the inner voids of the microcapsules.^{43,44} In this paper, we

report our recent progress in the chemistry of silica microcapsule preparation. We found that the reaction mechanism of sodium silicate with salts as precipitants on the W/O/W emulsion system was an important factor for the preparation of silica microcapsules. Furthermore, control of the particle sizes of the microcapsules was achieved by the suitable selection of precipitants and other preparation conditions.

Experimental Section

Materials. All chemicals used in this paper were commercially available and were used without further purification. Sodium silicate solution (water glass no. 3; SiO₂, 28.9 wt %; Na₂O, 9.4 wt %) was purchased from Kishida Chemical. Span 80, Tween 80, and all precipitants employed in this study were obtained from Kanto Kagaku Co. (Cica). Other compounds such as *n*-hexane were purchased from Wako Pure Chemical Industries.

Measurements. SEM (scanning electron microscopy) images were measured using a JEOL JSM-5200 microscope apparatus. Optical microscope images were obtained using a Nikon model Eclipse E600 POL apparatus. Nitrogen adsorption–desorption isotherms were measured using a Belsorp Mini instrument (Bel Japan). BJH plots were used for pore size distributions using adsorption branches. The particle sizes of microcapsules were measured by a laser diffraction particle analyzer (Shimadzu SALD-2000). XRD patterns of materials were recorded by using a Mac Science MOX3 diffraction meter with Cu Kα irradiation.

Preparation. Silica microcapsules (hollow spheres) were obtained by our interfacial reaction. A typical reaction procedure for the preparation of sample no. 4 (Table 1) is described using the following three solutions: water phase 1 (WP-1), a 4 M aqueous solution (36 mL) from ion-exchange water and sodium silicate solution (29.9 g, 144 mmol of Si); oil phase (OP), *n*-hexane solution (72 mL) of Tween 80 (1.0 g) and Span 80 (0.50 g) for the stabilization of the W/O emulsion well-claimed⁴⁵ (although the influence of these kinds of surfactants on

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mesoporous silica synthesis was reported,⁴⁶ the effects of these surfactants are not discussed in this paper); water phase 2 (WP-2), a 2 M aqueous solution (252 mL) of a precipitant (NH_4HCO_3 , 39.8 g, 503 mmol). OP was mixed using the homogenizer Heidolph DIAX 900 with 8200 rpm. To this solution was added WP-1 with emulsification. After being emulsified for 1 min, this mixture was poured into WP-2 in one portion with stirring. After the mixing, a white solid was formed in the resulting solution. The time period of this solid formation depended on the precipitants. For example, NH_4HCO_3 precipitant solution needed about 2–3 min for complete solid formation. On the other hand, NH_4Cl precipitant solution afforded solid immediately (within 1 min). The resulting solution was further mixed for 2 h for aging. The solid was filtered and washed with fresh ion-exchange water three times and with sufficient amounts of methanol. Finally, the solid was dried at 100 °C for 12 h. The influence of the volume ratio of the oil and water phases on the particle size was examined in the following manner. The concentrations of sodium silicate, precipitant, and surfactants in WP-1, WP-2, and OP, respectively, were not changed. As the molar ratio of precipitant to sodium silicate was also fixed to be 3.5 (precipitant/sodium silicate), the volume ratios of WP-1 and WP-2 were similar (WP-1/WP-2 = 1/7) in all runs. Only the total volume ratios of WP-1, OP, and WP-2 were varied, and the ratios are summarized in Table 1.

Observation of a Water Droplet in Oil of the W/O Emulsion. For estimating the size of the water droplet in oil (W/O emulsion), we used an optical microscope (Nikon model Eclipse E600 POL apparatus) just after the W/O emulsion formation. For measuring the laser diffraction particle analyzer, the dilution of the emulsion solution with suitable solvent is necessary to avoid multiple scattering. However, this dilution treatment probably influences the particle sizes of the droplets in the emulsion, which is not appropriate for the observation of water droplets in various preparation conditions, especially for different volume ratios of OP and WP-1. Therefore, we regarded the utilization of the laser diffraction particle analyzer as inadequate.

