IJCPE
Iraqi Journal of Chemical and Petroleum Engineering

Iraqi Journal of Chemical and Petroleum Engineering
Vol.18 No.2 (June 2017) 1 - 11
ISSN: 1997-4884

University of Baghdad
College of Engineering

The Effect of Crystallization Time and Acid Type on the Synthesis of Nano-Gamma Alumina Using Double Hydrothermal Method

Abdul-Halim A.K. Mohammed[1], Hussein Q. Hussein[2] and Mohammed Sabah Mohammed[3]
1. Gas and Petroleum Engineering Department, College of Al-Faraby University
2. Chemical Engineering Department, College of Engineering, University of Baghdad
3. Office of Assit. Dean for Scientific and Student Affairs, College of Engineering, Al-Nahrain University

Abstract

Double hydrothermal method was used to prepare nano gamma alumina using aluminum nitrate nano hydrate and sodium aluminate as an aluminum source, CTAB (cetyltrimethylammonium bromide) as surfactant, and variable acids: weak acids like; citric, and acitic acids, and strong acids like; hydrochloric and nitric acids as a bridge between aluminum salts and surfactant. Different crystallization times 12, 24, 48, and 72 hrs were applied. All the batches were prepared at pH equals to 9. XRD diffraction technique was used to investigate the crystalline nano gamma alumina pure from surfactant. N_2 adsorption-desorption (BET) was used to measure the surface area and pore volume of the prepared nano alumina, the average particle size and the morphology of the surface of nano gamma alumina were estimated using AFM and SEM techniques, respectively. The sharpness of the peaks increased with increasing of crystallization time. The surface area, pore volume, and average particle size were decreased with increasing crystallization time. The best result of surface area was 383 m^2/gm obtained using citric acid at 12 hr crystallization time, while the best results of pore volume and average particle size were 0.54cm^3/gm and 72.37nm obtained using hydrochloric acid at12 hr crystallization time. Low agglomeration with hexagonal structure obtained using weak acids, while agglomeration occurred and clusters formed using strong acids.

Key words: Gamma alumina, nanoparticle, double hydrothermal, CTAB, crystallization time and acid type.

Introduction

The nano structured alumina material is a porous crystalline system having a nano particle size range 1-100 nm used in form of particles. Aluminum oxide exists in various structures; only two phases are of interest, namely the nonporous crystallographically ordered alpha-Al_2O_3 which was composed to spherical shape, and the porous amorphous gamma-Al_2O_3 which was composed to spherical or non-spherical or irregular hexagonal shape. Gamma-Al_2O_3 is used as a catalyst by itself, and also used as adsorbent because of its porous structure [1, 2].

Gamma alumina is used as a support alone, or as a support of active metals in catalysis reactions due to its high thermal stability and the ability to be shaped into mechanically stable extrudes and pellets, also alumina is a poly anion of positive charge at pH values below 7 and negative at higher values, offering many possibilities to bind many ionic catalyst precursors [3].

Supported nano alumina with high surface area and pore volume is used extensively as catalyst, catalytic supports, and adsorbent for chemical processes. The surface of the nano particles plays an important role in their catalytic properties [4, 5 and 6].

The starting materials of synthesis nano gamma alumina are either expensiveand sensitive to moisture content like aluminium alkoxides or cheap and available materials like aluminium salts, clays, and pure aluminium powder [6]. different materials like; surfactant, dispercents and tamplets were used in the synthesis of nano gamma alumina with high texture properties using different methods like; sol gel, hydrothermal treatment, precipitation, lazer oblation, solution composition, spray pyrolysis…etc [7, 8, 9 and 10] . Aguado et al. 2005 [11] used sol-gel techniques to prepare nano gamma alumina using two types of surfactant and aluminum alkoxides source of aluminum, and hydrochloric acid. Uniform structure of produced catalyst was achieved with increasing acid/Al source (wt/wt) ratio, while decreasing the amounts of surfactant used causes decreasing in pore size of the prepared catalyst. Yi Jian Hong 2009 [12] used precipitation technique to prepare nano gamma alumina using sodium aluminate and oxalic acid as a precipitation agent. The effect of the pH of sodium aluminate and oxalic mixtures and the pH of washing at pH range 7-9 on the purity of the catalyst was studied, and found that Pure crystalline gamma alumina was obtained using pH >8, while beta alumina was obtained at pH <8. Ming Bao et.al.2010 [13] prepared nano gamma alumina in the presence of two sources of alumina, Cetyltrimethylammonium bromide (CTAB) as surfactant, citria acid, and different molar ratios of sodium citrate by double hydrothermal treatment using auto clave with temperature 170 ^{0}C for 24 hrs,the optimum results acting in 0.2 molar ratio of sodium citrate with respect to aluminium salts with surface area 398 m^2/gm, and pore volume 0.59 m^2/gm [12]. Dahlan et.al. 2012 [14] prepared nano alumina adding urea as a fuel with molar ratio 29:153:1:2028 of aluminium salt,CTAB,urea,and water using hydrothermal method producing 203 m^2/gm, 0.14 cm^3/gm of nano gamma alumina. Faramawy et.al. 2014 [15] synthesis of nano gamma alumina by hydrothermal technique using microwave irradiation for the crystallization of aluminium salt and CTAB surfactant and found that the increasing in the time and power of the reaction leads to increase the crystinallity and the texture properties of the prepared catalyst .Hawraa 2016 [16] prepared nano gamma alumina with 56 nm, 256 m^2/gm surface area, and 0.374 cm^3/gm pore volume by sol gel method using aluminum chloride dissolved in ethanol and ammonia.

The aim of this work is to prepare nano γ alumina by using double hydrothermal treatment method, and to study the effect of crystallization time and acid type on the characterstics of prepared catalyst like; XRD, AFM, surface area, pore volume and SEM.

