

Templated Synthesis of Silica Hollow Particles by Using Spray Pyrolysis

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It is commonly accepted that one hollow particle is formed from one droplet in conventional spray pyrolysis or drying. Therefore, the particles size distribution is closely related to the droplet size distribution. In this report, however, a new aerosol process was proposed, in which multiple hollow particles were produced from one liquid droplet with the aid of salt and polystyrene (PS) bead. In this process, the particles size and size distribution were determined by the PS beads, not by the droplets. Silica hollow particles of 160 nm in diameter and 10 nm in shell thickness were prepared after washing off the salt with water. Geometric mean dispersion of hollow particles were 1.02, whereas the geometric mean deviation of droplets was 1.3. The role of salt was to keep nano-size hollow particles desegregated while the PS template beads were burnt off at 500°C.

Introduction

Hollow particle is a special kind of core-shell particle in which the core consists of air. Compared to bulk materials, hollow particles have low density, enlarged surface area, and distinct optical and catalytic properties. Such properties are known to be important in a number of applications such as fillers, coatings, pigments and capsule agents for drug delivery (Aden and Kerker, 1951; Ohmori and Matijevic, 1992; Oldenburg *et al.*, 1998). Nowadays, hollow titania particles synthesized by templating methods have been reported (Iida *et al.*, 1998; Shiho and Kawahashi, 2000; Yang *et al.*, 2003).

One of the popular liquid phase methods for preparing hollow particle is an emulsion process in which self-organized surfactants are used as templates (Voiles *et al.*, 1994; Dhas *et al.*, 1999; Wang and Pan, 2000; Breen *et al.*, 2001). Hollow particles are also prepared by thermal or chemical degradation of organic beads on which inorganic shells of tailored structure are formed. For example, deposition of small particles on the cores (Kawahashi *et al.*, 1990; Kawahashi and Matijevic, 1991), or successive deposition of layers on core particles (Wang *et al.*, 2002).

These thermal or chemical degradation methods in liquid phase have some disadvantages. One is that the removal of templates requires time-consuming multi-processes. The other is that additional heat-treatment processes for eliminating a polymer core or improving the crystallinity of the shell cause the agglomeration between hollow particles.

In gas phase synthesis, spray drying or pyrolysis was used to produce hollow or coated particles (Chadda *et al.*, 1991; Powell *et al.*, 1997). In general, the spray drying produces one hollow or coated particle from one droplet. Therefore, the size and size distribution of particles are closely related to the characteristics of droplet generators. In this report, we propose an aerosol process in which multiple hollow particles are produced from one droplet and the hollow particle size and size distribution are determined by the template beads, not by the droplet size. In this process, salt is used to prevent hollow particles from agglomeration.

1. Experimental

1.1 Preparation of polystyrene (PS) bead template

As reported in the literature (Reese *et al.*, 2000), to prepare the PS template beads, 0.05 wt% of sodium hydrogen carbonate (CHNaO_3 , Sigma-Aldrich Co.), 0.02–0.12 wt% of 4-styrene sulfonic acid ($\text{C}_8\text{H}_7\text{NaO}_3\text{S}$, Sigma-Aldrich Co.), 1.17 mol of styrene monomer ($\text{C}_6\text{H}_5\text{CHCH}_2$, Sigma-Aldrich Co.), and 0.05 wt% of