Titration of Precipitant Solutions into the Aqueous Solution of Sodium Silicate. To 50 mL of the solution of sodium silicate (50 mM) was added dropwise a 1 M solution of a precipitant. The amounts of the precipitant solutions, when the silica precipitate was clearly found in the solution, were estimated by this titration experiment. The required amounts of the precipitant solutions were 78, 74, 65, 28, 28, and 12 mL in the cases of NH_4HCO_3 , KHCO_3 , NaHCO_3 , NH_4NO_3 , NH_4Cl , and $(\text{NH}_4)_2\text{SO}_4$, respectively.

Results and Discussion

Preparation and Properties of Silica Microcapsules. Silica microcapsules were obtained by the interfacial reaction of a W/O/W (WP-1/OP/WP-2) emulsion system using sodium silicate as the silica source. A W/O (WP-1/OP; WP-1 with sodium silicate and OP with Tween 80 and Span 80) emulsion was mixed with another aqueous solution (WP-2 with a precipitant) to form a W/O/W emulsion system, finally yielding silica precipitate. Some ammonium salts were suitable pre-

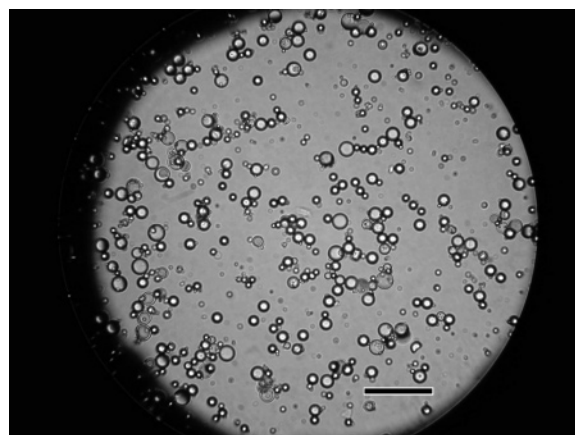


Figure 1. An optical microscope image of a silica microcapsule (sample no. 4) prepared from sodium silicate and NH_4HCO_3 . The length of the black bar is 50 μm .

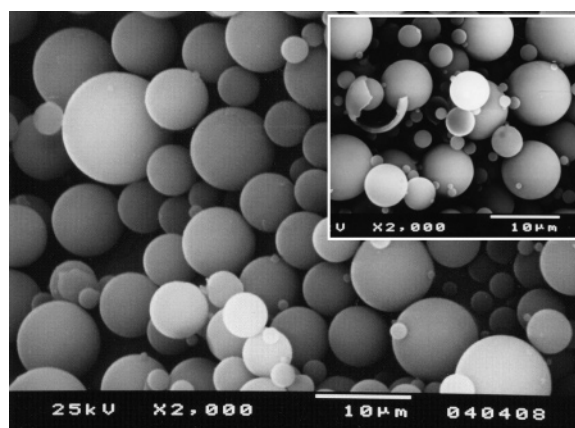


Figure 2. An SEM image of a silica microcapsule (sample no. 4) prepared from sodium silicate and NH_4HCO_3 , and in the inset another image with a broken silica microcapsule. The length of the scale bar is 10 μm .

cipitants for this preparation method. Optical microscopy and SEM images of a typical silica microcapsule prepared by using NH_4HCO_3 as precipitant (sample no. 4 in Table 1) are shown in Figures 1 and 2, respectively. The optical microscope image was recorded by a typical transmission light method. This image shows that silica is spherical and likely to be hollow due to a clear outline of the sphere. The SEM image in Figure 2 illustrates the good spherical shape of the silica microcapsule. Its high sphericity is remarkable in comparison with those of other reported silica hollow spheres.^{18–20,22–24,27,30} No hole was found in the silica shell of our microcapsules. Another SEM image of a silica microcapsule in the inset of Figure 2, where one silica microcapsule particle was partially broken, revealed that the silica microcapsule was really hollow because the broken silica particle looks like part of a shell. This collapsed particle was considered to be yielded by filtration treatment after the complete formation of the silica microcapsule. From this SEM image in the inset, the wall thickness of the shell was found to be about 1 μm , and the diameter of the silica particle was likely to be about 5–15 μm . Therefore, the shell wall was considerably thin, and its thickness was estimated to be about 10% of the total size of the particle, although most of the other reported silica hollow spheres have thicker shell walls.^{14,33} This silica microcapsule was mechanically fragile. When this mi-

