$CaCO_3$를 주형으로 사용한 나노실리카 중공구체 제조 및 특성분석

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Formation and characterization of hollow silica nanoparticles by using calcium carbonate as inorganic template

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1. Introduction

Hollow particles of inorganic and organic materials have an important role in multiphase system and microencapsulation processes [1]. There is a variety of synthesis techniques based on physical and chemical methods. One of the chemical methods mentioned in the literature involves inorganic systems for obtaining such hollow particles [2-4]. As synthesized hollow materials may find wide applications in many fields, because its high surface area, low densities, porosity, hollow structure and compatibilities with other materials [5,6].

The ion-exchange method was controlled more easily than the orther methods. The homogenous nucleation and the surface growth played important roles in the mechanisms of particle formation via ion-exchange method [7-9].

In this work, hollow silica nanoparticle was synthesized by using $CaCO_3$ nanoparticles as inorganic templates. Sodium ion of sodium silicate solution was removed by ion exchange resin. The silicic acid was hydrolyzed and the SiO_2 particles were continuously deposited on the surface of $CaCO_3$. It was proved that the important parameters influencing on the shell thickness of hollow silica were the concentration ratio of sodium silicate, the feed rate added with sodium silicate, and pH value.

Since sodium silicate and calcium carbonate can be produced with a low cost, the synthesis of hollow silica nanoparticle by in this method might benefit its commercialization [10].

2. Experimental

2-1 Starting materials

In this present work, the starting solutions were $CaCO_3$ (Extra Pure, Oriental Chemical Industries.), Sodium silicate (SiO_2(50%~55%) Na_2O(23%~27%), Daejung Chemicals & Metals Co. LTD.) powder, Amberlite (IR-120 cation exchange resin , Hydrogen type) and Hydrochloric acid (37%, Aldrich.). In order to solve sodium silicate powder completely it used the autoclave.

2-2 Ion exchange

Sodium silicate powder (commercial) were diluted with DI water and heating to 150°C. The active silicic acid was made by passing that diluted sodium silicate solution through a column where filled with cation exchange resin (Amberlite 120, pH=2.2). The sodium silicate solution was substitute by hydrogen ion on the exchange sites of cation resin. Sodium ion of sodium silicate solution was removed by ion exchange resin. The sodium ion from 3000ppm reduced with 20ppm.

2-3 Synthesis of hollow silica

In a process, calcium carbonate suspension solution was kept at 80°C under stirring. Silicic acid was then added dropwise into the suspension solution by using micro feed pump. The silicic acid was hydrolyzed and the SiO_2 particles were continuously deposited on the surface of $CaCO_3$. Therefore, it made a core-shell structure. Finally, hollow silica particles were made after sintering and dissolving $CaCO_3$ in HCl dilute solution. It was proved that the important parameters influencing on the shell thickness of hollow silica were the concentration ratio of sodium silicate and pH value.

2-4 Characterization

In addition, the morphology and particle size of hollow silica were characterized by , Transmission Electron Microscope (TEM ; JEOL JEM2010) , Energy Dispersive Spectroscope (EDS ; JEOL JSM-6330F) , Fourier Transform Infrared Spectroscopy (FT-IR ; Thermonicolet Avator360), X-ray Diffraction (XRD ; RIGAKU 12KW), Zeta-potential (ELS-8000 , Photal).

3. Results and discussion

Figure 1 present the TEM image of hollow silica with a wall thickness of about 30nm, 18nm and

10nm were obtained. The molar ratio of $SiO_2/CaCO_3$ were 1/3, 1/7.5, 1/10 respectively. The wall thickness was reduced as decreasing SiO_2 concentration.

Figure 2 present the TEM image of hollow silica with a $CaCO_3$ core structure was reduced as increasing the dissolving time in HCl solution. The $CaCO_3$ was completely removed by dipping the sample in an acidic solution kept for 12h.

Figure 3 shows a X-ray diffraction pattern of the silica particles, demonstrating their non-crystallization.

