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Short communication

Morphologies of Al_2O_3 shell prepared from Al/AlOOH·nH_2O core-shell particles

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Abstract

Influence of calcination temperature on the morphologies of Al_2O_3 shell with ~2 μm in diameter and ~200 nm in wall thickness, which were prepared via the calcination of the Al/AlOOH·nH_2O core-shell particles, was investigated. Scanning electron microscopy (SEM), transmission electron microscopy (TEM), SAED, and N_2 adsorption-desorption isotherms were used to characterize the as-prepared samples. The experimental results indicated that the intact Al_2O_3 shells were composed of nanorods-like particles when calcined at 900 °C, and increasing temperature lead to the evident growth of these nanoscale particles, with the surface morphology of Al_2O_3 shell variety from rough to smooth configuration. N_2 adsorption results revealed the specific surface area decreased from 114 m^2/g for shells obtained at 900 °C to 40 m^2/g for that obtained at 1100 °C, and the hollow sphere with porous shell provides the possibilities in the applications for catalyst and medical carriers due to its high specific surface area.

Keywords: A. Calcination; D. Al_2O_3; Chemical preparing

1. Introduction

Hollow spheres, which have high specific surface area and low density, are attracting great attention in both fundamental and industrial studies mainly due to their promising applications in medical, sensor, small containers, catalyst carriers and lightweight filler technology [1–5]. Various methods, including cosurfactant, Kirkendall effect, phase separation, rapid quench, and ultrasonication, have been reported for the preparation of hollow spheres with mesoporous shells [6–10]. Templating against colloidal particles is probably the most effective way to the formation of ceramic materials. In a typical procedure, a thin coating of the ceramic or its precursor is formed on the template to create a core-shell composite, and subsequent removal of the template generates ceramic hollow spheres. Recently, We reported a novel method for the preparation of hollow γ-Al_2O_3 and α-Al_2O_3 with about 2 μm in diameter and 200 nm in wall thickness microspheres using low-cost commercial aluminum powders as raw materials [11], and our precious work focused on the formation procedure and mechanism of as-prepared Al_2O_3 shell. In such a synthesis, the formation of hollow Al_2O_3 included two stages: the preparation of the Al/AlOOH·nH_2O core-shell composite particles and then the calcination of them. A formation mechanism was proposed to be a process following the formation of Al/AlOOH·nH_2O core/shell particles in solution, the decomposition of AlOOH·nH_2O shell to Al_2O_3 and the outflow and oxidation of Al core through calcination. During the process of calcination, the aluminum expands by 6.4% in volume at melting state, resulting in the outflow of aluminum from the core and attaching on the outer AlOOH shell. The outflow aluminum will be oxidized immediately into Al_2O_3 due to its high activity. With the increase of calcination temperature, aluminum core will run out and be oxidized continuously, and the AlOOH shell will also decompose into Al_2O_3, thus forms the hollow Al_2O_3 sphere. Recently, great efforts have been focused on the morphology control of nanocrystal due to their morphology dependent properties. Then the aim of this work is to study the influence of calcination temperature on the morphologies of as-synthesized Al_2O_3 shell. The specific

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surface area (SA) from Barrett–Emmett–Tellter (BET) analysis of particles calcined at 900 and 1100 °C revealed a high value of 114 and 40 m^2/g, respectively.

2. Experimental procedure

Aluminum powders (2–3 μm, >99.5%) were provided by Angang Group Aluminium Powder Co., Ltd., China. Concentrated sulfuric acid (95–98%), ammonium hydroxide (25–28% NH_3) and absolute ethanol (99.7%) were all supplied by Shanghai Lingfeng Chemical Reagent Co., Ltd., China. All the chemicals were of analytical grade and used as received without further purification. In a typical experimental procedure, 2 g of aluminum powders and diluted sulfuric acid (0.1 M), with a molar ratio of 4:3 for Al:H_2SO_4, were mixed under rapid stirring at 60 °C. After the dilute sulfuric acid was depleted completely, pyrogenation process was stopped. With the addition of ammonia solution (1 M) to the suspension drop by drop under stirring, white flocculent precipitates occurred, and the molar ratio of Al^{3+} and $NH_3{\cdot}H_2O$ was 1:3. The produced gray–white precipitates were collected and washed repeatedly with ethanol and distilled water, and then the products were dried in an oven at 80 °C for 10 h. The following calcination procedure was carried out at 900 and 1100 °C for 2 h in air, respectively.

The powder morphology and the microstructure were observed by scanning electron microscopy (SEM) (JSM-6700F, JEOL, Japan) and transmission electron microscopy (TEM) (Model 200CX, JEOL, Tokyo, Japan). N_2 adsorption-desorption measurements were performed on a Micromeritics ASAP 2010 apparatus.

