INTERNATIONAL JOURNAL OF
ENERGY AND ENVIRONMENT

Volume 9, Issue 3, 2018 pp.261-268

Journal homepage: www.IJEE.IEEFoundation.org

Preparation and characterization of γ-Al_2O_3 nanoparticles via chemical precipitation route: Effect of precursor concentration

Alaa Jassim Awadh[1], Saad H. Ammar[1], Ban A. Altabbakh[2]

[1] Department of Chemical engineering, AL-Nahrain University, Baghdad, Iraq.
[2] Petroleum Research and Development Center, Ministry of Oil, Iraq.

Received 23 Oct. 2017; Received in revised form 18 Jan. 2018; Accepted 13 Feb. 2018; Available online 1 May 2018

Abstract
In the present work, nano-sized γ-alumina powders have been successfully synthesized by control precipitation path using aluminum chloride as forerunner and water and ammonium solution as precipitating agents and at 70 °C. The synthesized γ-alumina samples have been characterized by XRD, AFM, SEM, and N_2-adsorption/desorption isotherm at -196 °C by the BET method. Different initial concentrations of aluminium chloride precursor in ethanol solvent were studied on the particle size and surface area of the prepared γ-alumina. Results indicates that the sample prepared by this method gave nano-sized particle with crystallite shape in the range 70-91 nm, surface area 260-291 m^2/g and pore volume 0.467-0.36 cm^3/g.

Keywords: Gama aluminum; Nanoparticles; γ-Al_2O_3; Co-precipitation.

1. Introduction
The preparation powders alumina has been an important field because of their wide range of enforcement in different fields of industry such as electronic ceramics, catalysts, adsorbents, composites and filters [1]. Alumina is an important material and vastly used in the various fields of industry such as ceramics, metallurgy, and electronics due to its good electrical insulation, high corrosion resistance, and catalytic properties. Among metastable phases of alumina (γ-Al_2O_3) is often utilized such as adsorbent and catalyst [2].
Diverse routes have been developed to products γ-alumina are classified into physical and chemical techniques. Mechanical milling, flame spray, laser ablation and thermal decomposition by plasma are classified as physical methods. Also co-precipitation, sol-gel, hydrothermal, combustion methods, vapor deposition and micro-emulsion are classified as chemical methods [2]. Among these methods, the chemical methods co-precipitation and sol-gel are the most commonly used for producing of γ-alumina because it can produce cheap, high quality and pinnacle specific surface area powders [8].
Precipitation route is the most generally used method not only because it can produce high-quality powders and also it is cheap [3].

In each method, different parameters such as concentration of the initial solution and raw material, pH, temperature and reaction time have important role on getting alumina powders with required shape and size [4].
In this work, γ-Al_2O_3 nanoparticles were synthesized and characterized by co-precipitation method. The effect of initial aluminum chloride (precursor) concentration was studied on the alumina properties such as particle size and surface area [5].

2. Materials and methods

2.1 Materials

Aluminum chloride ($AlCl_3.6H_2O$, 95%), ammonium solution (NH_4OH, 25%), ethanol (99.9%) and deionized water were used as raw chemicals. All reagents were of analytical category provided from Merck and used as standard.

2.2 Preparation of nano γ-Al_2O_3 by co-precipitation procedure

Initially, aluminium chloride (0.1-1 M) solution was equipped by dissolving appropriate amount of aluminium chloride in 300 ml of ethanol using magnetic stirrer. And then distilled water was added gradually until a transparent solution was appeared. 100 mL of 25% Ammonia solution was added while stirring as precipitant agent drop by drop to the $AlCl_3$ solution at a rate of 2 mL/min (from burette) until precipitation of $Al(OH)_3$ white gel. The temperature was fixed at 70 ºC through co-precipitation time. The white gel precipitate was aged at 70 ◦C for 1 h, filtered under vacuum, washed carefully with deionized water and with ethanol then drying at 90 ºC for about 24 h. The dried precipitate samples were calcined in furnace at 550 ºC for 2 h in air by the heating rate of 3 ºC/min to produce Al_2O_3 nano powders. The calcined samples prepared using 0.1 M, 0.3M, 0.5 M and 1 M were coded as γ-alumina-1, γ-alumina-2, γ-alumina-3 and γ-alumina-4 respectively. The synthesis process of nano γ-Al_2O_3 has been presented schematically as shown in Figure 1.