EDS spectrum reveals the presence of Si and O and the absence of Ca, indicating the complete removal of the calcium carbonate templates. FT-IR spectrum result confirm typical peak of SiO_2. BET surface area of the hollow silica is measured to be $628.7m^2/g \sim 684.4m^2/g$.

4. Conclusion

Hollow silica nanoparticle was successfully synthesized by using $CaCO_3$ nanoparticles as inorganic templates. Sodium ion of sodium silicate solution was removed by ion exchange resin effectively. Hollow silica had a uniform spherical hollow structure with a inner diameter of 50 ~ 80nm, wall thickness of 10 ~ 30nm and surface area of $628.7m^2/g \sim 684.4m^2/g$. The sodium ion from 3000ppm reduced with 20ppm.

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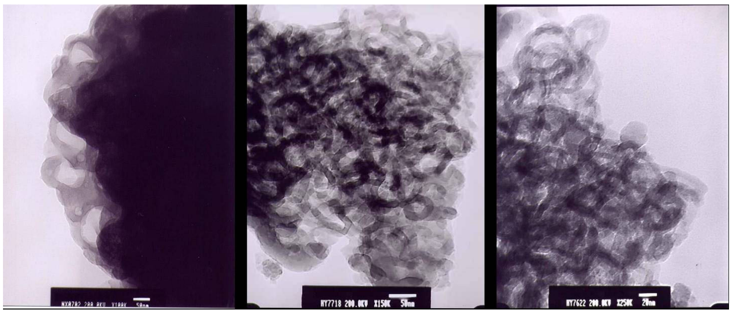

Figure 1. TEM image of hollow silica particle; spherical particle by $CaCO_3$ template. (molar ratio of $SiO_2/CaCO_3$ = 1/3, 1/7.5, 1/10)

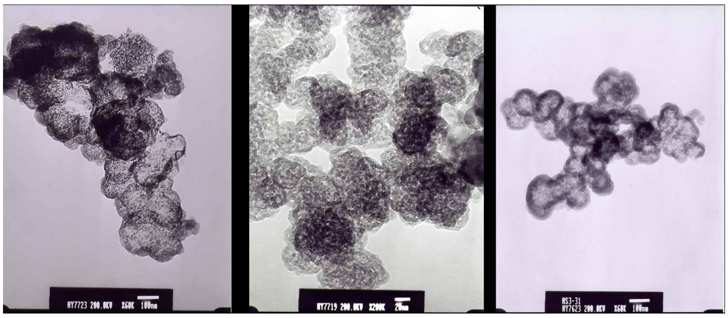

Figure2 . TEM image of hollow silica particle; spherical particle by $CaCO_3$ template. (dissolving $CaCO_3$ in HCl dilute solution - 6hr, 9hr, 12hr)

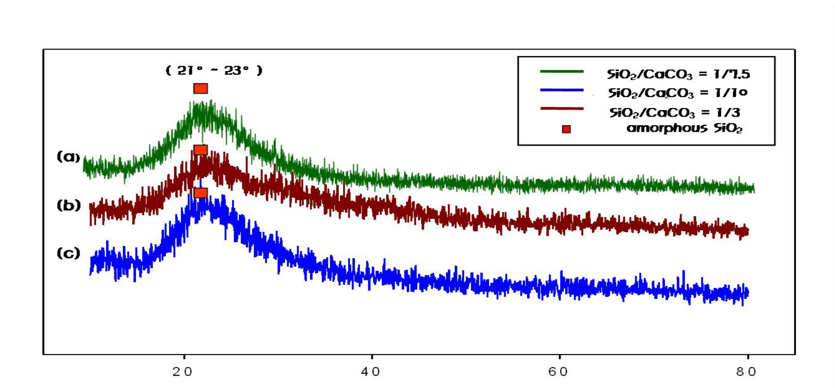

Figure 3 . XRD patterns of hollow silica (amorphous silica) ;
(a) molar ratio of $SiO_2/CaCO_3$ = 1/7.5 , (b) molar ratio of $SiO_2/CaCO_3$ = 1/3
(c) molar ratio of $SiO_2/CaCO_3$ = 1/10