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Size-controlled synthesis of nano α-alumina particles through the sol–gel method

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Abstract

Nano α-alumina particles were synthesized by a sol–gel method using aqueous solutions of aluminum isopropoxide and 0.5 M aluminum nitrate. 1/3-benzened disoulfonic acid disodium salt (SDBS) and sodium bis-2-ethylhexyl sulfosuccinate (Na(AOT)) were used as surfactant stabilizing agents. Solution was stirred for different periods (24, 36, 48 and 60 h) at 60 °C. The samples were then analyzed by X-ray diffraction (XRD), scanning electron microscopy (SEM) and transmission electron microscopy (TEM). Introduction of surfactant stabilizing agents and different stirring times will affect the size and shape of particle formed and also the degree of aggregation. SDBS, however, produced better dispersion, finer particles and spherical shape nanoparticles, compared to Na(AOT). The finest particle size (20–30 nm) was obtained at 48 h stirring time with SDBS surfactant.

Keywords: A. Sol–gel processes; B. X-ray methods; D. Al_2O_3

1. Introduction

Ceramics have many applications in high technology from structural to electrical and electronic because of their excellent properties, but sometimes their low mechanical properties limit their wide applications. However, nanocrystalline ceramics can enhance their mechanical properties. So nanometer size powder processing is of great importance in the range of nanotechnology since it affords to fabricate various kinds of nanocrystalline materials and the nanocomposite ceramics have such advantages over monolithic ceramics as high strength and high toughness [1,2].

To obtain nanostructure ceramics, nanoscale powders with high performance are necessary. However nanoscale α-alumina (α-Al_2O_3) powder is difficult to obtain, because of two reasons: First, α-Al_2O_3 is in a stable phase after calcining at high temperature, which easily prompt the grain growth of powder, and make it difficult to get nanoscale particles; secondly, α-Al_2O_3 particles tend to aggregate during dehydration process in wet chemistry method. Therefore, it is necessary to develop new methods to overcome this problem [3,4].

Conventional synthesis processes of α-Al_2O_3 involve mechanical milling, vapor phase reaction, precipitation, sol–gel, hydrothermal and combustion methods. Mechanical synthesis of α-Al_2O_3 requires extensive mechanical ball milling which easily introduces impurities. Vapor phase reaction for preparation fine α-Al_2O_3 powder from a gas phase precursor demands high temperature above 1200 °C. The precipitation method suffers from its complexity and time consuming (long washing times and aging time) [5,6]. The direct formation of α-Al_2O_3 via the hydrothermal method needs high temperature and pressure. The combustion method has been used to yield α-Al_2O_3 powders, whereas the powder obtained from the process is usually hard aggregated but contains nano-sized primary particles [7]. Sol–gel, a commonly used technique, involves the formation of an amorphous gel

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from a precursor solution. This method based on molecular precursors usually makes use of metal alkoxides as raw material. Some advantages of the sol–gel method are better homogeneity and purity from raw material, lower preparation temperature which save energy cost and the ability to form unique composition [8]. The purpose of this work is to synthesize nano-sized α-Al_2O_3 by controlling the particle size distribution and shape.

2. Experimental

Aluminum isopropoxide $Al(OC_3H_7)_3$ (Merck, German), aluminum nitrate $Al(NO_3)_3{\cdot}9H_2O$ (Merck, German), sodium bis-2-ethylhexyl sulfosuccinate (Na(AOT)) (Merck, German) and 1/3-benzened disoulfonic acid disodium salt (SDBS) (Merck, German) were used as raw materials to prepare nano α-Al_2O_3. The starting solution was prepared through using aluminum isopropoxide and 0.5 M aluminum nitrate aqueous solution as a solvent. The molar ratio of alumina sol (ALP/ALN) was 3:1. The solutions were continuously stirred for different periods (24, 36, 48 and 60 h). Then, the sodium bis-2-ethylhexyl sulfosuccinate (Na(AOT)) and 1/3-benzened disoulfonic acid disodium salt (SDBS) were added by adjusting the molar ratio between alkoxide and surfactants from 0.1 and stirred for 1 h. It is expected that this time be the optimal time for the addition of surfactant and it occurs prior to the onset of the nucleation and growth step.

