

Ultrafine alumina powders derived from ammonium aluminum carbonate hydroxide

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Ultrafine alumina powder is an important material for applications such as catalyst supports, fine ceramics and composite materials. Numerous techniques have been developed for the preparation of ultrafine alumina powders, which include gas phase synthesis [1, 2], liquid phase reaction [3–5] and hydrothermal reaction at high pressure [6, 7]. Among these, the liquid phase reaction method has been of considerable interest, because it allows a very fine and reactive powder to be prepared, and the powder characteristics can be easily modified by changing the conditions during powder synthesis.

In this letter, we report the preparation of ultrafine alumina powders via liquid phase synthesis of ammonium aluminum carbonate hydroxide (AACH) followed by thermal decomposition. The change of phase structure, specific surface area, particle size and morphology of AACH during calcination was studied and the sintering behavior of the alpha alumina powder obtained was examined.

Aluminum nitrate nonahydrate and ammonium carbonate (both analytical grade) were used as starting materials. AACH ($\text{NH}_4\text{AlO}(\text{OH})\text{HCO}_3$) was synthesized by adding dropwise an aluminum nitrate solution ($0.3 \text{ mol} \cdot \text{L}^{-1}$) to a rapidly stirred ammonium carbonate solution ($2 \text{ mol} \cdot \text{L}^{-1}$) in a mole ratio of $(\text{NH}_4)_2\text{CO}_3$ to $\text{Al}(\text{NO}_3)_3$ equal to 2.5. The precipitation was carried out at $37 \pm 2^\circ\text{C}$ for 0.5 h with the final pH of the resulting slurry being about 9. The system was further stirred for another 0.5 h after completion of the precipitation. The as-prepared powder was filtered, washed thoroughly with deionized water and then with ethanol (three times), and then dried at room temperature under vacuum. The calcination of the as-prepared powder was carried out at several selected temperatures between 300 and 1150°C for 1.5 h with an air atmosphere.

The crystalline phases in the as-prepared and calcined products were identified by X-ray diffraction (XRD) with a Rigaku D/MAX—III B diffractometer using $\text{Cu K}\alpha$ radiation. The particle morphology and size of the as-prepared and calcined powders were observed by transmission electronic microscopy (TEM) using a Jeol JEM-2010 electron microscope. Specimens were prepared by evaporation of an ethanolic dispersion of the powders on grids coated with perforated carbon film. The specific surface area of the calcined powders was measured via the Brunauer-Emmett-Teller (BET) method with nitrogen absorption using an Micromerit-

ics ASAP 2000 automated Volumetric analyzer. Samples were degassed at 150°C for 2 h under vacuum prior to analysis.

For sintering studies, the alpha alumina powders, prepared by calcining the as-prepared powders at 1150°C , were uniaxially dry-pressed at 50 MPa and subsequently isostatic pressed at 200 MPa. The powder compacts were sintered in air at various temperatures from 1200 to 1450°C for 2 h. The bulk densities of the sintered compacts were measured by the Archimedes' method. Relative bulk densities were calculated by taking the theoretical density of alpha Al_2O_3 as $3.98 \text{ g} \cdot \text{cm}^{-3}$ [8]. The microstructure of the polished and thermally etched sintered (1400°C , 0.5 h) specimen was observed by scanning electron microscopy (SEM) using a Jeol JSM-5600LV electron microscope.

The mole ratio (R) of $(\text{NH}_4)_2\text{CO}_3$ to $\text{Al}(\text{NO}_3)_3$ and the concentration (c) of $(\text{NH}_4)_2\text{CO}_3$ used in the process of precipitation affect significantly the properties of the as-prepared powders. AACH powders with desirable properties can be produced only in a narrow range of $2 < R \leq 3$ and $1.5 < c \leq 2 \text{ (mol} \cdot \text{L}^{-1})$. The as-prepared powders synthesized at $R < 2$ or $c < 1.5 \text{ mol} \cdot \text{L}^{-1}$ contain AACH together with gelatinous boehmite (AlOOH), which results in the formation of