Experimental Work

Materials

Aluminum nitrate nona hydrate ($Al(No_3)_3.9H_20$, 100% purity, Himedia Company), and sodium aluminate ($NaAlO_2$, 100 % purity, Himedia Company) were used as sources of aluminium. Cetyltrimethylammonium bromide (CTAB, 99% purity, Wuhan kemi-Works, Chemical Co.Ltd) was used as a surfactant, different acids like; cirtic acid (CA, 100% purity), acetic acid (AA, 100% purity), hydrochloric acid (HCL, 99% purity), and nitric acid(HNO_3, 99% purity) acting from Riedel-De Haen were used as a structure direct agent, and finally sodium hydroxide (NaOH, 99% purity, Sigma) was used to adjust the ph of the mixtures.

Preparation of Nano γ *Alumina*

The nano gamma alumina was prepared depending on the previous work of Ming Bao et. al. 2010 [13] by dissolving aluminium nitrate nonahydrate, citric acid and CTAB surfactant in suitable amount of dionized water, then sodium aluminate was dissolved in suitable amount of dionized water and added drop by drop to the first mixture under vigorous stirring 1000 rpm. The molar composition of the mixture AL/CTAB/citric acid/H_2O is 1.0/0.1/0.2/125, a white gel formed immediately, after further stirring for 3 hrs, the mixtures adjusted at pH equal to 9. The produced gel was then placed in a Teflon-Lined stainless steel auto clave to start the crystallization at 180 ^{0}C crystallization temperatures for crystallization time of 12, 24, 48, and 72 hrs. The crystallization product was filtered using nano filter papers (slow), and washed by deionized water and ethanol for several times to eliminate the contaminants. The product was dried at temperature 100 ^{0}C for 24 hrs, and then calcined at 600 ^{0}C. The procedure above was repeated using acetic acid, hydrochloric acid, and nitric acid instead of citric acid.

Characterization of NanoγAlumina

X-ray diffraction analysis was used to characteristic the phase of the prepared samples using X-Ray Diffract meter type Shimadzu SRD 6000, Japan, with Cu wave length radiation (1.54060) in the 2 theta range from 10-80 ^{0}, and fixed power source (40 Kv, 30 mA) by the Ministry of Science and Technology. The surface area, and pore volume of the samples were conducted at the Petroleum Research and Development Center in Baghdad using Brunauer Emmett and Teller (BET) method with Thermo analyzer/USA device. The average particle size and the morphology of surface of each sample were calculated at the Department of Chemistry / College of Science /University of Baghdad using Atomic Force Microscope device (type Angstrom, Scanning Probe Microscope, Advanced Inc, AA 3000, USA). The morphology of the structure of nano gamma alumina was studied using FEI NOVA NANO SEM device located at Chemical Engineering department / Tehran University. The specimen of prepared nano gamma alumina was dispersed in ethanol and coated by gold using special cell.

Results and Discussions

X-Ray Diffraction (XRD)

From the Figures 1 to 7 it is clear that all the coordinates of the peaks of prepared samples were accepted the three strong standard peaks of gamma alumina (311-65b intensity-2.39 d spacing), (400-80b intensity-1.98 d spacing), and (410-100 b intensity-1.4 d spacing) which represents the pure substantial crystallization of international alumina card (JCPDS) files no. (29.0063). All the XRD-diffraction Figures from 1 to 7 represented high crystalline gamma alumina at pH equal to 9. The broading of the peaks may be occurred due to the role of the CTAB surfactant used in the process which was released after calcination producing nano particle size [17, 11]. The increasing in crystallization time from 12 to 72 hrs causes little increasing in crystinallity and increasing in the sharpness of the peaks shown in Figures 1 to 4 as observed by Marzieh Jalilpour, 2012 [18]. The effect of varying the acid type on the XRD diffraction is shown in the Figures 1, 5, 6 and 7. The broading in the peaks occurred from using hydrochloric and nitric acids are larger than that occurred from using weak acids like; citric and acetic acids with the same degree of crystinallity because these experiments were attempted at the same conditions.

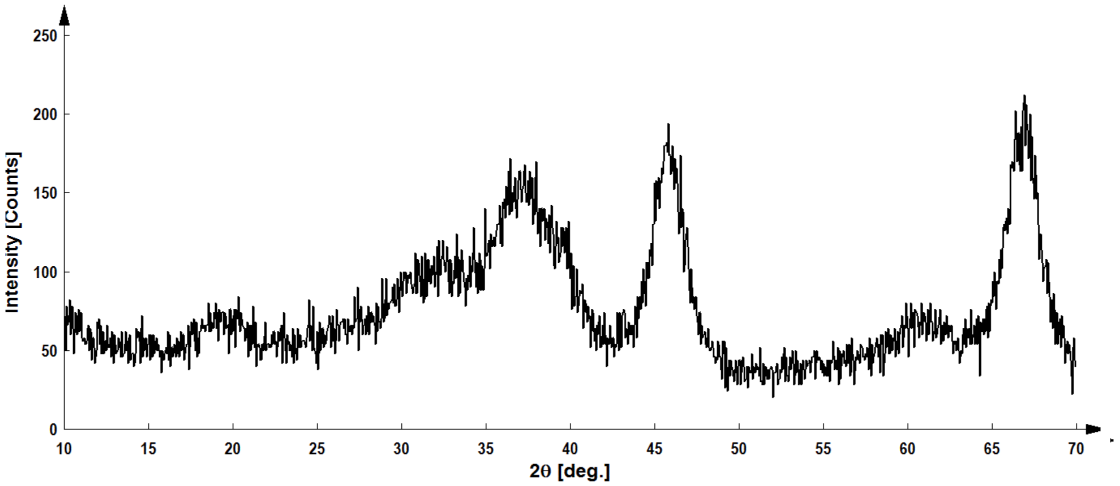

Fig. 1: XRD diffraction of the nano gamma alumina prepared using citric acid at 180 ^{0}C crystallization temperature, 12 hrs crystallization time and calcination temperature 600 ^{0}C