The solutions were heated up to 60 °C and stirred constantly for evaporation process. Viscosity and color changed as the sol turned into a transparent stick gel. The gels were then heat treated at 90 °C for 8 h. Dried gels were calcined at temperature between 1000 to 1200 °C. Finally, the calcined powders crushed by using mortar and pestle. Phase identifications were performed by X-ray diffraction (XRD) using nickel filtered Cu Kα radiation in the range of $2\theta = 10–80^\circ$ with a scanning speed of 5°/min. The ultrasonic bath was used to suspend calcined powders in ethanol, and subsequently a few droplets of it was used for microstructure evaluation by Phillips CM12 transmission electron microscopy (TEM) and Cambridge Stereoscan 200 and Leica Cambridge S-360 scanning electron microscopy (SEM). The process steps are illustrated in Fig. 1.

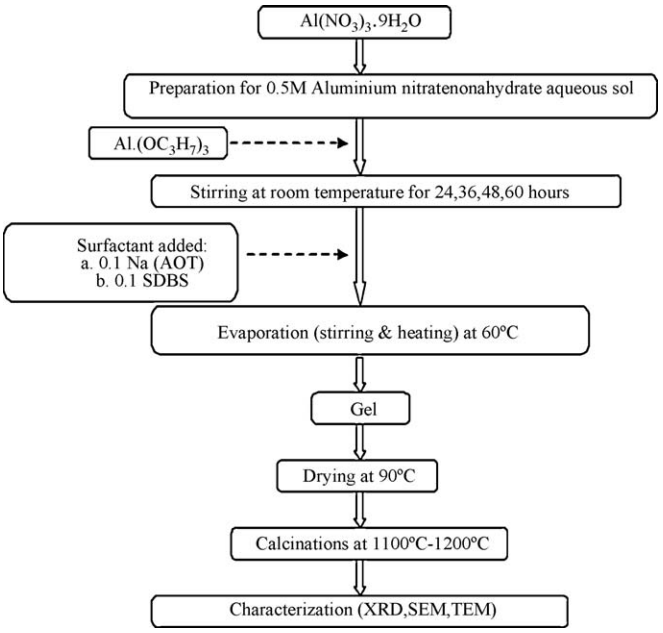

Fig. 1. Nano alumina synthesis process.

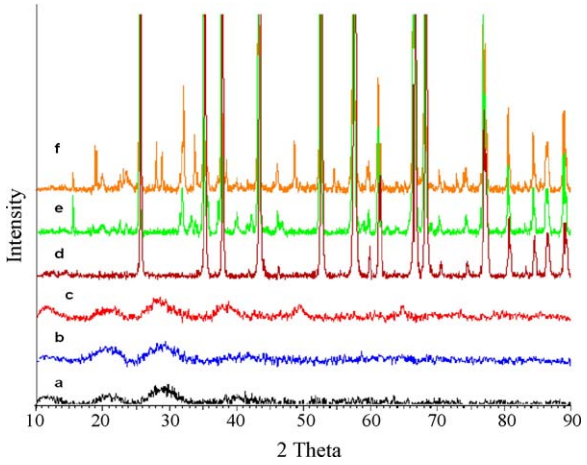

Fig. 2. XRD spectra of aluminum oxide obtained under various conditions: (a) XRD spectrum of bohemite formed without surface stabilizer before calcined, (b) XRD spectrum of bohemite formed after the addition of Na(AOT) before calcined, (c) XRD spectrum of bohemite, formed after the addition of SDBS before calcined, (d) XRD spectrum of α-Al_2O_3, formed without surface stabilizer, after calcined at 1200 °C, (e) XRD spectrum of α-Al_2O_3, formed after the addition of Na(AOT) after calcined at 1200 °C and (f) XRD spectrum of α-Al_2O_3, after the addition of SDBS after calcined at 1200 °C.

