PREPARATION OF NANO-SCALE α-Al₂O₃ POWDER BY THE SOL-GEL METHOD

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Sol-gel method was applied to synthesize ultrafine nano α-alumina particles using aqueous solutions of aluminum isopropoxide and 0.5 M aluminum nitrate hydrate. Sodium dodecylbenzen suffocate and Sodium bis-2ethylhexyl sulfosuccinate were also used as surfactant stabilizing agents. The prepared solution was stirred for 48 hours at 60°C, then, the resultant gelled mass was dried at 90°C, and finally, calcined at 1200°C for about 1 hour. The samples were characterized by different techniques such as, Brunauer-Emmet-Teller method, X-ray diffraction, Thermogravimetry analysis, Differential Scanning Calorimetry, Fourier transform infrared spectra, Scanning electron microscopy and Transmission electron microscopy. The results indicated that the addition of sodium dodecylbenzen sufonates and sodium bis-2ethylhexyl sulfosuccinate not only affected the particle size and shape of the produced nanoparticles but also the degree of aggregation. However, sodium dodecylbenzen sufonate produced better dispersion and finer particles, in range of 20-30 nm, compared to Sodium bis-2ethylhexyl sulfosuccinate.

INTRODUCTION

Alumina is one of the most widely used ceramic materials as catalysts, catalyst supports and absorbents and also wear resistant coating [1]. Among different forms of this worthwhile material, ultrafine α-Al₂O₃ powder has significant potential for a broad range of requests as high strength materials, electronic ceramics and catalysts. The wide utilization of ultrafine α-Al₂O₃ makes it a general material and increases the attentions for synthesis of ultrafine α-Al₂O₃ [2, 3]. Nano α-Al₂O₃ powder can be prepared through different methods such as sol-gel [3], hydrothermal [4], co-precipitation [4], mechanical milling, vapor phase reaction and combustion methods [3,5,6]. It is difficult to obtain nano α-Al₂O₃ powder, because the calcination temperature of >1000°C is often needed to produce the required α-Al₂O₃ phase. Nevertheless, such a high calcination temperature, unavoidably, leads to a considerable degree of particle coarsening and agglomeration [7, 8, 9]. Several attempts have been conducted to control the characteristics of the resulting alumina powders, including the introduction of surface controlling agents such as Sodium bis-2ethylhexyl sulfosuccinate (Na(AOT) and

Sodium dodecylbenzen sulfonate (SDBS).Surfactants have been found to promote, to slow down, or to prevent crystal growth in solutions. Surfactants are frequently used as growth delays for the period of crystal growth [9, 10]. Such agents like (Na (AOT) and (SDBS) interfere with the nucleating and growing particles to avoid agglomeration and control the particle size. The stabilization with surfactants, in general, occurs by the absorption of electric charges on the surface, causing a repulsion of the nanoparticles as long as a critical distance between the nanoparticles is increased [9]. Zhu et al. [10] also demonstrated that SDBS and Na(AOT) can be partially ionized in water and give anionic species, while the boehmite holds positive charges in a neural aqueous medium, showing a strong affinity for anionic groups. The negatively charged ions dissociated from the surfactants are adsorbed on the surface of the positively charged boehmite surface and hence the boehmite surface is negatively charged owing to the ionization of SDBS and Na (AOT). Accordingly, the effect of electrostatic stabilization is achieved. It was demonstrated that when more SDBS and Na (AOT) are added into the suspension, the concentration of Na⁺ group entering into the absorbed layer reduces the

net charge of the powder surface which causes a weak dispersion system [9,11]. The sol-gel method, based on molecular precursors, usually utilizes metal alkoxides as raw materials with a good control over the stoichiometry and morphology which help to tailor the required materials on atomic scale to suit specific applications [3, 4, 11]. This study tends to synthesize nanosized α-Al₂O₃ by controlling the particle size distribution and shape.
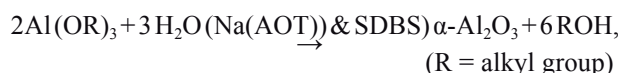
EXPERIMENTAL

