Preparation of Nano Activated γ-Alumina (Al_2O_3) with Surfactant and Surface Characterization

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Abstract:

This paper deals with the preparation of Alumina by sol-gel technique through the hydrolysis of aluminum ion mixed with the glucose as a surfactant and converting it to gel by ammonium hydroxide in aqueous media. The resulting sol composed of $Al(OH)_3$ particle is draying to become a transparent gel. The freshly prepared gel is heated at 700°C for 2hrs to obtain alumina (Al_2O_3)particles. The obtained particles are found to be γ-alumina particles with high porosity, Their characteristics are determined by LPSA, XRD, SEM, TEM and BET techniques. The results show that the particles are pure alumina, nano-sized=20nm, spherical shape, high surface area=210m^2/gm.

Keywords: γ-Alumina, synthesized, sol-gel technique, Surfactant, Surface characteristics

الخلاصه :

البحث هو لطريقه تحضير ماده الالومينا بطريقه المحلول–الجل بواسطة اذابه عنصر الالمنيوم وخلطه مع كلوكوز كعامل مساعد وتحويله الى جل باستخدام هيدروكسيد الامونيوم. الجل الناتج عباره عن ثلاثي هيدروكسيد الالمنيوم يتم تجفيفه ليتحول الى جل صلب. يتم تسخين الجل تحت درجه حرارة ٧٠٠ درجه مئويه لمده ساعتين للحصول على ثلاثي اوكسيد الالمنيوم (الالومنيا). الماده الناتجة ماده غير متبلورة نوعها كاما–الومينا ذات مسامية عالية. حددت خصائصها باستخدام عده تقنيات للفحص منها LPSA, XRD, SEM, TEM and BET. نتائج الفحوصات بينت ان حبيبات الماده كرويه الشكل وجدا نقيه وذات حجم =٢٠ نانومتر مع مساحه سطحيه كبيره تساوي =٢١٠ م²/غم.

الكلمات المفتاحيه: γ–الومينا، تحضير، طريقه المحلول–الجل،عامل مساعد، الخصائص السطحيه.

Introduction

Nanotechnology means the science of matter, material, and devices at the nanoscale, ranging from (1-100)nm in size. It is a multidisciplinary science integrating diverse fields of medicine, biology, chemistry, and engineering. Nanotechnology has recently received a lot of attention in the social media and financial backing because of its promising future. It has a multitude of applications ranging from energy production, textiles, cosmetics, and daily household items to medical devices, antibacterial creams, drugs, and diagnostics, all affecting the common man's day-to-day life, [Shivani *et. al*., 2015].

The synthesis of nanoparticles has been extensively investigated in the last two decades. Nano-sized materials exhibit novel and significant mechanical, electronic, magnetic and optical properties in comparison with their bulk counterparts. Aluminum oxide Al_2O_3, because of its excellent capability shown in the mechanical, electronic, magnetic, chemistry and thermodynamic fields, can be considered as one of the high-function materials, and is widely used in catalyst, fine ceramics, complex materials, fluorescent materials, waterish sensor and infrared- absorbing materials. Up to now, Al_2O_3 nanoparticles can be synthesized by many different methods, such as the co-precipitation, sol-gel , thermal decomposition. But the descriptions concerning the preparation of Al_2O_3 nanoparticles by the use of water-in-oil micro-emulsion have been limited, [Yin *et. al*., 2002].

Surfactant

Surfactants have been found to promote, to slow down, or to prevent crystal growth in solutions. Surfactants are frequently used as growth delays for the period of crystal growth. The presence of surfactants controls the size of the particles, their

degree of aggregation and their shape. The stabilization with surfactants, in general, occurs by the absorption of electric charges on the surface, causing a repulsion of the nanoparticles as long as a critical distance between the nanoparticles is increased, [Fatemeh *et. al*., 2011].

Materials

The materials used for preparation of nano activated alumina are listed in table 1

Table 1:The starting materials for preparation nano powder of alumina Al_2O_3.

No.	*Raw materials*	*Formulation*	*Molecular weight, (gm/mol)*	*Purity, %*	*Physical state*	*Origin*
1	Aluminum nitrate	$Al(NO_3)_3.9H_2O$	375.13	>98	Solid	England
2	Ammonium hydroxide	NH_4OH	35.05	—	Liquid	China
3	Ethanol absolute	C_2H_5OH	46.07	≥96	Liquid	Iraq
٤	Deionized water	H_2O	١٨	≥96	Liquid	Iraq
٥	Glucose	$C_6H_{12}O_6$	180.16	99.5	Solid	Iraq

Instruments

The following tools and equipments utilized in this work are : Laser Particle Size Analysis (LPSA) type (Bettersize 2000) (Korea), X-Ray Diffraction (XRD) type (Lab X Shamadzu), Scanning Electron Microscopy (SEM) type (Inspect S50), High Resolution Transmission electron microscope (HRTEM) type (CM12, Philips) and Brunauer–Emmett–Teller (BET) type (Micromeritics ASASP, 2020).

Preparation of γ-Alumina

A weight of(46.9 g) of $Al(NO_3)_3.9H_2O$ was dissolved in 125mL deionized water and 125 mL ethanol. Then the glucose surfactant with different percent (5% and 7%) and concentration (0.003, 0.005 and 0.007)mg/gm is add for each sample, as shown in table 2. Under continuous magnetic stirring added drops of ammonium hydroxide are added until the solution mixture was turn to gel and then filtered to remove any insoluble impurity. The gel was drying at 110ºC for around 12 h. The pH of the solution mixture was initially 2. As the reaction proceeds the pH gradually increased and rose sharply from 2 to 5 producing alumina gel. The drying gel was heated for 2 h at 700°C.