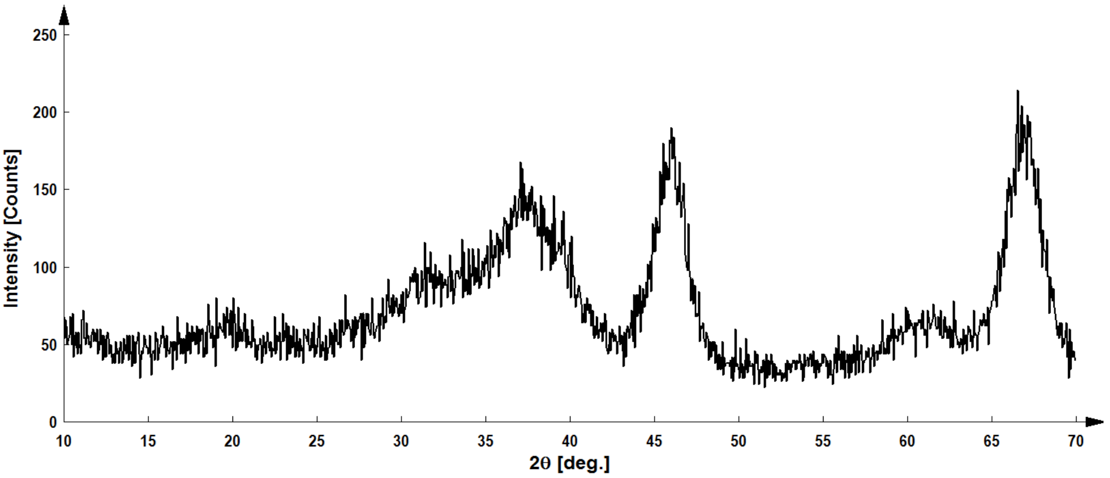

Fig. 2: XRD diffraction of the nano gamma alumina prepared using citric acid at 180 ^{0}C crystallization temperature, 24 hrs crystallization time and calcination temperature 600 ^{0}C

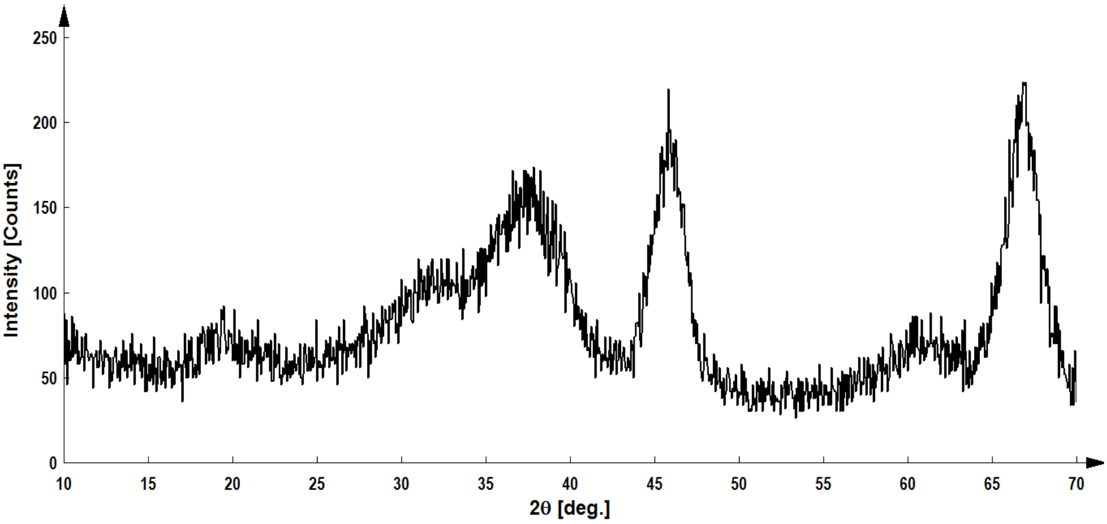

Fig. 3: XRD diffraction of the nano gamma alumina prepared using citric acid at 180 ^{0}C crystallization temperature, 48 hrs crystallization time and calcination temperature 600 ^{0}C

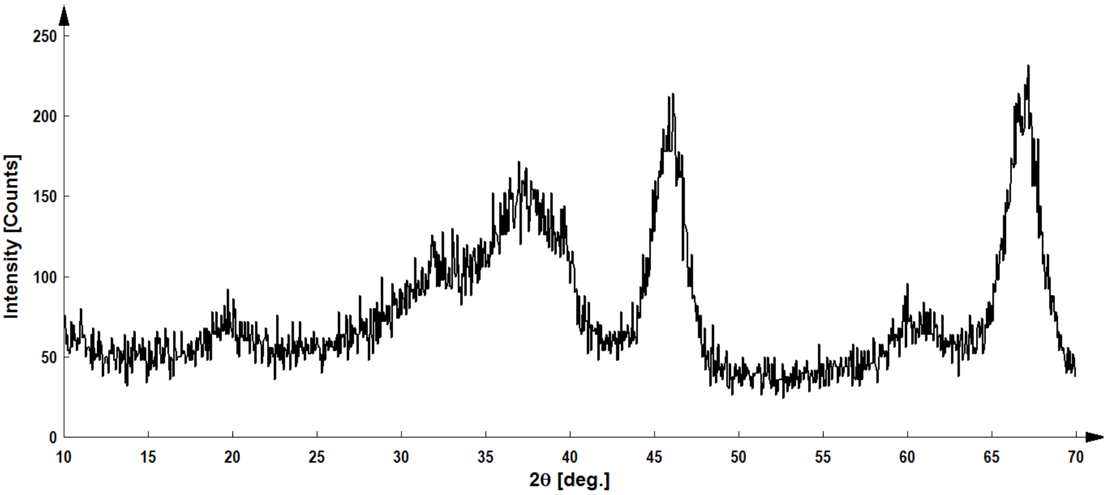

Fig. 4: XRD diffraction of the nano gamma alumina prepared using citric acid at 180 ^{0}C crystallization temperature, 72 hrs crystallization time and calcination temperature 600 ^{0}C