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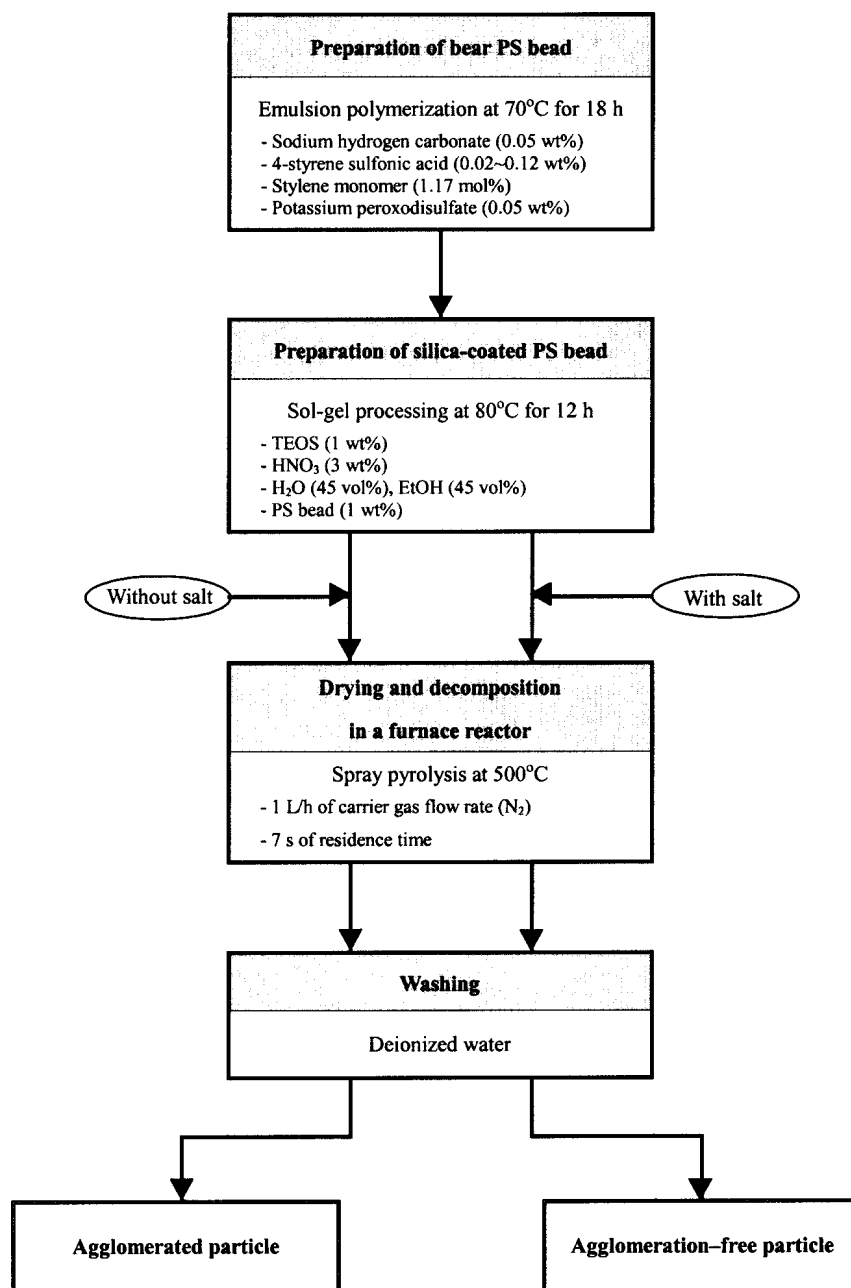


Fig. 1 Procedure for hollow particle production

potassium peroxydisulfate ($K_2O_8S_2$, Sigma-Aldrich Co.) were mixed in a reactor filled with distilled water. Sodium hydrogen carbonate and potassium peroxydisulfate were used as a seed and an initiator, respectively. The reactor was controlled to be maintained at 70°C throughout the reaction. Reactants were stirred at a rate of 360 rpm for 18 h. The prepared PS beads were 230 nm in diameter and the geometric mean dispersion was close to 1.00 as shown in Figure 2(a).

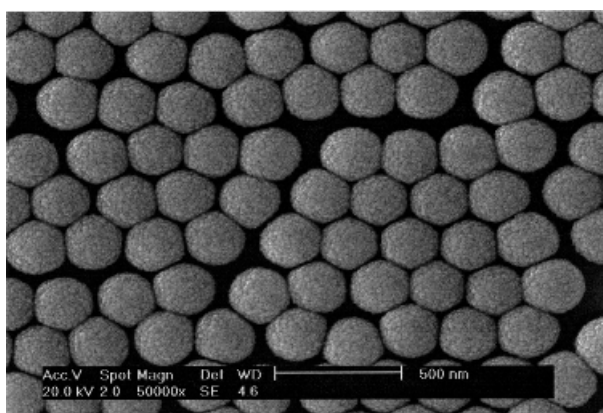
1.2 Preparation of silica-coated PS bead

Silica coated PS bead was prepared by sol-gel method. TEOS of 1 wt% ($C_8H_{20}O_4Si$, Sigma-Aldrich Co.) as a coating material and 3 wt% of nitric acid

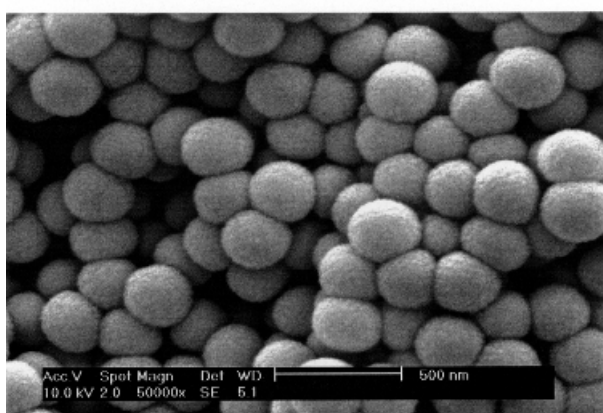
(HNO_3 , Sigma-Aldrich Co.) as a catalyst were added to water-ethyl alcohol mixture of an equal volume ratio. The prepared solution was stirred at room temperature until it became a clear solution. Finally, 1 wt% of PS template beads was added and stirred for 12 h at 80°C. At the end of this silica coating process, 1 wt% of salt (NaCl, Junsei Chemical Co., Ltd.) was added as a desegregation agent.