Aluminum isopropoxide (ALP) (Merck, German), aluminum nitrate nonahydrate (ALN) (Merck, German), Sodium bis-2ethylhexyl sulfosuccinate (Na(AOT)) (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 0.5 M aluminum nitrate aqueous solution as a solvent with the water purity of 99 % and aluminum isopropoxide in the power 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 clear solutions. The solutions were, continuously, stirred for 48 hours. Later, the Sodium bis-2ethylhexyl sulfosuccinate (Na (AOT)) and Sodium dodecylbenzen sulfonate (SDBS) were added by adjusting the molar ratio between alkoxide and surfactants from 0.1 so that optimum dispersion and size can be obtained. The ionization of surfactants results in negative charges dissociated from surfactants and adsorbed on the positively charged bohmite surface which in turn increases the repulsive forces. The solution, then, was stirred for one hour. This time is expected to be the optimal time for the addition of surfactant and occurs prior to the one set of the nucleation and growth step. The initial precipitation reaction is formed in the room temperature. 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 then calcined at the temperature range 1000-1200°C and finally, the calcined powders were crushed by mortar and pestle. The specific surface area of the samples was determined using N₂ adsorption/ desorption method at 77 K by standard Brunauer-Emmet-Teller method. Phase identifications were performed by X-Ray Diffraction using nickel fil-tered Cu Ka radiation in the range of 2θ = 10°-80° with a scanning speed of 5° per minute. Fourier transform infrared spectrometer by Perkin Elmer Spectrum 100 series was used by universal ATR sampling accessory.

The morphology of the gained α-Al₂O₃ powder was observed by Phillips CM12 transmission electron microscopy and Cambridge Stereoscan 200 and Leica Cambridge S-360 Scanning Electron Microscopy.

RESULTS AND DISCUSSION

The synthesis of nano a-Al₂O₃ was carried out with the concurrent addition of Sodium bis-2ethylhexyl sulfosuccinate (Na (AOT)) and Sodium dodecylbenzen sulfonate (SDBS). These chemicals prevent the excessive grain growth and aggregation of nanoparticles. The overall reaction scheme is shown below:

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

This reaction is a multi-step process involving the transformation of the aluminum alkoxide to aluminum hydroxide (Al(OH)₃), followed by dehydration of (Al(OH)₃) to ox-hydroxide aluminum intermediate, AlO(OH), constitution of AlO(OH) to the precursor in the sol-gel process [11, 12]. The surface area and particle size of the samples determined by Brunauer-Emmet-Teller (BET) analysis are presented in Table 1. The table shows that by increasing the amount of surfactant, the particle size decreased while the surface area increased. Besides that, SDBS produced finer particles with larger surface area compared to Na(AOT). The (XRD) patterns of the alumina precursors are demonstrated in Figure 1. The boehmite intermediate obtained in the absence of surfactant shows a crystalline phase in an amorphous background as illustrated in Figure 1a. However, the X-Ray Diffraction (XRD) spectrum of the boehmite formed without surfactant is the same as the XRD spectrum of the boehmite formed using Na (AOT) (Figure 1a, c).

Table 1. BET surface area and particle size for nano α-Al₂O₃ particles.

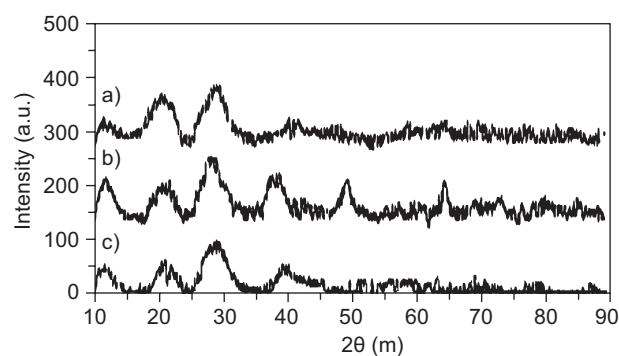|	Without surfactant	With Na(AOT)	With SDBS
Particle size (nm)	250-300	120-180	20-30
Surface area (m²/g)	153	276	412

Figure 1. XRD spectra of boehmite obtained under various conditions before being calcined: a) without surfactant; b) with SDBS; c) with Na(AOT).