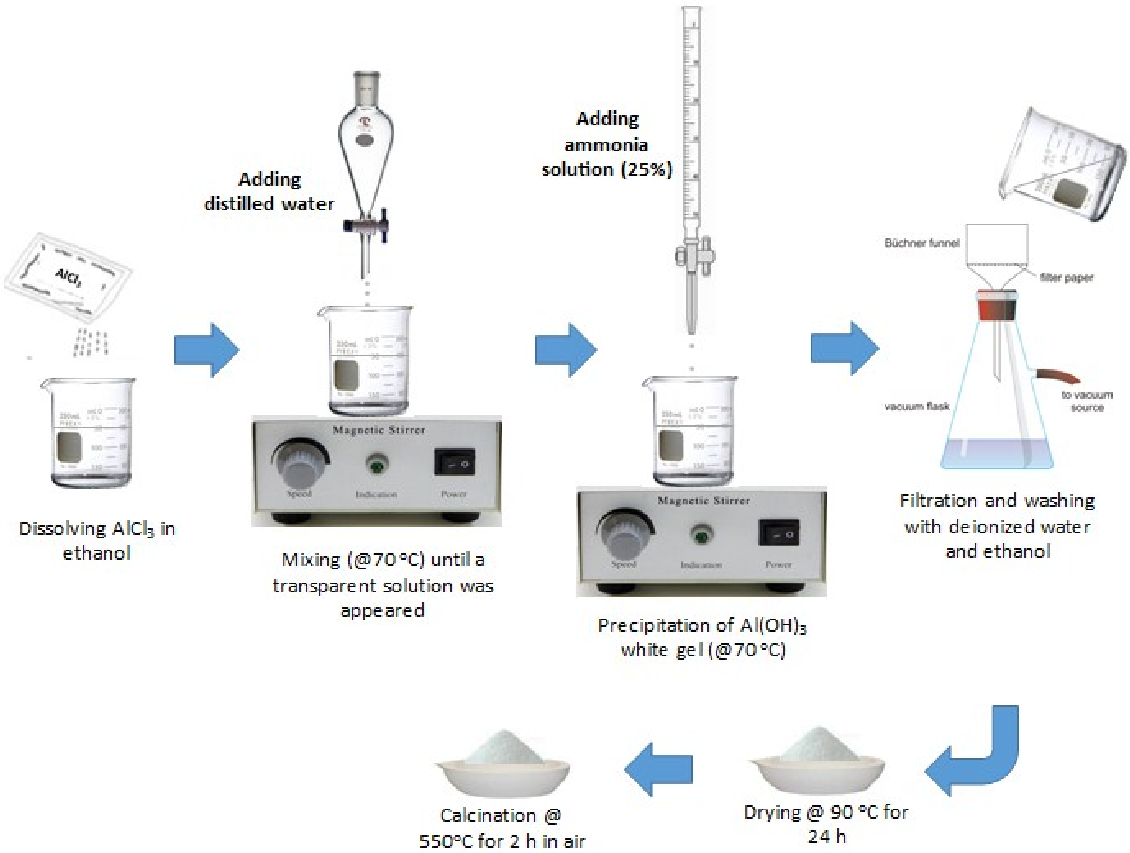


Figure 1. General scheme for the preparation of nano γ-Al_2O_3 using precipitation route.

2.3 Characterization

Structural phase analysis of alumina samples by X-Ray Diffraction (XRD) was performed by Rigaku, D/Max-2000 diffractometer using Cu Kα radiation using wavelength (λ) = 1.5406 A0, tube-voltage = 40 kV, tube-current = 30 mA, and at 2θ range = 10o to 80o. On all alumina samples, full N_2 adsorption-desorption isotherms at -196 °C in the partial pressure below 0.3 were measured using Surface Area and Pore volume Analyzer Quantachrome Autosorb-6iSA. The N_2 uptake provided a linear fit to the Brunauer-Emmett-Teller (BET) equation. Before BTE-surface area measurements, the samples were treated for 4 h at 200 ºC. The total pore volume of each sample was determined at a partial pressure of 0.99. Particle size distribution and morphology of samples are studied by a scanning electron microscope (SEM) and an *Atomic Force* microscope (AFM).

3. Result and discussion

3.1 X-Ray diffraction (XRD) analysis

The XRD spectra of the fourth prepared γ-Al_2O_3 samples at different aluminum chloride (precursor) concentration are shown in the Figure 2. For comparison, Figure 3 shows the XRD spectra of standard γ-Al_2O_3.

It is clear from Figure 2, that all the prepared samples of alumina represent gamma alumina after comparison with international alumina card, JCPDS files no. 29. 0063. The four clear standard peaks of all gamma alumina samples (400-35b intensity-4.33 d spacing), (311-65b intensity-2.39 d spacing), (400-80b intensity-1.98 d spacing), and (410-100b intensity-1.4 d spacing) were accepted.

