Research Article

Process for Producing Nano-Alpha-Alumina Powder

**Fatemeh Mirjalili,¹ Luqman Chuah Abdullah,^{2,3} Hasmaliza Mohamad,⁴
A. Fakhru'l-Razi,² A. B. Dayang Radiah,² and R. Aghababazadeh⁵**

¹ Maybod Branch, Islamic Azad University, Maybod, Iran

² Department of Chemical & Environmental Engineering, Faculty of Engineering, University Putra Malaysia, 43400 Serdang, Selangor, Malaysia

³ Institute of Tropical Forestry and Forest Products (INTROP), University Putra Malaysia, 43400 Serdang, Selangor, Iran

⁴ School of Material & Mineral Resources Engineering, University Sains Malaysia, Seri Ampangan 14300, Nibong Tebal, Pulau Pinang, Malaysia

⁵ Institute for Colorants, Paint and Coatings, Tehran 16688-14811, Iran

Correspondence should be addressed to Fatemeh Mirjalili, fm.mirjalili@gmail.com

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This paper is trying to explore the effect of stirring time on the synthesis of nano- α -Alumina particles. In this study, alumina nanoparticles were synthesized through alkoxide route using sol-gel method, where aqueous solutions of aluminum isopropoxide and 0.5 M aluminum nitrate nanohydrate were used for preparing alumina sol. Sodium dodecylbenzen sulfonate (SDBS) was used as the surfactant stabilizing agent. The prepared solution was stirred at different times (24, 36, 48, and 60 hours) at 60°C. The Samples were, then, characterized by X-ray diffraction, thermogravimetry analysis (TGA), differential scanning calorimetry (DSC), scanning electron microscopy (SEM) and Transmission Electron Microscopy (TEM). The introduction of different stirring times affected the particle size and shape and the degree of aggregation. By increasing the stirring time, (starting from 24 to 48 hours) the particle size decreased, but agglomeration became hard for 60 hours of stirring time. The finest particle size (20–30 nm) was obtained at 48-hour stirring time.

1. Introduction

Alumina is one of the most widely used ceramic materials as catalysts, catalyst supports and absorbents, and also wear resistant coating [1]. It can be prepared through methods such as sol-gel [2, 3], hydrothermal [4], coprecipitation, mechanical milling, vapor-phase reaction and combustion methods [5, 6]. However, nanoscale alpha-alumina (α -Al₂O₃) powder is difficult to obtain. It is due to two reasons first, α -Al₂O₃ is in a stable phase after calcining at high temperature, which easily prompts the grain growth of powder and makes it difficult to get nanoscale particles; secondly, α -Al₂O₃ particles tend to aggregate during dehydration process in wet chemistry method. Therefore, it is necessary to develop a new method to overcome this problem [7, 8]. Sol-gel synthesis offers relatively inexpensive scale processing of mixed oxide materials with a good control over the stoichiometry and morphology which helps to

tailor the required materials on atomic scale to suit specific applications [5].

This study tends to synthesize nanosized α -Al₂O₃ by controlling the particle size, distribution, and shape.

2. Material and Method

Aluminum isopropoxide Al (OC₃H₇)₃ (Merck, German), aluminum nitrate nonahydrate Al (NO₃)₃·9H₂O (Merck, German), and Sodium dodecylbenzen sulfonate (SDBS) (Merck, German) were used as raw materials to prepare nano- α -Al₂O₃. The starting solution was prepared through using aluminum isopropoxide and 0.5 M aluminum nitrate aqueous solution as a solvent with the water purity of 99% and aluminum isopropoxide in the powder form gradually added to it.

The molar ratio of alumina sol (ALP/ALN) was 3 so that the raw materials can be completely dissolved and provide

FIGURE 1: Nano- α -alumina synthesis process.

clear solutions. The solutions were continuously stirred for 24, 36, 48, and 60 hours. Later, Sodium dodecylbenzen sulfonate (SDBS) was added by adjusting the molar ratio between alkoxide and surfactants to 0.1 and stirred for one hour. It is expected that the optimal time for the addition of surfactant is 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 hours. Dried gels were calcined at temperature between 1000 and 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 K α radiation in the range of $2\theta = 10^\circ$ – 80° with a scanning speed of 5° per minute. The ultrasonic bath was applied to suspend calcined powder in ethanol, and subsequently, few droplets of it were 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 Figure 1.

3. Results and Discussion

The synthesis of nano- α -Al₂O₃ was achieved through increasing the stirring time so that the excessive grain growth and aggregation of nanoparticles could be prevented. The

FIGURE 2: XRD spectra of Al₂O₃ at 1200°C.

FIGURE 3: TGA curve of the as-synthesized precursor.

FIGURE 4: DSC curve of the as-synthesized precursor.

XRD analysis (Figure 2) showed the most stable phase, α -Al₂O₃ occurred dominantly at 1200°C.

The observation reported by Hyuk-Joon et al. [9] indicated that completion of the most stable phase of α -alumina occurs at this temperature. During thermal treatment, stable α -Al₂O₃ phase can be obtained through the following series of phase transformation before conversion to α -Al₂O₃:

(see [12]).

