Synthesis of Flake Type Micro Hollow Silica Using $\text{Mg}(\text{OH})_2$ Inorganic Template

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(Received March 22, 2017; Revised May 10, 2017; Accepted May 11, 2017)

ABSTRACT

Flake-type micro hollow silica was synthesized by precipitation method using an $\text{Mg}(\text{OH})_2$ inorganic template and sodium silicate and ammonium sulfate as the silica precursors. We investigated the effects of the silica precursor concentration on the shape, shell thickness, and surface of the hollow silica. When the concentration of the silica precursor was 0.5 M, the hollow silica had a smooth and translucent thin shell, but the shell was broken. On the other hand, the shell thickness of the hollow silica changed in the range of 12 nm to 18 nm with the increase of the precursor concentration from 0.7 M to 1.1 M. Simultaneously, unintended spherical silica satellites were created on the shell surface. The number of satellites and the size rose according to the increased concentration of silica precursor. The reason for the formation of spherical silica satellites is that the NH_4OH nucleus generated in the synthesis of hollow silica acted as another silica reaction site.

Key words : Powders, SiO_2 , Hollow silica, Inorganic Template, Core/Shell

1. Introduction

Hollow structure materials exhibit properties different from conventional materials due to their unique structure where the particles are surrounded by a porous or non-porous shell. Such materials offer the advantage that both the particle surface and interior can be utilized. Also, these materials have high specific surface area, low density, and high loading capacity, which are all attractive material properties for application to dye-sensitized solar cells, lithium ion batteries, supercapacitors, catalysts, drug delivery systems, sensors, and fuel cells.¹⁻⁶⁾ In particular, hollow silica offers outstanding optical properties and high thermal, electrical, and chemical stability in addition to the various advantages of a hollow structure material. Moreover, control of the material properties through the hollow silica size, shape, and combination with other materials has led to active technology development and application research worldwide.⁷⁻⁹⁾

The most common hollow silica synthesis method is liquid phase synthesis using a spherical polystyrene latex (PSS) organic template.¹⁰⁻¹⁴⁾ When using an organic template, the silica coats the surface of the organic template, forming a shell, and the final product of spherical hollow silica particles can be obtained by removing the organic template using heat treatment or organic solvents. In the case of the hollow silica synthesis method using an organic template, the template particle size can conveniently control the particle size

of the final product, the hollow silica. However, the organic template residue washing process is difficult and cumbersome when using an organic solvent to remove the organic template. When high temperature heat treatment is used to remove the organic template to resolve this problem, agglomeration of the synthesized hollow silica occurs. Also, previous hollow silica research showed greater preference towards spherical synthesis of the hollow structure and studies on the synthesis method for hollow silica with different structure formations are lacking.

The aim of the present study was to synthesize flake type hollow silica using a $\text{Mg}(\text{OH})_2$ inorganic template, which allows for convenient removal through acid treatment without using additional heat treatment or organic solvent. Furthermore, the silica precursor concentration was varied as a hollow silica synthesis variable to investigate the resulting hollow silica shape, shell thickness, and surface. Sodium silicate was used as the silica raw material, which is more economical and environmentally friendly compared to the conventionally widely used TEOS (Tetraethyl orthosilicate).

2. Experiment Procedure

In this study, $\text{Mg}(\text{OH})_2$ inorganic template particles were used to synthesize hollow silica through a precipitation method.

A microscale flake type magnesium hydroxide ($\text{Mg}(\text{OH})_2$, KISUMA 5A, 98%, average particle size 0.8 μm , KISUMA, Netherlands) was used as the inorganic template particles and sodium silicate (Na_2OSiO_2 , sodium silicate solution, Na_2O 9 ~ 10%, SiO_2 28 ~ 30%, DAEJUNG, Korea) was used as the silica precursor. After dissolving in DI water, sodium

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silicate aqueous solutions in a range of 0.7 M to 1.1 M were prepared. Ammonium sulfate ($(\text{NH}_4)_2\text{SO}_4$, Ammonium sulfate, 99.5%, JUNSEI, Japan) was used as the metal salt and aqueous solutions had the same mole fractions as the sodium silicate aqueous solutions.

