Synthesis and Characterization of γ-Alumina Porous Nanoparticles from Sodium Aluminate Liquor with Two Different Surfactants

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Abstract

Among the various phases of alumina, two phases γ and α are the most widely used in various industries. In this paper, γ-Al_2O_3 porous nanoparticles have been successfully synthesized from a simple aqueous sol–gel method using inexpensive material such as: sodium aluminate liquor, HCl, NaOH, Polyethylene glycol (PEG) and polyvinyl alcohol (PVA). Sodium aluminate liquor was extracted from Bayer liquor of alumina product processed in the Jajarm alumina factory. PEG and PVA were used as structure-stabilizing agents. The structures and properties of samples calcined at 800 ºC, were performed utilizing X-ray diffraction (XRD), infrared spectroscopy (FTIR), scanning electron microscopy (SEM), termogeravimetery analysis (TG/DTA), and N_2 adsorption/desorption techniques. Prepared sample of γ-Al_2O_3 with polyethylene glycol surfactant has an average crystallite size of 2.313 nm, average particle size of 20 nm, specific surface area (SSA) of 138.8 m^2/g, and pore volume of $\sim$ 0.166 cm^3/g. The average crystallite size of 2.063 nm, average particle size of 46 nm, specific surface area of 201.1 m^2/g, and pore volume of $\sim$ 0.246 cm^3/g, were achieved using polyvinyl alcohol surfactant.
Keywords: *γ-alumina, Porous, Sodium aluminate liquor, Nanoparticles, Surfactant.*

1. INRODUCTION

Alumina is one of the most significant industrial material which is used as catalysts or a catalyst support, adsorbents, functional ceramics, reinforcements for composite materials abrasives, electronic, structural composites for spacecraft, thermal wear coatings, petroleum industries, wastewater treatment and surface coatings in various industrial fields [1-6]. The variety of applications is due to combination of several properties (amphoteric and textural) of alumina which contains good pore distribution, large pore volume and large specific surface area [4]. Alumina has eight different polymorphs, seven metastable phases (γ, δ, κ, ρ, η, θ and χ), and the thermally stable α phase. The nature of metastable (or transition) alumina powders are intrinsically nano-crystalline and can be simply synthesized through a variety of methods [7]. Among these metastable, γ-alumina is a very essential nanosized material used in the industry. Recent studies have revealed that γ-alumina is thermodynamically stable compared to α-alumina when a critical surface area is achieved, and that nano γ-alumina can promote the sintering behavior of alumina and silicon carbide fibers. The use of single phase of γ-alumina powders creates the densification temperature shift to lower temperature compared to samples

consisting of γ- and χ-alumina [8]. Up to now, the synthesis of γ-alumina nanopowders has been a longstanding goal and there are several methodologies existing for the synthesis of nano γ-alumina that may be grouped into physical, gaseous and wet phase chemical processes [9, 10]. Besides, among the various synthesis methods, sol–gel method is the most promising and thus has been widely investigated because it produces solid particles of ultrafine sizes, it is highly homogeneous, with controlled chemical purity and crystallinity, and has highly specific surface area [11, 12]. The sol–gel process is a wet chemical method that provides an alternative approach to the synthesis of nanomaterials. Therefore, sol–gel technology plays an important role in a diverse range of scientific and engineering fields such as the ceramic industry, the nuclear-fuel industry, and the electronic industry. Sol–gel technique has been widely used for the synthesis of high nano-porous aluminas according to the procedures directly related to the original work of Yoldas. These methods allow to control the pore size and surface area by adjusting the main synthesis variables (e.g. pH, water content, and solvent nature) [13, 14].

In most of the previous work using the sol-gel route in an aqueous system, crystalline mesoporous γ-alumina has been attained [15, 16]. Li et al. have prepared dispersed spherical amorphous alumina nanoparticles with a narrow size distribution by facial homogeneous precipitation and subsequent calcination [15]. Maensiri et al. have synthesized mesostructured γ -Al$_2$O$_3$ with a simple chitosan-polymer complex solution route. The crystallite sizes of the prepared powders were in the range of 4–49 nm [16]. Renuka et al. have synthesized well-ordered porous alumina nanoparticle by template method using dodecylamine with average pore diameter in the 3–12 nm range [17]. In the present contribution, we report a novel processing method for the synthesis of

porous γ-Al$_2$O$_3$ nanoparticles from sodium aluminate liquor obtained from natural bauxite and by two types of surfactants as structure-directing agents. The aim of this study is to synthesis the nanoparticles with very fine crystallite size, low cost, and high synthesis rate, and also to investigate the effects of the two surfactants on the synthesis of nanoparticles of γ-alumina from sodium aluminate liquor.

