IJCPE
Iraqi Journal of Chemical and Petroleum Engineering

Iraqi Journal of Chemical and Petroleum Engineering
Vol.18 No.1 (March 2017) 1- 16
ISSN: 1997-4884

University of Baghdad
College of Engineering

The Effect of Temperature on the Synthesis of Nano-Gamma Alumina Using Hydrothermal Method

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

Abstract

Nano gamma alumina was prepared by double hydrolysis process using aluminum nitrate nano hydrate and sodium aluminate as an aluminum source, hydroxyle poly acid and CTAB (cetyltrimethylammonium bromide) as templates. Different crystallization temperatures (120, 140, 160, and 180) ^{0}C and calcinations temperatures (500, 550, 600, and 650) ^{0}C were applied. All the batches were prepared at PH equals to 9. XRD diffraction technique and infrared Fourier transform spectroscopy were used to investigate the phase formation and the optical properties of the nano gamma alumina. N_2 adsorption-desorption (BET) was used to measure the surface area and pore volume of the prepared nano alumina, the particle size and the morphology of the surface of nano gamma alumina were estimated using AFM and SEM techniques ,respectively. All the samples represented pure nano gamma alumina with high crystalline and irregular hexagonal structure shape. The best results obtained were 456.5 m^2/gm surface area, 0.49 cm^3/gm pore volume, and 59.26 average particle size for the sample prepared at 180 ^{0}C crystallization temperature, and 500 ^{0}C calcinations temperature with nano spherical surface structure.

Key words: Gamma alumina, nanoparticle, double hydrothermal, CTAB.

Introduction

Aluminium oxide or alumina is the most cheap and effective oxide in the group of ceramic industry. Alumina is used in ceramic and metal manufacturing due to its hardness, abrasion resistance, and heat resistance, used in synthesis of electronic circuits due to its electrical insulation and low thermal conductivity [1]. 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 nanoparticles plays an important role in their catalytic properties [2, 3, and 4]. Different methods were used to prepare nano gamma alumina like; sol gel, hydrothermal treatment, precipitation, lazeroblation, solution composition, spraypyrolysis…etc [5, 6, 7 and 8]. The starting materials of synthesis nano gamma alumina are either expensive and sensitive to moisture content like aluminium alkoxides or cheap and available materials like aluminium salts, clays, and pure aluminium powder [4]. To produce nanoparticle with optimum conditions of purity, high surface area, and pore volume different structure-direct-agent like surfactant and others were used in the synthesis using either room temperature (sol gel) method or high temperature over 100 ^{0}C (hydrothermal treatment) by auto-clave reactors or microwave irradiation [9, 10].

Using of surfactant-sol gel-technique is accompanied with some problems during process represented by the fast condensation of the mixtures causes cracks of prepared gel and phase transformation by the thermal treatment during eliminating of surfactant rather than hydrothermal treatment [11]. Few reports were recognized using hydrothermal technique to prepare nano alumina like; Ming Bao et.al. 2010 prepared nano gamma alumina in the presence of two sources of alumina, 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]. Xiang Li et.al. 2011 [13] succeeded in the synthesis of nano gamma alumina using inorganic salt of alumina, ammonium carbonate, and 20000 molecular weight of PEG by hydrothermal treatment with auto-clave in the temperature 100 ^{0}C for 24 hrs, and calcination temperature 500 ^{0}C to produce nano gamma alumina with particle size between 10-38 nm, surface area 494 m^2/gm, and pore volume 1.1 cm^3. 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 [10] 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 [11] 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 temperature and calcination temperature on the characterstics of prepared catalyst like; XRD, FTIR, AFM, surface area, pore volume, and SEM.

Experimental Work

Materials

Aluminum nitrate nonahydrate ($Al(No_3)_3.9H_20$, 100% purity), and sodium aluminate ($NaAlO_2$, 100 % purity) were used as sources of aluminium. Cetyltrimethylammonium bromide (CTAB, 99% purity) was used as a surfactant, cirtic acid (CA, 100% purity) was used as a bridge between the aluminum source and the surfactant, and finally sodium hydroxide (NaOH, 99% purity) was used to adjust the pH of the mixtures.

Preparation of Nano γ - Alumina

The nano gamma alumina was prepared 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 different crystallization temperatures 120-180 ^{0}C for 12 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. Alumina powders produced from various crystallization conditions were dried at temperature 100 ^{0}C for 24 hrs, and calcined at 600 ^{0}c, while nano alumina which is crystallized at 180 ^{0}C calcined at different calcination temperatures 500- 650 ^{0}C to study the effect of the calcination temperature besides the crystallization temperatures on the characteristics of the prepared nano alumina.

Characterization of Nanoγalumina

The structure of the samples was obtained by X-ray diffraction analysis in the Ministry of Science and Technology. Analysis was carried out 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 (40Kv, 30mA). To study the functional groups and the characteristics of the bonds of the prepared samples Fourior –transform infrared spectroscopy (FTIR) applied using (IR-Affinity,S himazdo, Japan) with wave range between 400-4000 CM^{-1} loacated at the University of Baghdad /College of Science / Central Environmental Laboratory, the samples were made by pressing the to disk shape after added 1% nano alumina to 99% KBr. The texture properties 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. The average particle size and the morphology of surface of each sample were calculated at the University of Baghdad /College of Science /Department of Chemistry 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 prepared samples represent gamma-alumina after comparison with international alumina card (JCPDS) files no. (29. 0063) where they 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 substantial crystallization. These figures represent the high crystalline gamma alumina because the pH of the operation condition is over 8 while using pH under 8 leads to produce beta alumina which very easy transform to alpha alumina after thermal treatment [16]. It is clear that the broading of the peaks occurs due to the role of the CTAB surfactant used in the process producing nano particle size while the surfactant is released after calcinations [17, 18]. The increasing in crystallization temperature from 120 ^{0}C to 180 ^{0}C in Figures 1 to 4 leads to more matching of the (d) spacing and the intensity between the standard peaks and the peaks of the samples prepared, and any increasing in crystallization temperature leads to increase the intensity (crystinallity) and some of the particles were solubilized and grain growth occurred causes enlargement of the crystal size [19].The increasing in calcinations temperature Figures 4 to 7 causes increasing in crystinallity of the prepared samples beginning from 500 ^{0}C which represents width of the peaks due to low crystinallity to the high crystalline and sharp peaks in the calcinations temperatures 600, 650 ^{0}C [19, 20].

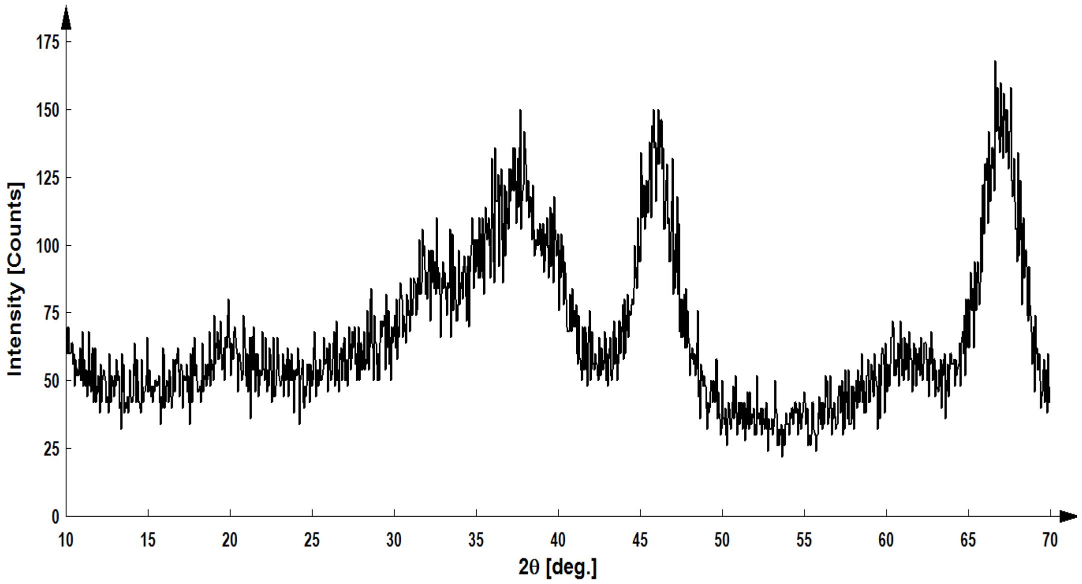


Fig. 1: XRD diffraction of nano gamma alumina prepared at 120 ^{0}C crystallization temperature and 600 ^{0}C calcination temperature