3.2 Atomic force microscopy (AFM)

In this examination, by using Atomic Force Microscope, the morphology of equipped the alumina is studied. Figures (4-7) and (8-11) shows the images of AFM on (two-dimensional) surface and (three-dimensional) exterior of γ-Al_2O_3 samples prepared at different aluminum chloride concentrations, respectively. The shapes of nonagamma alumna (γ-Al_2O_3) crystal in two-dimensional is the irregular hexagonal structure as shown in Figures (4-7). Whereas the shapes of nonagamma alumna (γ-Al_2O_3) crystal in three dimensional are in form of irregular and hexagonal layers and also spherical and rough in shape with height terraces up to (9.8)nm as shown in Figures (8-11) [2].

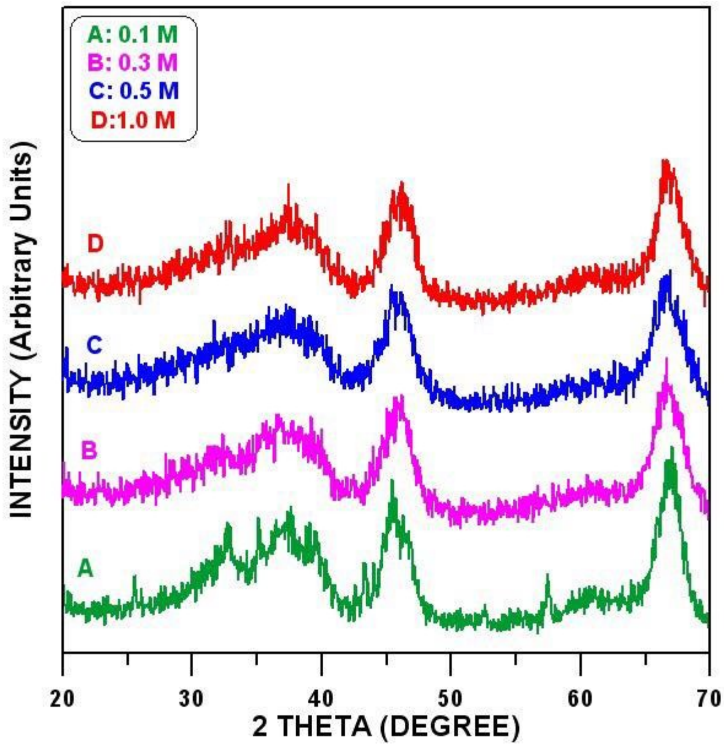


Figure 2. XRD diffraction of nano gamma alumina samples prepared at different aluminum chloride concentration.