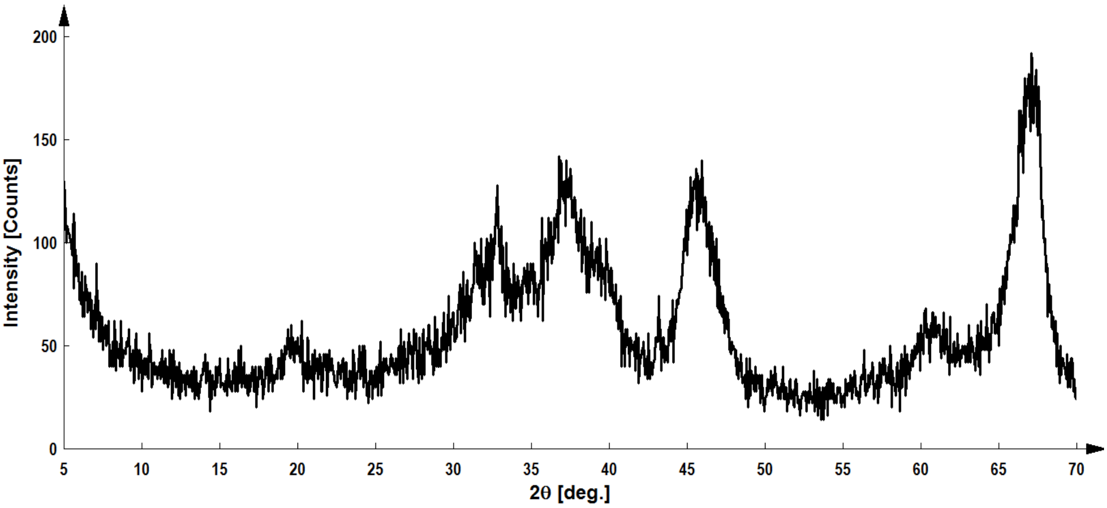

Fig. 5: XRD diffraction of the nano gamma alumina prepared using acetic acid at 180 ^{0}C crystallization temperature, 12 hrs crystallization time and calcination temperature 600 ^{0}C

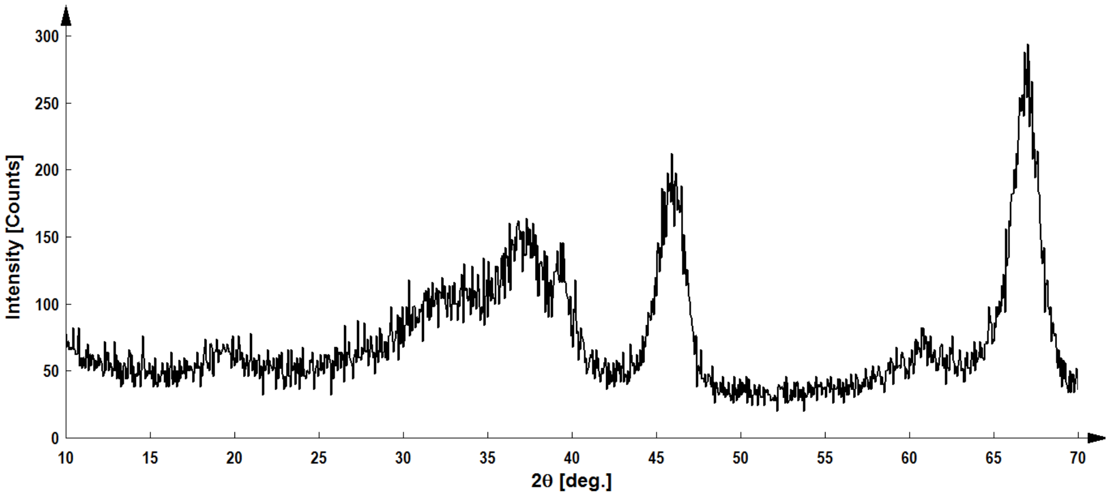

Fig. 6: XRD diffraction of the nano gamma alumina prepared using hydrochloric acid at 180 ^{0}C crystallization temperature, 12 hrs crystallization time and calcination temperature 600 ^{0}C

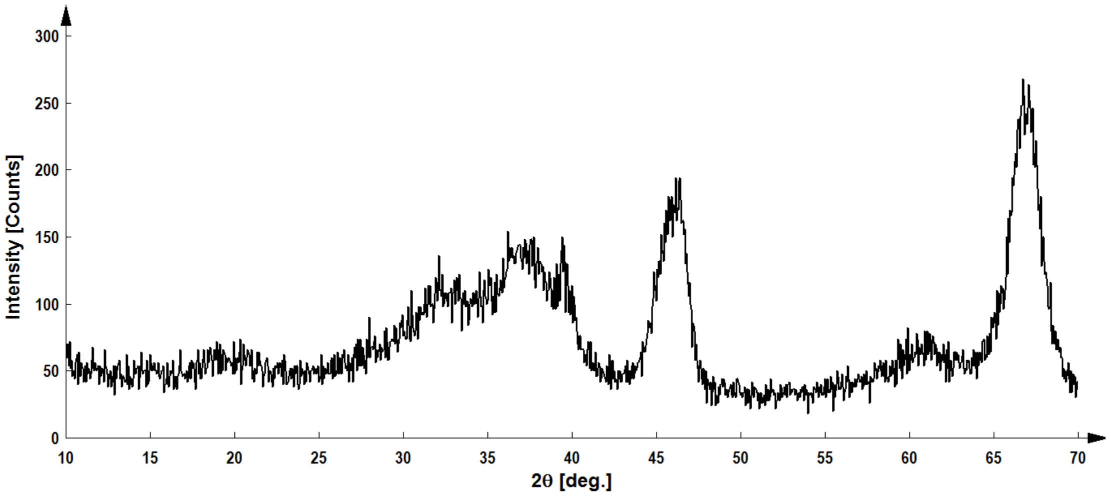

Fig. 7: XRD diffraction of the nano gamma alumina prepared using nitric acid at 180 ^{0}C crystallization temperature, 12 hrs crystallization time and calcination temperature 600 ^{0}C

Surface Area and Pore Volume

The surface area and pore volume of the nano catalyst play a very important role for the activity of the nano catalyst, because high surface area leads to high active sites causes increasing in activity. Table 1 shows the results of surface area and pore volume of the samples for different conditions.

