A Facile Preparation Method of ZrO_2 Hollow Sphere Using PVA Microcapsule as a Template

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Abstract. In this study, we proposed a simple and facile preparation method of ZrO_2 hollow sphere using PVA microcapsule as a template. The prepared hollow sphere was characterized by XRD, FESEM, N_2 adsorption/desorption isotherms, FT-IR techniques. PVA microcapsule were prepared by polymerization in a water-in-oil emulsion and coated by adding of zirconia sol. Uniform and spherical shaped zirconia hollow sphere with very narrow size distribution was obtained after calcination at 700 °C by removing the PVA microcapsule template. No other carbon residues and carbon-zirconium compounds were observed. These results indicate that the zirconia capsule formed without deformation of the zirconia shell structure, and CO_2 and H_2O gases by decomposition of the PVA microcapsule during sintering process removed through the zirconia shell.

Keywords: Micro hollow sphere; PVA microcapsule; Zirconia; Template

1 Introduction

Hollow sphere materials have unusual properties such as special shape, low density and large interior void space fraction. Due to their potential application in many industrial fields, it has received much interest by researches [1-5]. It is generally understood that the physical and chemical properties of hollow spherical materials are strongly dependent on their shape and structural characteristics. In recent years, many researchers reported that inorganic hollow spherical materials, especially hierarchical nanostructured hollow materials, because the two or more levels of structure can provide both extraordinarily high activated surface and robust stability [6-8]. However, the complexity of synthetic methods for hollow sphere materials, it is required to develop simple synthetic methods [9-10].

In this study, we report a facile method to fabricate a hollow type particle structure which includes the core material inside the shell. Poly (vinyl alcohol) (hereinafter "PVA"), which may include a core substance, used as a template to synthesize the micro (or sub-micro)

capsules in water in oil (w/o) emulsion interface reaction by polymerization. For the formation of inorganic shell, zirconium sol was added into the w/o emulsion to coat the PVA microcapsule. By calcination, inside PVA microcapsule can be removed and ZrO_2 core-shell structured resulted. Compare with the conventional core-shell preparation technique which using emulsion/hydrophobic polystyrene polymer capsule as a template, PVA microcapsule template has many advantages. For example, PVA microcapsules are easily generated by the surface reaction to the state of containing the core material. It can also contain hydrophilic substance due to its hydrophilicity. Since it can be a hydrophilic nanoparticle, such as most of the inorganic particles on the surface of PVA microcapsule can be coated and core PVA microcapsule can be easily removed by extraction using chemicals or calcination process.

The method proposed in this study is very simple because all of the synthesis procedure is carried out in one place. It also has the advantage of fabrication of nano-structured materials. Fig 1 shows the simplified schematic diagram of the method used in this study.

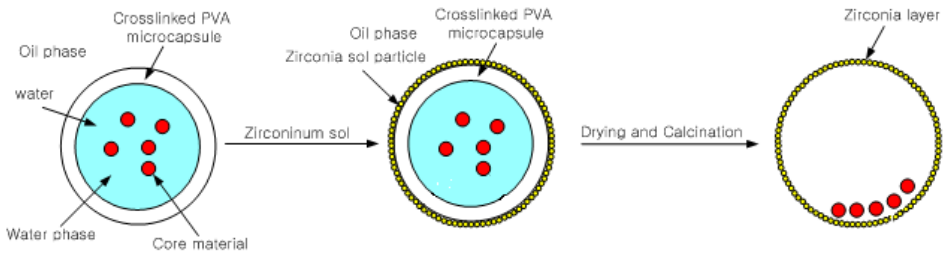

Fig. 1. Schematic representation for the preparation of zirconia hollow sphere.

2 Experimental

2.1 Materials

All following reagents used in this study were chemical grade and used without further purification. Zirconium (IV) propoxide (70 wt%, solution in 1-propanol, Sigma-Aldrich); poly (vinyl alcohol) (PVA, 98~99%, Mw: 31,000~50,000, Sigma-Aldrich); hydroxyproply cellulose (HPC, Mw: 370,000, Sigma-Aldrich); span #80 (Samchun pure chemical); glutaric dialdehyde (GA, 25 wt% solution, Samchun pure chemical); n-Hexane (95%, Samchun pure chemical); hydrochloric acid (35.0~37.0%, Samchun pure chemical); petroleum ether (90%, Samchun pure chemical); ethanol (99.5%, Samchun pure chemical).

2.2 Preparation of PVA Microcapsule and Capsulation

PVA microcapsule were prepared by polymerization in a w/o emulsion method. HPC dissolved in deionized water and then mixed it into n-hexane with stirring for 30 min. 5 wt% of PVA solution was added in HPC/n-hexane solution and mixed with high speed homogenizer for emulsifying of mixture. HCl and GA, as catalyst and cross-linking agent, were mixed with n-hexane and slowly added into PVA/HPC/n-hexane solution with vigorous stirring for one hour. After esterification reaction between the surface function group of PVA and GA, PVA microcapsule was resulted.