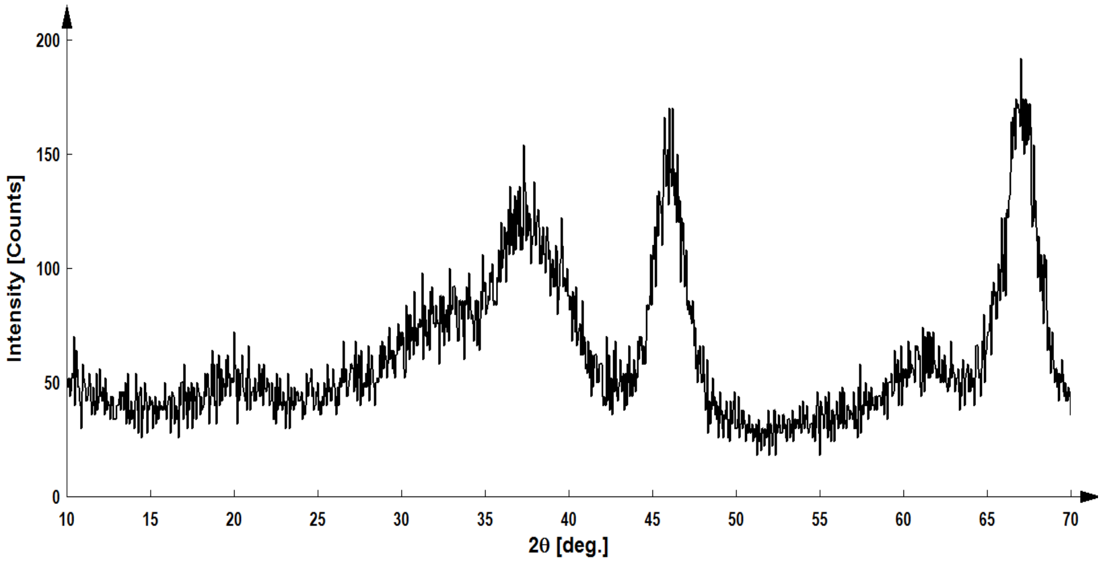


Fig. 2: XRD diffraction of nano gamma alumina prepared at 140 ^{0}C crystallization temperature and 600 ^{0}C calcination temperature

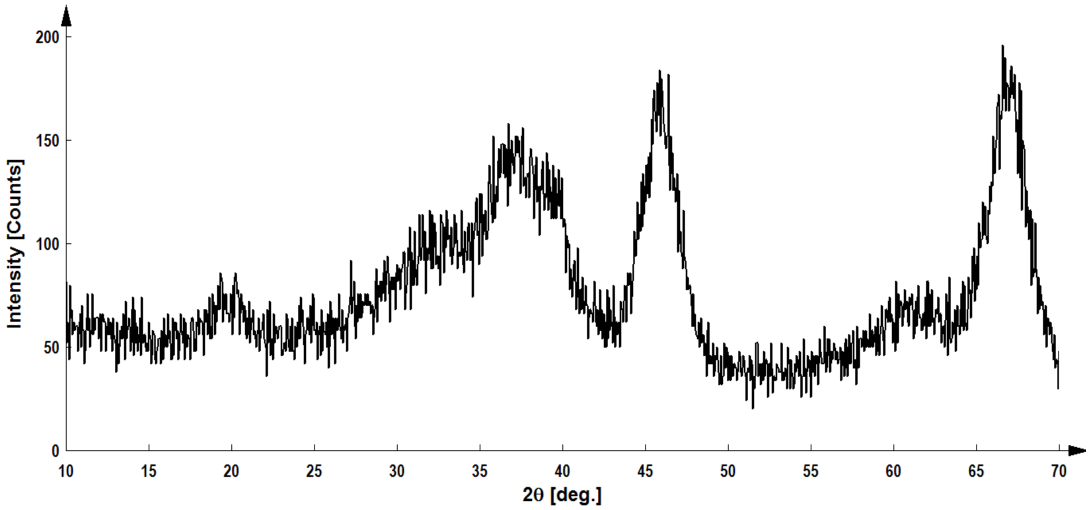


Fig. 3: XRD diffraction of nano gamma alumina prepared at 160 ^{0}C crystallization temperature and 600 ^{0}C calcination temperature

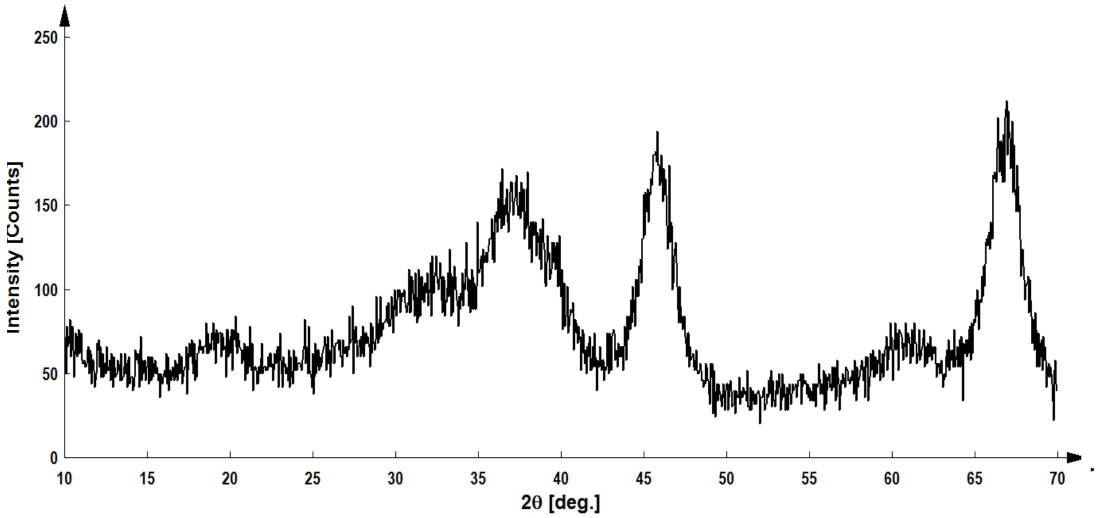


Fig. 4: XRD diffraction of nano gamma alumina prepared at 180 ^{0}C crystallization temperature and 600 ^{0}C calcination temperature