Before the silica shell formation reaction, $\text{Mg}(\text{OH})_2$ was mixed with DI water and dispersed for 20 minutes using ultrasonic processor. If the $\text{Mg}(\text{OH})_2$ inorganic template particles are agglomerated or precipitated before the shell formation reaction, the surface area of the $\text{Mg}(\text{OH})_2$ inorganic template particles changes and the intended shell thickness or shape cannot be obtained. The fabricated $\text{Mg}(\text{OH})_2$ dispersions were poured into 3-neck reaction vessels and stirred at 350RPM while raising the temperature to 50°C. When this temperature was reached, a metering pump was used to drop the sodium silicate and ammonium sulfate aqueous solutions at a constant rate for the reaction to take place over 3 h, and silica shells were obtained on the surfaces of the $\text{Mg}(\text{OH})_2$ inorganic template particles.

In order to finally obtain hollow silica by removing the $\text{Mg}(\text{OH})_2$ inorganic template particles, the washed $\text{Mg}(\text{OH})_2$ /silica core-shell particles were dispersed in 1 L of DI water and mixed followed by the addition of H_2SO_4 diluent at a rate of 7 g/min. When the H_2SO_4 diluent is added to the $\text{Mg}(\text{OH})_2$ /Silica core-shell dispersion, the diluent seeps into the pores of the silica shell and the $\text{Mg}(\text{OH})_2$ template particles are dissolved, yielding microscale flake type hollow silica. Figs. 1 and 2 show a schematic diagram and the process flow of the experiment.

A pH meter was used to observe the pH variation according to the reaction time during the silica shell formation reaction, and SEM and TEM analyses were carried out to observe the shape, shell thickness, and surface morphology of the hollow silica according to the precursor concentration. Through an XRD analysis, silica synthesis and crystallinity variation according to the precursor concentration were identified and the oil absorption was measured in order to compare the hollow volume ratio according to the hollow silica shape. The oil absorption was calculated by measuring the maximum paraffin weight absorbable by the hollow silica

Fig. 1. A schematic diagram of the experimental apparatus for the synthesis of hollow silica.

Fig. 2. Hollow silica synthesis process.

Table 1. Content of Reactants for Synthesis of Hollow Silica

No	$\text{Mg}(\text{OH})_2$	$\text{Na}_2\text{OSiO}_2 : (\text{NH}_4)_2\text{SO}_4$ mole ratio	Na_2OSiO_2
1	0.8 M	1:1	0.5 M
2			0.7 M
3			0.9 M
4			1.1 M

when minute amounts of liquid paraffin of 25 ~ 35 cst viscosity were dropped on 1 g of the synthesized hollow silica powder and the measured maximum absorbed paraffin weight was divided by the paraffin density (0.85 g/cc).

Table 1 shows the conditions of the constant 0.8 M concentration of $\text{Mg}(\text{OH})_2$ for the hollow silica synthesis, the constant mole ratio of 1:1 for sodium silicate and ammonium sulfate, and the various concentrations of the sodium silicate ranging from 0.5 M to 1.1 M.

3. Results and Discussion

By forming silica shells on the surface of the $\text{Mg}(\text{OH})_2$ inorganic template and removing the inorganic template through acid treatment, micro flake type hollow silica was obtained. Fig. 3 shows Scanning Electron Microscope images (SEM, Nova SEM 450, FEI Co., acceleration voltage 10 kV, Spot size 3.5) of the hollow silica particles according to the silica precursor concentration.

While flake type hollow silica with smooth and clean shell was synthesized when the sodium silicate molarity was 0.5 M, the partial formation of hollow silica, which appeared to be broken, was also observed. The partial formation was ascribed to the amount of the silica precursor being insuffi-

Fig. 3. FE-SEM images of hollow silica particles synthesized at different concentration of precursor.

cient to completely coat the surface area of the $\text{Mg}(\text{OH})_2$ template particles. On the other hand, for molar concentrations of 0.7 M and greater, all particles had complete flake type hollow structures, but the formation of unintended spherical silica particles on the shell surface was observed. The number of spherical silica satellites on the shell surface tended to increase as the silica precursor molar concentration increased.

Figure 4 shows Transmission Electron Microscope images (TEM, Tecnai G2 F20, FEI Co, acceleration voltage 200 kV, Spot size 3, BF mode) obtained to identify the presence of residual $\text{Mg}(\text{OH})_2$ template particles, the hollow silica shell thickness variation according to the silica precursor concentration, and the size variation of silica satellites formed on

Fig. 4. TEM images of hollow silica particles synthesized at different concentrations of precursor.