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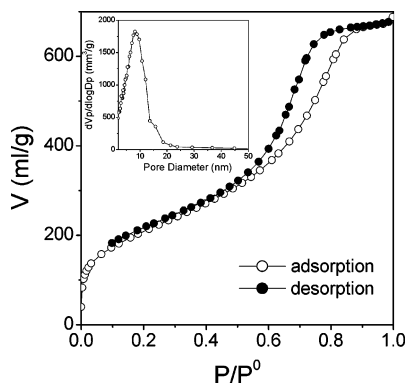


Figure 3. Nitrogen adsorption-desorption isotherm of a silica microcapsule (sample no. 4) prepared from sodium silicate and NH_4HCO_3 , and its pore size distribution calculated by the BJH method using the adsorption branch (inset).

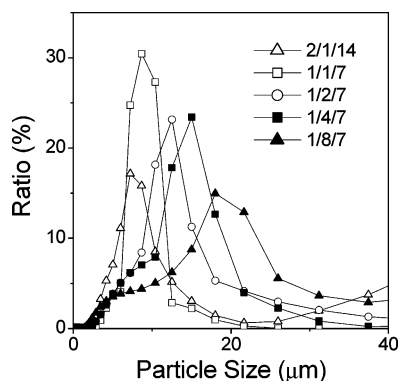


Figure 4. Particle size distribution of silica microcapsules using NH_4HCO_3 as precipitant in the cases of various volume ratios of WP-1 to OP to WP-2. Concentrations of sodium silicate in WP-1, surfactants in OP, and NH_4HCO_3 in WP-2 were 4 M, 13.9 g/L Tween 80 and 6.9 g/L Span 80, and 2 M, respectively. The rotation number of the homogenizer was 8200 rpm.

microcapsule was pounded hard in a mortar, considerable parts of the microcapsule were broken. By XRD measurement, the shell wall of the silica microcapsule was amorphous (not shown in this paper). In Figure 3, the nitrogen adsorption-desorption isotherm of a silica microcapsule (sample no. 4) is displayed, and its pore size distribution calculated by the BJH method using the adsorption branch is given in the inset. A kind of type IV isotherm (IUPAC) indicates the presence of large amounts of mesopores, and the peak pore diameter was evaluated to be about 8.21 nm. The particle size distribution of this silica microcapsule was analyzed by laser diffraction measurement (as 1/2/7 in Figure 4). The distribution was highly monodispersed, and the peak particle size was estimated to be approximately 12.5 μm .

Control of the Particle Size of a Silica Microcapsule by the Preparation Conditions. The control factors studied were the volume ratio of WP-1 to OP to WP-2, the rotation number of the homogenizer, and the concentration of sodium silicate in WP-1. When NH_4HCO_3 was employed as precipitant, the effect of the volume ratios of WP-1 to OP to WP-2 on the particle size was more prominent than when $(\text{NH}_4)_2\text{SO}_4$ was employed as precipitant,⁴² and the range of particle size variation was over 10 μm . The concentrations of WP-1, WP-2, and OP were fixed, and only their volume ratios were altered. Silica microcapsules were successfully

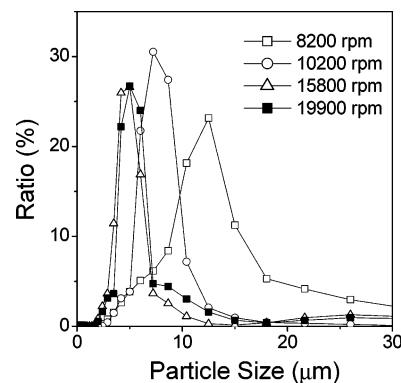


Figure 5. Particle size distribution of silica microcapsules using NH_4HCO_3 as precipitant in the cases of various rotation numbers of the homogenizer. The volume ratio of WP-1 to OP to WP-2 was 1/2/7. Concentrations of sodium silicate in WP-1, surfactants in OP, and NH_4HCO_3 in WP-2 were 4 M, 13.9 g/L Tween 80 and 6.9 g/L Span 80, and 2 M, respectively.