As a consequence, addition of Na (AOT) did not play a significant role in the formation of an amorphous boehmite phase coupled with some hydrates of surfactant. In other word, the most difference observed was due to the presence of SDBS surfactant, as Figure 1b shows. This observation is in agreement with Yoldas [12] and Bokhimi et al. [13] works who reported addition of SDBS resulted in the formation of an amorphous boehmite phase coupled with some hydrates of SDBS. It is believed the adsorption of surfactant layer on the surface of the initial boehmite nuclei, prevents the aggregation and grain growth of the boehmite.

Figure 2 indicates that the XRD analysis of the aluminum oxide after being calcined. It also exhibits that the most stable phase, α-Al_2O_3, was obtained at 1200°C. Hyuk-Joon et al. [14] reported that completion of the most stable phase of α alumina occurs at this temperature. During thermal treatment, stable α-Al_2O_3 phase can be obtained through the following series of phase transformation before conversion to α-Al_2O_3:

hydrous alumina → boehmite → γ → δ → Θ → a

When ionic surfactant is used, it can cause additional substances entering into the structure during the heat treatment [15]. Also with regard to the XRD patterns of
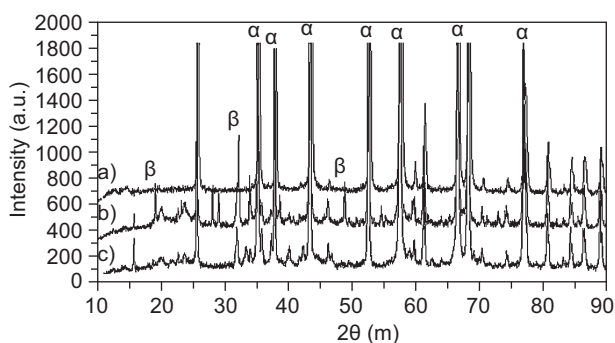
alumina precursors which were capped with surfactants (SDBS and Na (AOT), two phases namely a-Al_2O_3 phase and sodium aluminum oxide (Na Al $_{5.9}$O $_{9.4}$) phase were formed as shown in Figure 2b,c.

Figure 3 illustrates the Thermogravimetry analysis (TGA) curves for the aluminum oxide under various conditions using a heating rate of 10°C/min in air. A sharp decrease is observed in the weight of the specimen (~5% for the particle with SDBC, 2 % for the sample with Na(AOT) and 3-4 % for the sample without any surfactants) at temperature below 400°C. This decrease is due to the elimination of residual water content absorbed on the surface of nanocrystalline boehmite particles [7]. The weight loss of the mat is less than 1% in the temperature range of 400-750°C. Accordingly, it is fair to note that; volatilization does not take place [16]. The thermograph also reveals no weight loss for the particles capped with Na (AOT) and the ones without any surfactants in the range of 750-1200°C. However, for the particles capped with SDBS, a weight loss is observed during this temperature range and the temperature oscillates obviously that indicates an exothermic reaction. The TGA results show that the magnitude of weight loss also increases when SDBS is used as a surfactant because the surface area is increased. This observation is in consistence with the results presented by Yong and Wang [7]. They annotated the creation of a large amount of newly formed surfaces is a reason for observing a steady weight loss during high temperatures. When SDBS is used as a surfactant the surface area is increased and agglomeration of particles is decreased hence a steady weight loss is occurred at high temperatures.