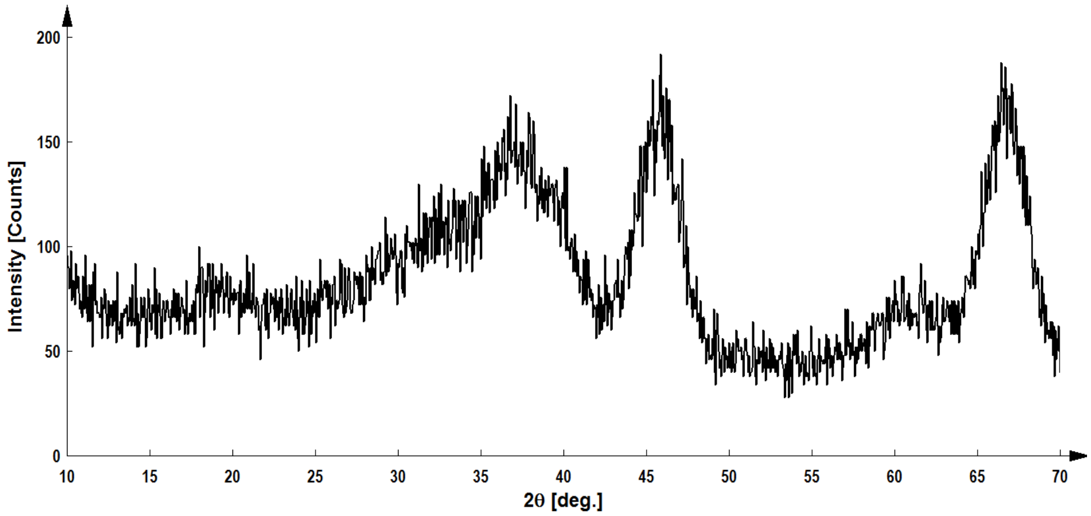


Fig. 5: XRD diffraction of nano gamma alumina prepared at 180 ^{0}C crystallization temperature and 500 ^{0}C calcination temperature

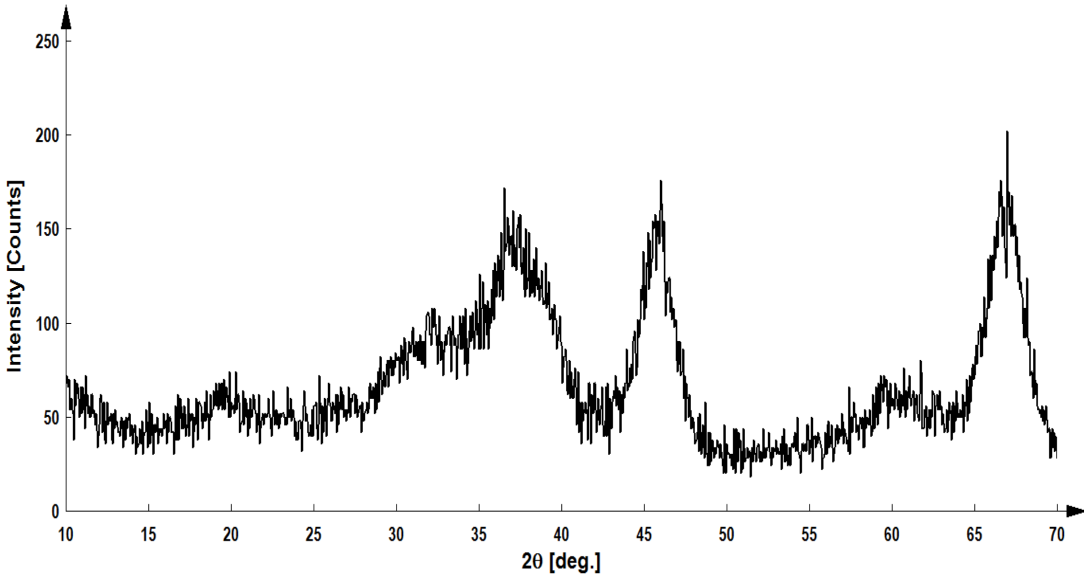


Fig. 6: XRD diffraction of nano gamma alumina prepared at 180 ^{0}C crystallization temperature and 550 ^{0}C calcination temperature

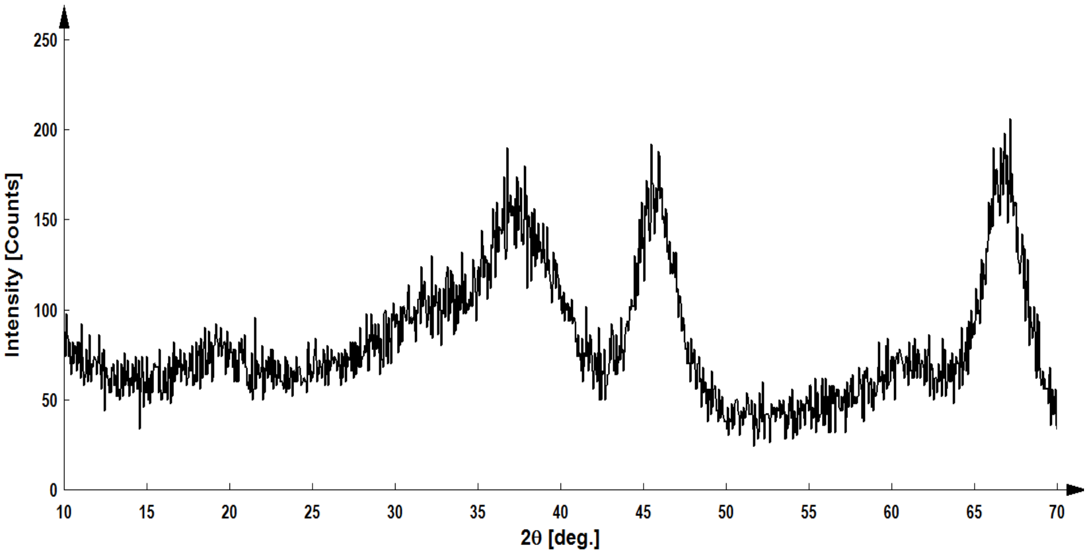


Fig. 7: XRD diffraction of nano gamma alumina prepared at 180 ^{0}C crystallization temperature and 650 ^{0}C calcination temperature

Fourier Transport Infrared (FTIR) FTIR-spectra of the prepared nano gamma alumina are shown in Figures from 8 to 14 shows large bands in the region between 400-1000 CM^{-1} represent the stretching vibration of Al-O-Al bands, the broad bands between 500-750 CM^{-1} refers to gamma alumina with nanoparticle size [17, 21]. The absence of bands around 1371CM^{-1} refers to absence of surfactant after calcination in the prepared samples [17], while The absence of bands around 1380 CM^{-1} refers that the samples are free from No_2 after calcination which is clear from its white colour [7]. The bands around 1640 CM^{-1} and 3500 CM^{-1} represent the bending bands of OH bands [22], so that these results of broad bending and stretching bands leads to prepare pure nano gamma alumina which are in agreed with the results obtained from XRD diffraction.

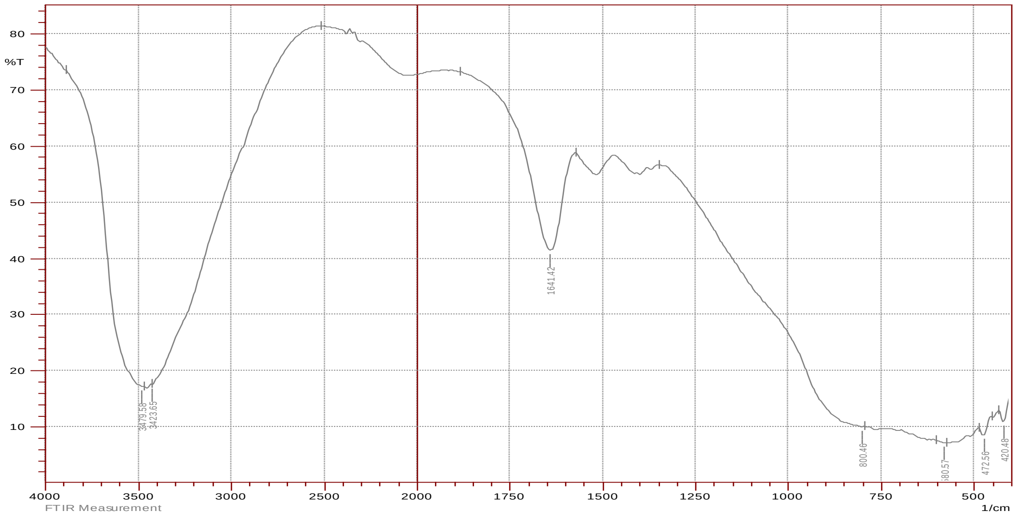


Fig. 8: FTIR-spectra of the nano gamma alumina prepared at 120 ^{0}C crystallization temperature and calcination temperature 600 ^{0}C