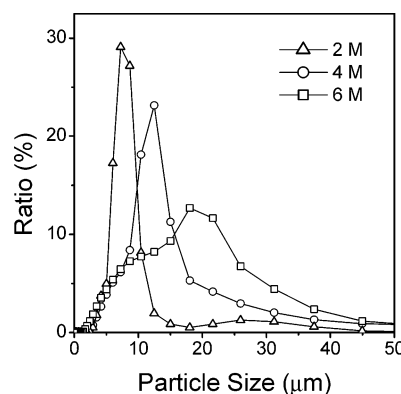


Figure 6. Particle size distribution of silica microcapsules using NH_4HCO_3 as precipitant in the cases of various concentrations of sodium silicate in WP-1. The volume ratio of WP-1 to OP to WP-2 was 1/2/7. Concentrations of surfactants in OP and NH_4HCO_3 in WP-2 were 13.9 g/L Tween 80 and 6.9 g/L Span 80 and 2 M, respectively. The rotation number of the homogenizer was 8200 rpm.

produced when the volume ratio of OP to WP-1 was between 0.5 (WP-1/OP/WP-2 = 2/1/14) and 8 (WP-1/OP/WP-2 = 1/8/7). The distributions of the particle sizes of these silica microcapsules are summarized in Figure 4, indicating that the particle size of the microcapsule increased with the OP/WP-1 volume ratio. It is well-known that the sizes of the water droplets in the oil phase decreased with the rotation number of the homogenizer. We also found that the particle size of the silica microcapsule was controlled by the rotation number. As shown in Figure 5, a clear dependence of the particle size on the rotation number was observed. However, even when the rotation number was higher than 15800 rpm, no further decrease of the particle size was found. This suggests that some limitation of the small size of the particle (water droplet) existed in this preparation process using homogenizer. Furthermore, the particle size of the silica microcapsule could be controlled by the concentration of sodium silicate in the water phase (WP-1). When the concentration of sodium silicate in WP-1 was high, the particle size of the microcapsule became larger. On the contrary, the particle size was smaller in the case of lower concentration of sodium silicate (Figure 6). Thus, when NH_4HCO_3 was used as precipitant, the particle size of the silica

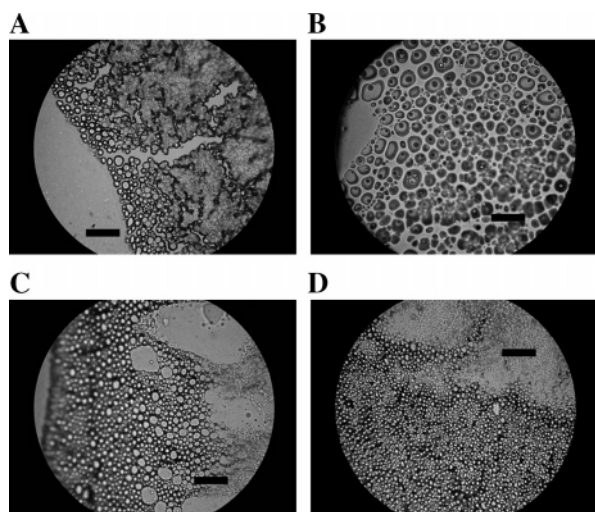


Figure 7. Optical microscope images of water droplets in W/O emulsions formed under various conditions: (A) OP/WP-1 volume ratio 2, rotation number 8200 rpm; (B) OP/WP-1 volume ratio 8, rotation number 8200 rpm; (C) OP/WP-1 volume ratio 0.5, rotation number 8200 rpm; (D) OP/WP-1 volume ratio 2, rotation number 15800 rpm. The length of the bars is 50 μm .

microcapsule was successfully controlled by the volume ratio of WP-1 to OP to WP-2, the rotation number of the homogenizer, and the concentration of sodium silicate in WP-1.