Keeping the mixtures at 180 ^{0}C crystallization temperature during 24 hrs may allow the particles to become close to each other causes decreasing in surface area besides the reduction in pore volume. The increasing in crystallization time from 48 to72 hrs did not effect on the results of surface area and pore volume because the stable structure of boehmite occurred causes no change in these values as mentioned by Yvan J.et al. 2012. The addition of acids beside the surfactant to the starting materials had very important role, because it represents the bridge between the surfactant and the source of aluminum ions, besides its role as a dispersant agent as mentioned by Ki Wom Jun et al. 2009. The dispersant degree varies from acid to another one in the order of hydrochloric acid >nitric acid >acetic acid > citric acid prevent the agglomeration of the particles causes low surface area with high pore volume.

Table 1: the values of surface area and pore volume at different conditions

Synthesis conditions	Acid type	Surface area,m^2/gm	Pore volume,cm^3/gm
180^0C,12hrs,and 600^0C	Citric acid	383.0	0.430
180^0C,24hrs,and 600^0C		338.8	0.430
180^0C,48hrs,and 600^0C		339.0	0.430
180^0C,72hrs,and 600^0C		338.8	0.365
180^0C,12hrs,and 600^0C	Acetic acid	203.0	0.500
180^0C,12hrs,and 600^0C	Hydrochloric acid	183.4	0.540
180^0C,12hrs,and 600^0C	Nitric acid	183.1	0.500

Particle Size

The atomic force microscopy (AFM) method was used to find the average particle size, particle size distribution, and the results of the particle size are listed in Table 2.

The average particle size of the prepared nano alumina was in the nano scale catalyst for all crystallization temperatures. Increasing the crystallization time at 180 ^{0}C causes drop in surface area and pore volume of the prepared samples, and the particles became bigger due to agglomeration reaching to the levels out of the nano scale level at crystallization time higher than 24 hrs as observed by Y van.et al.2012 [19]. Using variable acids in the presence of the surfactant produced different ranges of average nano gamma alumina. hydrochloric and nitric acids produced nano gamma alumina with average particle size less than 75 nm,while weak acids like; aceti and citric acids produced nano gamma alumina with average particle size above 95 nm.These results are near the results obtained by Hawraa 2016 [16].

Table 2: the values of particle size distribution and average particle size at different conditions

Synthesis conditions	Acid type	particle size distribution,nm	average particle size,nm
180^0C,12hrs,and 600^0C	citric acid	75-160	92.72
180^0C,24hrs,and 600^0C		50-140	103.17
180^0C,48hrs,and 600^0C		40-160	106.59
180^0C,72hrs,and 600^0C		70-150	110.37
180^0C,12hrs,and 600^0C	acetic acid	70-130	96.44
180^0C,12hrs,and 600^0C	hydrochloric acid	35-100	72.37
180^0C,12hrs,and 600^0C	nitric acid	55-130	74.82

Scanning Electron Microscopy (SEM)

The morphology of the surface of prepared nano gamma alumina samples is obtained at magnification of 60 kx and zoom of 500 nm. Increasing crystallization time shown in Figures 8 to 11. Using crystallization time above 12 hrs causes agglomeration in particles, and reduces nano particles lead to drop in surface area and pore volume as observed by Y van. et al. 2012 [19]. Uniform hexagonal shape of particles with low agglomeration is observed by using weak acids like; citric and acetic acids shown in Figures 8 and 12. Agglomeration and formation of clusters is observed by using strong hydrochloric and nitric acids shown in Figures 13 and 14 leads to low surface area with high pore volume. This morphology is the same with the morphology acting by hawraa 2016 [16].

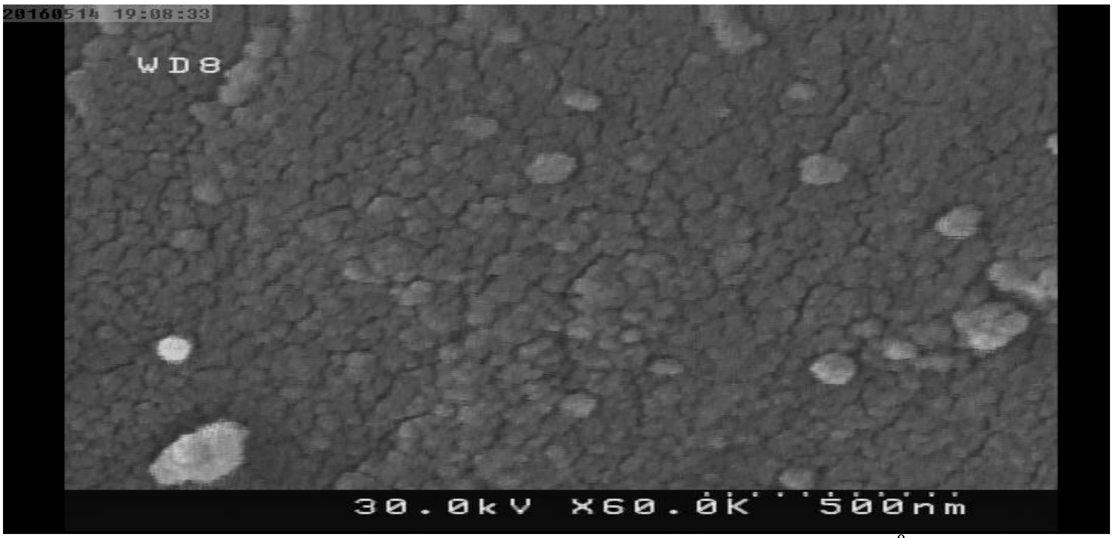

Fig. 8: SEM image of the nano gamma alumina prepared using citric acid at 180 ^{0}C crystallization temperature, 12 hrs crystallization time and calcination temperature 600 ^{0}C