3. Results

SEM images of the microspheres are shown in Fig. 1. Fig. 1a illustrates a typical image of Al_2O_3 hollow spheres obtained via calcination at 900 °C for 2 h, and it reveals that the surface of the intact sphere is comprised of uniform packed vermicular crystals with about 50 nm in diameter and several hundreds nanometer in length, which is the typical morphology of γ-Al_2O_3. To further examine the interior structure of these microspheres, Fig. 1b shows the cross section of a cut particle in Fig. 1a. The hollow nature of as-synthesis particle is confirmed successfully, and the regularity and uniformity of the shell wall with a thickness of 200 nm is also perfectly demonstrated. It is observed that the shell consists of individual nanoscale particles, which is accordance with the surface morphology in Fig. 1a. It is worthy to note that Fig. 1b indicate the hollow sphere is porous, and a high specific surface may be expected. With increasing the calcination temperature up to 1100 °C and maintain the calcination time constant, Fig. 1c indicates no evident variety is observed for the diameter of these microspheres, however, the surface morphology of them become much smoother.

Fig. 2 illustrates the TEM images of these hollow microspheres. Morphologies of particles obtained via calcina-

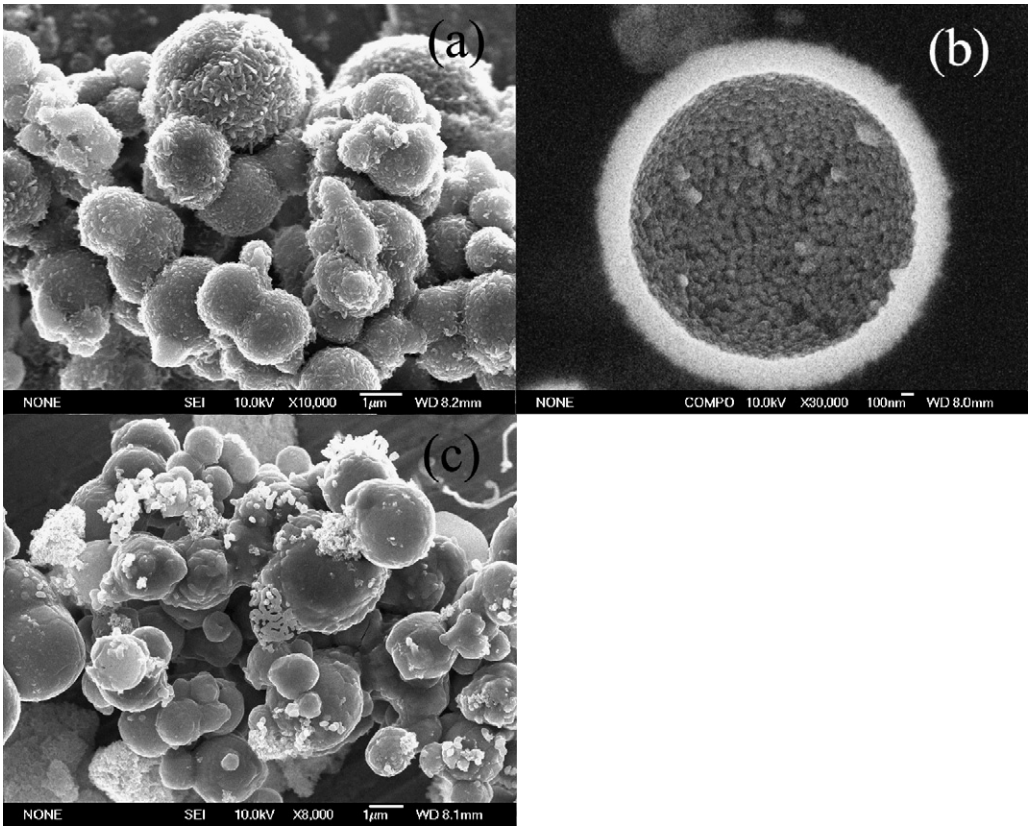

Fig. 1. SEM images of Al_2O_3 prepared from calcining Al/AlOOH·nH_2O core-shell particles at 900 °C (a and b) for 2 h. (a) Overall product morphology. (b) The cross section of a cut particle. The particles obtained via calcination at 1100 °C (c) for 2 h.