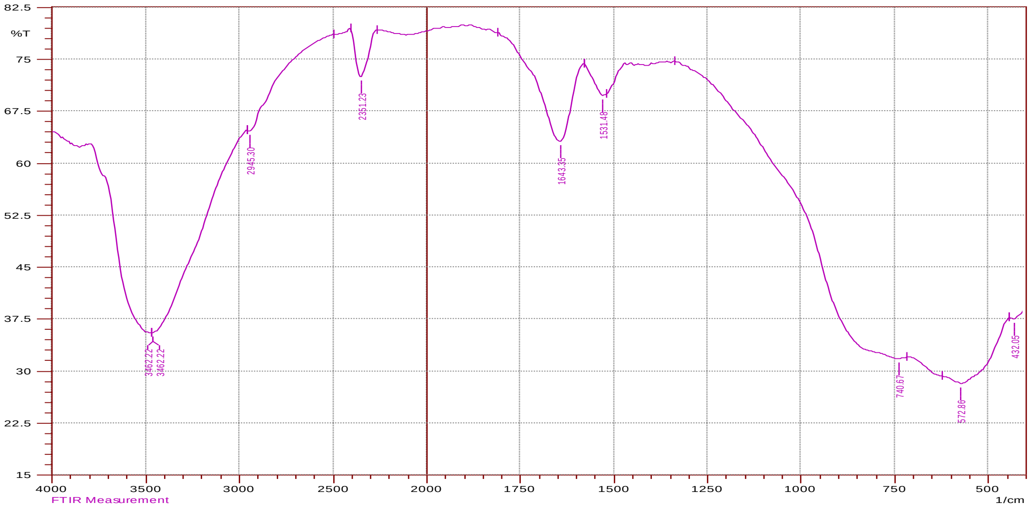


Fig. 9: FTIR-spectra of the nano gamma alumina prepared at 140 ^{0}C crystallization temperature and calcinations temperature 600 ^{0}C

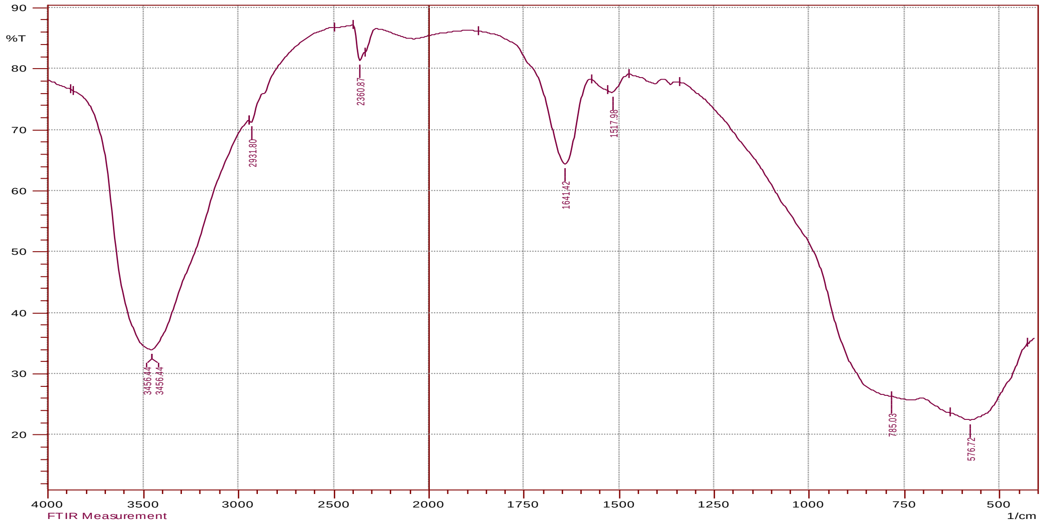


Fig. 10: FTIR-spectra of the nano gamma alumina prepared at 160 ^{0}C crystallization temperature and calcinations temperature 600 ^{0}C

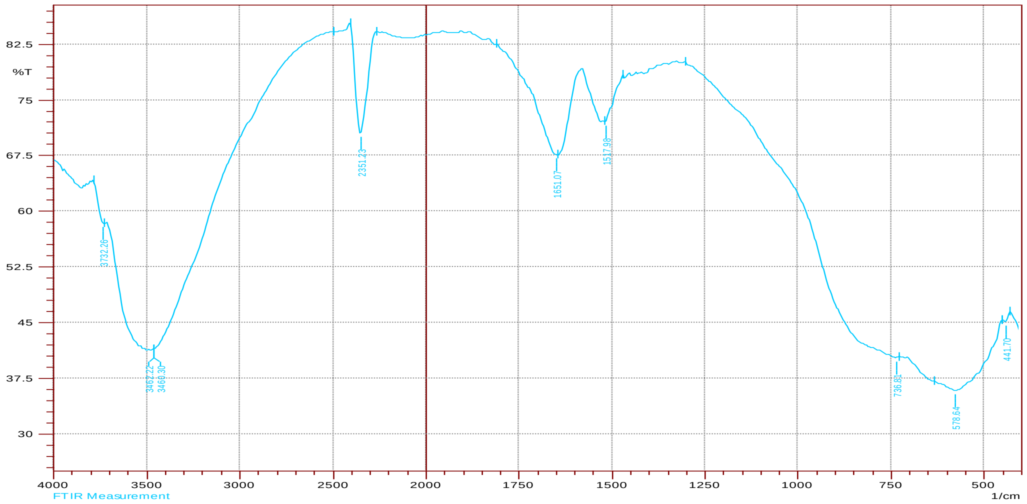


Fig. 11: FTIR-spectra of the nano gamma alumina prepared at 180 ^{0}C crystallization temperature and calcinations temperature 600 ^{0}C

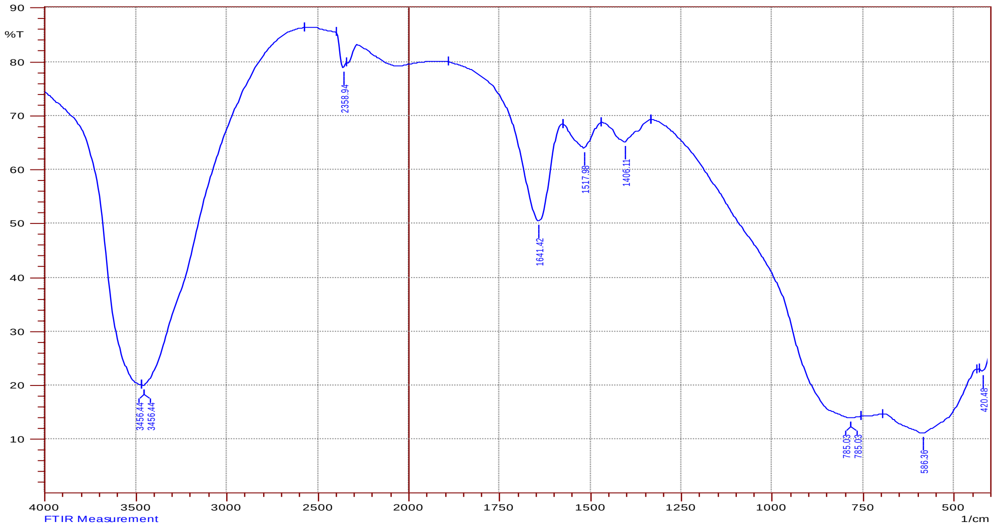


Fig. 12: FTIR-spectra of the nano gamma alumina prepared at 180 ^{0}C crystallization temperature and calcinations temperature 500 ^{0}C