Figure 3 illustrates the TGA curve, at heating rate of 10°C/min in air. There is a sharp decrease observed in

FIGURE 5: SEM micrographs of α - Al_2O_3 at different stirring time.

specimen weight ($\sim 6\%$) at temperature of $<400^\circ\text{C}$; seemingly, this decrease is due to the elimination of the residual water content which is absorbed on the surface of nanocrystalline bohemite particles [10].

From 400 – 750° , weight loss of the mat is less than 1% , and also there is less decrease in temperature. So, the volatilization does not happen obviously [11]. From 750 to 1200°C , weight loss is observed again, and the temperature oscillates obviously, and it shows an exothermic reaction.

The DSC curve of the precursor is illustrated in Figure 4. In the temperature region of 25 – 270°C , a broadened endothermic peak as well as a slight endothermic peak around 279.83°C emerges which is associated with the vaporization of physically bound absorbed water [2] and [12].

Three small exothermal peaks at 420 , 456 , and 479°C are attributed to the pseudomorphic phase transformation of bohemite to γ - Al_2O_3 . [2, 12, 13]. The endothermic peaks at 882 and 953°C are attributed to the phase transformation of γ - Al_2O_3 to δ - Al_2O_3 and θ - Al_2O_3 . Also, α - Al_2O_3 phase formation occurred at around 1035 and 1130 with two exothermic peaks [13]. This is in consistence with the XRD results which indicate that α - Al_2O_3 phase occurred at 1100 – 1200°C .

Figure 5 shows SEM micrographs that by increasing the stirring time, the particle become finer and less agglomerated until 48 hour stirring. The particle started to agglomerate and to be more dense in structure at 60 h.

Novakovic and Korthaus [7] and Hasmaliza et al. [5] 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 Figures (6(a), 6(b), 6(c), and 6(d)) of the α - Al_2O_3 particles show that the Particles, after 24, 36, and 60 hours of stirring, predominantly were in irregular angular shapes. As for the sample with stirring time of 48 hours, the particle shapes were mainly spherical Figure 6(c). The size of particles, after 24 hours of stirring, is in the range of 270 – 320 nm and had a lot of agglomeration, and the size of particles, after 36 hours of stirring, fell in the range of 250 – 300 nm, and had a lot of agglomeration, but after 48 hours, the particle sizes were in the range of 20 – 30 nm and had a good quality of dispersion. After 60 hours

FIGURE 6: TEM micrographs of α - Al_2O_3 at different stirring time.

of stirring, the sizes of particles were in the range of 150–200 nm and a lot of agglomeration and only little dispersion were observed.

Takhashi et al. [8] found that during stirring of the solution, the viscosity increased; therefore, the particle size improved but, due to the spinner revolution, the particle size decreased. As it proceeded, after 48 hours, more water evaporated from the sol, the supersaturated solution, thus, supplied the material necessary to bond colliding particles and form agglomerates. According to Lin et al. [14], agglomeration of solid products from two liquid ionic solutions A and B is as follows:

This reaction involves the 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 the competition between the nucleation and the growth of the crystal. However, at high supersaturation, the process is dominated by agglomeration.

As it proceeds, more water evaporates from sol, the supersaturated solution, thus, supplies the material necessary to bond colliding particles and form the agglomerates. Local concentrations, also, determine the electrical interaction

between the small colloidal particles because most particles in aqueous media are charged and the resulting repulsion force depends on the solution composition.

Hence, due to these reasons, the agglomeration process enhances after 60 hours of stirring time, and there was strong agglomeration observed in the samples. This is in agreement with the observation of this study as shown in Figure 6(d).

Consequently, despite the high temperature (1200°C), the obtained particle size ranged between 20 and 30 nm after 48 hours of stirring time. Furthermore, Wright and Sommerdijk [15] explained that the colloidal particles tend to obtain surface charge by ionization or adsorption of ions or polar molecules from the solution in stable sols. The charged surface layer, in turn, attracts a second more diffuse layer of ions of opposite charge in the neighboring solution. The van der Waals attractive forces which potentially lead to aggregation fall as r^{-6} . On the other hand, the electrostatic repulsions vary as r^{-1} , between the link-charged ions of the diffuse layers around the nearest charged colloid particles.

Therefore, the repulsions dominate the van der Waals attractions, and the particles are stable in opposition to the aggregation unless the thickness of the diffuse layer can be significantly decreased.

The main way in which the diffuse layer thickness can be decreased is raising the ionic strength of the solution, and in particular, increasing the charge on the counterion. Hence, the stirring time was effective in controlling the size of the particles and their degree of aggregation.

4. Conclusions

In this research, the sol-gel method for the synthesis of aluminum oxide from aluminum alkoxide complexes was explained. However, selecting and controlling the exact stirring time for controlling the size of particles and the degree of aggregation are important. The evolution in the alumina precursor involved the decomposition which was followed by amorphous-to- γ - Al_2O_3 and γ -to- α - Al_2O_3 phase transformation. Nano- α - Al_2O_3 was observed at 1200°C, when the transformation had just completed. The microstructural observation showed nanoscale α - Al_2O_3 powder with 48 hours of stirring time were obtained in the range of 20–30 nm. Moreover, the particle size after 48 hours, in comparison with 24, 36, and 60 hours, generated a better dispersion as well as finer particles.

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