1.3 Atomization of silica-coated PS bead solution and decomposition of PS in the aerosol reactor

The silica-coated PS solution was atomized by an ultrasonic nebulizer, of which vibrating frequency was 1.67 MHz. The generated droplets of 3–5 μm in



(a)



(b)

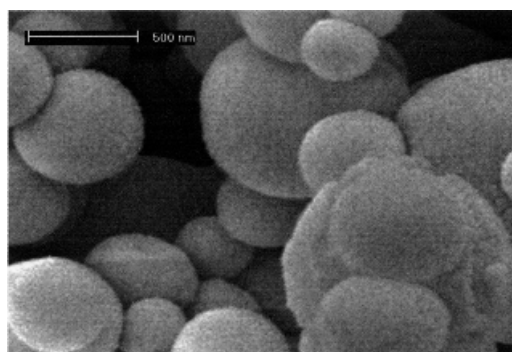
Fig. 2 SEM micrographs of (a) bear PS beads and (b) silica-coated PS beads

diameter were carried into the reactor, which was maintained at 500°C. Water solvent was evaporated and PS bead was burnt off within 7 s of residence time while passing through the furnace reactor. The flow rate of nitrogen carrier gas was fixed at 1 L/min for all the samples. At the end of the reactor, particles were collected with a thimble filter (28 × 100 nm, Toyo Roshi Kaishu, Ltd.) and the salt was washed off with deionized water.

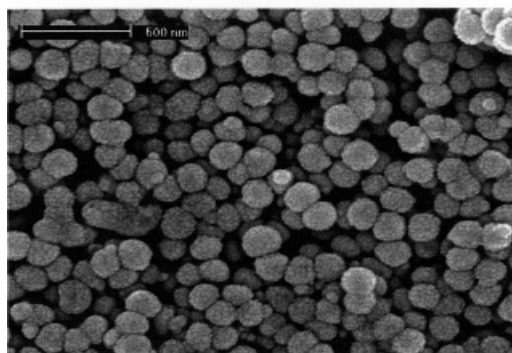
Figure 1 is a summary of the experimental procedure. The morphology and the size of the prepared hollow silica particle were characterized by using SEM (Scanning Electron Microscopy, model: 535M, Philips Co. Ltd.) and TEM (Transmission Electron Microscopy, model: 2000EX, JEOL Ltd.).

2. Results and Discussion

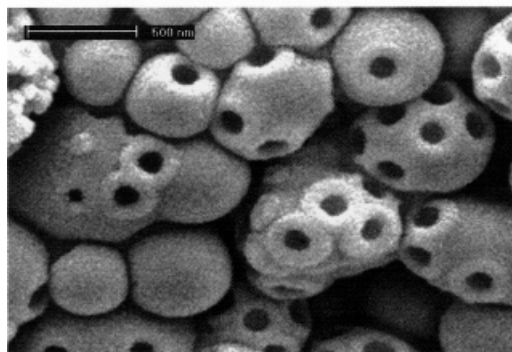
Figures 2(a) and (b) are micrographs of PS beads before and after silica coating, respectively. The mean diameter changed from 230 to 280 nm after silica coating. So the average coating thickness would be 25 nm.



(a)



(b)



(c)

Fig. 3 SEM micrographs of hollow particles (a) before and (b) after washing off salt, and (c) particles prepared without adding salt

If TEOS is assumed to be completely converted into silica and coated the surface of PS bead uniformly and densely, the thickness of the coated-layer is calculated to be 5 nm. If the TEOS was not hydrolyzed at all and coated the surface of PS beads, the thickness should be 38 nm. Therefore, the measured thickness of coating is reasonable because the silica layer is not a dense silica structure and some partially reacted TEOS remains on the surface of PS beads.

