

Effect of stirring time on synthesis of ultra fine α - Al_2O_3 powder by a simple sol-gel method

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The present paper tends to explore the effect of stirring time on the synthesis of nano α - Al_2O_3 particles. In this study, alumina nanoparticles were synthesized through an alkoxide route implementing sol-gel method in which aqueous solutions of aluminum isopropoxide and 0.5 M aluminum nitrate nanohydrate were used to prepare an alumina sol. Sodium dodecylbenzen sulfonate was used as the surfactant stabilizing agent. The prepared solution was stirred for different times (24, 36, 48 and 60 hours) at 60 °C. The samples were, then, characterized by Brunauer-Emmet-Teller method, X-ray diffraction, thermogravimetry analysis, differential scanning calorimetry, Fourier transform infrared spectrometry, scanning electron microscopy and transmission electron microscopy. 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 there was a harder agglomeration for the samples with 60 hours stirring time. The finest particle size (20-30 nm) was obtained at 48 hours stirring time.

Key words: α - Al_2O_3 , X-ray methods, Electron Microscopy.

Introduction

Alumina is one of the most widely used ceramic materials as a catalyst, catalyst support and absorbent and also as a wear resistant coating [1]. It can be prepared through methods such as sol-gel [2, 3], hydrothermal [4], co-precipitation [5], mechanical milling, vapor phase reaction and combustion [3, 5, 6].

However, nanoscale alpha- alumina (α - Al_2O_3) powder is difficult to obtain. This is due to two reasons: first, α - Al_2O_3 is a stable phase after calcining at high temperature which easily promotes the grain growth of powder, and makes it difficult to obtain nanoscale particles; secondly, α - Al_2O_3 particles tend to aggregate during the dehydration process in a wet chemistry method. Therefore, it is necessary to develop a new method to overcome this drawback [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 an atomic scale to suit specific applications [5, 9].

This study intends to synthesize nanosized α - Al_2O_3 by controlling the particle size, distribution and shape.

Material and Method

Aluminum isopropoxide $\text{Al}(\text{OC}_3\text{H}_7)_3$ (Merck, German), aluminum nitrate nonahydrate $\text{Al}(\text{NO}_3)_3 \cdot 9\text{H}_2\text{O}$ (Merck, German), and sodium dodecylbenzen sulfonate (SDBS) (Merck, German) were used as raw materials to prepare nano α - Al_2O_3 . The starting solution was prepared using aluminum isopropoxide and 0.5 M aluminum nitrate aqueous solution as a solvent with distilled water and aluminum isopropoxide power gradually added to it. The molar ratio of alumina sol (aluminum isopropoxide/ aluminum nitrate nonahydrate) was 3 so that the raw materials could be completely dissolved and provide clear solutions. The solutions were continuously stirred for 24, 36, 48 and 60 hours. Later, sodium dodecylbenzen sulfonate was added to adjust the molar ratio between alkoxide and surfactant to 0.1. The solution, was, then stirred for one hour after which it was considered to be the optimal time for the addition of the surfactant which occurred prior to the onset of the nucleation and growth step. The solutions were heated to 60 °C and stirred constantly for an evaporation process. The viscosity and color changed as the sol turned into a transparent thick gel. The gels were, then, heat treated at 90 °C for 8 hours. Dried gels were calcined at 1000-1200 °C. Finally, the calcined powders were crushed using a mortar and pestle.

The specific surface area of the samples was determined

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using N_2 adsorption/desorption method at 77 K by standard Brunauer-Emmet-Teller (BET) method. Phase identifications were performed by X-ray diffraction (XRD) using nickel filtered $\text{Cu K}\alpha$ radiation in the range of $2\theta = 10^\circ - 80^\circ$ with a scanning speed of 5° per minute. A Fourier transform infrared spectrometer (FTIR) by Perkin Elmer Spectrum 100 series was used with the universal attenuated total reflection (UATR) method. Thermogravimetry analysis (TGA) was performed using a Perkin Elmer TGA 7 and differential scanning calorimetry (DSC) analysis was performed using a Mettler Toledo DSC 823. An ultrasonic bath was applied to suspend the calcined powder in ethanol, and subsequently, a few droplets of it were used for microstructural evaluation by a Philips CM12 transmission electron microscope (TEM) and Cambridge Stereoscan 200 and Leica Cambridge S-360 scanning electron microscopes (SEM). The process steps are illustrated in Fig. 1.