For estimating the size of the water droplet in oil (W/O emulsion), we observed the water droplets directly by an optical microscope. Figure 7 shows the images of W/O emulsions recorded by an optical microscope under some representative conditions. It is likely that the size of the water droplet in oil increased with the volume ratio of the oil and water phases (OP/WP-1) by the comparison of the pictures among Figure 7A–C. The water droplets from a W/O emulsion (OP/WP-1 = 8) in Figure 7B are clearly larger than those from other emulsions in Figure 7A,C. The dark black dots are water droplets, whose sizes were estimated from 10 to 30 μm (Figure 7B, OP/WP-1 = 8). In Figure 7A (OP/WP-1 = 2), smaller droplets (about 5–15 μm) are found in the emulsion. On the other hand, the increase of the rotation number of the homogenizer reduced the particle sizes of the water droplets in oil (Figure 7D). When the sizes of the water droplets were compared between Figure 7A (8200 rpm) and Figure 7D (15800 rpm), the droplets in Figure 7D were obviously smaller than those in Figure 7A. These results suggest that the sizes of the water droplets in the W/O emulsion influence the particle sizes of the silica microcapsules. However, the effect of precipitants is not considered in these cases. Then, we examined the same kinds of experiments using precipitants other than NH_4HCO_3 .

Effect of Precipitants on Silica Microcapsules.

The profiles of microcapsules produced by using various precipitants are summarized in Table 1. No microcapsule was obtained when HCl aqueous solution was used, although the mixing of sodium silicate solution with HCl solution is a representative method of silica gelation. Microcapsules were successfully produced in the cases using NH_4Cl , $(\text{NH}_4)_2\text{SO}_4$, and NH_4NO_3 as precipitants. Metal hydrogen carbonates such as those of sodium (NaHCO_3) and potassium (KHCO_3) also afforded mi-

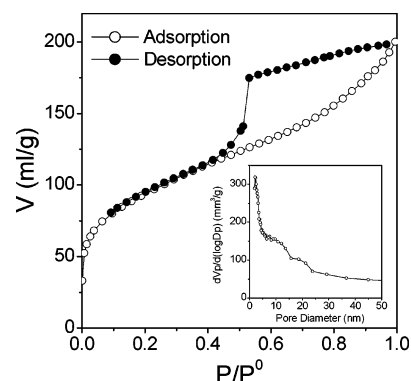


Figure 8. Nitrogen adsorption-desorption isotherms of a silica microcapsule (sample no. 1) using NH_4Cl as precipitant. The pore size distribution calculated from the BJH method with the adsorption branch is shown in the inset.

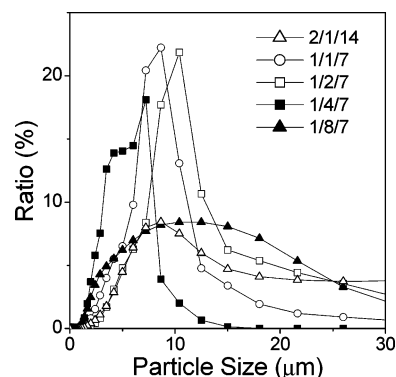


Figure 9. Particle size distribution of silica microcapsules using NH_4Cl as precipitant in the cases of various volume ratios of WP-1 to OP to WP-2. Concentrations of sodium silicate in WP-1, surfactants in OP, and NH_4Cl in WP-2 were 4 M, 13.9 g/L Tween 80 and 6.9 g/L Span 80, and 2 M, respectively. The rotation number of the homogenizer was 8200 rpm.

crocapsules effectively. If the size of the water droplet in the W/O emulsion is the single factor to determine the properties of a silica microcapsule including particle size, the particle size is not affected by precipitant used. However, a clear dependence of the properties of the silica microcapsule on the precipitant was found. As mentioned before, the shell wall of the silica microcapsule obtained from NH_4HCO_3 (sample no. 4) was mesoporous. The pore volume reached over 1000 mm^3/g . On the other hand, in the case of NH_4Cl precipitant, the porosity of the shell wall of the microcapsule (sample no. 1) was low and its pore volume was found to be 245 mm^3/g (Table 1). In BJH pore size distribution, no clear peak of the mesopore was detected (inset of Figure 8).