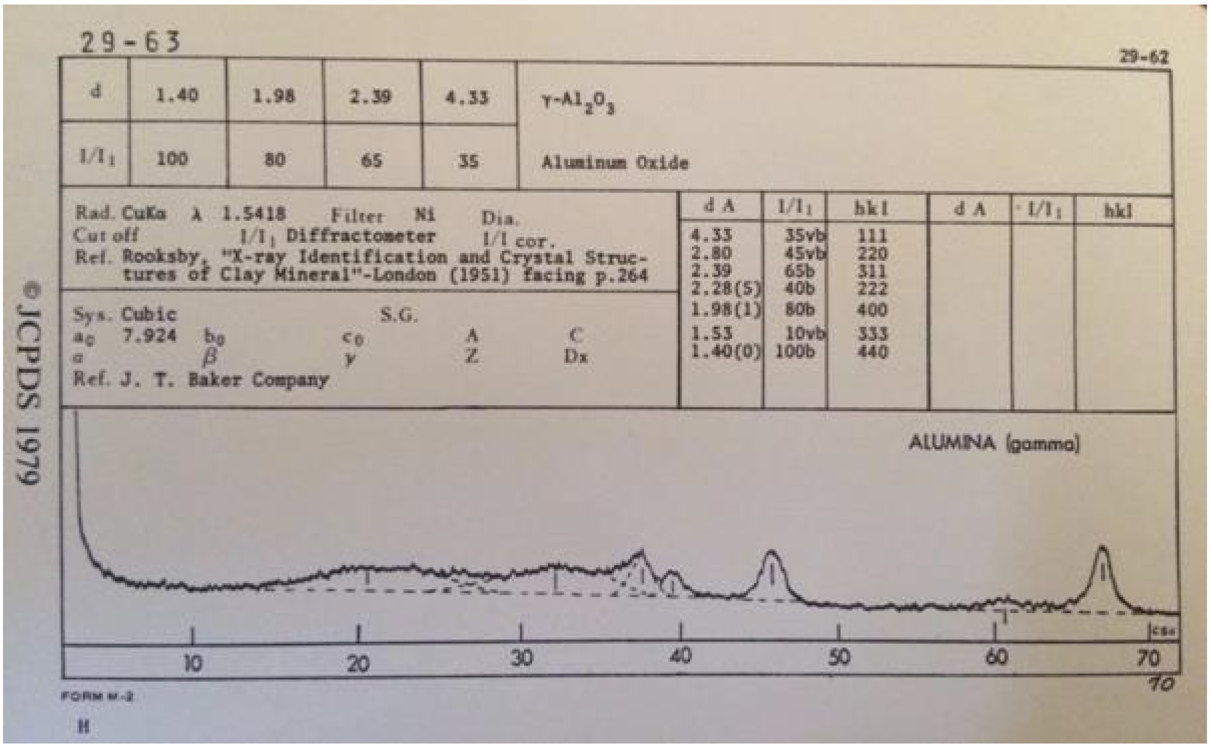


Figure 3. The XRD spectrum of standard gamma alumina.

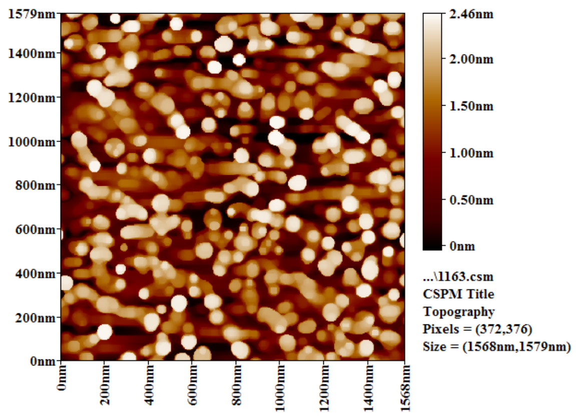


Figure 4. Two-dim. surface of prepared nano-alumina at concentration 0.3M.

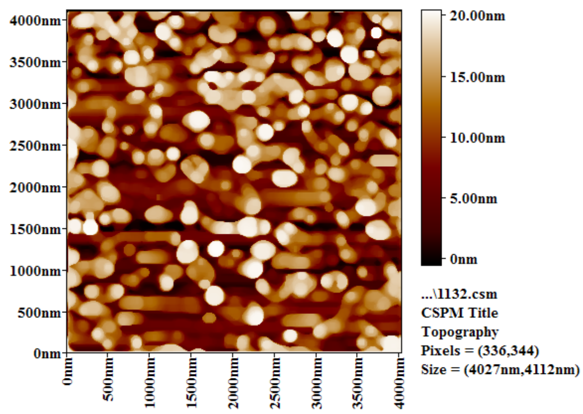


Figure 5. Two-dim. surface of prepared nano-alumina at concentration 0.1M.

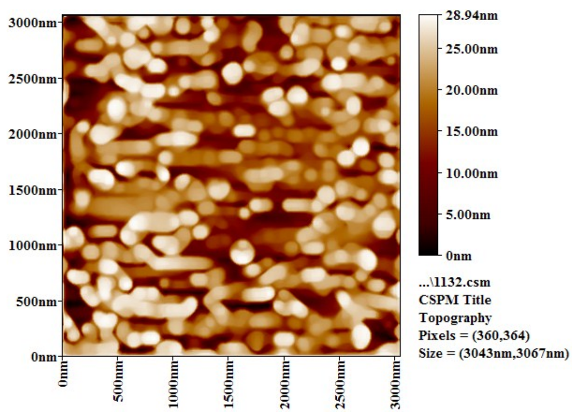


Figure 6. Two-dim. surface of prepared nano-alumina at concentration 0.5M.

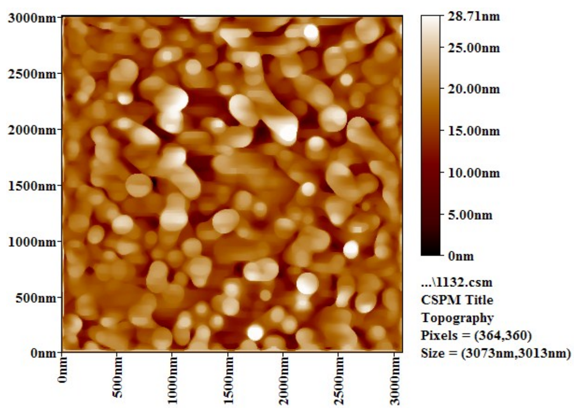


Figure 7. Two-dim. surface of nano- alumina at concentration 1M.