Results and Discussion

The synthesis of nano α - Al_2O_3 was achieved through increasing the stirring time so that the excessive grain growth and aggregation of nanoparticles could be prevented.

The surface area and particle size of the samples are shown in Table 1. By increasing the stirring time (starting from 24 to 48 hours), the particle size decreased, but there was a harder agglomeration for the samples with 60 hours stirring time. The finest particle size (20-30 nm) was obtained at 48 hours stirring time.

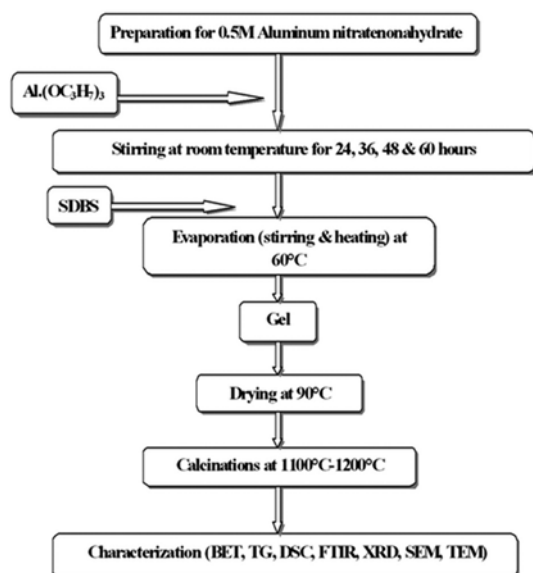


Fig. 1. Nano α -alumina synthesis process.

Table 1. BET surface area and particle size for nano α - Al_2O_3 particles at different stirring times

	24 h	36 h	48 h	60 h
Particle size/nm	250-320	270-300	20-30	150-200
Surface area/ m^2g^{-1}	149	155	412	276

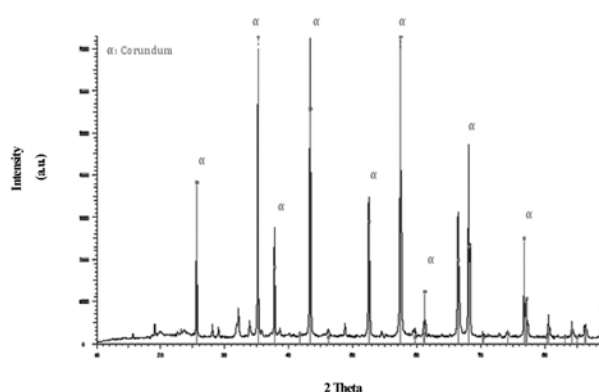


Fig. 2. XRD pattern of Al_2O_3 at 1200°C .

The XRD analysis (Fig. 2) showed the most stable phase, α - Al_2O_3 occurred dominantly at 1200°C . The observation reported by Hyuk-Joon *et al.*, [6] indicated that complete formation of the most stable phase of α alumina took place at this temperature. During the thermal treatment, the stable α - Al_2O_3 phase can be obtained through the following series of phase transformations before conversion to α - Al_2O_3 :

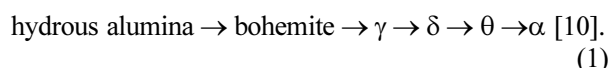


Fig. 3 illustrates the TGA curve, at a heating rate of $10^\circ\text{Kminute}^{-1}$ in air. There is a sharp decrease observed in the specimen weight ($\sim 6\%$) at temperature of $< 400^\circ\text{C}$; seemingly, this decrease is due to the elimination of the residual water content which is absorbed on the surface of nanocrystalline bohemite particles [11]. From 400 – 750°C , the weight loss of the material is less than 1% and also there is less decrease in temperature. So, the volatilization does not happen obviously [12]. The endothermic peak at 750°C was associated with dehydration [13]. From 750 – 1200°C , a 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 Fig. 4. In the temperature region of 25 – 270°C , a broadened endothermic peak as well as a slight endothermic peak around 279.83°C emerge which are associated with the

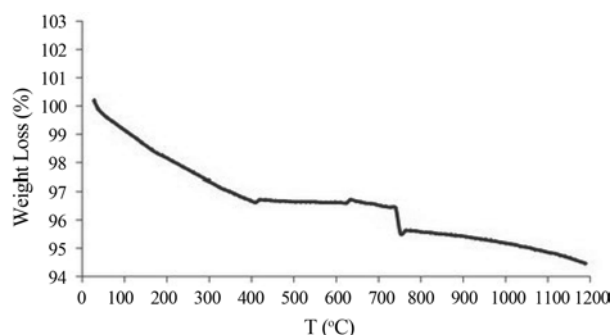


Fig. 3. TGA curve of the as-synthesized precursor.