2. EXPERIMENTAL PROCEDURE
2.1. Synthesis of γ-alumina nanoparticles

Sodium aluminate liquor, HCl (37 %wt, Merck), NaOH (Merck), polyvinyl alcohol (2000-6000, Merck), and polyethylene glycol (2000-6000, Merck) were used as raw materials to prepare γ-alumina nanoparticles. In order to investigate the effect of surfactant type and addition amount on the structural properties of γ-alumina, two surfactants, including polyethylene glycol (PEG) and polyvinyl alcohol (PVA) were systematically trialled. The sodium aluminate liquor which contains 148.41 g/L of Al$_2$O$_3$ was used as the starting material. It was obtained from Bayer liquor of alumina product processed in the Jajarm (North Khorasan, Iran) alumina production plant. At first, a little amount of HCl was added to the raw material, which consisted of impurities such as Na$_2$O$_c$ (c = NaOH) and Na$_2$O$_t$ (t = NaOH + Na$_2$Co$_3$), and then the suspension was stirred at 500 K for 2 h using a magnetic stirrer until the pH was adjusted to 7±0.5 and Al(OH)$_3$ was precipitated as the product. The resultant product was leached with double-distilled water and then filtered precipitated to obtain pure Al(OH)$_3$. NaOH (18 gr) was then added to the pure Al(OH)$_3$ (100 gr) until pure product of Al(OH)$_4$Na was formed in the solution. HCl (15 gr) solution was then added dropwise to the vigorously stirred Al(OH)$_4$Na solution with the same volume as the former to produce a white, gelatinous Al(OH)$_3$. PEG (0.5 gr) and PVA (0.5 gr) were used as structure-directing

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agents and as a dispersant to prevent the aggregation of solid particles. The solid phase was then rinsed with distilled water in order to remove extra PEG and other impurities. The obtained gel was dried at 100 ℃ for 2 h. The dried gel was then ground and calcined in a furnace at 800 ℃ for 4 h. The schematic process of the sol–gel synthesis of γ-Al$_2$O$_3$ nanoparticles is illustrated in Figure 1.

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┌─────────────────────────────┐
│     Al(OH)₄Na (liquor)      │
└─────────────────────────────┘
              ⇓
┌─────────────────────────────┐
│   Elimination of impurities │
└─────────────────────────────┘
              ⇓
┌─────────────────────────────┐
│ Stirring at room temperature│
└─────────────────────────────┘
  PEG or PVA added            ⇓
- - - - - - - - - - - ►
┌─────────────────────────────┐
│ Stirring at room temperature│
└─────────────────────────────┘
  HCl added                   ⇓
- - - - - - - - - - - ►
┌─────────────────────────────┐
│            Gel              │
└─────────────────────────────┘
              ⇓
┌─────────────────────────────┐
│      Drying at 100°C        │
└─────────────────────────────┘
              ⇓
┌─────────────────────────────┐
│    Calcination at 800°C     │
└─────────────────────────────┘
              ⇓
┌─────────────────────────────┐
│       Characterization      │
│   (XRD, TGA, SEM, FTIR,     │
│   N2 adsorption/desorption) │
└─────────────────────────────┘
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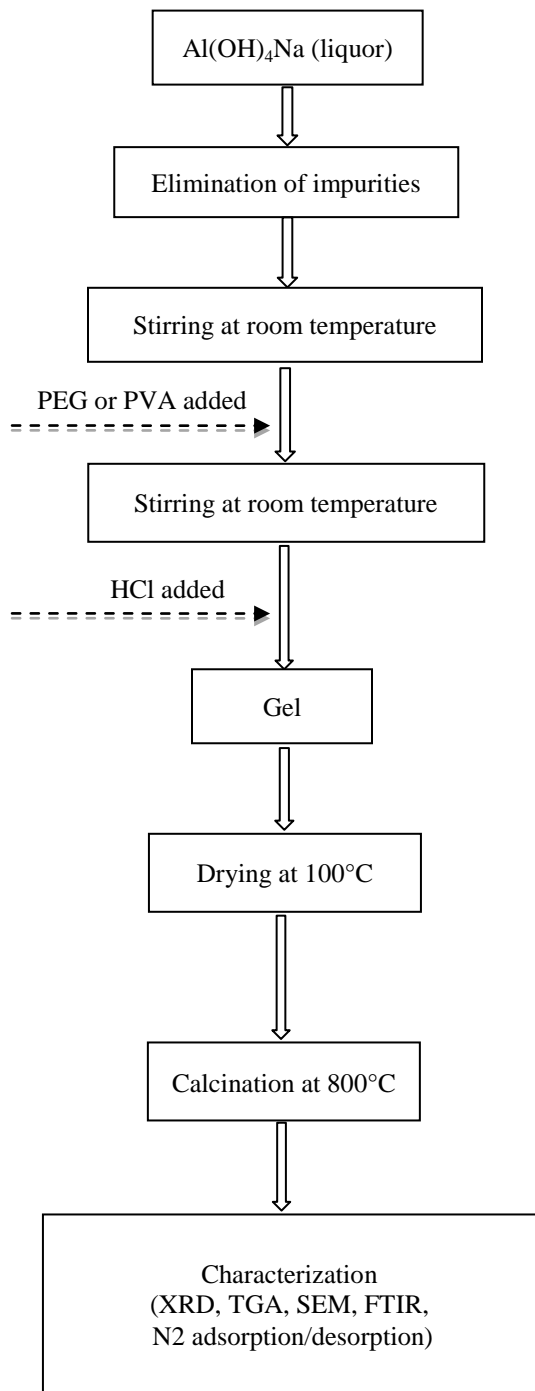
Figure 1. *Nano γ-alumina synthesis process.*