3. Results and discussion

The synthesis of nano α-Al_2O_3 was carried out with the concurrent addition of sodium bis-2-ethylhexyl sulfosuccinate (Na(AOT)) and 1/3-benzened disoulfonic acid disodium salt (SDBS) and increasing the stirring time, to prevent excessive grain growth and aggregation of nanoparticles. The overall reaction scheme is shown below [8]:

$$2Al(OR)_3 + 3H_2O \xrightarrow{(Na(AOT))\ \&\ SDBS)} \alpha\text{-}Al_2O_3 + 6ROH,$$
$$(R = \text{alkyl group})$$

This is a multi-step process that involves the transformation of the aluminum alkoxide to an aluminum hydroxide ($Al(OH)_3$) followed by the dehydration to form an oxo-hydroxide aluminum intermediate, AlO(OH) (bohemite), that will constitute the precursor in the sol–gel process and that will involve the following chemical transformation [8,9]:

$$2AlO(OH) \xrightarrow{(Na(AOT))\ \&\ SDBS)} \alpha\text{-}Al_2O_3 + H_2O[8-9]$$

The XRD analysis in Fig. 2 showed the most stable phase, α-Al_2O_3 occurred dominantly at 1200 °C. The observation reported by Hyuk-Joon et al. [10] indicated that completion of the most stable phase, α-alumina occurs at this temperature. Although the thermodynamically stable α-Al_2O_3 phase can be

obtained through a sequence of topotactic and reconstructive transformations (i.e. boehmite → γ → δ → θ → α), the morphology remains unchanged and the final products have the same shape as the initial phases [6,7].

The bohemite intermediate obtained in the absence of surfactant, exhibits a crystalline phase in a amorphous background Fig. 2a.

The addition of the surfactants resulted in the formation of an amorphous bohemite phase coupled with some hydrates of surfactant. This may be the result of the adsorption of surfactant layer on the surface of the initial bohemite nuclei, which prevented the aggregation and grain growth of bohemite, in the absence of surfactants that would allow the formation of crystalline phase [8–9]. However, addition of Na(AOT) did not play a significant role in the formation of an amorphous bohemite phase coupled with some hydrates of surfactant, and the most difference observed was in the presence of SDBS surfactant which is shown in Figs. 2[b and c] and 3[b–d].

Fig. 3 shows SEM micrographs that by increasing the surfactant and stirring time the particle become finer and less agglomerated until 48 h stirring. The particle started to agglomerate and more dense in structure at 60 h. Wu et al. [9] and Novakovic and Korthaus [11] had reported that drying of the sol invariably leads to agglomeration because the residual salts present in the sol as the water evaporates forms solid bridges between particles. Besides that, the particle size and shape of the α-alumina is determined by the crystal structure of the original hydroxide and the series of phase transformations which occur during calcinations. The TEM micrographs of the α-Al_2O_3 particles show that the particles were capped with Na(AOT) and SDBS after 24, 36 and 60 h stirring predominantly the particles had irregular angular shape. As for the sample with stirring time of 48 h the particle shapes were mainly spherical (Fig. 4(b and d)). Particles formed with SDBS as surfactant after 24 and 36 h stirring were in the range of 270–320 and 250–300 nm and had a lot of agglomeration and only little dispersion was observed. However, after 48 h, the particle sizes were in the range of 20–30 nm and possessed a good quality of dispersion (Fig. 4(b)). The size of particles with 60 h was in the range of 150–200 nm with a lot of agglomeration and only little dispersion was observed. The size of particles was capped with Na(AOT)) after24 and 36 h stirring were in the range of 280–330 and 200–250 nm and also had agglomerated. After 48 h the particle size was in the range of 120–180 nm and agglomeration had formed (Fig. 4(d)). The sizes of particles with 60 h of stirring were in the range of 200–250 nm and a lot of agglomeration was observed.

Ming et al. [7] reported the maximum number of hydrogen bonds with the OH groups on boehmite surfaces was achieved by the SDBS surfactant micelles, reducing the free energy of the boehmite crystallites with low dimensions. Yong et al. [9] also reported the shape of particles were capped with surfactant at the higher 600 °C temperature were mainly spherical. This is in agreement with the observation of this study as shown in Fig. 4(b and d).