Fig. 5. The shell thickness and satellite of hollow silica synthesized at different concentrations of precursor.

the surface. The TEM analysis results revealed that the $\text{Mg}(\text{OH})_2$ template particles were completely removed through the H_2SO_4 acid treatment as hollow shapes were observed for all specimens. In addition, as the silica precursor concentration increased, the hollow silica shell thickness increased along with the silica satellite size. The thickness of hollow silica shell according to the silica precursor concentration was approximately 8 nm for 0.5 M, 12 nm for 0.7 M, 15 nm for 0.9 M, and 18 nm for 1.1 M, which revealed shell thickness increments of around 3 nm for every 0.2 M increase in the silica precursor concentration.

Figure 5 shows a graph of changes in thickness of hollow silica shells and the size of silica satellite according to the silica precursor concentration based on the TEM analysis results.

Figure 6 shows the crystallinity change according to whether silica satellite synthesis occurred and the precursor concentration as analyzed through the X-Ray Diffractometer (XRD, D/MAX-22000/PC). The results revealed wide peaks at $\theta = 24^\circ$, which signified the synthesis of amorphous silica. There was virtually no change in the hollow silica crystallinity according to the concentration of precursor.

Fig. 6. Effect of concentration of precursor on the hollow silica XRD patterns.

Fig. 7. Oil absorption of the hollow silica.

This verified that spherical single particles formed at the hollow silica shell surface were the same silica, rather than different components.

The oil absorption was measured to identify the hollow volume ratio of the hollow silica according to the silica precursor concentration and the results are shown in Fig. 7. The oil absorption was 7.51 cc/g for the hollow silica synthesized with 0.5 M sodium silicate, which was the lowest oil absorption measurement among the four conditions. This result was due to the hollow silica particles with broken hollow structures failing to exhibit the maximum effect of the hollow structure. Meanwhile, the oil absorption for the 0.7 M sodium silicate case, where complete flake type hollow silica was obtained, was measured at 10.40 cc/g, which was the highest measurement of all the conditions. However, for concentrations of sodium silicate of 0.9 M and higher, the shell thickness increased and the number of hollow silica particles in relation to the weight was low due to the spherical silica satellites on the surface, resulting in lower hollow efficiency and consequently reduced oil absorption. For generic solid silica (SiO_2 , Spherical, 1 ~ 3 μm , SUNSIL-20, SUNJIN BEAUTY SCIENCE, Korea), a low oil absorption value of 1.1 cc/g was measured. The hollow silica synthesized in this study had an oil absorption value 9.45 times greater than that of the generic solid silica, which verified that the hollow structure particles had low density and high loading capacity.

In order to investigate the cause of the formation of unintended spherical silica satellites where the silica precursor was not completely utilized to form the shell, the silica precursor concentration was set to 0.9 M and synthesis of the hollow silica was conducted to examine the surface morphology of the $\text{Mg}(\text{OH})_2$ /silica core-shell particles and the pH variation of the reaction solution according to the time duration.

Figure 8 shows the SEM images of the $\text{Mg}(\text{OH})_2$ /silica core-shell particle surface morphology according to the hollow silica synthesis time duration. In the initial stages of the reaction, as shown in Figs. 8(b) and (c), silica satellites were not observed on the $\text{Mg}(\text{OH})_2$ /silica core-shell particle

Fig. 8. FE-SEM images of $\text{Mg}(\text{OH})_2$ /silica core-shell particles synthesized at reaction time. (a) 0 min (b) 20 min (c) 40 min (d) 60 min (e) 100 min (f) 180 min.

surface, but after 60 minutes into the reaction, the formation of silica satellites was observed. Through this result, it was predicted that an additional reaction site other than the $\text{Mg}(\text{OH})_2$ template particle surface that can be produced independently was formed on the silica during the reaction.

Figure 9 shows the reaction solution pH value variation plot according to the hollow silica synthesis time. The pH value was decreased from 10.1 to 8.83 when the sodium silicate solution and ammonium sulfate solution were added, respectively. It was also observed that there was almost no pH change after the silica shell precursor addition was finished (100 minutes).

Fig. 9. pH value of solution at reaction time.