2.2. Characterization and analysis

ITAL STRUCTURES, APD 2000 model was used for phase analysis of synthesized alumina samples in X-ray diffraction. The samples were scanned in the 2θ range from 10 to 80° at a scanning rate of 5° min^{-1}. The average crystallite size of the alumina samples was calculated using the Sherrer's formula:

$$D = \frac{K\lambda}{\beta \cos \theta} \qquad (1)$$

Where D is the crystallite size, k the Sherrer constant (k = 0.9), λ the wavelength, β peak width at half height, and θ the diffraction angle.

The morphology and particle size of synthesized nanoparticles were characterized by scanning electron microscopy (SEM, Philips-XL30).

Using a Perkin-Elmer TG/DTA instrument the thermogravimetric method (TG) and differential thermal analysis (DTA) measurements of synthesized nanoparticles can be performed (PE Diamond) in the temperature range of 32.32 to 900 ℃. The temperature scanning rate was 10 ℃ per minute.

The BET surface areas and pore volumes were estimated from nitrogen adsorption/ desorption isotherm data obtained at −196 ℃ on a constant-volume adsorption apparatus (Quantachrome Instruments, 1994-2006). The pore volumes were determined at a relative pressure (P/P_0) of 0.99. The pore size distribution, average pore diameter and total pore volume were calculated according to the DFT method.

The FTIR spectroscopy for the nano-alumina materials was carried out using the KBr pellet technique and a Fourier transform infrared spectrometer, Perkin-Elmer Spectrum 65, in the range 4000–400 cm^{-1}.