The Differential Scanning Calorimetry (DSC) curves of the precursor are illustrated in Figure 5. In the temperature region of 25-270°C, a broadened endothermic peak as well as a slight endothermic peak around 209°C emerge for the particles without surfactant. Similarly, a broadened endothermic peak and a slight

Figure 2. XRD spectra of Al_2O_3 obtained under various conditions at 1200°C: a) without surfactant; b) with SDBS; c) with Na(AOT).
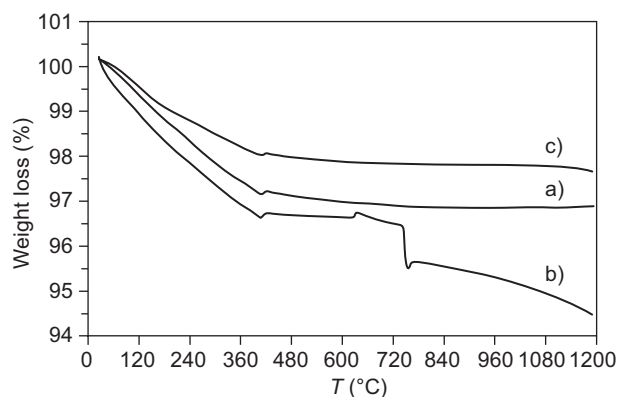

Figure 3. The TGA curves of the aluminum oxide under various conditions: a) without surfactant; b) with SDBS; c) with Na(AOT).
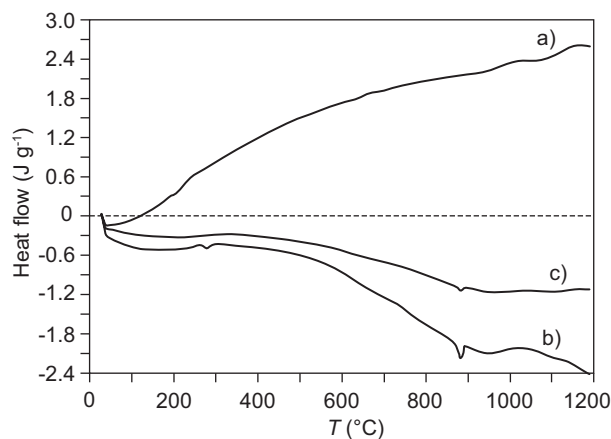

Figure 4. DSC curve of the aluminum oxide under various conditions: a) without surfactant; b) with SDBS; c) with Na(AOT).

endothermic peak appeared at 240°C and 279.83°C for the particles capped with Na(AOT) and SDBS, respectively. This observation can be attributed to the vaporization of physically bound absorbed water [3, 17]. In the absence of the surfactant, a small endothermic peak at 420°C presents the transformation of boehmite to γ-Al₂O₃. Further peaks a 775, 835, 929 and 1072°C are attributed to the phase transformation of γ-Al₂O₃ to δ-Al₂O₃ and Θ-Al₂O₃ and α-Al₂O₃, respectively[11]. When Na(AOT) and SDBS are present in the system, a weak transformation of the boehmite to γ-Al₂O₃is detected at a higher temperature , *i.e.*, around 432°C for the particles capped with Na(AOT) and 479°C for the particles capped with SDBS [3, 11, 17]. The endothermic peaks at 882 and 953°C are attributed to the phase transformation of γ-Al₂O₃ to δ-Al₂O₃ and Θ-Al₂O₃ for the particles capped with Na(AOT) and 882 and 964°C for the particles capped with SDBS. Besides that, α-Al₂O₃ phase formation is occurred at around 1035 and 1130-1153°C with two exothermic peaks for both samples [11]. An overview of the curves reveals that the particles capped with SDBS need higher temperature for starting the partial formation of the γ-Al₂O₃ phase. This is in consistent with the results obtained from XRD and TGA that, indicate the SDBS molecules stabilize the forming of AlO(OH) nuclei early, resulting the formation of an amorphous oxide structure. The formation of the surfactants capping layer onto the surface of the boehmite retards the aggregation of the oxide amorphous phase and increase the temperature that the partial formation of the γ-Al₂O₃ phase starts [18, 8].