Fig. 10. Concept of NH_4OH nucleation and silica satellite growth based on Lamer theory.¹⁸⁾

This was because NH_4OH and H^+ ions were formed due to hydrolysis reaction of ammonium sulfate ($(\text{NH}_4)_2\text{SO}_4$) as shown in the chemical reaction formula in Eq. (1), thereby having acidity.^{15,16)}

In this study, the other reaction site of the silica was judged to be the NH_4OH produced during the hollow silica synthesis. The mechanism that formed silica shells at the surface of $\text{Mg}(\text{OH})_2$ template particle was that since $\text{Mg}(\text{OH})_2$ had the OH group at the surface, the OH group of $\text{Mg}(\text{OH})_2$ and the OH group of silicate ion incur a dehydration condensation reaction, thereby creating silica synthesis at the surface of $\text{Mg}(\text{OH})_2$.¹⁷⁾ Based on this mechanism, the NH_4OH produced during the hollow silica synthesis also has an OH group and hence there is the possibility of reaction with the silicate ions. In the initial stage of the reaction, as shown in Fig. 8, the silica satellites are not formed whereas they are formed after 60 minutes, and this phenomenon is thought to be determined by the nucleation of NH_4OH .

Figure 10 shows a conceptual diagram of the NH_4OH nucleation and silica satellite formation during the hollow silica synthesis reaction based on the Lamer theory. As stated by the Lamer theory,¹⁹⁾ the amount of the $(\text{NH}_4)_2\text{SO}_4$ aqueous solution added before 60 minutes was small and supersaturation could not be reached, and thus NH_4OH existed in a very loose agglomerated cluster or embryo, returning to individual particles, and the silica reaction site existing at this point can only be the $\text{Mg}(\text{OH})_2$ inorganic template. However, as the reaction time elapses, the input amount of the $(\text{NH}_4)_2\text{SO}_4$ aqueous solution increases to reach supersaturation, resulting in the NH_4OH growing beyond the critical size to form and grow as one nucleus. The NH_4OH nucleus has an OH group and as such there is the possibility that it acts as the reaction site of the silica. At this stage, silica synthesis occurs not only at the surface

of $\text{Mg}(\text{OH})_2$ but also at the NH_4OH nucleus, simultaneously forming spherical silica satellites independent of the silica shell growth. The protrusions on the hollow silica surfaces were thought to be caused by the produced spherical silica satellites existing in a dispersed state in the reaction solution followed by agglomeration and adhesion on the hollow silica particle surface in the filtration and drying process. As the added silica precursor molar concentration increased, supersaturation was reached at a faster pace, where the NH_4OH nucleation occurred earlier, meaning that there was more formation and growth of the spherical silica satellite, causing the number and particle size of the satellites to increase.

4. Conclusions

A $\text{Mg}(\text{OH})_2$ inorganic template was used to synthesize microscale flake type hollow silica from sodium silicate using the precipitation method. Silica shells were formed on the surface of the $\text{Mg}(\text{OH})_2$ inorganic template, and microscale flake type hollow silica was obtained by removing the inorganic template through H_2SO_4 treatment.

Observation of the hollow silica shape, shell thickness, and surface while varying the concentrations of sodium silicate and ammonium sulfate as the hollow silica synthesis process variable revealed that when the silica precursor concentration was low, flake type hollow silica with thin and smooth shells was synthesized along with hollow structures that appeared to be broken. On the other hand, as the precursor concentration increased, the thickness of silica shell increased and unintended spherical silica satellites were formed on the shell surface. The number and size of the silica satellites increased as the precursor concentration increased.

XRD analysis revealed that silica was synthesized, and measurement of oil absorption carried out to identify the loading capacity of the synthesized hollow silica was 10.40 cc/g, which was 9.45 times greater than that of generic solid silica.

Unintended silica satellites were formed on the hollow silica surface, and this was ascribed to the NH_4OH produced during the hollow silica synthesis acting as an additional silica reaction site, where silica synthesis occurred on the $\text{Mg}(\text{OH})_2$ inorganic template as well as the NH_4OH nucleus, resulting in the simultaneous formation of spherical silica satellites independently from the silica shell coating. The spherical silica satellites, which existed in a dispersed state in the reaction solution, were thought to agglomerate or adhere to the hollow silica particle surface in the filtration and drying process, producing a hollow silica surface morphology with observable protrusions.

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