3. RESULTS AND DISCUSSINS
3.1. Characterization of γ-alumina nanoparticles

Figure 2a and 2b, show SEM images of as-synthesized alumina nanoparticle prepared with the two surfactants after calcination at 800°C. From Figure 2a and 2b, it can be seen that the size of as-synthesized alumina nanoparticles are about 20 nm and 46 nm. The morphologies of the synthesized nanoparticles after adding the surfactant to the sol did not change to a great extent. Furthermore, characterization is required to confirm the pore structure by using the nitrogen gas sorption method. As reported in Figure 3a and 3b, XRD profiles reveal the alumina nanoparticles [16-18] already after the calcination at 800°C. The intensity of XRD peaks and the peak width indicating that a larger amount of *γ-alumina* crystals are formed throughout the sample. As shown in their XRD pattern, diffraction peaks appear at 2θ, 67°, 46° and 37°, of γ-alumina without other diffraction peaks. The average sizes of resultant nano-alumina with PEG and PVA were estimated from the half-height width of the strong peaks to be 2.0313 nm and 2.063 nm, respectively. As shown in Figure 4, the most weight loss (7.26%) occurs at temperatures lower than 600 ºC due to the evaporation of volatile components, such as water residues, including adsorbed water, free water, crystal water, and also PEG template. The adsorbed water and crystal water in the sample are released at 100-120 ºC and 340 ºC, respectively. Because the boiling point of PEG is less than 300 ºC the mass loss up to 340 ºC is attributed to the removal of PEG and free bonded water. The mass loss process is stabilized at over 600 ºC.
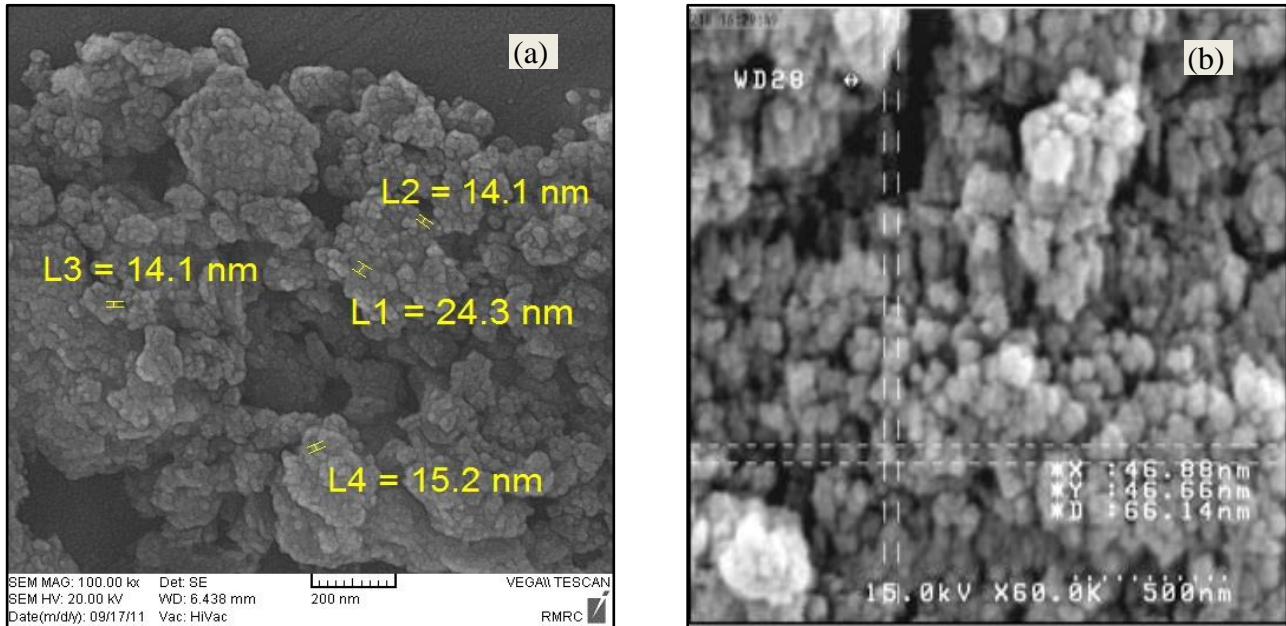