indicate some changes in the surface chemistry of Al₂O₃ particles when surfactants was used. The bands at 1121-1122-1328 and 1394 cm⁻¹ are due to the typical signals of C–N and bands at 1556 and 1570 cm⁻¹ are
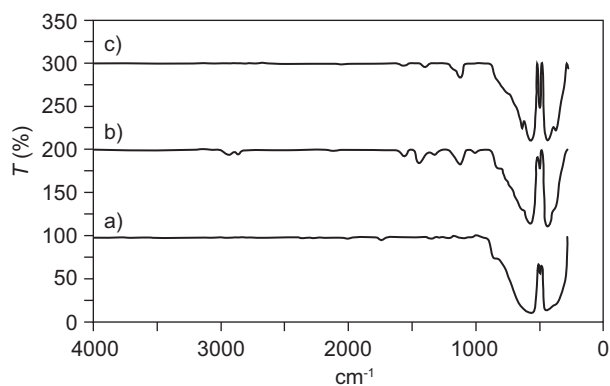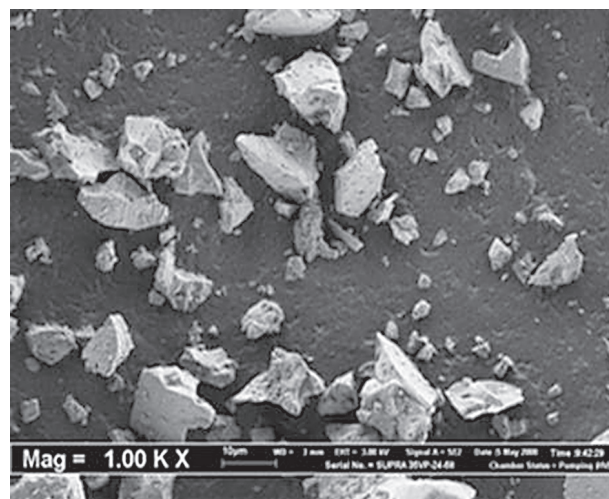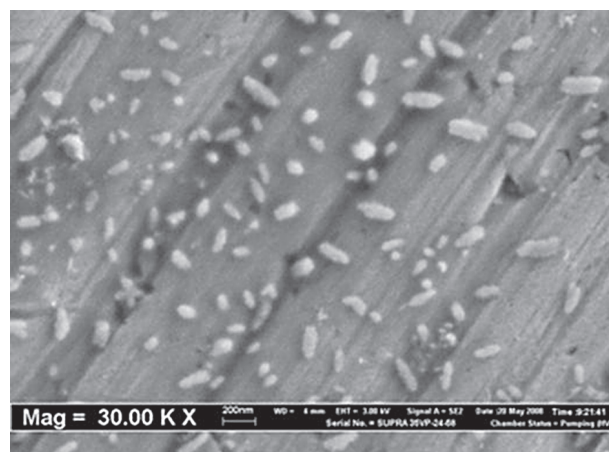

a) without surfactant

b) with SBDS

Figure 5. FTIR spectra of Al₂O₃ at different conditions: a) without surfactant; b) with SDBS; c) with Na(AOT).

Fourier transform infrared spectra (FTIR) analysis was also performed for characterization of the aluminum oxide in the absence and presence of surfactants in the wave number region of 4000-280 cm⁻¹. The FTIR analysis is demonstrated in Figure 5. The absorption recorded at about 3500 and ~ 650 cm⁻¹, that is due to stretching vibration and deformation vibration characteristics of the hydroxylate (O-H) [3]. The absorption peaks, at 1740.29, 1570 and 1457 cm⁻¹, presented in Figure 5,

