

Rapid and high yield synthesis of hollow silica nanoparticles using an NH_4F catalyst

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Abstract

The rapid synthesis of hollow silica nanoparticles based on the CaCO_3 template method is proposed. Typically, it contains two steps for the silica coating on a CaCO_3 template by a sol-gel reaction and template removal by a dilute acid solution. To promote the conversion of tetraethoxysilane (TEOS) to a silica shell on the CaCO_3 template, the effects of fluoride catalysts on the TEOS consumption rate during the silica coating was investigated using energy dispersive spectroscopy (EDS). The TEOS consumption rate of the NH_4F -catalyzed system reached 100 % within 15 minutes while the conventional NH_4OH system took 120 minutes to consume the TEOS. The obtained samples using the NH_4F system for 15 minutes showed a uniform hollow structure with a thin silica shell. For the KF system as the other fluoride catalyst, the TEOS consumption rate did not reach 100 % even after 120 minutes. When the polystyrene (PS) template was used with the NH_4F system, dense silica particles were formed as well as hollow structures. Based on these results, a rapid and high yield of hollow silica nanoparticles can be achieved by not only F^- , but also NH_4^+ using the CaCO_3 template method.

Keywords: hollow silica nanoparticles; sol-gel reaction; catalyst; NH_4F ; NH_4OH ; KF

1. Introduction

Hollow silica nanoparticles, which are composed of a solid shell and nano-sized hollow interior, can be expected to have unique properties of a high specific surface area [1], thermal insulation [2,3], optical property [4], etc. A number of techniques to prepare hollow nanoparticles have been reported, which can be classified into two categories of the hard template method and soft template method. The former mainly utilizes polystyrene (PS) beads [5] because it is easy to control their size and narrow size distribution. Typically, the preparation process has two steps; silica coating on the PS beads surface mostly by a sol-gel reaction and template removal by dissolution in an organic solvent or by thermal decomposition.

The inorganic template method to fabricate hollow nanoparticles via the sol-gel route has been previously developed by Fuji et al. Cubic-shaped CaCO_3 with a calcite crystal structure, as the template, was dispersed in an ethanol (EtOH) medium. With the addition of tetraethoxysilane (TEOS), ammonium hydroxide (NH_4OH) and distilled water, the negatively charged silicic acid, (SiOH) which is generated by hydrolysis of the TEOS, adsorbs on the positively charged site of CaCO_3 surface to become a thin silica shell [6]. After CaCO_3 removal by dilute acid etching, silica hollow nanoparticles were obtained as a replica of the cubic shape from the template [1,7]. This technique has an advantage because the template can be recycled by collection of the byproduct CO_2 gas and CaCl_2 solution when compared to the heat decomposition of organic bead templates.

NH_4OH as a catalyst accelerates the hydrolysis and condensation of TEOS which converts to the silica coating on the CaCO_3 surface. To design a silica shell structure with a specific thickness, porosity, and apparent density, the process conditions, such as temperature, catalyst amount, reaction time, and additives, should be optimized [8]. The reagent TEOS cost is relatively high, therefore, it is desirable to consume all of the added TEOS. However, a high amount of NH_4OH and long reaction rate induce a dense silica particle formation as well as a silica coating on the template

surface.[9] Therefore, the catalyst, which can effectively promote the hydrolysis and condensation of TEOS near the CaCO_3 surface, is required.

Various kinds of catalysts including basic and acidic have been used to evaluate the sol-gel reaction progress. A fluoride ion (F^-) is a known material which promotes the hydrolysis of TEOS because the small radius F^- easily attacks the Si of TEOS. Pope et al. reported that the gelation times in the HF, KF catalyzed systems were 6 minutes and 12 hours compared to 1000 hours in the NH_4OH catalyzed system, respectively. This remarkable improvement of the catalyst ability of KF is caused by the basic pH of the starting solution (pH 8.5 in KF, 1.9 in HF) [9]. The other reported F catalysts were NH_4F [10], NaF, HF, etc. [11]. In the proposed inorganic template method, a basic catalyst which does not dissolve the CaCO_3 template is needed. In this study, NH_4F was chosen as the basic catalyst. The TEOS conversion to silica was defined as the TEOS consumption rate [%] which indicates the reacted TEOS analyzed by energy dispersive spectroscopy (EDS). By comparison to the conventional NH_4OH and KF as another fluoride system, the effects of NH_4^+ and F^- ions on the silica shell formation on the CaCO_3 surface were investigated.