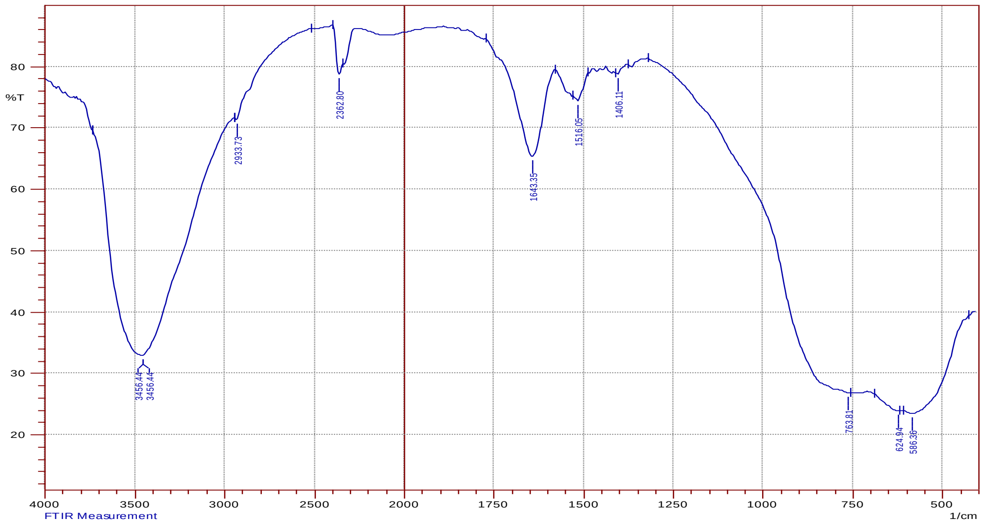


Fig. 13: FTIR-spectra of the nano gamma alumina prepared at 180 ^{0}C crystallization temperature and calcinations temperature 550 ^{0}C

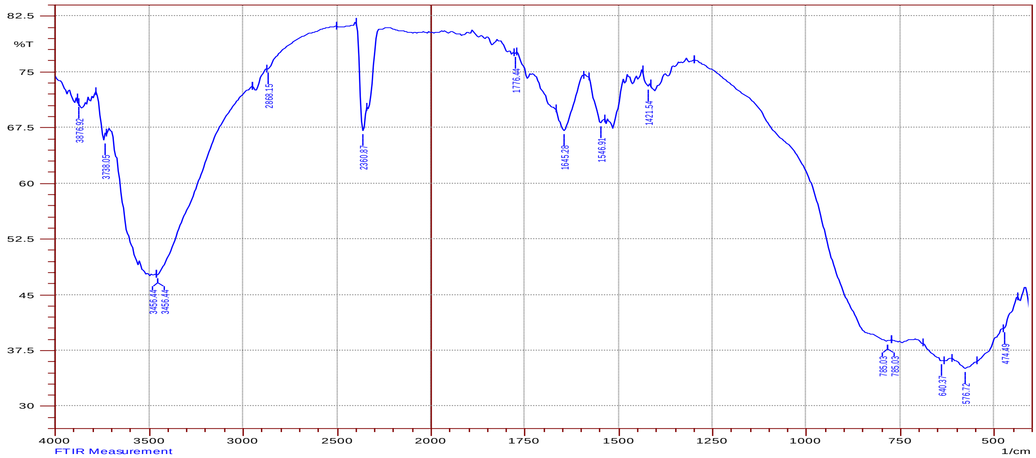


Fig. 14: FTIR-spectra of the nano gamma alumina prepared at 180 ^{0}C crystallization temperature and calcinations temperature 650 ^{0}C

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.

Table 1: The values of surface area and pore volume at different crystallization and calcinations temperatures

Crystallization Temp. ^{0}C	Calcination Temp. ^{0}C	Surface area (m^2/gm)	Pore volume (cm^3/gm)
120^{0}C	600^{0}C	352	0.47
140^{0}C	600^{0}C	356.37	0.4598
160^{0}C	600^{0}C	359.37	0.4548
180^{0}C	600^{0}C	383.01	0.43
180^{0}C	500^{0}C	456.5	0.49
180^{0}C	550^{0}C	401.02	0.53
180^{0}C	650^{0}C	338.93	0.43

In spite of that the increasing of the crystallization temperature leads to densification of some of the pores reducing the pore volume but the surface area still increased due to the dispersion role of the surfactant [23]. The increasing of calcinations temperature causes decreasing in the surface area and pore volume values because at low calcination temperature about 500 ^{0}C the dehydroxelation begins and the bonds of H_2 atoms eliminated causes increasing in surface area reached to 456 m^2/gm which is higher than the results obtained by Ming 2010 [13], while in the temperature of 600 ^{0}C and above the particles become [close to each other's causes agglomeration and reduce the open pores so that the surface area and pore volume of the samples decreased [24].

Particle Size and the Morphology of the Catalyst

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

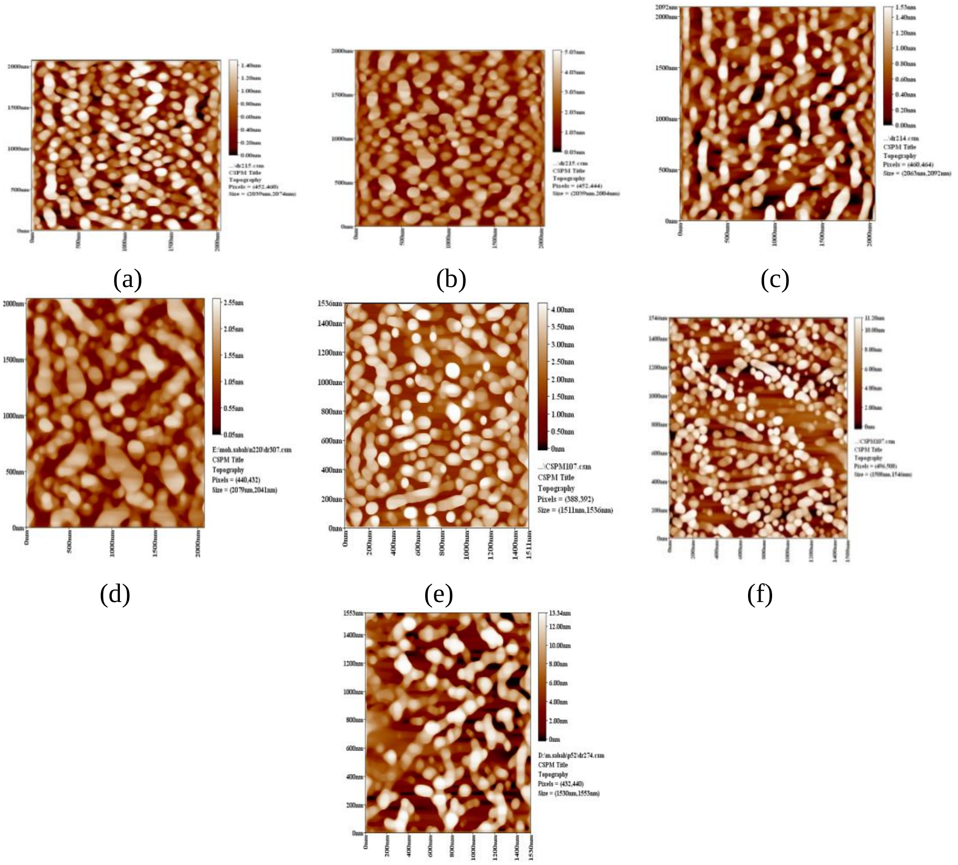
The average particle size of the prepared nano alumina was in the nano scale catalyst for all crystallization temperatures. The increasing in crystallization temperature from 120 ^{0}C to 180 ^{0}C at constant calcinations temperature 600 ^{0}C leads to increase the average particle size gradually from 90.56 nm to 92.72 nm with little effect in the temperature between 140 ^{0}C to 160 ^{0}C. This behavior causes gradual rising in surface area associated with drop in pore volume reaches to its high values at a temperature 180 ^{0}C.