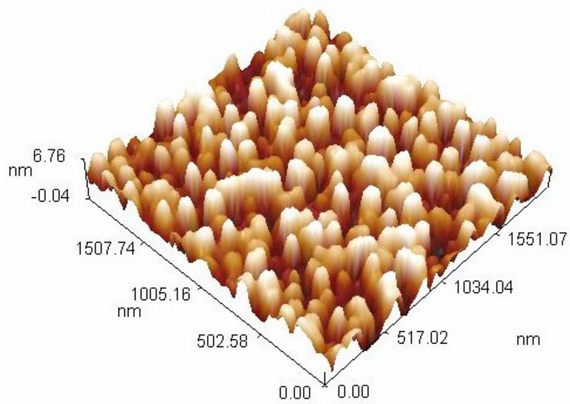


Figure 8. Three-dimensional surface of prepared nano-alumina at concentration 0.1M.

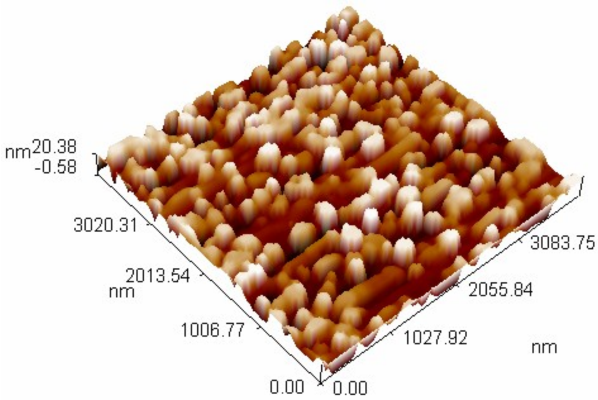


Figure 9. Three-dimensional surface of Prepared nano-alumina at contraction 0.3M.

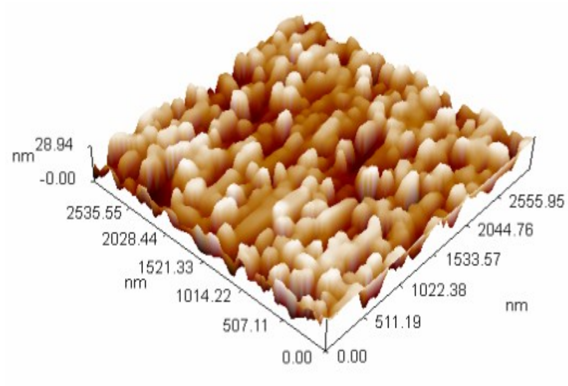


Figure 10. Three-dim. surface of Prepared nano-alumina at concentration 0.5M.

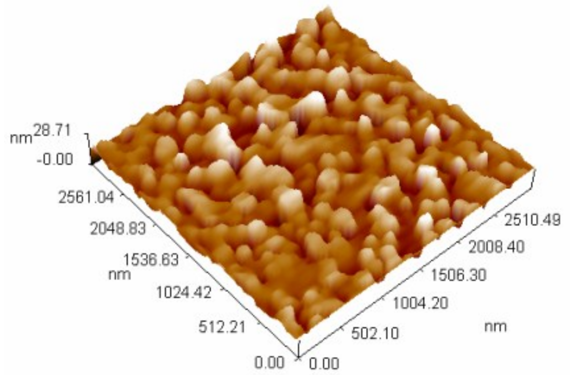


Figure 11. Three-dim. surface of prepared nano-alumina at concentration 1M.

Figures (12-15) at different concentration, the particle size distribution of gamma alumina nanoparticles are demonstrate. The highest volume percentage at concentration (0.1M) is (11.55%) at (60) nm whereas the lowest volume percentage at the same concentration is (0.4%) at (98-100) nm. The diameter of particles found in the gamma alumina at (0.1M) concentration is ranges between (40-95) nm and average (70) nm. This results obtained from present study is near from the previous author [8]. Who prepared nano structured gamma alumina powder 40.00 nm [6]. The highest volume percentage at concentration (0.3M) is (22.37%) at (85) nm whereas the lowest volume percentage at the same concentration is (0.34%) at (98.98-100). The diameter of particles found in the gamma alumina at (0.3M) concentration is ranges between (0-120) nm and average (95.93) nm. The highest volume percentage at concentration (0.5M) is (34.09%) at (100) nm whereas the lowest volume percentage at the same concentration is (0.76%) at (95.45-100) nm. The diameter of particles found in the gamma alumina at (0.5M) concentration is ranges between (0-130) nm and average (110) nm. The highest volume percentage at concentration (1.0M) is (16%) at (150) nm whereas the lowest volume percentage at the same concentration is (0.8%) at (60-90) nm. The diameter of particles found in the gamma alumina at (1M) concentration is ranges between (90-160) nm and average (130) nm.