For the zirconia capsulation, zirconia solution (zirconia sol) was prepared by reacting with 0.1 M nitric acid solution and zirconium propoxide. The zirconia sol was dropped into PVA microcapsule solution for an hour with stirring. After 3 hours aging, the solution was divided into two phases and filtrated by vacuum filter. The filtered cake was washed with

petroleum ether and ethanol for several times to remove the residual oil and unreacted reactants. The resulted powder was dried for 24 h at the room temperature and then completely dried under vacuum condition at 60 °C.

The dried powder was re-suspended in the deionized water before calcination. To remove the core PVA template and formation of ZrO_2 shell structure, it was calcinated to 700 °C with a heating rate of 4 °C/min. Finally, white colored-powder was resulted.

2.3 Characterization

The morphologies of PVA microcapsules and zirconia hollow microsphere were observed by field emission scanning electron microscope (FESEM, JEOL Co, Japan) with gold coating. Transmission electron microscope (TEM, JEOL Co, Japan) was performed to analyze the structure of hollow sphere and X-ray diffraction (XRD, Rigaku Co, Japan) characterization was carried out using CuKα radiation (λ = 1.54 nm), operated at 40 kV and 30 mA at a scan rate of 4 ° min^{-1} in the range of 2θ = 10-70 °. The particle size of the PVA microcapsule and zirconia hollow microsphere was analyzed by the dynamic light scattering (DLS) method using the suspension of PVA microcapsule and zirconia hollow sphere. The interaction between the PVA microcapsule and zirconia shell was studied by Fourier transform-Infrared (FT-IR) analysis and the specific surface area, the pore volume was determined by the BET method using N_2 adsorption-desorption at 77 K.

3 Results and Discussion

Fig 2 (a) shows the morphologies of prepared zirconia hollow sphere before calcination. Spherical particles having a clean surface of approximately 1-5 μm was observed. It is indicated that polymerization was successfully proceeded during the PVA microcapsule preparation stage. The original shape was almost maintained after removing PVA mircocapsule template by calcination at 700 °C. The formation of CO_2 and H_2O gases by decomposition of the PVA microcapsule during sintering process does not significantly affect on the exterior of zirconia shell.

In general, structural deformation such as crushing or cracking might be occurred during template removing process by heat treatment, which is closely associated with the thermal decomposition behavior of the substance that was used as a template. Additionally, the heat treatment temperature and heating rate become crucial factors for formation of core-shell structure because surface composing materials such as inorganic oxide particles such as zirconia, silica, and titania can be strongly affected its formation condition including the condensation rate, thermal expansion or condensation. The morphology hardly changed before and after sintering of the hollow sphere under the conditions used in this study. It may due to the formation of hydrogen bond such as Zr-O-C or ZrOH-COOH between surface of zirconia and PVA microcapsule template. This result indicates that the direct decomposition of polymer during heat treatment process without morphological transformation. From the results, zirconia capsule formed without deformation of the zirconia shell structure.

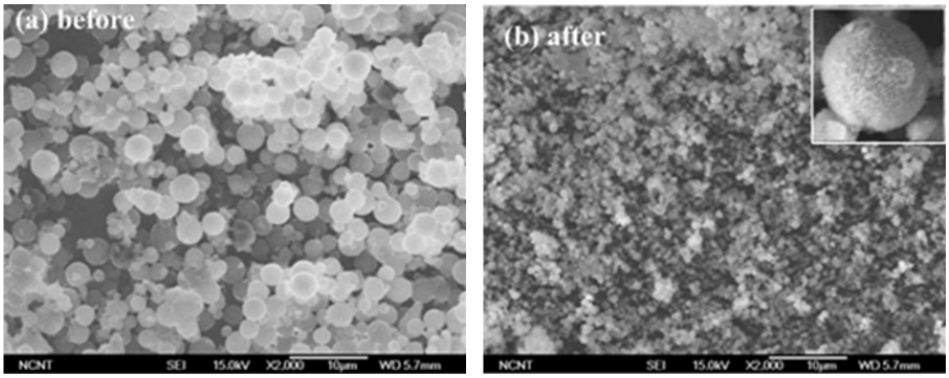

Fig. 2. Surface morphologies of prepared zirconia hollow spheres a) before calcination b) after calcination at 700 °C.