Increasing the calcination temperature from 500 ^{0}C to 650 ^{0}C leads to very high enlargement from 59.26 nm to 93.84 nm causes increasing in surface area associated in decreasing in pore volume. In the calcination temperatures 500 ^{0}C and 550 ^{0}C the pores between the particles are opened cause high surface area and pore volume, while any increasing in calcinations temperature causes blockage in these pores reaching to the sentring. These results are near the results obtained by Hawraa 2016 [11].

Figure 15 represents the two dimension surface morphology of the prepared samples with non spherical structure, while Figure 16 represents the three dimension surface morphology of the prepared samples with hexagonal layers.

Table 2: the values of particle size distribution and average particle size at different crystallization and calcinations temperatures

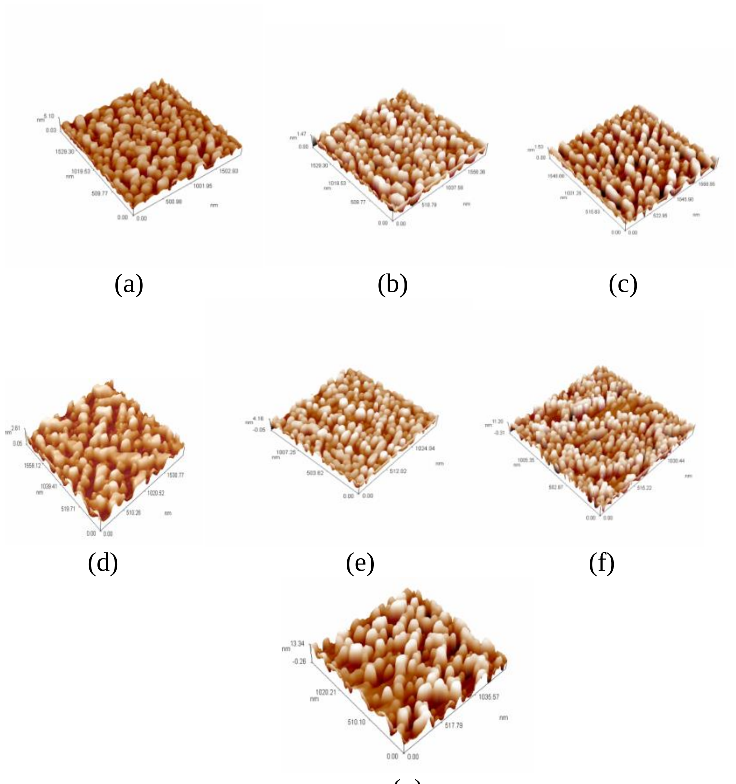
Crystallization Temperature ^{0}C	Calcination Temperature ^{0}C	Particle size distribution, nm	Average particle size, nm
120^{0}C	600^{0}C	30-145	90.56
140^{0}C	600^{0}C	45-125	92.15
160^{0}C	600^{0}C	20-155	92.57
180^{0}C	600^{0}C	75-160	92.72
180^{0}C	500^{0}C	50-110	59.26
180^{0}C	550^{0}C	30-85	59.53
180^{0}C	650^{0}C	93.84	75-125


(a) (b) (c)

(d) (e) (f)

(g)

Fig. 15: AFM images for samples [a-d at T=120-180 °Ccrystallization temperature, Time=12 h,600^{0} C calcination temperature,e-f at180 °Ccrystallization temperature, Time=12 h,500,550,650^{0} C calcination temperature



(a) (b) (c)

(d) (e) (f)

(g)

Fig. 16: AFM three – dimensional surface profile for samples [a-d at T=120-180 °C crystallization temperature, Time=12 h,600^0 C calcination temperature, e-f at180 °C crystallization temperature, Time=12 h, 500,550,650 ^{0}C calcination temperature

Scanning Electron Microscopy (SEM)

The effect of crystallization and calcination temperatures is shown in Figures 17 to 23. At 120 ^{0}C non uniform shape of particles is observe .Using crystallization temperature between 140-180 ^{0}C leads to crystal growth with low agglomeration and uniform irregular hexagonal shape and size because of the active role of CTAB surfactant in these temperatures as mentioned by Kianinia 2014 and Dahlan . 2012 [24, 25].

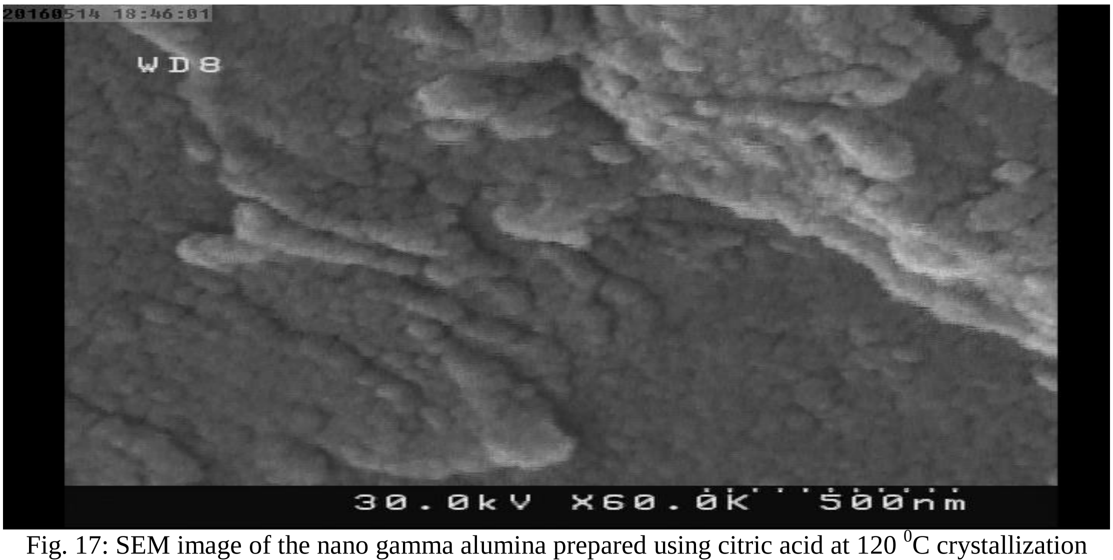


Fig. 17: SEM image of the nano gamma alumina prepared using citric acid at 120 ^{0}C crystallization temperature, 12hrs crystallization time and calcination temperature 600 ^{0}C

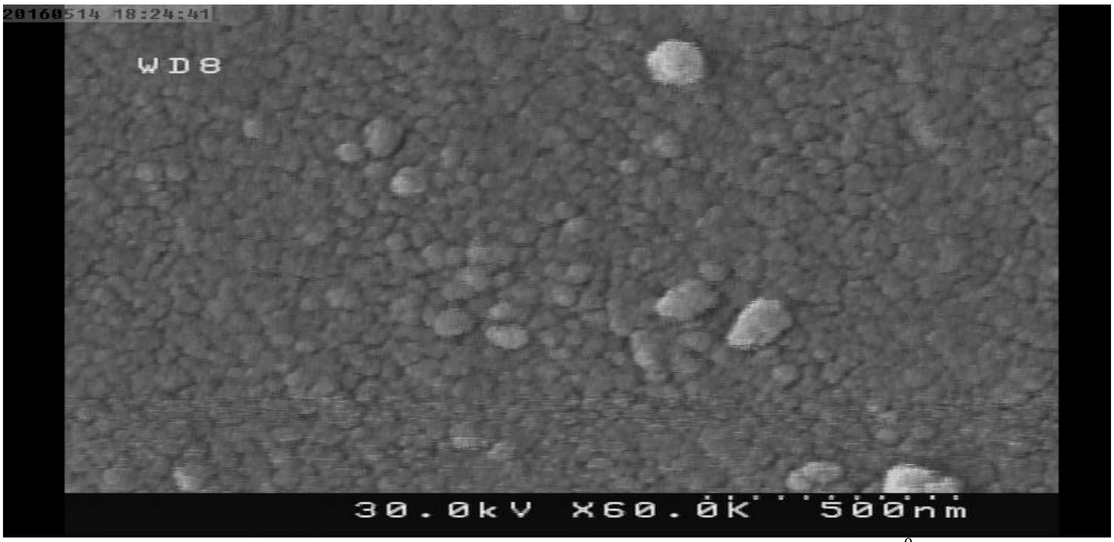


Fig. 18: SEM image of the nano gamma alumina prepared using citric acid at 140 ^{0}C crystallization temperature, 12hrs crystallization time and calcination temperature 600 ^{0}C