Figure 3(a) is a micrograph of spray pyrolyzed particles. The mean diameter was 540 nm and geometric mean dispersion was 1.3, which is a typical

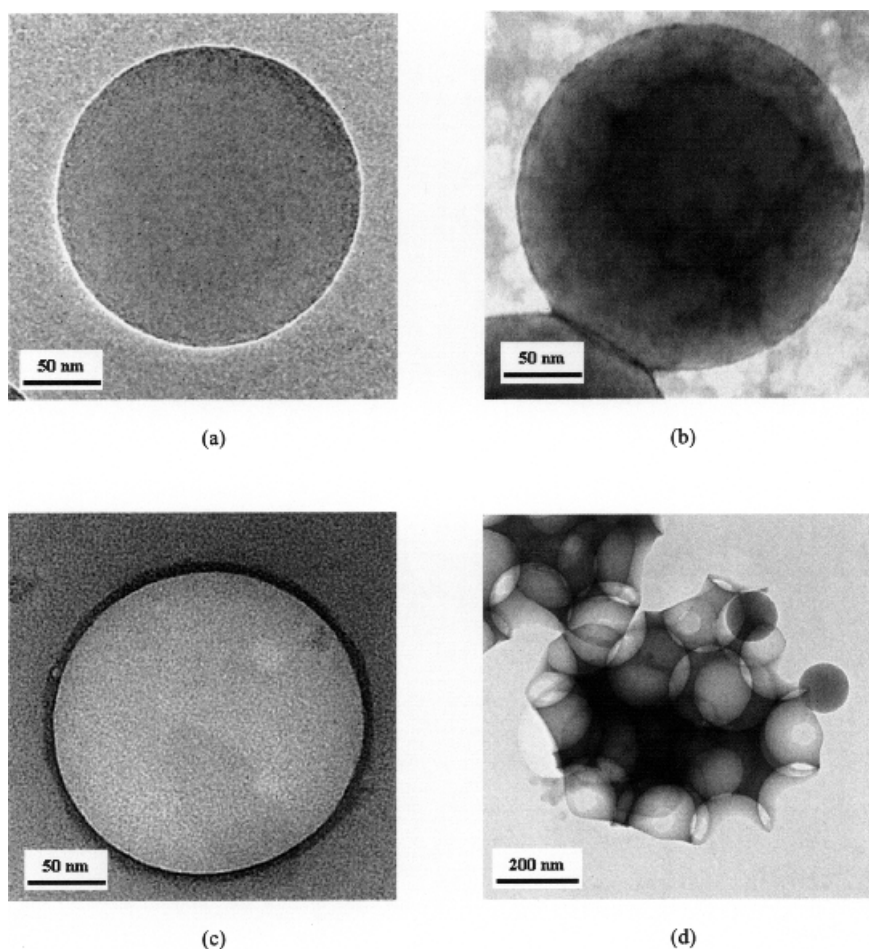


Fig. 4 TEM micrographs of a (a) bare PS bead, (b) silica-coated PS bead, (c) hollow silica particle prepared with salt and (d) that without salt

geometric mean dispersion value of ultrasonically atomized droplets. After washing off salt, particles in Figure 3(a) turned into hollow particles shown in Figure 3(b). The mean diameter of the hollow particles was 160 nm and the geometric mean dispersion was 1.02, which was far smaller than that of the droplets. If hollow particles of 160 nm were packed in the fcc structure inside the sphere of 540 nm, the average number of hollow particles should be around 30. If one droplet assumes to contain 30 PS beads, the average droplet diameter would be 3.3 micrometer. This value is slightly smaller than the droplet size of atomized pure water, of which diameter ranges from 4 to 5 μm (Kang and Park, 1995). It is not surprising to observe this small value because the droplet size is known to become smaller as the ratio of surface tension to the density of solution increases (Moon *et al.*, 2000).

Figure 3(b) also shows that 7 s of residence time was long enough to decompose all PS template beads and to form hollow particles and that salt plays a role of desegregating hollow particles at 500°C of reactor temperature. This desegregation role of salt is very similar to the role of salt in the preparation of

nanoparticles by the spray pyrolysis (Xia *et al.*, 2001).

It should be noted that the diameter of the hollow particles was smaller than that of the original PS template beads because of the shrinkage of hollow particles. The shrinkage explains how the decomposed gas went off without explosion from the inside of the hollow silica particles. At the first stage of the decomposition of PS beads, the silica layer stayed as porous film so that the gas could penetrate out of the silica layer. Once the decomposition was completed, the porous layer became dense and the cooling process made the shrinking accelerated.