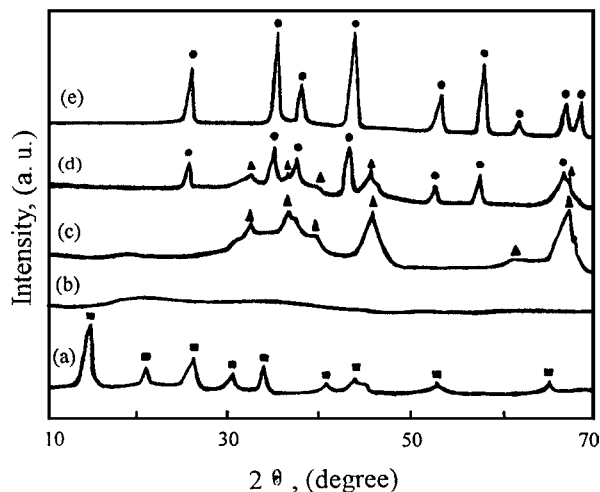


Figure 1 XRD patterns of the as-prepared powder and powders calcined at various temperatures for 1.5 h: (a) as-prepared powder, (b) 300°C , (c) 850°C , (d) 1000°C , and (e) 1150°C . ■, $\text{NH}_4\text{AlO}(\text{OH})\text{HCO}_3$; ▲, $\gamma\text{-Al}_2\text{O}_3$; ●, $\alpha\text{-Al}_2\text{O}_3$.

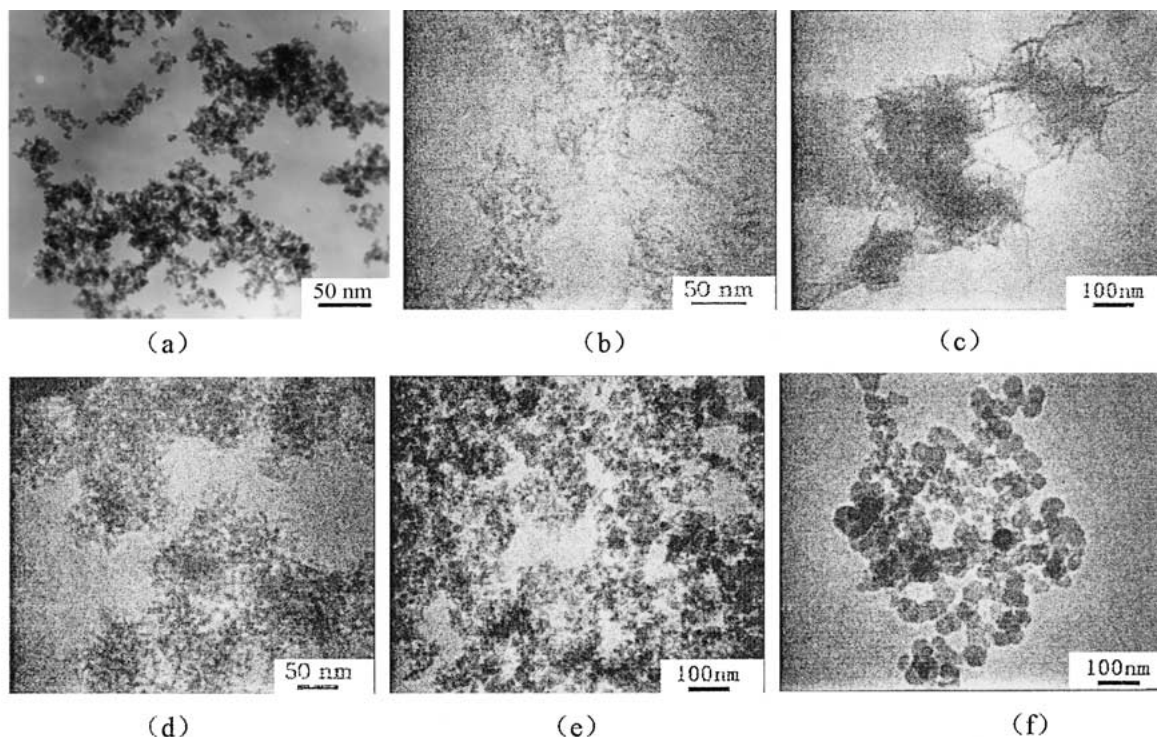


Figure 2 TEM micrographs of the as-prepared powder and powders calcined at different temperatures: (a) as-prepared powder, (b) 300 °C, (c) 600 °C, (d) 850 °C, (e) 1000 °C, and (f) 1150 °C.