3.3 Scanning electron microscopy (SEM)

At calcination temperature (550 ºC), SEM images of prepared gamma alumina at concentration (0.1)M are shown in Figure 16. At magnification of 1.00, 5.00, 10.0, and 25.0 k x.

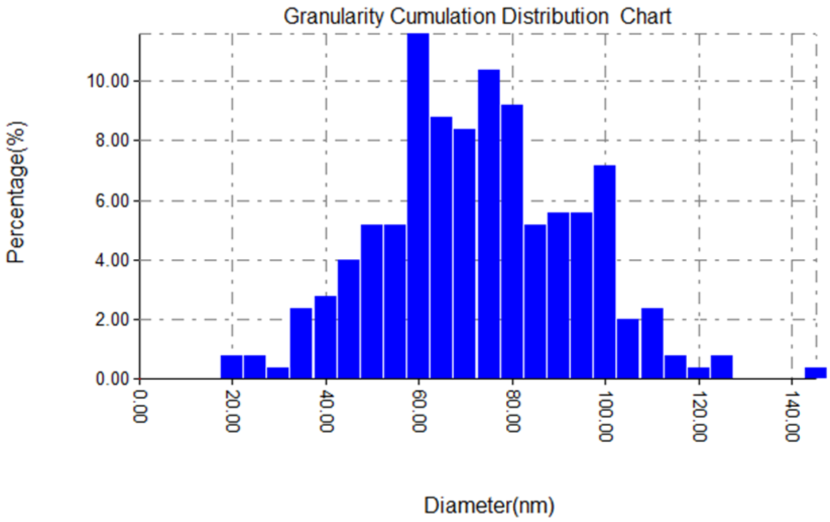


Figure 12. Bar-chart representation distribution of particle size for prepared alumina at concentration 0.1M.

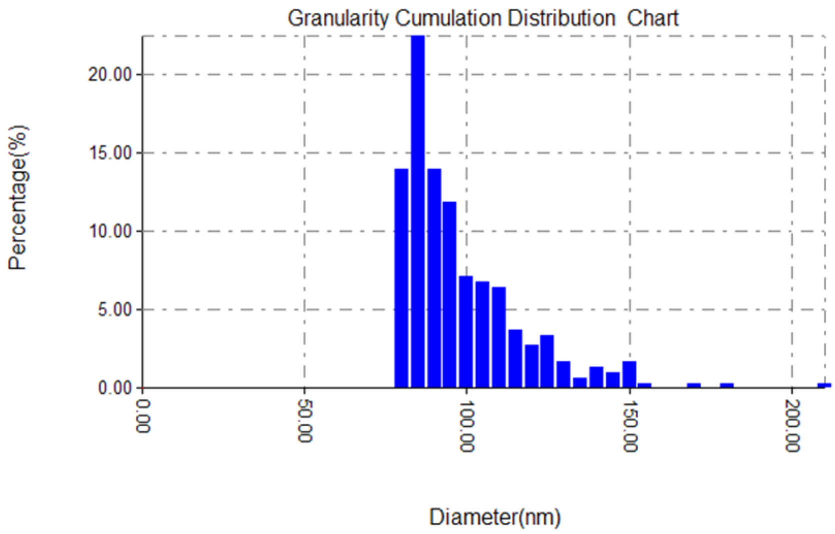


Figure 13. Bar-chart representation distribution of particle size for prepared alumina at concentration 0.3M.

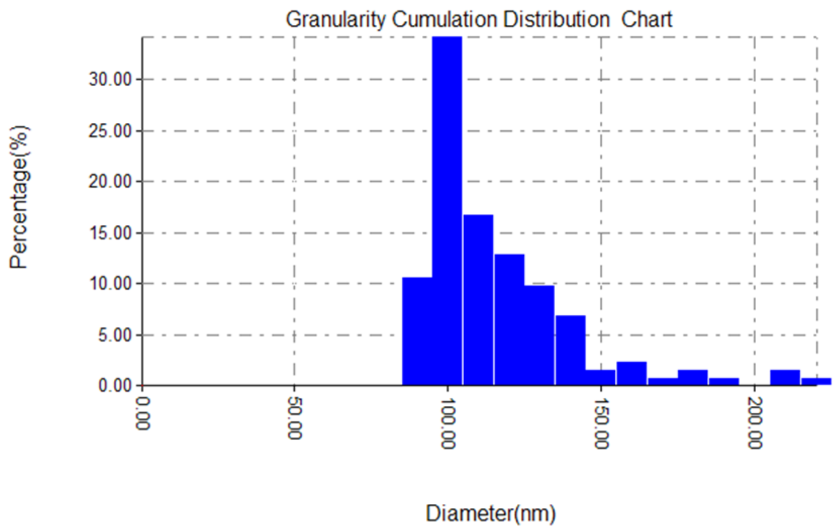


Figure 14. Bar-chart representation distribution of particle size for prepared alumina at concentration 0.5M.