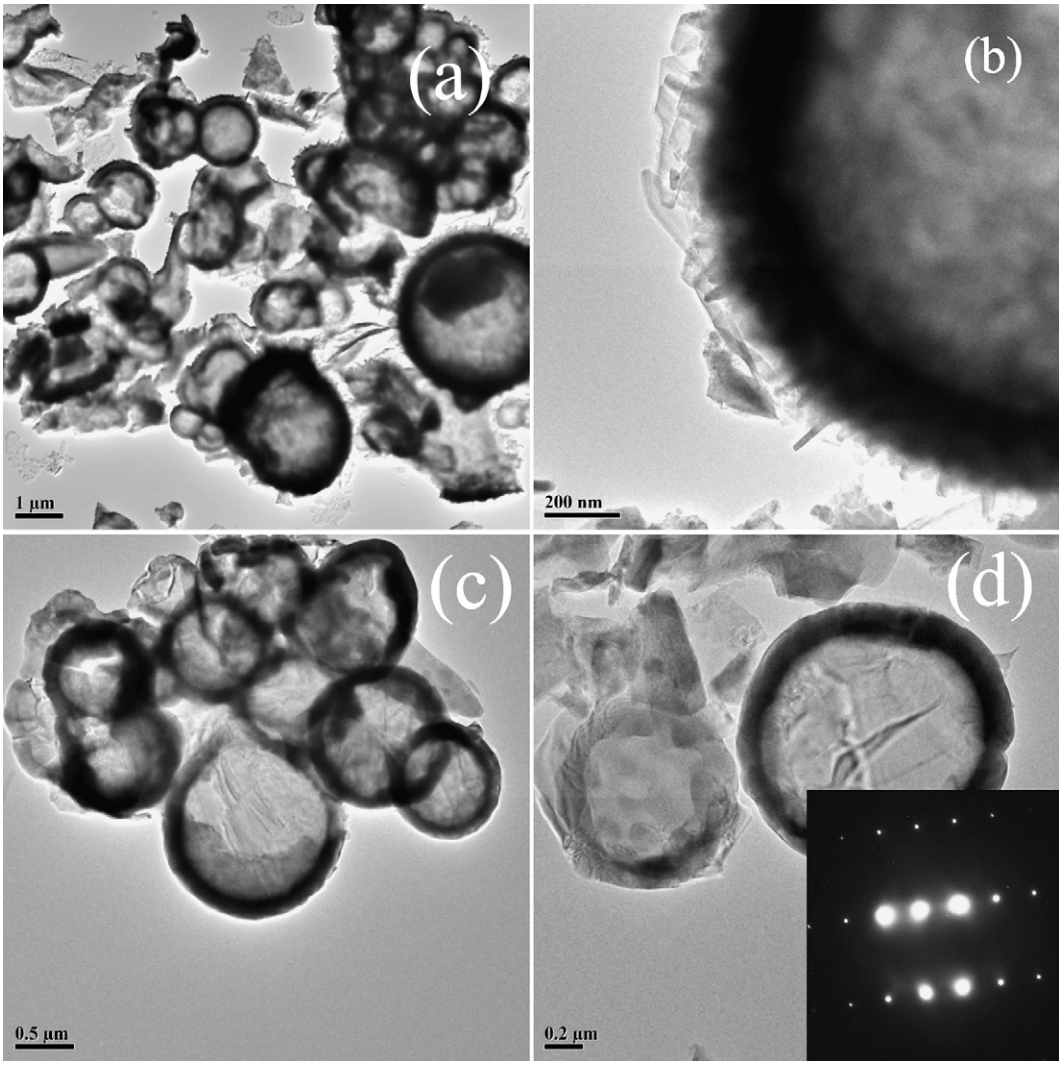

Fig. 2. TEM images of the particles obtained via calcining Al/AlOOH·nH$_2$O core-shell particles at 900 °C (a and b) for 2 h. (a) Overall product morphology. (b) Enlarged the rim of the particle. The particles obtained via calcination at 1100 °C (c and d) for 2 h. (inset) Selected-area electron diffraction of the smaller shell particle in (d) (SAED).

tion Al/AlOOH·nH$_2$O core/shell particles at 900 °C for 2 h is shown in Fig. 2a. In this case, some microspheres contain a small core because of the incomplete removal of Al core, and the formation procedure of hollow Al_2O_3 spheres have been analyzed elsewhere [11]. A higher magnification of a hollow sphere in Fig. 2a indicates some degree of surface roughness. Nanorod-like particles can be seen on the surface, which is well accordance with the result from Fig. 1a. Particles obtained via calcination at 1100 °C lead to the smooth surface of these hollow Al_2O_3 spheres (Fig. 2c and d). The electron diffraction (SAED) recorded on of the small shell in Fig. 2d indicates the single crystalline nature, suggesting significant grain growth occurrence at higher calcination temperature.