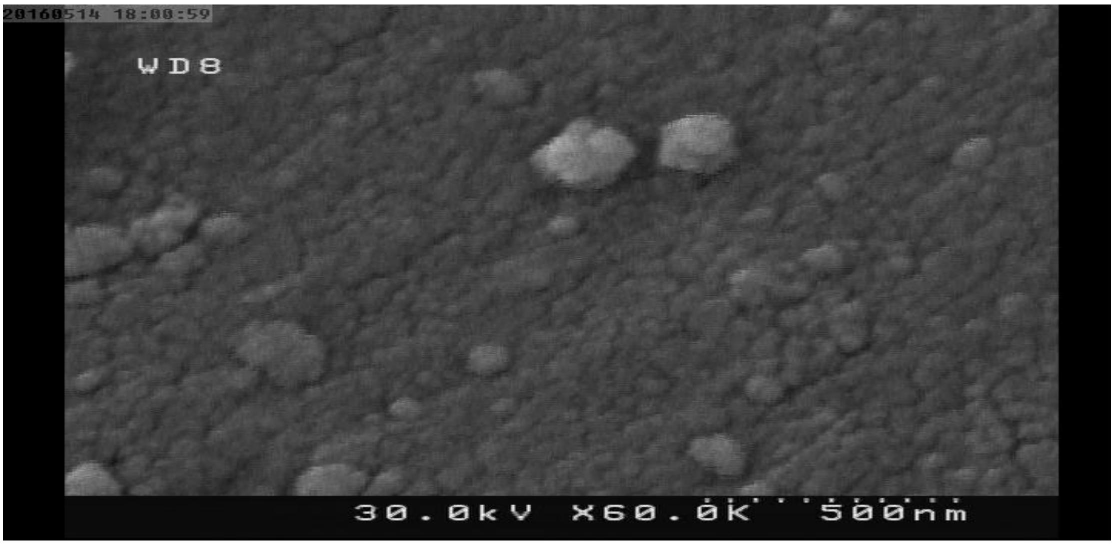


Fig. 19: SEM image of the nano gamma alumina prepared using citric acid at 160 ^{0}C crystallization temperature,12hrs crystallization time and calcination temperature 600 ^{0}C

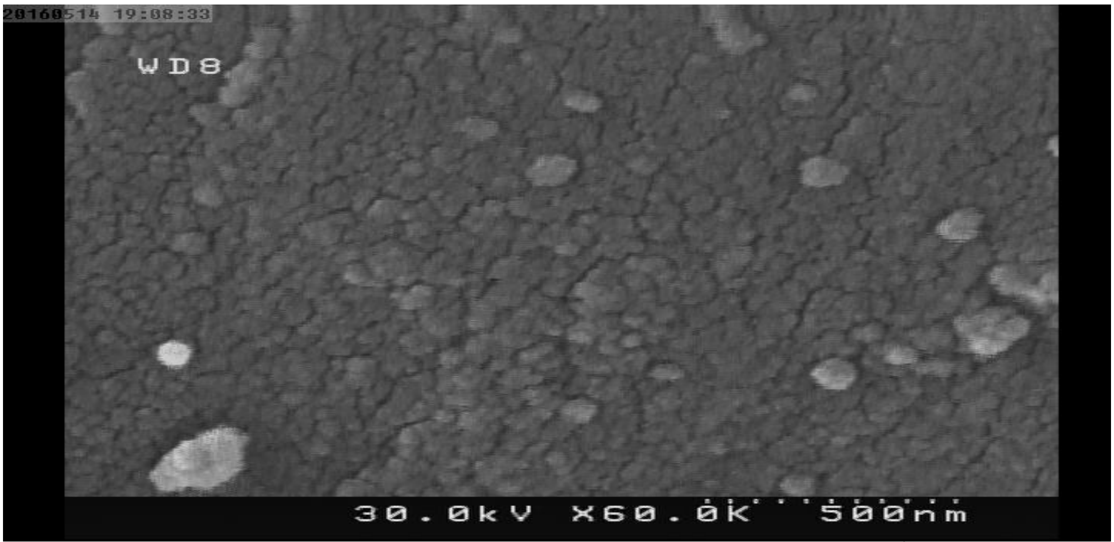


Fig. 20: SEM image of the nano gamma alumina prepared using citric acid at 180 ^{0}C crystallization temperature,12hrs crystallization time and calcination temperature 600 ^{0}C

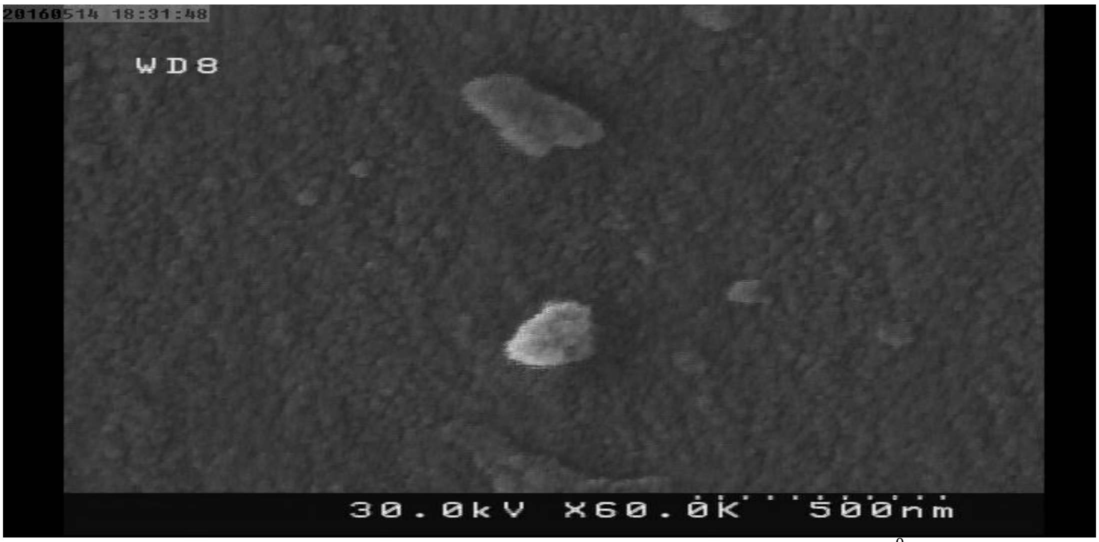


Fig. 21: SEM image of the nano gamma alumina prepared using citric acid at 180 ^{0}C crystallization temperature, 12hrs crystallization time and calcination temperature 500 ^{0}C