The thickness of zirconia shell was observed 50 nm. Moreover, it confirms that the pores were created by the gaps between the particles. This result indicates that material can pass through the zirconia shell. Such characteristics can be considered as a very important physical property which can be used in areas such as chemical reactions or drug delivery system. If nano-sized particles can be coated in place of the sol particles, the pore size of the particles considered to be adjustable. Fig. 3 shows the particle size distribution analysis of a prepared hollow sphere. Very narrow distribution with a range from 1-5 μm size was observed in a sample of before calcination. Also, uniform sized hollow sphere was observed after calcination as similar with before calcination, but the particle size was decreased after calcination compare to that of before calcination. These results indicate that the shrinkage of zirconia shell during the calcination process.

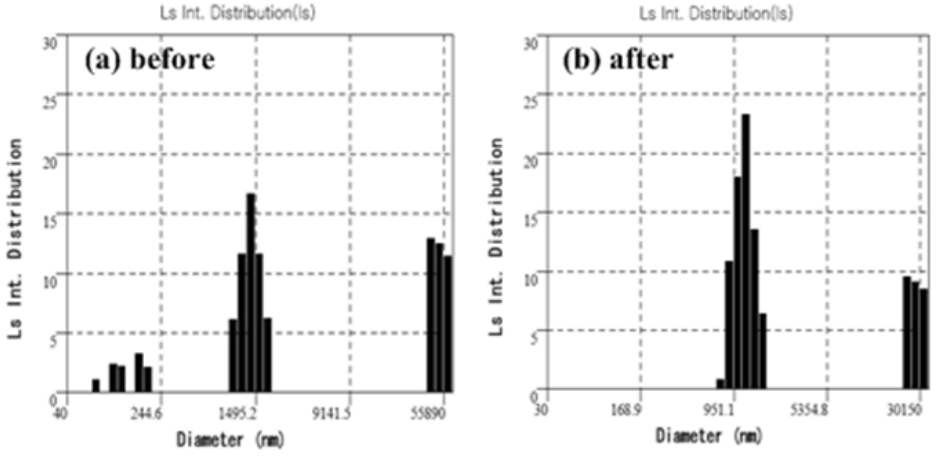

Fig. 3. Particle size distribution of prepared zirconia hollow sphere (a) before and (b) after calcination at 700 °C.

The typical monoclinic ZrO_2 structure of zirconia sphere after calcination process was observed by XRD analysis shown in Fig. 4. No carbon residues and other complex structures were observed. From the result, PVA microcapsule was completely removed by calcination.

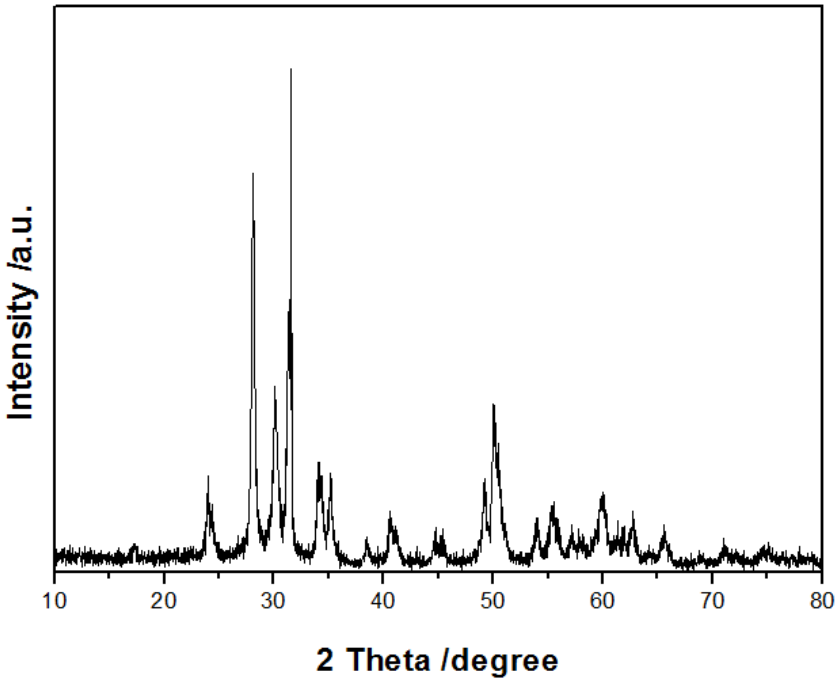

Fig. 4. X-ray diffraction patterns of the ZrO_2 hollow sphere after calcination at 700 °C.

Conclusion

In this study, we successfully demonstrate a simple preparation method of the zirconia hollow sphere by self-assembly of nanoparticles of zirconia sol on the surface of the capsule by using PVA microcapsules as a template. The proposed method is composed of simple process as compared to the previous methods. It was confirmed that the PVA template removed without changes of spherical shape during the high temperature calcination. The suggested method can be considered as a simple way to include the core material, and there can be expected potential applications in various fields such as DDS, catalyst carrier, heat resistance materials due to high thermal stability of ZrO_2 shell.

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