The effects of the volume ratios of WP-1 to OP to WP-2 on the particle sizes were examined even in the cases using various precipitants. The particle size distribution using NH_4Cl is shown in Figure 9. From this figure, particle sizes of microcapsules are altered by the volume ratio even in these cases. However, no clear relationship between the volume ratio and the particle size was observed. Figure 10 summarizes the correlation between the peak particle size and the volume ratio of OP to WP-1. The peak particle sizes were determined by charts of the particle size distributions. In the volume ratios not plotted in Figure 10, no microcapsule was formed. The plot of NH_4HCO_3 had a clear relation between the volume ratio of OP to WP-1 and the particle size. In the

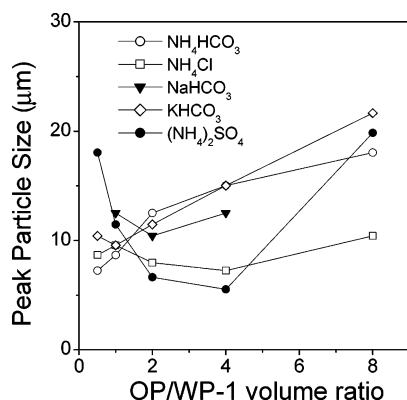


Figure 10. Variation of the peak particle size of the microcapsule obtained with various precipitants as a function of the volume ratio of OP to WP-1.

cases of NaHCO_3 and KHCO_3 , considerable relationships were observed when the volume ratio was high. On the other hand, in other cases [NH_4Cl and $(\text{NH}_4)_2\text{SO}_4$], no remarkable correlation was observed in the entire range of volume ratios. Furthermore, the control of the particle size of the microcapsule by the rotation number of the homogenizer was not successful in the case of NH_4Cl . The particle size of the microcapsule with a higher rotation number (speed 15800 rpm) was smaller than that with a lower rotation number (10200 rpm). These results conclude that NH_4HCO_3 is an effective precipitant for the control of the particle size of the microcapsule by preparation conditions such as the volume ratio of three solution phases and rotation number of the homogenizer.

Mechanism Aspect of the Preparation of Silica Microcapsules. It is noteworthy that the peak particle sizes of microcapsules obtained from various precipitants were different even when other reaction conditions were identical as summarized in Table 1 and Figure 10. For example, in the case of the volume ratio 1/2/7, the peak particle size of the microcapsule was $12.51\ \mu\text{m}$ with NH_4HCO_3 precipitant. On the other hand, the peak particle size was $6.63\ \mu\text{m}$ when $(\text{NH}_4)_2\text{SO}_4$ was used. It is obvious that the particle size of the microcapsule strongly depends on the precipitant employed. In general, hydrogen carbonate salts such as NH_4HCO_3 produced larger microcapsules than other acid salts such as NH_4Cl . In the cases of simple mixing of the solutions of sodium silicate with precipitant solutions, a clear difference of reaction mechanism was observed between hydrogen carbonate salt and acid salt. When the solution of sodium silicate was added to the solution of NH_4HCO_3 , the whole mixed solution became a white opaque gel after a few minutes. On the other hand, NH_4Cl solution afforded silica precipitate at the bottom of the vessel immediately. The nitrogen adsorption–desorption isotherms of these two silicas are shown in Figure 11. Highly porous silica was obtained with NH_4HCO_3 ($1660\ \text{mm}^3/\text{g}$), whereas the pore volume of silica using NH_4Cl was low ($189\ \text{mm}^3/\text{g}$). On the other hand, the required amounts of precipitant for the formation of silica precipitate were also different. For example, more than 6 times more NH_4HCO_3 (78 mL) was required compared with $(\text{NH}_4)_2\text{SO}_4$ (12 mL). The order of the required amounts of precipitant, $\text{NH}_4\text{HCO}_3 > \text{KHCO}_3 > \text{NaHCO}_3 > \text{NH}_4\text{NO}_3 > \text{NH}_4\text{Cl} > (\text{NH}_4)_2\text{SO}_4$, as noted

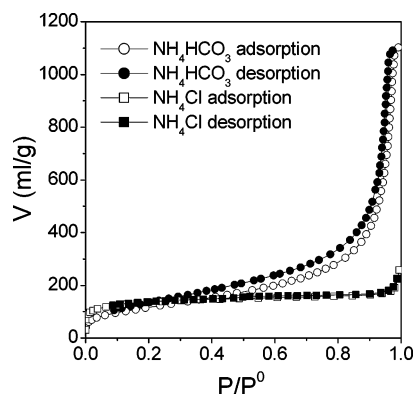


Figure 11. Nitrogen adsorption–desorption isotherms of silicas obtained by the simple mixing of sodium silicate with NH_4HCO_3 or NH_4Cl .