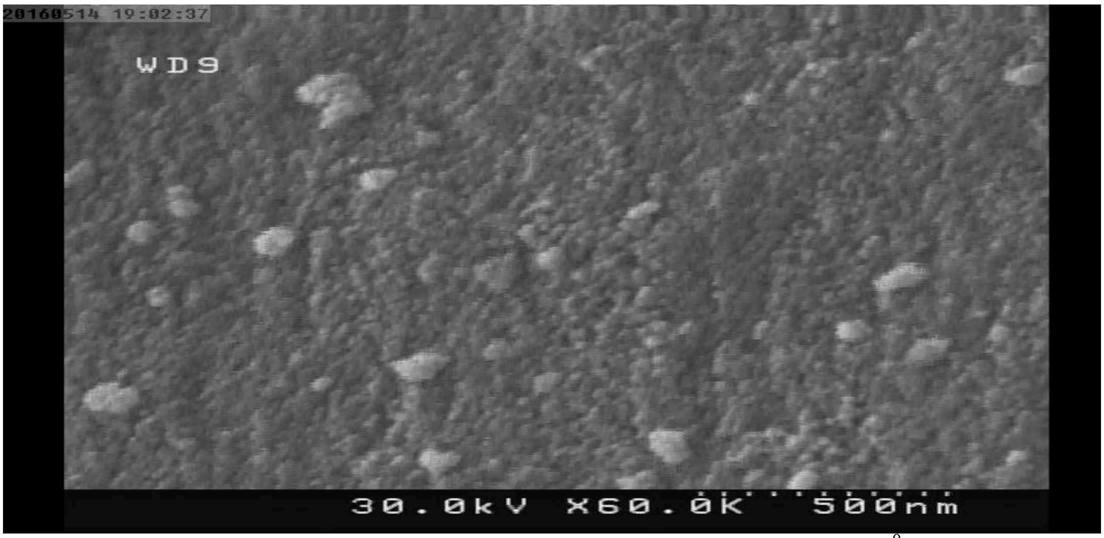

Fig. 9: SEM image of the nano gamma alumina prepared using citric acid at 180 ^{0}C crystallization temperature, 24 hrs crystallization time and calcination temperature 600 ^{0}C

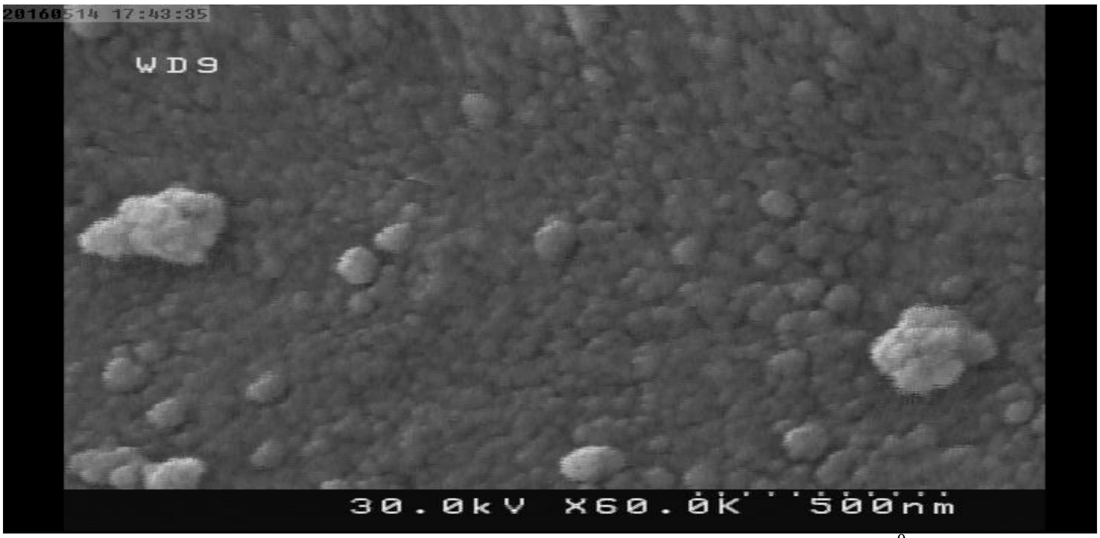

Fig. 10: SEM image of the nano gamma alumina prepared using citric acid at 180 ^{0}C crystallization temperature, 48 hrs crystallization time and calcination temperature 600 ^{0}C

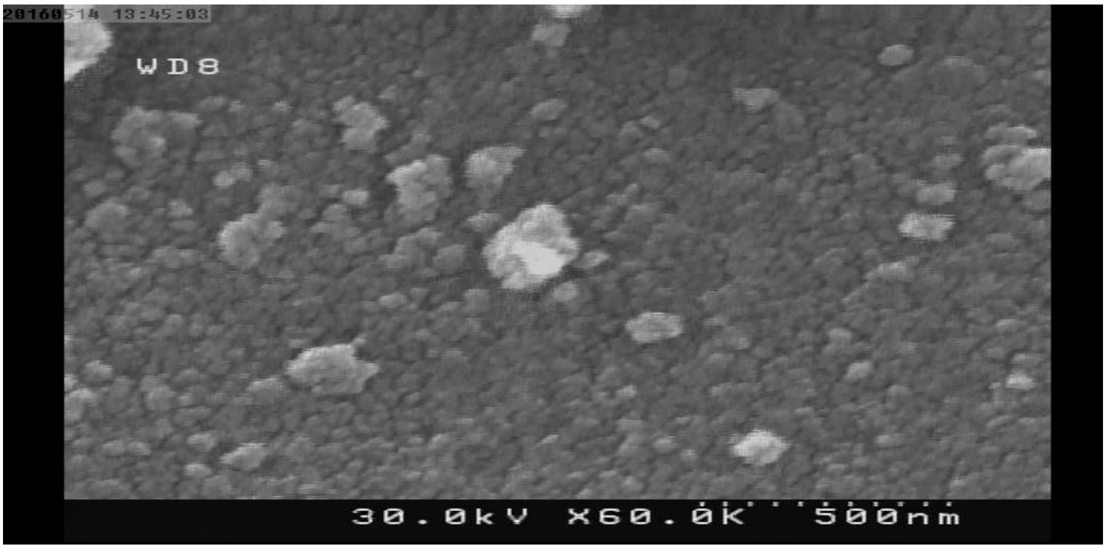

Fig. 11: SEM image of the nano gamma alumina prepared using citric acid at 180 ^{0}C crystallization temperature,72 hrs crystallization time and calcination temperature 600 ^{0}C