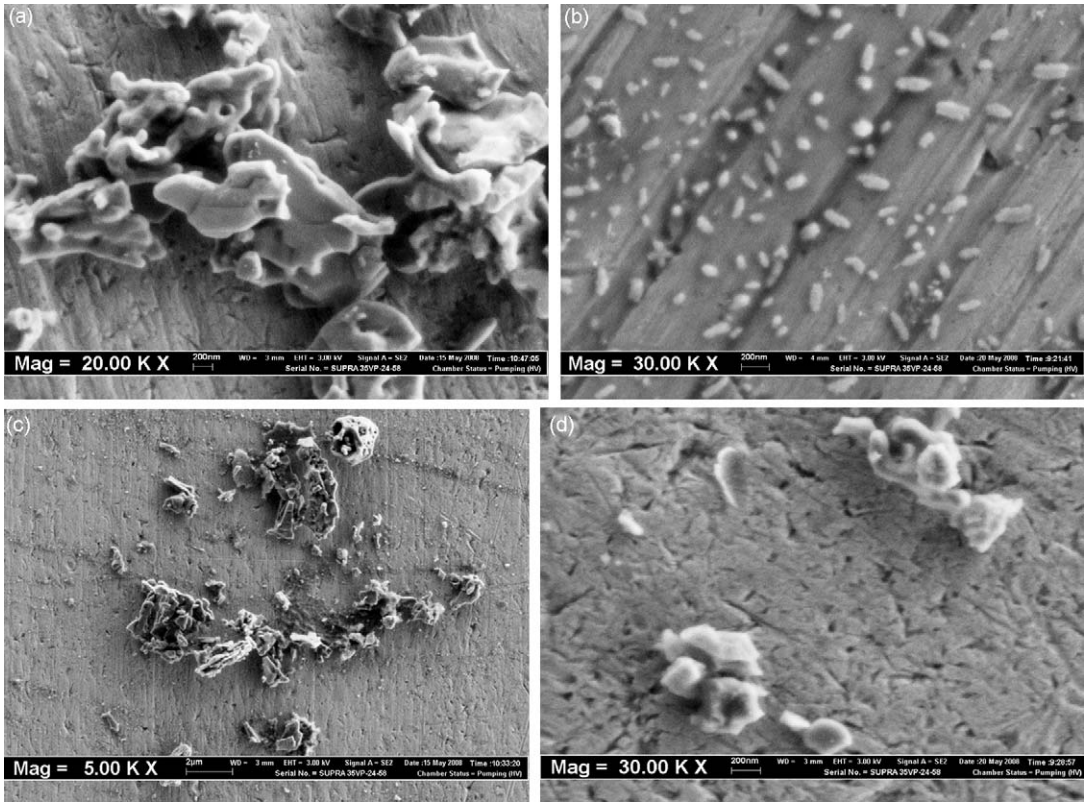

Fig. 3. SEM images of the alumina powder; (a and b) SEM micrograph of α-Al_2O_3 in the present of 0.1 SBDS at 24 and 48 h stirring time and (c and d) SEM micrograph of α-Al_2O_3 in the present of 0.1 Na(AOT) at 24 and 48 h stirring time.