Figure 2. *SEM image of as-synthesized nanoparticles at 800 ºC by: (a) polyethylene glycol. (b) polyvinyl alcohol.*
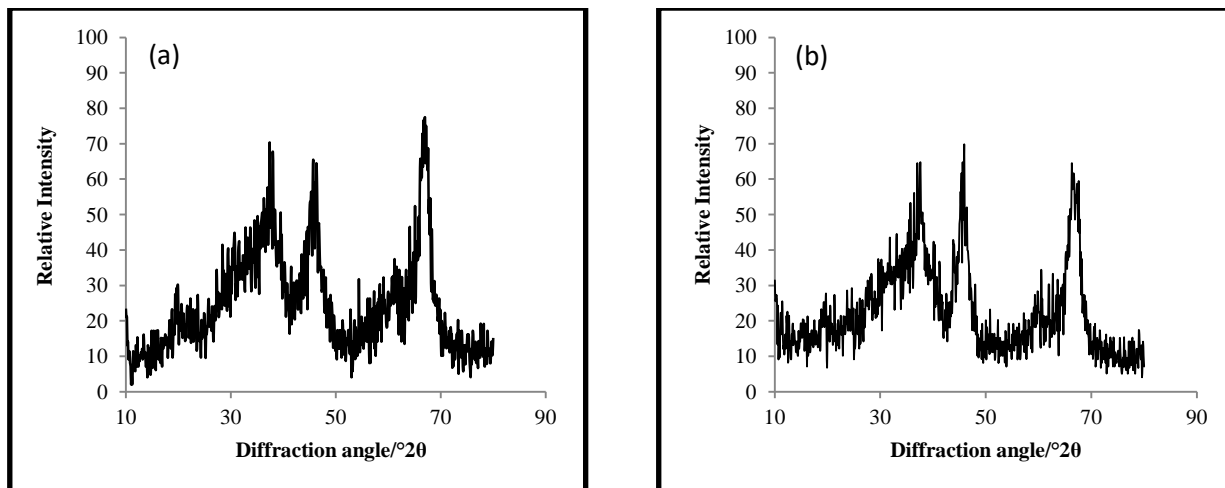
Figure 3. XRD patterns of as-synthesized nanoparticles γ-alumina using: (a) polyethylene glycol. (b) polyvinyl alcohol.
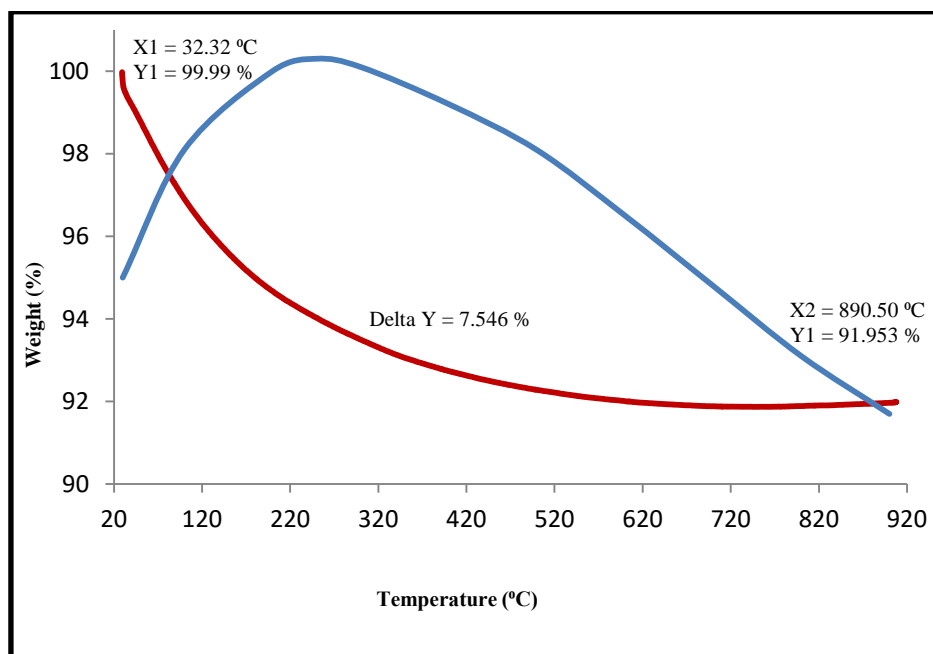

Figure 4. TG/DTA curves of the as-synthesized nanoparticles.

Figure 5a and 5b, illustrate IR spectra of two alumina samples studied. The stronger broadening bands from 300 to 1000 cm^{-1} for –Al– OH and –O–Al–O–Al– correspond to the characteristic vibration of Al_2O_3 at 800 °C. The vibration bonds in Fig. 5a at 3508.01 and 1644.04 cm^{-1} and in Fig. 5b at 3457.89 and 1637.81 cm^{-1} can be explained by the stretching and bending vibration of OH bonds. This shows the number of hydroxyl groups on the surface of nano-γ-

alumina. According to this data, the synthesized nano-γ-alumina is a pure product and a number of hydroxyl groups exist on its surfaces. The nitrogen adsorption/desorption isotherms at 77.3 K and the DFT pore size distributions of γ-alumina nanoparticles produced by using PEG and PVA surfactant are shown in Figure 6 and Figure 7. It interprets from Figure 6a and 6b, we can interpret the BET surface area, the shape of

adsorption/desorption isotherms, and the hysteresis loop. DFT pore-size distributions of this tested sample are shown in Fig. 7a and 7b. It demonstrates that at 800 °C the pores diameter range is between 1.9-16 nm by using PEG, which increases to 1.4-25 nm by using PVA. Obviously with changing surfactant, the pore diameter increases and the pore-size distribution becomes broader. The pores ranging from 4 nm to 25 nm decrease, also in the 16 nm and 25 nm is almost stable.