Fig. 3 shows the nitrogen adsorption-desorption isotherms of hollow Al_2O_3 spheres resulting from different calcination temperature at 77 K. As can be seen clearly from this chart, specific surface area of sample obtained at 900 °C (Fig. 3a) is much larger than that obtained at 1100 °C (Fig. 3b), which

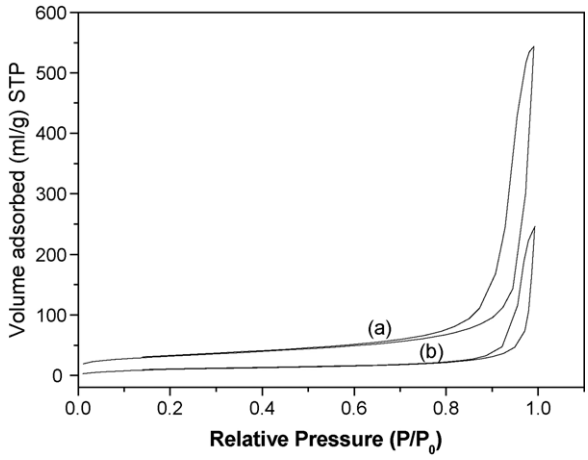

Fig. 3. Nitrogen adsorption-desorption isotherms of the particles obtained via calcining Al/AlOOH·nH$_2$O core-shell particles at: (a) 900 °C and (b) 1100 °C for 2 h.

demonstrate our conjecture from Fig. 1b. By applying BET equation for specific surface area, the specific surface area decrease from 114 m^2/g for particles calcined at 900 °C to 40 m^2/g for products obtained at 1100 °C. Crystal growth and bridging (as a result of sintering) between neighboring particles may responsible for the drastic decrease in BET surface area.

4. Discussion and conclusion

We concentrate on only influence of calcination temperature on the morphologies of Al_2O_3 shell prepared via the calcination of the Al/AlOOH·nH_2O core-shell particles in this work, and the results indicate that the calcination temperature play an important role on the morphologies of as-prepared Al_2O_3 shell. The surface of Al_2O_3 shell obtained at 900 °C is comprised of individual nanorod particles and the shell is porous, corresponding to a high specific surface area of 114 m^2/g. The hollow sphere with porous shell highlights the advantages associated with the application for catalyst and medical carriers due to its high specific surface area. With the calcination temperature increasing to 1100 °C, nanorods-like particles on the shell grow and some of the pore between the neighboring particles is built up, leading the great decrease of specific surface area of sample obtained at this temperature to 40 m^2/g, and surface of the shell becomes much smoother accordingly. Single crystalline nature of some shell is another proof of grain growth.

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References

[1] Z.Y. Zhong, Y.D. Yin, B. Gates, Y.N. Xia, Preparation of mesoscale hollow spheres of TiO_2 and SnO_2 by templating against crystalline arrays of polystyrene beads, Adv. Mater. 12 (3) (2000) 206–209.
[2] M. Fujiwara, K. Shiokawa, Y. Tanaka, Y. Nakahara, Preparation and formation mechanism of silica microcapsules (hollow sphere) by water/oil/water interfacial reaction, Chem. Mater. 16 (2004) 5420–5426.
[3] Y.D. Yin, Y. Lu, B. Gates, Y.N. Xia, Synthesis and characterization of mesoscopic hollow spheres of ceramic materials with functionalized interior surfaces, Chem. Mater. 13 (2001) 1146–1148.
[4] K. Zhang, X.H. Zhang, H.T. Chen, X. Chen, L.L. Zheng, J.H. Zhang, B. Yang, Hollow titania spheres with movable silica spheres inside, Langmuir 20 (2004) 11312–11314.
[5] W.J. Li, M.O. Coppens, Synthesis and characterization of stable hollow ti-silica microspheres with a mesoporous shell, Chem. Mater. 17 (2005) 2241–2246.
[6] S.P. Naik, A.S.T. Chiang, R.W. Thompson, F.C. Huang, Formation of silicalite-1 hollow spheres by the self-assembly of nanocrystals, Chem. Mater. 15 (2003) 787–792.
[7] Y.D. Yin, R.M. Rioux, C.K. Erdonmez, S. Hughes, G.A. Somorjai, A.P. Alivisatos, Formation of hollow nanocrystals through the nanoscale Kirkendall effect, Science 304 (2004) 711–714.
[8] C. Radloff, R.A. Vaia, Metal nanoshell assembly on a virus bioscaffold, Nano Lett. 5 (2005) 1187–1191.
[9] R.G. Yang, G. Chen, Thermal conductivity modeling of core-shell and tubular nanowires, Nano Lett. 5 (2005) 1111–1115.
[10] W.F. Dong, J.K. Ferri, T. Adalsteinsson, M. Schönhoff, G.B. Sukhorukov, H. Möhwald, Influence of shell structure on stability, integrity, and mesh size of polyelectrolyte capsules: mechanism and strategy for improved preparation, Chem. Mater. 17 (2005) 2603–2611.
[11] H.M. Kou, J. Wang, Y.B. Pan, J.K. Guo, Hollow Al_2O_3 microspheres derived from Al/AlOOH·nH_2O core-shell particles, J. Am. Ceram. Soc. 88 (6) (2005) 1615–1618.