In order to confirm the role of salt in the formation of agglomeration-free hollow particles, silica-only-coated PS bead solution was atomized, decomposed and washed off without salt. Figure 3(c) shows that particles of 550 nm in diameter were produced and the surface of particles had small holes that were formed after the removal of PS beads. The geometric mean dispersion was 1.2. Without using salt, silica-coated PS particles were sintered during the thermal decomposition process.

Figures 4(a) and (b) are the TEM micrographs of

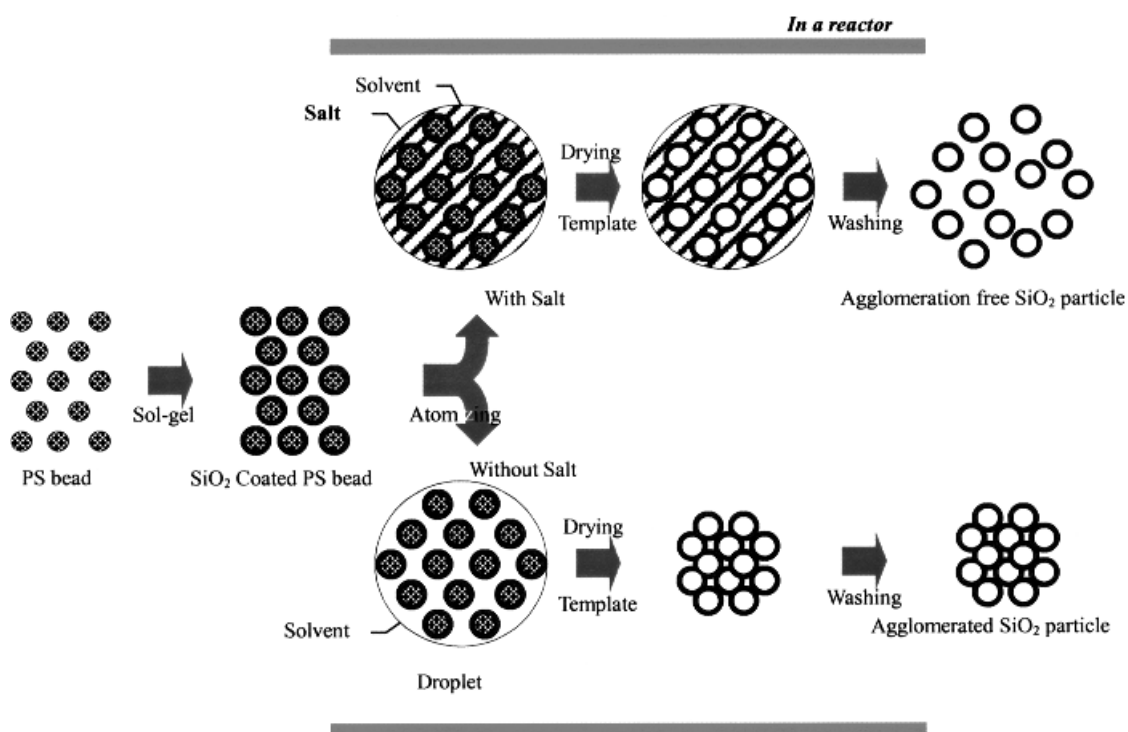


Fig. 5 Schematics of changes in particle morphology

the PS template beads before and after silica coating, respectively. No visible difference in contrast was observed between silica shell and PS particle core because of dense PS particles. From the TEM micrograph in Figure 4(c), however, thin layer of 10 nm in thickness was clearly observed after the removal of PS bead core. Figure 4(d) is the TEM micrograph of sintered particles of hollow morphology, which confirmed that hollow particles prepared without salt were severely agglomerated.

Figure 5 summarizes the changes of particle morphology during the process of hollow particle preparation. The first two steps were carried outside of the furnace reactor and the next two steps were inside the furnace reactor. Finally, the last washing step was performed after the sample was cooled down to room temperature.

Conclusion

A new aerosol process, in which were produced hollow silica particles of 160 nm in diameter and 10 nm in thickness and was the geometric mean dispersion close to 1.02, was proposed. The key concepts of this process include polystyrene beads as template and salt as a desegregation agent. The size of hollow particles was determined by the size of the template beads, not by the size of droplets of aerosol generator. Comparison of SEM and TEM micrographs of particles that were produced with and without salt, revealed that salt

was effective to desegregate hollow particles even at 500°C of the reactor temperature. Shrinkage of silica layer turned out to be important for the formation of a dense silica layer of hollow particles without fragmentation caused by the explosion of decomposition gas. Variation of size and core material of template would make this process versatile and attractive to many applications ranging from photonic crystals to novel catalyst supports.

Acknowledgment

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