Table 1. *Surface area, pore size, and pore volume of synthesized MA samples*

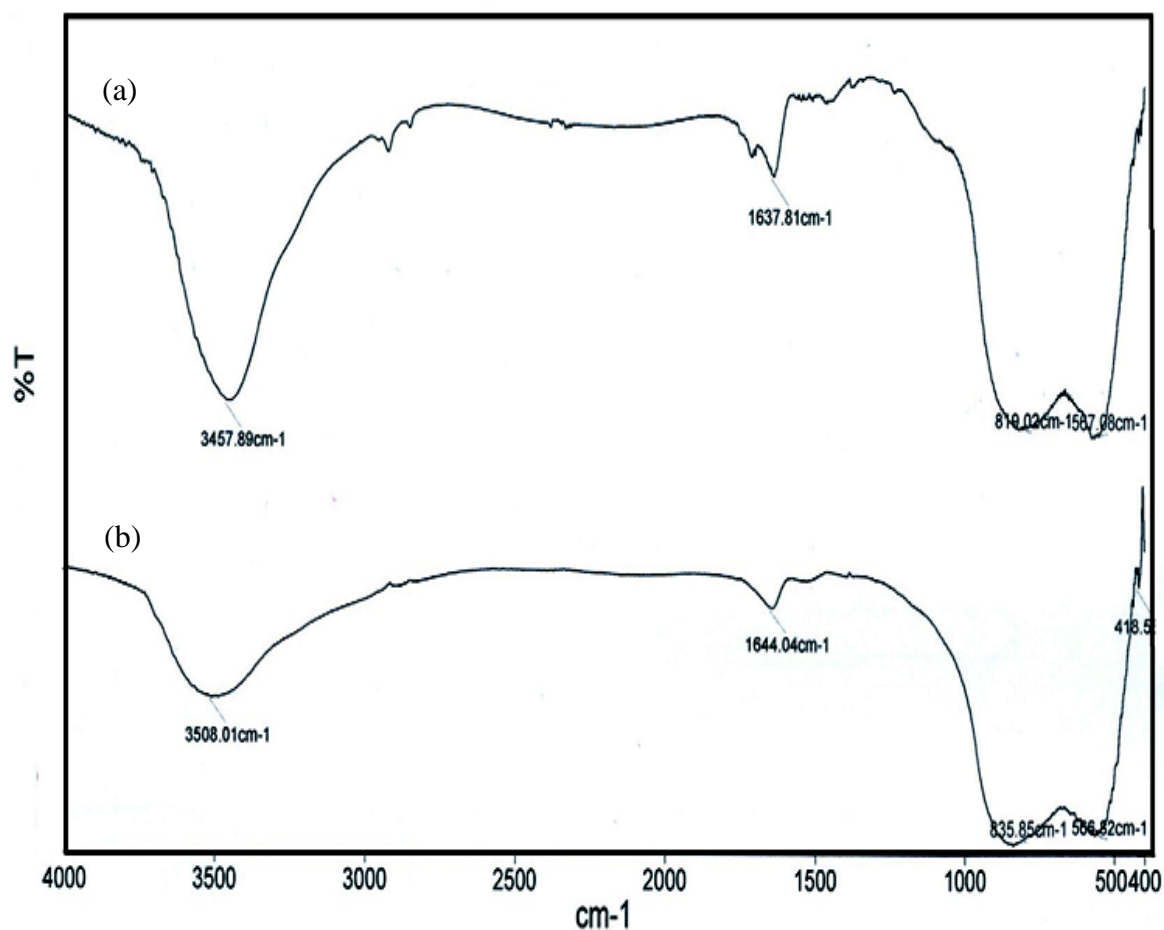| sample	Surface area (m² g⁻¹)	Pore diameter (nm)	Pore volume (cm³ g⁻¹)
nano-γ-alumina with PEG	138.8	4.7	0.1658
nano-γ-alumina with PVA	201.1	7.8	0.2463