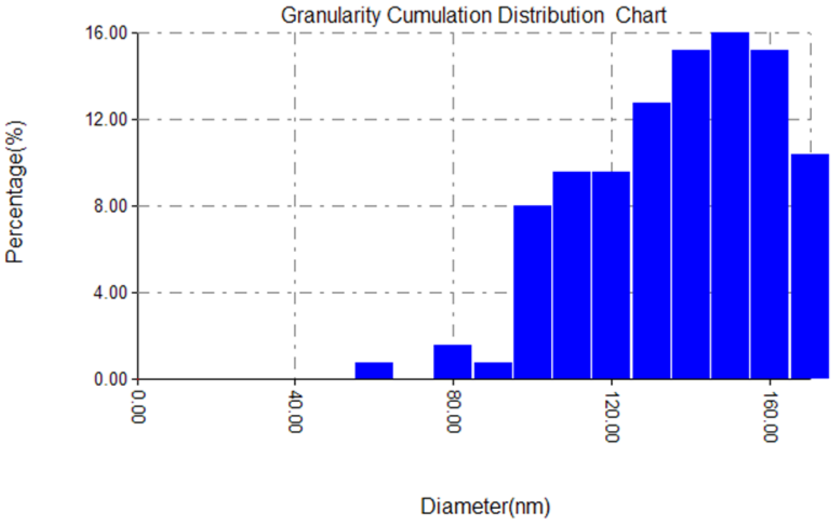
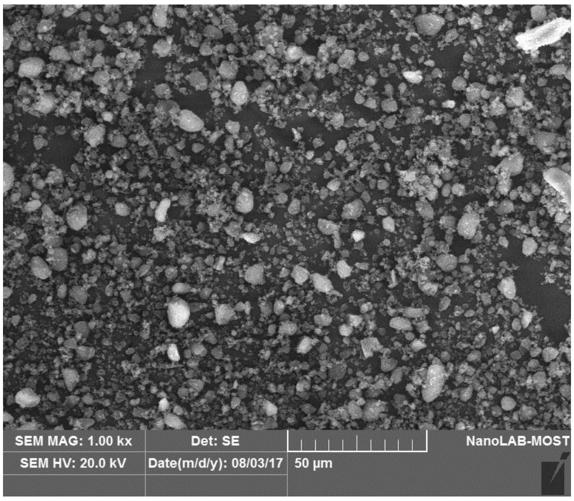
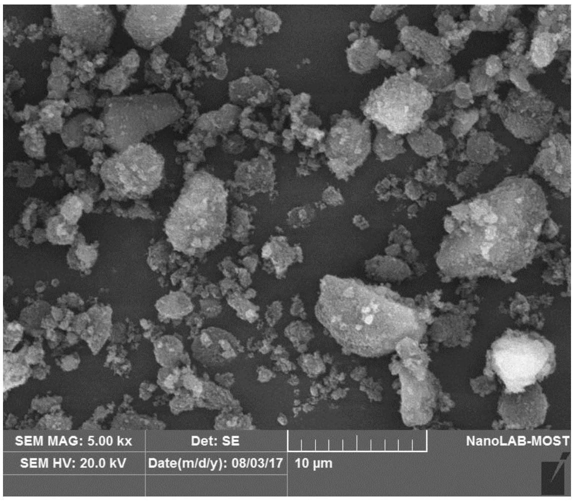


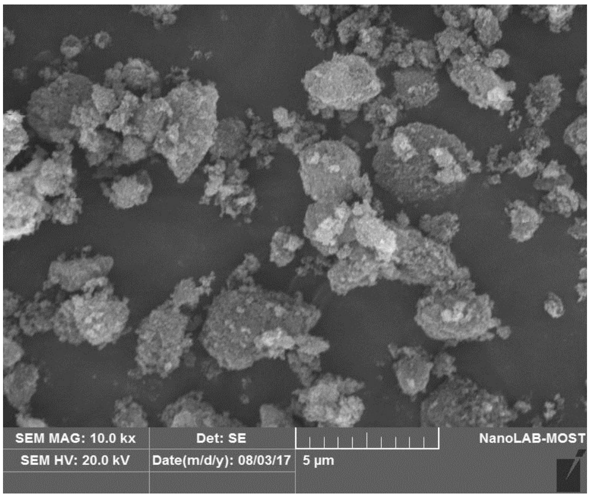
Figure 15. Bar-chart representation distribution of particle size for prepared alumina at concentration 1M.