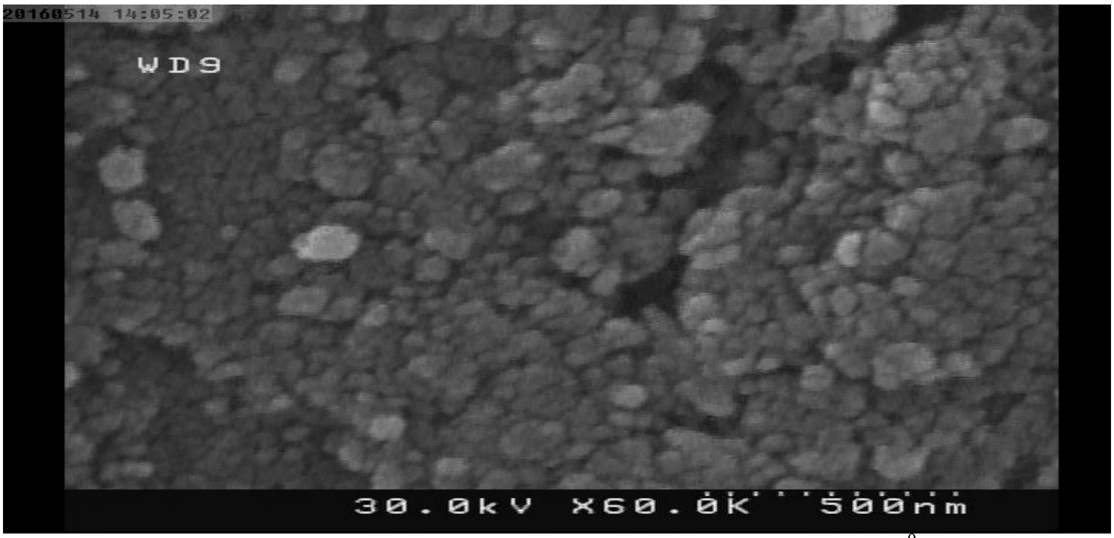

Fig. 12: SEM image of the nano gamma alumina prepared using acetic acid at 180 ^{0}C crystallization temperature, 12 hrs crystallization time and calcination temperature 600 ^{0}C

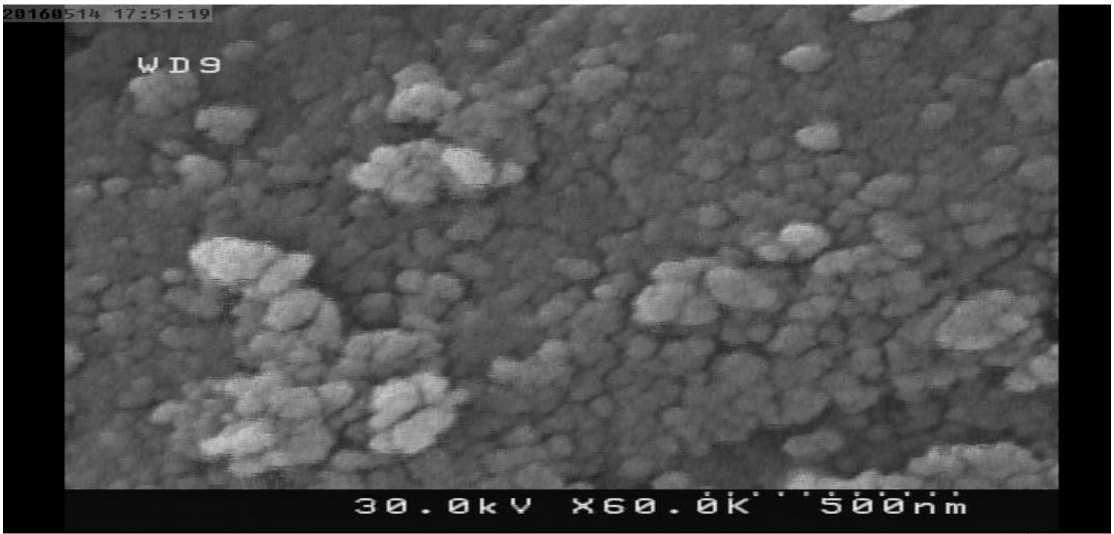

Fig. 13: SEM image of the nano gamma alumina prepared using hydrochloric acid at 180 ^{0}C crystallization temperature, 12 hrs crystallization time and calcination temperature 600 ^{0}C

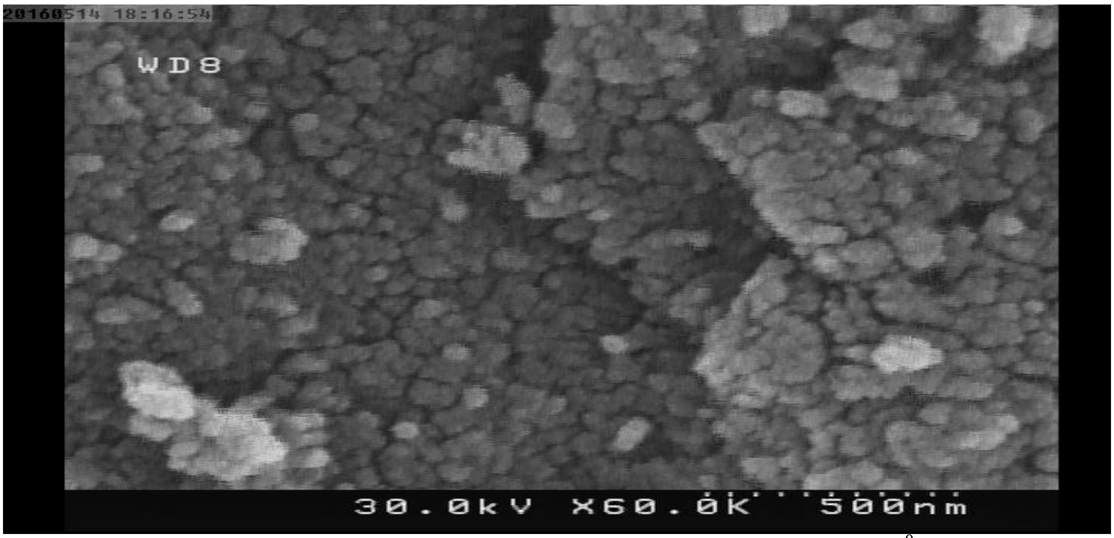

Fig. 14: SEM image of the nano gamma alumina prepared using nitric acid at 180 ^{0}C crystallization temperature, 12 hrs crystallization time and calcination temperature 600 ^{0}C