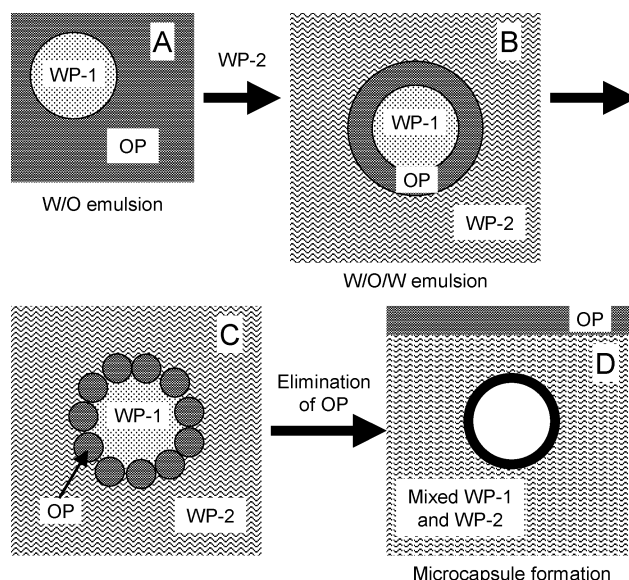


Figure 12. A plausible scheme of microcapsule formation using the W/O/W emulsion system.

in the Experimental Section, was well consistent with the order of the particle sizes of the microcapsules listed in Table 1. Thus, it is clear that the activity of the precipitant for silica formation influences the particle size of the corresponding silica microcapsule.

In the interfacial reaction of the W/O/W emulsion system, OP droplets where WP-1 droplets are included are first formed in WP-2, and the organic solution of OP eliminates slowly from between WP-1 and WP-2. During the elimination of OP, oil droplets are probably formed and silica precipitate is produced along this W/O/W emulsion system to give a silica microcapsule as shown in Figure 12. Although the reaction schemes in Figures 12 and 13 are still hypothetical, they provide full accountings of all our experimental results. While WP-1 and WP-2 are mixing on the W/O/W emulsion interface, a concentration gradient of the sodium silicate and precipitant is temporarily formed (Figure 13). On the side of WP-1 located at the inner interface of the W/O/W emulsion system, the concentration of sodium silicate is higher than that of precipitant. On the contrary, the concentration of sodium silicate is lower than that of precipitant on the side of WP-2 at the outer interface. In the case that silica precipitate can be yielded under lower precipitant concentration condi-

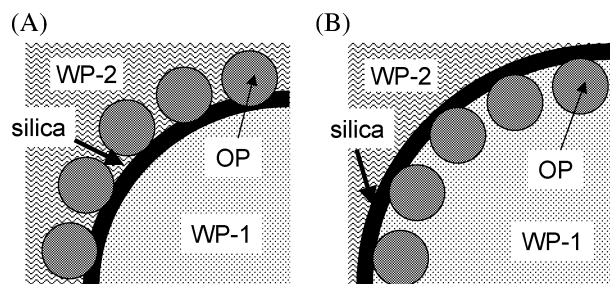


Figure 13. Expected schemes of silica microcapsule formation using NH_4Cl (A) or NH_4HCO_3 (B) as precipitants in step C in Figure 12.

tions, silica is likely to be produced around the side of WP-1 (around the inner interface of the W/O/W emulsion system), affording a smaller microcapsule (Figure 13A). Acid salt precipitants such as NH_4Cl correspond to this case, and smaller microcapsules were indeed produced as listed in Table 1. On the other hand, when more concentrated or a greater amount of precipitant is required to afford silica precipitate as in the cases of hydrogen carbonate salts, a larger microcapsule is obtained (Figure 13B), because of the formation of silica precipitate around the side of WP-2 where the concentration of precipitants is high (outer interface).