2. Experimental section

2.1. Preparations of hollow silica nanoparticles with different catalysts

Formation of the hollow silica nanoparticles using the inorganic template method is as follows. Twelve ml of ethanol (EtOH, Wako Pure Chemical Industries, Ltd.) and 2.24 ml of distilled water were mixed in a 100-ml polystyrene bottle. A 1.63 g sample of calcium carbonate (CaCO_3 , nanocube60, Nittetsu Mining Co., Ltd., average particle size is 60 nm) was added in the solution and ultrasonicated (UH-600S, SMT Co., Ltd., probe diameter of 7 mm) for 10 min. One ml of 25% ammonia solution (NH_4OH , Wako Pure Chemical Industries, Ltd.) and 1.0 ml of tetraethoxysilane (TEOS, Wako Pure Chemical Industries, Ltd.) were then added to the suspension and the suspension

was mixed using a shaking water bath (196 rpm). After 120 min, the suspension was separated by centrifugation and washed with ethanol to remove any unreacted TEOS and NH_4OH . By the addition of a 3.0 M HCl solution (HCl, 5.0 M HCl solution, Wako Pure Chemical Industries, Ltd.), the CaCO_3 was removed by stirring. The suspension was washed with ethanol to remove the residual HCl and dried under vacuum at room temperature for 24 hours. In a similar way, potassium fluoride (KF) and ammonium fluoride (NH_4F) were used as catalysts. Except for 2.92 ml of water and 0.38 g of KF or 0.24 g of NH_4F , the conditions and procedures were the same. For comparison, hollow silica nanoparticles were prepared using a polystyrene template and NH_4F .

2.2. Determine TEOS consumption rate

The TEOS consumption for the silica coating on CaCO_3 or formation of dense silica nanoparticles was estimated as follows. After the mixing process of TEOS/EtOH/ NH_4OH / H_2O with/without CaCO_3 by the shaking water bath, the supernatant of the suspensions was immediately removed using a syringe and filtered by a syringe filter (Ministart RC15, pore size 0.20 μm , Sartorius stedim biotech). The Si contents in the supernatants were characterized by energy dispersive X-ray spectroscopy (EDX, EDX-800HS2, Shimadzu, 15 kV, He atmosphere). The Si weight concentration was estimated by a calibration curve of a known TEOS/EtOH solution. Based on these results, the TEOS consumption rate [%] for each stirring time was calculated based on the fact that one TEOS molecule contains one Si atom. The value for the stirring time of 0 minutes is the value assuming that all the added TEOS remains in the supernatant. For comparison, dense silica nanoparticles were prepared using each catalyst without CaCO_3 and the TEOS consumption rates were calculated in the same way.

2.3. Observation of obtained particles

The obtained particles were observed using a transmission electron microscope (TEM, 2000-EX, JEOL Ltd.) at 160 kV and a scanning electron microscope (SEM, JSM-7600F, JEOL, 15.0 kV) with

secondary electron image (SEI) and transmission electron diffraction (TED). The particles were dispersed in EtOH by ultrasonication and the suspension was dropped on a microgrid (STEM150Cu, Oken Shoji), then dried in the air.

3. Results and discussion

Figure 1 shows the TEOS consumption rates of the NH_4OH -catalyzed system with CaCO_3 (white square) and without CaCO_3 (black circle) as a function of the stirring time from 0 to 120 minutes. Both of the TEOS consumption rates rapidly increased up to 80 % within 1 hour while stirring and then it gradually reached near 100 % at 120 minutes. The first rapid increase of the TEOS consumption with CaCO_3 is slightly faster than without CaCO_3 within 1 hour.

When NH_4OH and TEOS were added to EtOH/ H_2O , the NH_4^+ ion gathers around the TEOS molecules by an electrostatic force between the NH_4^+ ion and ethoxy (-OEt) groups of TEOS. Once a sufficient amount of NH_4OH was supplied in the suspension, the OH^- ion attacks the Si of TEOS and one -OEt group is replaced by OH. Hydrolysis of the other three -OEt groups then immediately occurs. As the hydrolysis proceeds, the OH^- ion concentration decreases. Therefore, the hydrolysis speed decreases. This is the two steps of the TEOS consumption rate seen in Fig. 1. The difference in the first rapid increase in the TEOS consumption with/without CaCO_3 within 1 hour is due to promotion of the TEOS hydrolysis by the presence of CaCO_3 . The TEOS hydrolysis selectively occurs on the CaCO_3 surface because the NH_4^+ or OH^- ion tends to gather on the CaCO_3 surface.

Instead of the OH^- ion, the effect of the F^- ion on the TEOS consumption was investigated using the NH_4F catalyst. Figure 2 shows the TEOS consumption rate of the NH_4F catalyzed system (a) with and (b) without CaCO_3 as a function of the stirring time from 0 to 15 minutes (with CaCO_3) and to 90 minutes (without CaCO_3). The TEOS consumption in the NH_4F system were significantly improved compared to that of the NH_4OH system (Fig. 1). Especially, the TEOS consumption

without CaCO_3 reached 100% at only 5 minutes after the reaction started. For the system with CaCO_3 , only 15 minutes was required to complete the TEOS consumption.