c) with Na(AOT)
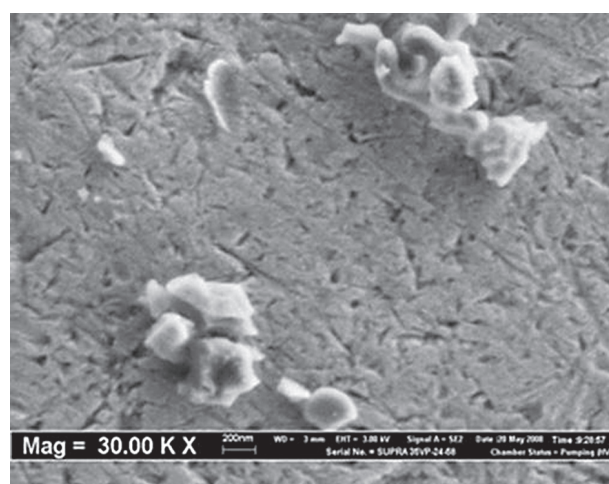
Figure 6. SEM micrographs of the various microstructures of α-Al₂O₃ under different conditions.

the characteristic of absorption peaks or SDBS and Na (AOT) [11, 18]. There are also some wide and high peaks of AL–O stretching (AlO_4 or AlO_6 vibration) in the range of 500-1000 cm^{-1} (636.16, 559.23, 568.15 cm^{-1}) that are relates to the transitional phases of alumina and stable phase of alumina (Alpha) [17].

a) without surfactant
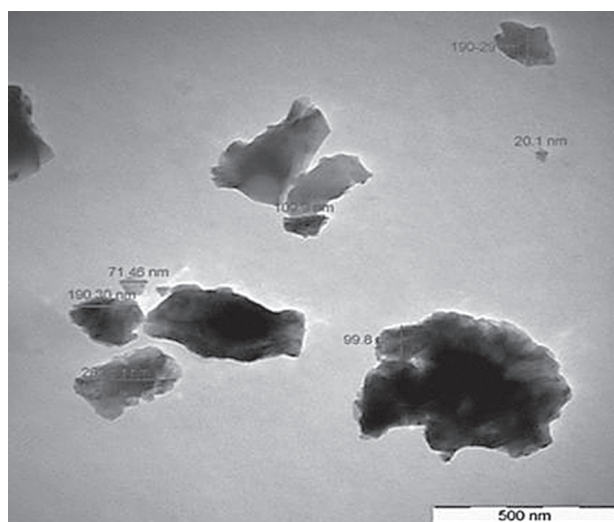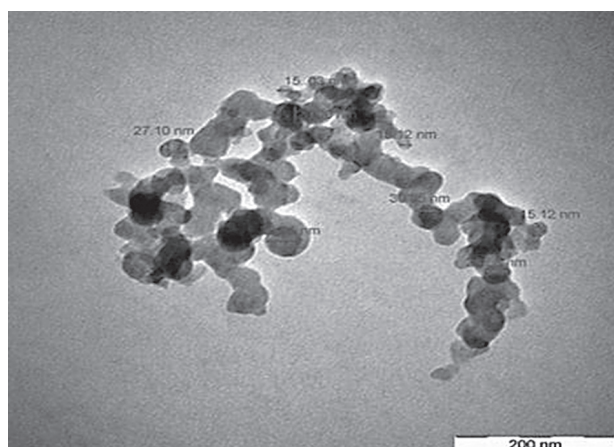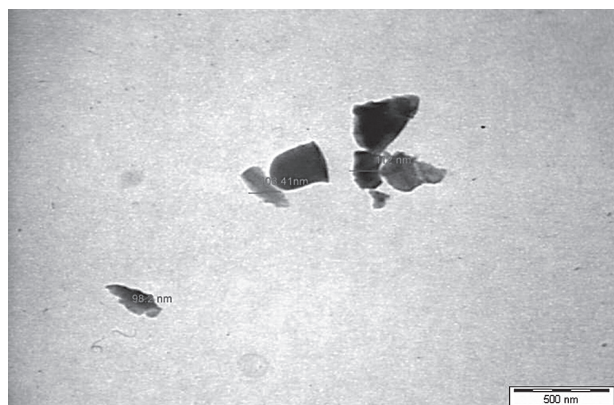

b) with SBDS

c) with Na(AOT)

Figure 7. TEM micrographs of the various microstructures of α-Al_2O_3 under different conditions.