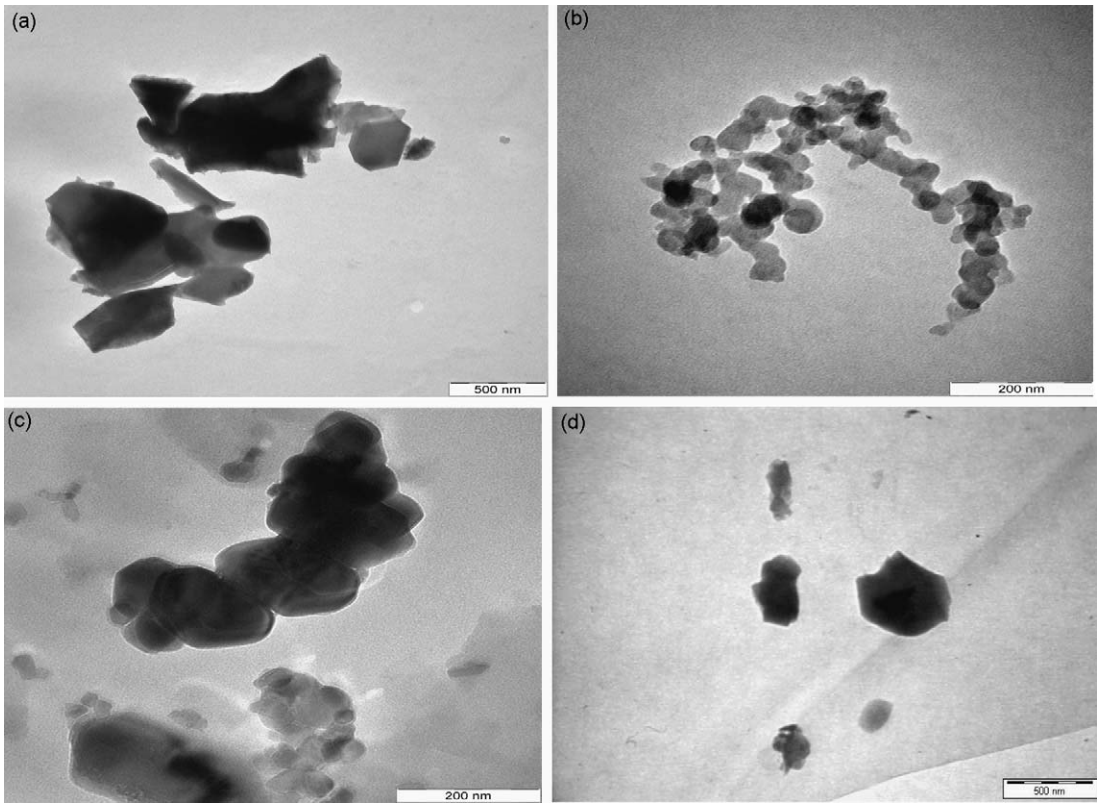

Fig. 4. TEM micrographs of the various microstructures of α-Al_2O_3 under different conditions: (a and b) TEM micrograph of α-Al_2O_3 in the presence of 0.1 SBDS at 24 and 48 h stirring and (c and d) TEM micrograph of α-Al_2O_3 in the presence of 0.1 Na(AOT) at 24 and 48 h stirring.

Consequently, despite the high temperature (1200 °C), the obtained particle size ranged between 20 and 30 nm in the presence of SDBS surfactant after 48 h stirring time. This is consistent with the XRD results for these samples which seem to indicate that the SDBS performed better than Na(AOT).

According to Zinchenko and Davis [12] agglomeration of solid products from two liquid ionic solutions A and B is as follows:

$$An^+ + B\,n^- \longrightarrow C\downarrow$$

This reaction involves instantaneous (mixing controlled) chemical reaction, subsequent crystallization of the product (i.e. nucleation and growth of crystals) and its agglomeration. At low supersaturation there are usually negligible effects of agglomeration, and the crystals size distribution is mainly affected by competition between nucleation and growth of crystal. At high supersaturation the process is dominated by agglomeration. As it proceeds, more water evaporated from sol, the supersaturated solution thus supplies material necessary to bond colliding particles and form agglomerates. Local concentrations also determine electrical interaction between small colloidal particles, because most particles in aqueous media are charged, and resulting repulsion force depends on solution composition [12,13]. Hence, it will further enhance the agglomeration process for these reasons after 60 h of stirring time we can see the strongly agglomeration in samples was observed.

4. Conclusions

The sol–gel method was used for the synthesis of nano α-Al_2O_3 from aluminum alkoxide complexes which were coupled with the presence of surface active agents, like Na(AOT) and SDBS. Selection and control of the precise stirring time together with surface active agents proved to be important in controlling the particles size, degree of aggregation and the particles shape. Nano α-Al_2O_3 was checked at 1200 °C, when the transformation was just completed. In comparison to Na(AOT), SDBS indicated a better dispersion and finer particles. Similarly, the shape of the nano α-alumina nanoparticles with SDBS was basically spherical. The micro structural observation showed that nanoscale α-Al_2O_3 powder with SDBS surfactant with 48 h stirring time was produced in the range of 20–30 nm.

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