Figure 5. *The FTIR spectra of as-synthesized nanoparticle at 800 °C by: (a) polyethylene glycol. (b) polyvinyl alcohol.*
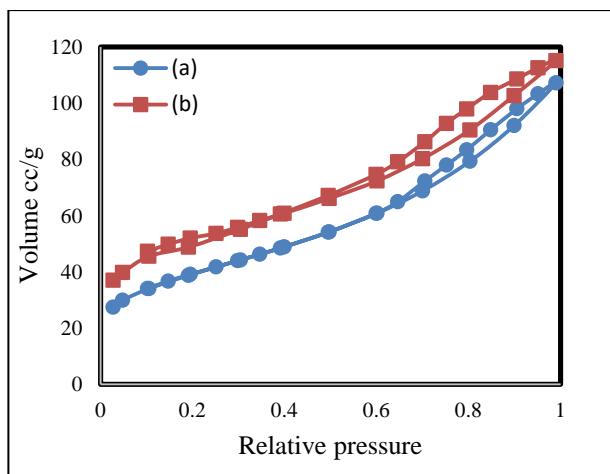
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Figure 6. *The nitrogen adsorption/desorption isotherms of γ-alumina nanoparticles calcined at 800∘C produced by: (a) polyethylene glycol. (b) polyvinyl alcohol.*
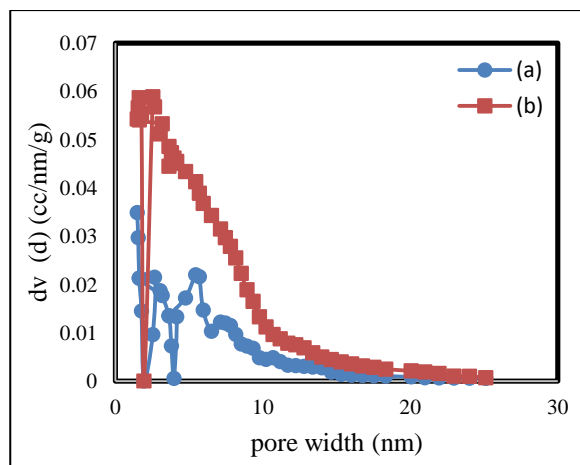

Figure 7. *DFT pore-size distributions of γ-alumina nanoparticles calcined at 800ºC produced by: (a) polyethylene glycol. (b) polyvinyl alcohol.*

3.2. Effect of two types of surfactants on preparing nanoparticles alumina

The application of PEG led to the formation of much smaller solid particles during the synthesis of nanoparticles probably because PEG inhibits the hydrolysis and condensation of formed aluminum hydroxide particles; thus, forming small particles by adsorption at the particle surface through hydrogen bonding and the basic oxygen of the ethoxyl group of PEG or electrostatic interaction [19]. The contribution of PVA is similar to PEG. PEG and PVA act as structure-directing agents and make the porous γ-alumina nanoparticle. Application of PEG leads to form smaller particles but with PVA the particles will become larger and adhesion between the particles will be less (in the similar qualification).

4. CONCLUSION

The porous γ-alumina was successfully synthesized using sodium aluminate liquor as the precursors along with two different surfactants as the structure-directing agents. When the calcination temperature was 800 °C, γ-alumina porous nanoparticles made by using PEG and PVA surfactant were obtained with the surface area of 138.8 m^2/g and 201 m^2/g, respectively. Also, the average crystallite sizes of synthesized nanoparticles made by using PEG and PVA surfactants were 2.58 nm and 3.07 nm. Examination by SEM identified that the particle average sizes were 20 nm by using PEG and 46 nm by using PVA. The use of PEG and PVA leads to the formation of much smaller solid particles during the aluminum hydroxide precipitate formation process. In comparison to PEG, PVA resulted in a better dispersion (in the qualification similar). The PVA surfactants were shown to more strongly influence the structural properties compared to PEG.

REFERENCES

1. Qi, Y. E., Zhang, Y. S., Hu, L. T. (2012). "High-temperature self-lubricated properties of Al 2 O 3/Mo laminated composites", *Wear*, 280: 1-4.

2. Isfahani, T. D., Javadpour, J., Khavandi, A., Dinnebier, R., Goodarzi, M., Rezaie, H. R. (2012). Mechanochemical synthesis of alumina nanoparticles: Formation mechanism and phase transformation", *Powder technology*, 229: 17-23.