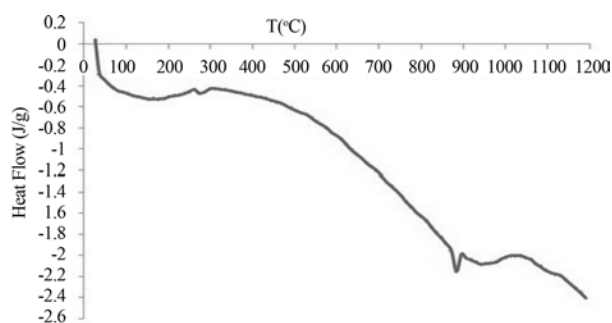


Fig. 4. DSC curve of the as-synthesized precursor.

vaporization of physically bound absorbed water [3, 10].

Three small exothermal peaks at 420 °C, 456 °C and 479 °C are attributed to the pseudomorphic phase transformation of bohemite to γ - Al_2O_3 [3, 10, 14]. The endothermic peaks at 882 °C 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 °C and 1130 °C with two exothermic peaks [14]. This is in agreement with the XRD results which indicate that the α - Al_2O_3 phase formed at 1100-1200 °C.

FTIR analysis was carried out for the aluminum oxide precursor in the wave number region of 4000-280 cm^{-1} . The related spectrum is presented in Fig. 5. Absorptions were recorded at about 3500 and $\sim 650 \text{ cm}^{-1}$, and this is because of the stretching vibration as well as the deformation vibration characteristics of hydroxylate (O-H) [15]. The absorption peaks presented in Fig. 5 at 1556.73 cm^{-1} prove that there are some changes in the surface chemistry of Al_2O_3 particles when SDBS is added.

The bands at 1121-1328 cm^{-1} are due to the typical signals of C-N and the band at 1556 cm^{-1} is the characteristic absorption peak of SDBS [13]. There are wide and high peaks of Al-O stretching (AlO_4 or AlO_6 vibration) in the range of 500-1000 cm^{-1} . These peaks are attributed to transitional phases of alumina and the stable phase of alumina (Alpha) [3]. For the sample calcined at 1200 °C, significant spectroscopic bands at 568.15, 499.19 and 431.99 cm^{-1} emerge which are recognized to be the characteristic absorption bands of α - Al_2O_3 . This is in complete agreement with XRD observations.

Fig. 6 shows SEM micrographs in which increasing the stirring time made the particles become finer and less

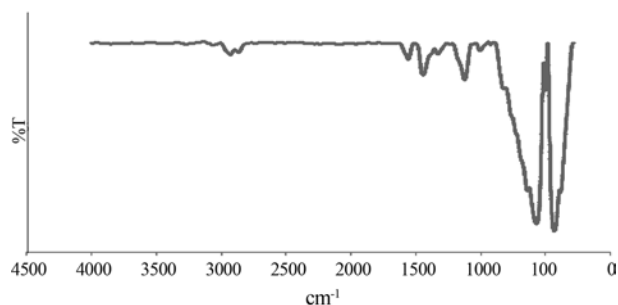


Fig. 5. FTIR spectra of Al_2O_3 precursor calcined at 1200 °C.