hard-agglomerates during the following calcinations. On the other hand, the as-prepared powders obtained at $R > 3$ or $c > 2 \text{ mol} \cdot \text{L}^{-1}$ consist of submicrometer-sized AACH particles, from which the $\alpha\text{-Al}_2\text{O}_3$ powder prepared via calcinations at 1150 °C has a lower BET specific surface area. It is obvious that preparation conditions are important in influencing powder characteristics.

Fig. 1 shows the XRD patterns of the as-prepared and calcined powders. The crystalline phase present in the as-prepared powder is AACH, which decomposes to amorphous Al_2O_3 after being heated at 300 °C, and this persists on further heating until to 850 °C, at which temperature Al_2O_3 transforms from amorphous to gamma phase. When the heating temperature is increased to 1000 °C, $\alpha\text{-Al}_2\text{O}_3$ appears as the predominant phase and the diffraction peaks of $\gamma\text{-Al}_2\text{O}_3$ becomes significantly reduced. After heating at 1150 °C the XRD pattern shows that $\gamma\text{-Al}_2\text{O}_3$ transforms to $\alpha\text{-Al}_2\text{O}_3$ completely.

Fig. 2 shows the TEM photographs of the as-prepared and calcined powders. The as-prepared powders are composed of AACH particles of about 5–10 nm in size (Fig. 2a). The amorphous Al_2O_3 derived from the calcination of AACH at 300–600 °C exhibits a fibrillar morphology (Fig. 2b and c), which converts to dendritic morphology after the transformation of amorphous Al_2O_3 to $\gamma\text{-Al}_2\text{O}_3$ at 850 °C (Fig. 2d). The powders calcined at 1000 °C consist of grained particles with a broad size distribution, some of which were observed to begin to spheroidize via the aggregation and growth of Al_2O_3 particles (Fig. 2e). The $\alpha\text{-Al}_2\text{O}_3$ powders obtained by calcination at 1150 °C exhibits spherical morphology, and the particle size is about 40–50 nm (Fig. 2f). From Fig. 2e and f it can be seen that the for-

mation of $\alpha\text{-Al}_2\text{O}_3$ is accompanied by the grain growth and spheroidization of Al_2O_3 particles.

The BET specific surface areas of the Al_2O_3 powders calcined at different temperatures are given in Fig. 3. It can be seen that the powder calcined at 300 °C has a specific surface area of about $420 \text{ m}^2 \cdot \text{g}^{-1}$, which decreases continuously with increasing temperature. The variation of specific surface areas with calcination temperature can be explained by the change of particle size and morphology of Al_2O_3 powders as shown in Fig. 2b–f. After calcining at 300 °C the Al_2O_3 powder takes the shape of fibrils with a smaller size, in the aggregates of which an abundance of pores exist, so the powder has a large specific surface area. As the calcining temperature is increased from 300 to 1000 °C, the particle

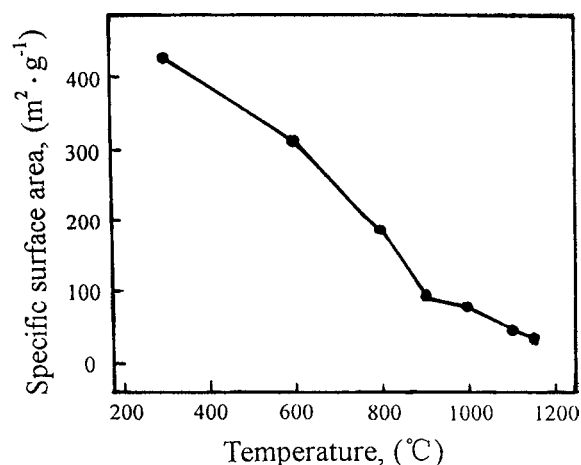


Figure 3 Dependence of the specific surface area of Al_2O_3 powders on calcination temperatures.