Conclusions

Nano gamma alumina was successfully synthesized using double hydrothermal method in the presence of CTAB surfactant using different crystallization times, and different structure direct agent. XRD diffractions represent the crystalline nano gamma alumina pure from surfactant. The sharpness of the peaks increased with increasing of crystallization time. Using strong acids causes broading in peaks larger than that occurred in peaks using weak acids. The surface area, pore volume, and average particle size were decreased with increasing crystallization time. The best result of surface area obtained using citric acid at 12 hr crystallization time, while the best results of pore volume and average particle size obtained using hydrochloric acid at 12 hr crystallization time. Low agglomeration with hexagonal structure obtained using weak acids, while agglomeration occurred and clusters formed using strong acids.

References

1. Speight[b], J.G., 2002, ″Chemical and process design handbook", the McGraw-Hill Companies.
2. Suzuki,, M., 1990, ″Adsorption Engineering handbook" ,Kodansha Ltd, Tokyo and Elsevier Science B.V., Amsterdam.
3. Zaki, T., Mohmed, N.H., Nessim, M.I., and Salam, H. A.,2013, ″Characterization znd application of nano-alumina sorbents for desulfurization and dearomatization of suez crude petroleum", Fuel processing technology, 106:625-630.
4. Marino F., Descorme C., and Duprez D., 2005, "Supported base metal catalysts for the preferential oxidation of carbon monoxide in the presence of excess hydrogen", j. of Appl.Cat. vol.58, pp. 175-183.
5. Carmo M., Paganin V.A., Roselen J.M., 2005, "Alternative supports for the preparation of catalysts for low temperature fuel cells: the use of carbon nanotubes", j. of power sources, vol.142, pp. 169-176.
6. Parida, K.M., and Amaresh C., 2009, "Synthesis and Characterization of nano-Sized porous Gamma –Alumina by

Control Precipitation Method", Institute of Minerals and Materials Technologies, India, vol (113), 244-248.

7. Chengchao Liu, Jinlin Li, Kongyong Liew, and Junjiang Zhu, 2012, "An Enviromental friendly method for the synthesis of nano-alumina with controllable morphologies", J. of RCS advances, vol.2, pp.8352-8358.
8. Veeradate Piriyawong, Voranuch Thongpool, and Piyapong asanithi, 2012, "Praparation and characterization of alumina nanoparticles in Deionized water using lazer ablation technique", J. of nanomaterials, article ID 819403, 6 pages.
9. Bustan Afruz A., and Tafreshi M.J., 2014, "Synthesis of gamma alumina nanoparticle by different combustion modes using ammonium carbonate", Indian J. of pure and applied physics, vol.52, pp. 378-385.
10. Yousif Jawad, 2009, "Synthesis and characterization of zeolite nanoparticles catalysis used for N-hexane conversion.", Phd thesis, University of Baghdad, college of engineering, chemical engineering department.
11. Aguado J., Escola J. M., and Castro M.C., 2005, "Sol-gel synthesis of nanostructured gamma alumina templated by cationic surfactant",j. of micro. And meso. Mater., vol.82, pp.181-192.
12. Yi Jian Hong, Sun You Yi, and Gao Jian Feng, 2009 "Synthesis of crystalline γ alumina with high purity", Trans. Nonferrous Met. Soc. China, vol.19 pp.1237-1242.
13. Ming Bo Yue, Wen Qian Jiao, Yi Meng Wang, and Ming Yuan He, 2010, "CTAB-directed synthesis of mesopores gamma alumina promoted by hydroxyl polyacids", J.of Micro., and Meso. Mat., vol.132, pp.226-231.
14. Dahlan, I Nyoman Marsih, and JoonJai Panpranot, 2012, "gamma alumina nanotubes prepared by hydrothermalmethod as support of iron,cobalt,and nickel for Fischer-Tropsch catalysts", J. of chemistry and materials research, vol.2, No.3, pp.31-38.
15. Faramawy S., El-shall M. S., and Abd El Wahed M.G., 2014 "Synthesis of high surface area gamma alumina by microwave irradiation process", J. of American science, vol.10, pp.9.
16. Hawraa H., 2016, " Preparation of Nano Ni-Mo/ϒ-Al_2O_3 Catalyst for Hydrodesulphurization of Iraqi gas oil", MSC.thesis, Chemical engineering department, college of engineering, university of Baghdad.
17. Kianinia Y., Darban A.K., and Rahnama B., 2014, "Synthesis of nano sized mesoporous gamma alumina powder from domestic hamedan kaolin", Iranian j. of materials and eng., vol.12, no.1, pp.59-65.
18. Marzieh Jalilpour, and Mohammad Fathalilou, 2012, "Effect of aging time and calcination temperature on the cerium oxide nanoparticles synthesis via reverse co-precipitation method", Int. J. of physics and science, vol.7, no.6, pp.944-948.
19. Y van J.O., Maria R., 2012 "Synthesis of high surface area γ alumina from aluminium scrap and its use for the adsorption of metals:Pb(II),Cd(II), and Zn(II)", J. of applied science, vol.258, pp.10002-10011.
20. Ki Won jun, Yun Jo Lee, Scung Moon Kim, 2009, "Method of preparing boehmite and gamma alumina with high surface area", US patent, No.0104108 A1.