FTIR results showed that both surfactants were absorbed by the nano-alumina powders. However, the FTIR spectra for particles capped with SDBS tend to possess a double-peak at 1570 and 1457 cm^{-1}, which are identified to be the more absorption bands of SDBS compared to Na (AOT). This observation is in good agreement with the XRD and BET results, which indicate that the SDBS played a significant role in the formation of finer particles and less agglomeration compared to Na (AOT). Figure 6, which is Scanning Electron Microscopy (SEM) micrographs of the particles, shows that a finer nanoparticle with less agglomeration is achieved by increasing the surfactant. Figure 6a shows that the particles had irregular angular shapes with a lot of agglomeration, and only a little dispersion was observed that is a major problem in producing nanopowders. As shown in Figures 6b,c by increasing the surfactants, the particles become finer and less agglomeration is formed. Particles capped with SDBS as surfactant possessed a good quality of dispersion and finer particle size than the particles capped with Na (AOT).

Lin et al. [19] had reported that drying of the sol invariably leads to the agglomeration, since the residual salts present in the sol forms 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 that occur during calcinations [16, 20]. Transmission Electron Microscopy (TEM) micrographs of the various samples are illustrated in Figure 7. The uncapped α-Al_2O_3 particles (Figure 7a) shows predominantly irregular angular shaped particles with an average size of about 250-300 nm. The particle sizes of α-Al_2O_3 capped with SDBS were in the range of 20-30 nm with a good quality of dispersion (Figure 7b). Moreover, the size of particles capped with Na (AOT)) were in the range of 120-180 nm with a lot of agglomeration (Figure 7c).

Ming et al. [2] reported that the maximum number of hydrogen bonds with the OH groups on boehmite surfaces can be achieved by the SDBS surfactant micelles, since the free energy of the boehmite crystallites with low dimensions is reduced. Park et al. [11] also annotated that at the temperature higher 600°C, the shape of the particles capped with the surfactant were mainly spherical. This result is in accordance with the observation made in this study as shown in Figure 7b. Suchanek and Garces [21] and Shojaie-Bahaabad and Taheri-Nasssaj [22], produced nanoscale α-Al_2O_3 powder through two methods, hydrothermal and sol-gel respectively. They had particle size distribution ranging from 30 to 100 nm with lots of agglomeration after heat treatment at 1200°C. Comparing with them, in the proposed method, nanoscale α-Al_2O_3 powder was synthesized by using SDBS surfactant at about 1100-1200°C and the nanoparticles were spherical in shape and a good quality of dispersion. Consequently, despite the high temperature

(1200°C) applied in this research, the size of the particles formed were in the range of 20-30 nm when SDBS surfactant and 48 hours stirring time were used. Therefore, the presence of surfactants controls the size of the particles, their degree of aggregation and their shape. However, among two different surfactant used, SDBS showed a better dispersion and finer particles compared to Na (AOT). This observation can be explained by the fact that, the ionization of SDBS is more than Na (AOT) that results in negative charges adsorbed on the positively charged initial boehmite. This phenomenon decreases the possibility of the particles aggregation and grain growth of boehmite and hence enhances the dispersion of the particles. As a consequence finer nanoparticles are formed.

CONCLUSIONS

Nano a-Al₂O₃ was obtained from aluminum alkoxide complexes through a sol gel method coupled with the presence of surface active agents, like Na(AOT) and SDBS. The surfactants facilitate the control of nanoparticles size, shape and their dispersion. Completion of the most stable phase of nano α alumina occurs at 1200°C, when the transformation was just completed. However, among two different surfactant used in this research, using SDBS indicated a better dispersion of particles and formation of finer particles. The shape of the nano α-Alumina nanoparticles with SDBS was predominately spherical. The micro structural observation of the particles indicated that nanoscale α-Al₂O₃ powder with SDBS surfactant was produced in the range of 20-30 nm.

Acknowledgment

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