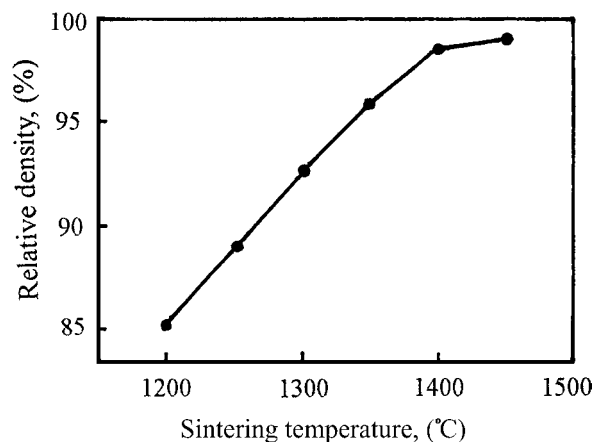


Figure 4 Change in relative sintered density with sintering temperature. Sintering time is 2 h.

morphology transforms from fibrils to dendrites, and then to grains, and in the meanwhile the particles grow in size progressively, which results in the gradual diminution of the specific surface area. The decrease in specific surface area above 1000 °C is due to the particle growth and spheroidization. The α - Al_2O_3 powders obtained at 1150 °C has a specific surface area of $32.5 \text{ m}^2 \cdot \text{g}^{-1}$, based on which the average particle size is calculated to be about 46 nm, corresponding to the result of the TEM observation.

Fig. 4 shows the sintering curve of the α - Al_2O_3 powders. It can be seen that the powder can be sintered to 98.7% of theoretical density at 1400 °C, and on increasing the temperature to 1450 °C the relative density of the sintered compact can be further increased to >99%. Fig. 5 shows the microstructure of the compact sintered at 1450 °C for 2 h. The sintered body exhibits a very fine equiaxed morphology with grain size in the range of 0.2–0.3 μm , and the residual pores are mainly located at the grain boundaries.

In summary, ultrafine spherical α - Al_2O_3 powders with particle size in the range of 40–50 nm and a BET specific surface area of $32.5 \text{ m}^2 \cdot \text{g}^{-1}$, can be prepared from $\text{Al}(\text{NO}_3)_3$ and $(\text{NH}_4)_2\text{CO}_3$ via the synthesis of ammonium aluminum carbonate hydroxide followed by calcination. The powder obtained exhibits excellent sinterability and can be sintered to >99% of theoretical density at 1450 °C for 2 h. The high sintered density

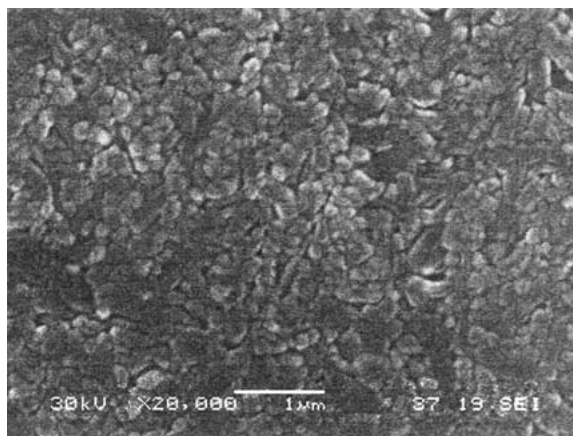


Figure 5 SEM micrograph of polished and thermally etched surface of sample sintered at 1450 °C for 2 h.

and fine microstructure of the Al_2O_3 ceramic obtained in this study benefit from the good dispersion and ultrafine particle size of the α - Al_2O_3 powders.

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