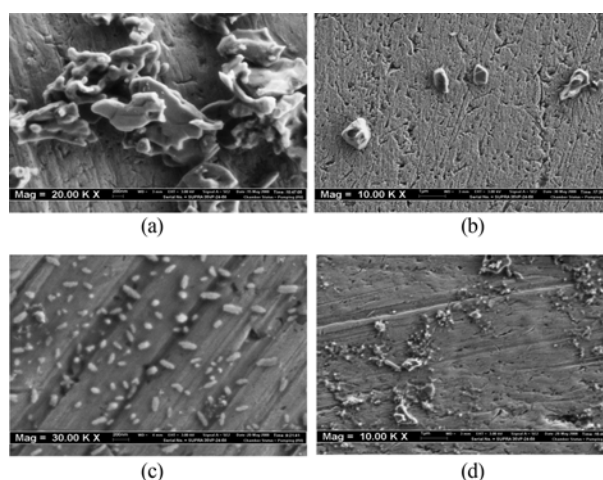


Fig. 6. SEM micrograph of α - Al_2O_3 at different stirring times (a) 24 h (b) 36 h (c) 48 h (d) 60 h.

agglomerated up to 48 hours stirring. The particles started to agglomerate and become more dense in structure at 60 hours.

Novakovic and Korthaus [8] and Hasmaliza and Rahayu [5] have reported that drying of the sol invariably leads to agglomeration because the residual salts present in the sol form solid bridges between particles as the water evaporates. Besides that, the particle size and shape of the α -alumina are determined by the crystal structure of the original hydroxide and the series of phase transformations which occur during calcination.

The TEM micrographs in Fig. 7(a, b, c, 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 a stirring time of 48 hours, the particle shapes were mainly spherical (Fig. 7(c)). The size of particles, after 24 hours of stirring, was in the range of 250-320 nm and with much agglomeration while the size of particles, after 36 hours of stirring, fell in the range of 270-300 nm again with much agglomeration. However,

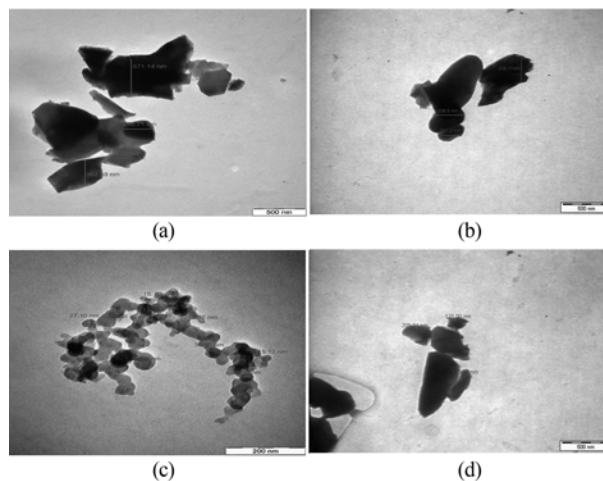


Fig. 7. TEM micrographs of α - Al_2O_3 at different stirring times (a) 24 h (b) 36 h (c) 48 h (d) 60 h

after 48 hours, the particle sizes were in the range of 20-30 nm and had a good quality of dispersion. After 60 hours of stirring, the sizes of particles were observed to be in the range of 150-200 nm with much agglomeration and there was only a little dispersion observed.

Takahashi and Yamaguchi [9] found that during stirring of a 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, thus the supersaturated solution supplied the material necessary to bond colliding particles and form agglomerates.

According to Lin et al., [16], 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 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 growth of the crystals. However, at a high supersaturation, the process is dominated by agglomeration. As it proceeds, more water evaporates from the sol, the supersaturated solution, thus, supplies the material necessary to bond colliding particles and form the agglomerates. Also, local concentrations determine the electrical interaction between the small colloidal particles, because most particles in an aqueous media are charged, and the resulting repulsive force depends on the solution composition. Hence, the agglomeration process enhances after 60 hours of stirring time and there is strong agglomeration observed in the samples. The results are shown in Fig. 7(d). Consequently, despite the high temperature (1200 °C), the particle size obtained ranged between 20-30 nm after 48 hours of stirring time.

Furthermore, Wright and Sommerdijk [17] explained that the colloidal particles tend to obtain a 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 off as r^{-6} . On the other hand, the electrostatic repulsions vary as r^{-1} , between the like-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 counter-ions. Hence, the stirring time is proved to be effective in controlling the size of the particles and their degree of aggregation.

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 transformations. Nano α - Al_2O_3 was observed at 1200 °C, when the transformation had just completed. The microstructural observations showed nanoscale γ - Al_2O_3 powder with 48 hours of stirring time was obtained in the size 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.

Acknowledgment

The authors would like to thank Ministry Science, Technology and Innovation, Malaysia, University Putra Malaysia and University Sains Malaysia in providing fund and support toward this work.

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