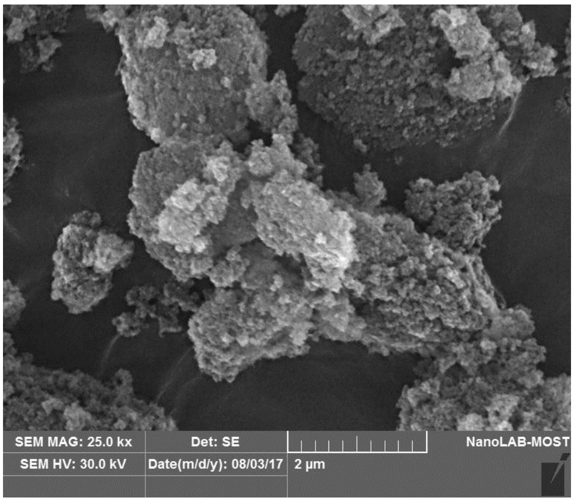
(a) SEM test at a magnification of 1.00 kx.



(b) SEM test at a magnification of 5.00 kx.



(c) SEM test at a magnification of 10.0 kx.



(d) SEM test at a magnification of 25.0 kx.

Figure 16. SEM test images of prepared nano gamma alumina.

3.4 Surface area and pore volume

Physical and chemical properties surface area, and pore volume of prepared gamma alumina at different aluminum chloride concentration were determined by BET device and presented in Table 1. In this table, It's noticed by increasing aluminum chloride concentration, the surface area is decrease. The maximum surface area obtained from the present study is (261.24 m^2/g) prepared at concentration (0.1 M). This result of maximum surface area obtained from present study is near from the previous author [8] was 206 m^2/g. The pores in higher surface area usually are very small [7].

Table 1. Physical properties of prepared nano γ-Al_2O_3.

Concentration (M)	Surface Area (m^2/g)	Pore Volume (cm^3/g)
0.1	261.2404	0.3555
0.3	260.5342	0.3558
0.5	238.1757	0.36176
1	229.366	0.3795

4. Conclusions

In This study, effects of concentration of cloride aluminiom on the size of nanoparticles was studied. by changes of $ALCL_3$ concentration by four different concentration the change in surface area and pore volume were changed. Decreasing the aluminum chloride concentration from 1 to 0.1M, leads to decrease in the particles size from 130 to 70 nm, increase in surface area from 229.36 to 261.24 m^2/g, and decrease in pore volume from 0.3795 to 0.3555 cm^3/g.

References

[1] S. A. Hosseini, "Production of γ-Al_2O_3 from Kaolin," Open J. Phys. Chem., vol. 1, no. 2, pp. 23-27, 2011.

[2] S. A. Hassanzadeh-Tabrizi and E. Taheri-Nassaj, "Economical synthesis of Al_2O_3 nanopowder using a precipitation method," Mater. Lett., vol. 63, no. 27, pp. 2274-2276, 2009.

[3] H. S. Potdar, K. W. Jun, J. W. Bae, S. M. Kim, and Y. J. Lee, "Synthesis of nano-sized porous ??-alumina powder via a precipitation/digestion route," Appl. Catal. A Gen., vol. 321, no. 2, pp. 109-116, 2007.

[4] L. C. Pathak, T. B. Singh, S. Das, A. K. Verma, and P. Ramachandrarao, "Effect of pH on the combustion synthesis of nano-crystalline alumina powder," Mater. Lett., vol. 57, no. 2, pp. 380-385, 2002.

[5] J. hong YI, Y. yi SUN, J. feng GAO, and C. yan XU, "Synthesis of crystalline ??-Al_2O_3 with high purity," Trans. Nonferrous Met. Soc. China (English Ed., vol. 19, no. 5, pp. 1237-1242, 2009.

[6] H. Wang, S. Pu, J. Li, L. Zhu, and J. Li, "Preparation and characterizations of monodisperse porous ?? -Al_2O_3 nanoparticles," Mater. Lett., vol. 124, pp. 296-298, 2014.

[7] A. Eliassi and M. Ranjbar, "Application of Novel Gamma Alumina Nano Structure for Preparation of Dimethyl ether from Methanol," Int. J. Nanosci. Nanotechnol., vol. 10, no. 1, pp. 13-26, 2014.

[8] A. Rajaeiyan, M. M. Bagheri- Mohaghi, "Comparison of Sol- gel and Co-precipitation Methods on The Structural Properties and Phase Transformation of γ and α-Al_2O_3 Nanoparticales", Springer, 1: 176-182, 11. May, 2013.