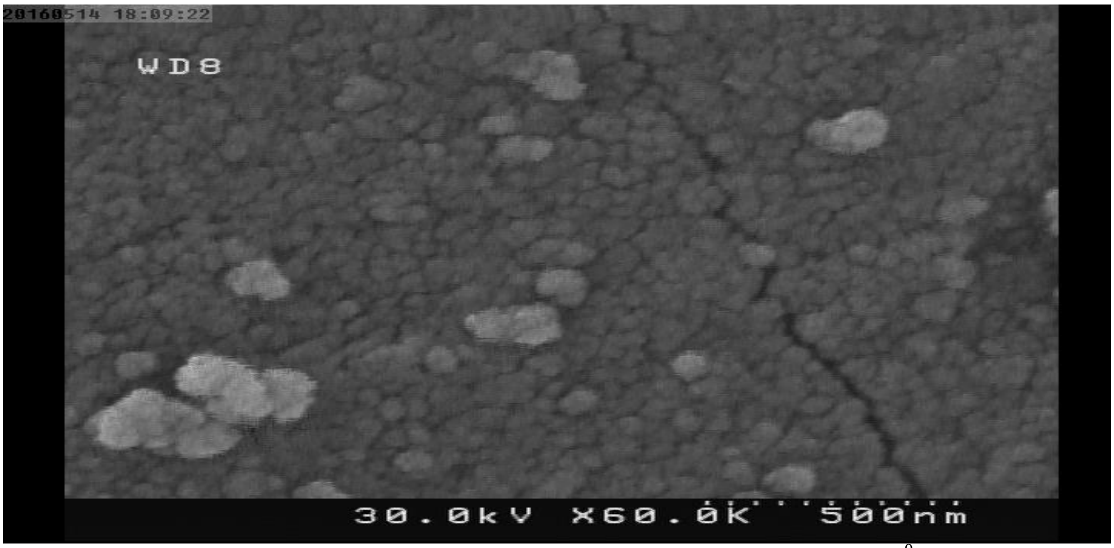


Fig. 22: SEM image of the nano gamma alumina prepared using citric acid at 180 ^{0}C crystallization temperature, 12hrs crystallization time and calcination temperature 550 ^{0}C

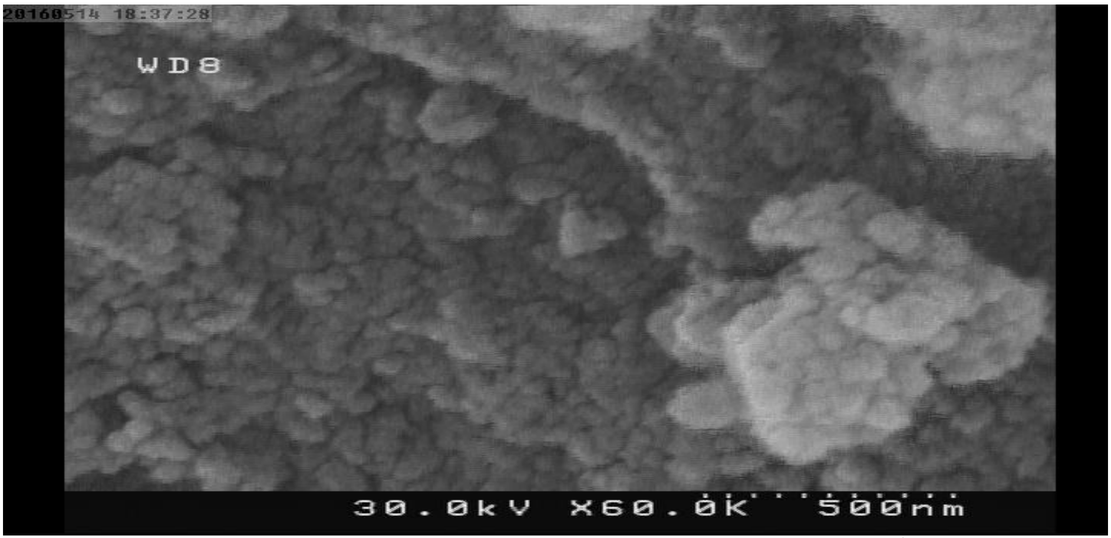


Fig. 23: SEM image of the nano gamma alumina prepared using citric acid at 180 ^{0}C crystallization temperature, 12hrs crystallization time and calcination temperature 650 ^{0}C

At 500 ^{0}C fine nano particles with low agglomeration is observed. Increasing the calcination temperature above 500 ^{0}C makes the particles close to each others causes increasing in particle size and decreasing in surface area and pore volume as mentioned by Amirsalari A. 2015 [26].

Conclusions

Nano gamma alumina was successfully synthesized using double hydrothermal method in the presence of CTAB surfactant and citric acid. Different techniques were used to characterize the prepared samples with different crystallization and calcination temperature. XRD diffractions and FTIR-spectra represent the crystalline nano gamma alumina pure from surfactant. The surface area increased during increasing of crystallization temperature and decreased during increasing calcinations temperature, while pore volume was increased with the rising of the crystallization and calcinations temperature. All the prepared samples were in the nano scale particle size with irregular hexagonal surface structure, and this morphology is the same with the morphology acting by hawraa 2016 [11].

References

1. Amirsalari A.,and Farjami Shayesteh, 2015, "Effect of PH and calcinations temperature on structure and optical properties of alumina nanparticle" , J. of superlattics and microstructure,department of physics, University of Guilan, Iran,vol.82,pp.507-524.
2. 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.
3. 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.
4. 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.
5. 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.
6. 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 819403,6pages.
7. 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.
8. 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.
9. Mandana Akia,Sayad Mahdi Alavi,and Zi Feng Yan,2010,"Promoted platinum dehydrogenation catalyst on a nano-sized gamma alumina support",J. of

petroleum and coal,vol.52,pp.280-289.

10. 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.
11. 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.
12. Mandana Akia,Sayad Mahdi Alavi,and Zi Feng Yan,2011,"Dehydrogenation catalysts of higher normal paraffins on a nanocrystalline gamma alumina:different impregnation sequences",J. of petroleum and gas Eng.,vol.2,No.3pp.64-73.
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. Xiang Li,Dezhi Han,and Zifeng Yan,2011,"A simple hydrothermal route to bimodal mesoporous nanorod gamma alumina with high thermal stability",Int. J. of Mat. Research,pp.1473-1476.
15. Dahlan,I Nyoman Marsih,and JoonJai Panpranot,2012,"gamma alumina nanotubes prepared by hydrothermal method as support of iron,cobalt,and nickel for Fischer-Tropsch catalysts",J. of chemistry and materials research,vol.2,No.3,pp.31-38.
16. Jian hong Yi,Son You Yi,and Gao Jian Feng,2009,"Synthesis of crystalline gamma alumina with high purity",J.of nanoferrous matrials society ,China,vol.19,pp.1237-1242.
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. 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.
19. 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.
20. Baichao An,Guijun Ji,and Guanghuan Li,2010,"Azeotropic distillation assisted preparation of nanoscale gamma alumina powder from waste oil shale ash",J. of chem. Eng. ,vol.157,pp.67-72.
21. Parida K. M.,Amaresh C. Pardhan,2009,"Synthesis and characterization of nano-sized porous alumina by control precipitation method",J. of mater. Chem..and physic.,vol.113,pp.244-248.
22. Shuchismita Dey, 2010,"Synthesis and application of gamma alumina nanopowder",MSC thesis,National institute of technology,Rourkela.
23. Hyun Chul Lee,Hae Jin Kim,and Chang Houn Rhee,2005,"Synthesis of nanostructured gamma alumina with a cationic surfactant and controlled amounts of water",j. of meso. And micro. Mater.,vol.79,pp.61-68.
24. Padmaja P.,Krishina Pillai,2004,"Adsorption isotherm and pore characteristics of nano alumina derived from sol-gel

boehmite",J. of porous mater.,vol.11,pp.147-155.

25. 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.
26. Dahlan,I Nyoman Marsih,and JoonJai anpranot,2012,"gamma alumina nanotubes prepared by hydrothermal method as support of iron, cobalt, and nickel for Fischer-Tropsch catalysts" , J. of chemistry and materials research,vol.2,No.3,pp.31-38.
27. Amirsalari A.,and Farmaji S.,2015,"Effect of PH and calcination temperature on structure and optical properties of alumina nanoparticles"j.of suprelattics and microstructures,vol.82,pp.507-524.