The effective controls of the particle size of the microcapsule by the volume ratio of WP-1 to OP to WP-2 and the concentration of sodium silicate in WP-1 using NH_4HCO_3 as precipitant are also explained by the above-mentioned reaction mechanism. The formation of silica precipitate takes place around the outer interface between OP and WP-2 in this case. The size of the oil droplet of OP including WP-1 in the W/O/W emulsion system (B in Figure 12) increases with the volume ratio of OP to WP-1, because much more organic solution for OP is used. Therefore, the silica microcapsule obtained becomes larger with the volume ratio of OP to WP-1. On the contrary, a lower OP/WP-1 volume ratio results in the production of a smaller microcapsule because less utilization of organic solution leads to a thinner OP. When the concentration of sodium silicate in WP-1 is higher, a higher concentration of NH_4HCO_3 is necessary for silica precipitate production. The outer interface between OP and WP-2 is suitable to result in the formation of a larger particle of the silica microcapsule. In the case of a lower concentration of sodium silicate in WP-1, the silica precipitate is readily yielded near the inner interface between WP-1 and OP where the amount of NH_4HCO_3 is sufficient for silica production. Finally, a smaller microcapsule is obtained. On the other hand, when NH_4Cl and other acid salts are used as precipitants, silica precipitate is formed mainly around the inner interface between OP and WP-1. Therefore, the control of the particle size of the silica microcapsule by the volume ratio of WP-1 to OP to WP-2 is scarcely elicited.

Conclusions

A silica microcapsule (hollow sphere) can be prepared by a simple interfacial reaction using a W/O/W emulsion system. A W/O emulsion consisting of WP-1 with sodium silicate and OP (*n*-hexane solution) containing Span 80 and Tween 80 for stabilizing the emulsion was added

to another aqueous solution of a precipitant (WP-2). The inorganic reaction occurred during the elimination of the oil phase from between WP-1 and WP-2, and silica precipitate was formed along this interface. When the preparation conditions were appropriate, the hollow structure of silica was formed spontaneously, and no core compound was required. When NH_4HCO_3 is employed as precipitant, the particle size of the silica microcapsule can be dominated by the volume ratio of WP-1 to OP to WP-2, the rotation number of the homogenizer, and the concentration of sodium silicate in WP-1. These controls of the particle sizes were not achieved when other precipitants such as NH_4Cl were used. More NH_4HCO_3 is necessary to form silica precipitate than NH_4Cl . When NH_4HCO_3 was used as precipitant, the silica formation was likely to take place at the outer interface of the W/O/W emulsion system (between OP and WP-2). On the other hand, using NH_4Cl and other acid salts as precipitants, silica was yielded at the inner interface between OP and WP-1. The successful controls of the particle size of the silica microcapsule in the case of NH_4HCO_3 precipitant were achieved by the formation of silica precipitate along the outer interface of the W/O/W emulsion system. We are already aware that the interfacial reaction using the W/O/W emulsion system is a unique reaction condition aside from microcapsule formation. For example, when a CaCO_3 microcapsule is prepared from K_2CO_3 and CaCl_2 by this W/O/W emulsion system, a vaterite phase is formed.³⁷ However, it is well-known that the direct mixing reaction of these two compounds affords a calcite phase of CaCO_3 mainly and no vaterite phase. These unique features of interfacial reaction using the W/O/W emulsion system will create novel methodologies in inorganic materials. The details of the unique features of the interfacial reaction and further applications are under investigation in our institute.

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Supporting Information Available: Detailed explanation of W/O/W interfacial reaction for silica microcapsule synthesis and figures showing a conceptual scheme of silica microcapsule formation by W/O/W interfacial reaction, particle size distributions of a silica microcapsule prepared from sodium silicate and NH_4HCO_3 , silica microcapsules using KHCO_3 as precipitant in the cases of various volume ratios of WP-1 to OP to WP-2, and silica microcapsules using NH_4Cl as precipitant in the cases of various rotation numbers of the homogenizer, and TGA profiles of silica microcapsules (PDF). This material is available free of charge via the Internet at <http://pubs.acs.org>.

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