For the NH_4OH catalyzed system, the TEOS hydrolysis starts once a sufficient amount of NH_4^+ ion gathers around TEOS in the NH_4F system. The difference is that the F^- ion has easy access to the Si of TEOS because the ionic radius of F is much smaller than that of OH. Through the $[(\text{OEt})_4\text{-Si-F}]^-$ intermediate, $(\text{OEt})_3\text{-Si-F}$ forms. This compound makes a complex with H_2O in the system, then one OEt group hydrolyzes to OH. The F^- ion also contributes to the condensation among the $\text{Si}(\text{OH})_4$. Consequently, the TEOS consumption rate of the NH_4F system is much faster than of the NH_4OH system. Interestingly, even if CaCO_3 exists, such a rapid TEOS consumption can be seen for 15 minutes. Therefore, it can be said that the NH_4^+ ion tends to gather around the CaCO_3 surface.

The obtained samples in the NH_4F catalyzed system for 15 minutes were observed by STEM as shown in Figure 3(a). Hollow cubic structures similar to template shape can be confirmed. When compared to the samples obtained in the NH_4OH system for 120 minutes (Figure 3(b)), the shell thickness is a half-time thinner (7.02 nm in NH_4F for 5 minutes, 15.12 nm in NH_4OH for 120 minutes) and the shell outline is not sharply defined. From the surface observation in the SEI mode, the shell surface is slightly rough but no pores were observed in the NH_4F system. How thin and rough shell formed in NH_4F system is still under investigation. Although NH_4F is certainly effective catalyst, it is true that its high toxicity. Currently, no existence of fluorine compounds was detected in the obtained hollow particles by spectroscopic analysis.

As another fluoride catalyst, KF whose cation is not NH_4^+ was used. Figure 4 shows the TEOS consumption rate of the KF catalyzed system with CaCO_3 (white square) and without CaCO_3 (black circle) as a function of the stirring time from 0 to 120 minutes. The TEOS consumption without CaCO_3 rapidly increased within 30 minutes, which is faster than in NH_4OH . After 30 minutes, it

gradually increased and reached nearly 90 %. With the addition of CaCO₃, the TEOS consumption increased within 60 minutes and gradually reached only 70 % of the 120 minutes. The F⁻ ion possibility promotes the sol-gel reaction, however, selection of the cation is also important especially when CaCO₃ is added.

How the NH₄⁺ ion contribution to the reaction is now discussed. On the top of the CaCO₃ surface, Ca²⁺ or CO₃²⁻ ions exist. Neagle and his coworker reported that Lewis-acidic Ca²⁺ sites of CaCO₃ surface have weak interaction with NH₃ molecules investigated by FT-IR study [15]. Therefore, the CaCO₃ surface could be ready for the NH₄⁺ ion presence during the sol-gel reaction. That is, hydrolysis and condensation of the TEOS selectively occurs near the CaCO₃ surface and the silica shell can be formed. This could be typical phenomena for CaCO₃ and the NH₄⁺ ion. Instead of CaCO₃, PS nanoparticles were used as the template. Figure 5 shows an STEM observation of the obtained particles in the NH₄F system. A hollow structure was formed, however, the silica shell was not uniform and many dense silica particles were observed.

4. Conclusion

A rapid and high-yield process for hollow silica nanoparticles via the inorganic template method has been developed using NH₄OH catalysis. The TEOS consumption of NH₄F reached 100 % within 15 minutes and the obtained particles had uniform hollow structures.

In the conventional NH₄OH system, it took 120 minutes to complete the TEOS consumption, while in the KF system, it did not reach 100 % after 120 minutes. In the NH₄F system with the PS template, it reached 100 % similar to that with the CaCO₃ template, however, dense particles were observed as well as hollow structures. Based on these results, the F⁻ ion significantly improves the hydrolysis and condensation of the TEOS, and the NH₄⁺ ion is proper for producing selective silica coating on the CaCO₃ surface.

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Figure captions

Figure 1 TEOS consumption rate of NH_4OH catalyzed system with CaCO_3 (white square) and without CaCO_3 (black circle) as a function of the stirring time.

Figure 2 TEOS consumption rate of NH_4F catalyzed system with CaCO_3 (white square) and without CaCO_3 (black circle) as a function of the stirring time.

Figure 3 TEM images of hollow particles in (a) NH_4F system for 15 minutes and (b) NH_4OH system for 120 minutes, which are the conditions when the TEOS is completely consumed.

Fig. 4 TEOS consumption rate of KF catalyzed system with CaCO_3 (white square) and without CaCO_3 (black circle) as a function of the stirring time.

Fig. 5 STEM images of hollow particles from PS template with the addition of NH_4F catalyst for 15 minutes.