3. Huang, B., Bartholomew, C. H., Smith, S. J., Woodfield, B. F. (2013). "Facile solvent-deficient synthesis of mesoporous γ-alumina with controlled pore structures", *Microporous and Mesoporous Materials*, 165: 70-78.

4. Ibrahim, A. R., Zhu, L., Xu, J., Hong, Y., Su, Y., Wang, H., Li, J. (2014). "Synthesis of mesoporous alumina with CO 2 expanded carbonation and its catalytic oxidation of cyclohexanone", *The Journal of Supercritical Fluids*, 92: 190-196.

5. Ranjbar, M., Yousefi, M. (2016). "Sonochemical Synthesis and Characterization of a Nano-Sized Lead (II) Coordination Polymer; A New Precursor for the Preparation of PbO Nanoparticles", *International Journal of Nanoscience and Nanotechnology*, 12(2): 109-118.

6. Almasi Kashi, M., Ramazani, A. (2010). "Ordered Nanoporous Alumina Membranes Formed in Oxalic/Phosphoric Acid Using Hard Anodization", *International Journal of Nanoscience and Nanotechnology*, 6(2):78-87.

7. Kathirvel, P., Chandrasekaran, J., Manoharan, D., Kumar, S. (2014). "Preparation and characterization of alpha alumina nanoparticles by in-flight oxidation of flame synthesis", *Journal of Alloys and Compounds*, 590: 341-345.

8. Hosseini, S. A., Niaei, A., Salari, D. (2011). "Production of γ-Al2O3 from Kaolin", *Open Journal of Physical Chemistry*, 1(02): 23.

9. Wu, W., Wan, Z., Zhu, M., Zhang, D. (2016). "A facile route to aqueous phase synthesis of mesoporous alumina with controllable structural properties", *Microporous and Mesoporous Materials*, 223: 203-212.

10. Da Costa Cunha, G., Romão, L. P. C., & Macedo, Z. S. (2014). "Production of alpha-alumina nanoparticles using aquatic humic substances", *Powder Technology*, 254: 344-351.

11. Zaki, T., Kabel, K. I., & Hassan, H. (2012). "Preparation of high pure α-Al 2 O 3 nanoparticles at low temperatures using Pechini method", *Ceramics International*, 38(3): 2021-2026.

12. Kango, S., Kalia, S., Celli, A., Njuguna, J., Habibi, Y., Kumar, R. (2013). "Surface modification of inorganic nanoparticles for development of organic–inorganic nanocomposites—A review", *Progress in Polymer Science*, 38(8): 1232-1261.

13. Wang, J., Ge, L., Li, Z., Li, L., Guo, Q., Li, J. (2016). "Facile size-controlled synthesis of well-dispersed spherical amorphous alumina nanoparticles via homogeneous precipitation", *Ceramics International*, 42(7): 8545-8551.

14. Saengkwamsawang, P., Pimanpaeng, S., Amornkitbamrung, V., Maensiri, S. (2014). "Synthesis and characterization of Al$_2$O$_3$ nanopowders by a simple chitosan-polymer complex solution route", *Ceramics International*, 40(4): 5137-5143.

15. Alphonse, P., Faure, B. (2013). "Synthesis of highly porous alumina-based materials", *Microporous and Mesoporous Materials*, 181: 23-28.

16. Bleta, R., Alphonse, P., Pin, L., Gressier, M., Menu, M. J. (2012). "An efficient route to aqueous phase synthesis of nanocrystalline γ-Al 2 O 3 with high porosity: from stable boehmite colloids to large pore mesoporous alumina", *Journal of colloid and interface science*, 367(1): 120-128.

17. Renuka, N. K., Shijina, A. V., Praveen, A. K. (2012). "Mesoporous γ-alumina nanoparticles: synthesis, characterization and dye removal efficiency", *Materials letters*, 82: 42-44.

18. Dionigi, C., Ivanovska, T., Liscio, F., Milita, S., Corticelli, F., Ruani, G. (2016). "Fabrication and properties of non-isolating γ-alumina meso-foam", *.Journal of Alloys and Compounds*.

19. Yang, H., Liu, M., Ouyang, J. (2010). "Novel synthesis and characterization of nanosized γ-Al$_2$O$_3$ from kaolin", *Applied Clay Science*, 47(3): 438-443.