Table (2): Preparation of gels at different surfactant concentration (A=0, A3=0.03mg/L, A5=0.05mg/L, A7=0.07mg/L).

Sample code	**Aluminum Nitrate, gm.**	**50/50 water–Ethanol ratio, mL.**	**Surfactant, %.**	**NH_4OH, mL.**	**pH**	**Room Temperature, ºC.**	**Test Time, min.**
A	46.893	250	----	22	4.58	21	20
A3	46.893	250	5	26	4.69	18	15
A3	46.893	250	7	27	5.14	18	15
A3	93.78625	500	16	125	4.5	22	180
A5	46.893	250	5	18	5.12	15	15
A5	46.893	250	7	25	4.83	15	15
A7	46.893	250	5	26	5.17	15	15
A7	46.893	250	7	24	4.79	15	15

Drying and Calcination

The filtered gel will be drying to the next day at room temperature 25ºC until separated from filtered paper, then it is put in fire proof crucibles to be dried at temperature 110°C for 12 hours in programmed electrical oven (type, DZF 2060) to get solid aluminum hydroxide $Al(OH)_3$.

That causes the gel transference to the sold state and we will note shrinkage in volume and change in color of gel from white to brown. Then, the gel is crushed by hand in mortar to dispose the agglomeration of particles, After that the samples is calcinated at temperature 700°C with heating rate 5°C/min for 2 hours by using furnace (type Lindberg , Germany) to get nano aluminum oxide and water as illustratedin Eqs. (1 to 4) [Yvan, and Maria, 2012] and shown in plate (1a).

$$Al(NO_3)_{3(s)} + H2O \quad 3NH_4OH \longrightarrow Al(OH)_{3(S)} + 3NH_4NO_3 + H_2O \quad .....(1)$$

$$2Al(OH)_{3(S)} \xrightarrow{110^oC\ draying} 2AlO.OH_{(S)} + 2H_2O_{(g)} \quad .....(2)$$

$$2AlO.OH_{(S)} \xrightarrow{700^oC\ burning} \gamma\text{-}Al_2O_{3(S)} + H_2O \quad .....(3)$$

$$2Al(OH)_{3\ (s)} \rightarrow \gamma\text{-}Al_2O_{3(s)} + 2H2O_{(g)} \quad ..... (4)$$

The powder is slowly cooled by switching off the furnace and let it cool at room temperature until the next day. The next step is powder crashing .The utilization active alumina is crashed by hand by using a mortar and hammer as shown in plate (1) to get final result which is nano activated alumina.

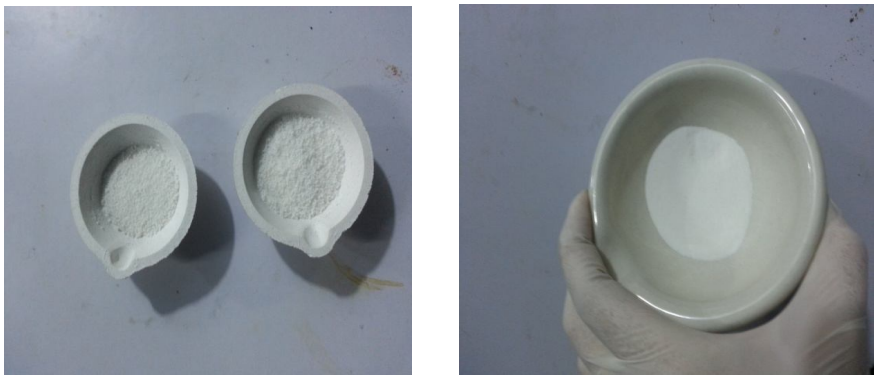

plate 1: (a) Sample after calcination (b) Mortar (hand crashing after calcination)

Characteristics of nano powders

The characteristics of the prepared nano powders include the following tests and results:-

1. Laser Particle Size Analysis Result (LPSA)

Laser Particle Size Analysis type (Bettersize 2000) are used to find the particle size and their diffraction. As the results shown in table 3 show, the alumina had a particle size distribution ranged from (0.44 to 467.2) μm with an effective grain size, d_{10}, ranging from (2.8 to 15.2) μm, a median grain size, d_{50}, ranging from (23 to 99) μm.

Table (3): Summary of Laser Particle Size Analysis result for Preparation alumina at different surfactant concentration (A=0, A3=0.03mg/L, A5=0.05mg/L, A7=0.07mg/L).

Sample code	Surfactant, %.	particle size dmin	particle size dmax	d_{10}	d_{50}
A	----	0.561-0.715	390.2-497.2	5.227	41.41
A3	5	0.440-0.561	147.9-188.5	2.884	23.06
A3	7	0.561-0.715	306.2-390.2	4.280	36.59
A3	16	0.561-0.715	479.2-633.6	15.21	99.07
A5	5	0.561-0.715	27.12-34.56	1.865	8.996
A5	7	0.440-0.561	188.5-240.3	3.518	24.82
A7	5	0.440-.561	306.2-390.2	4.963	36.31
A7	7	0.440-0.561	56.13-71.52	2.19	13.43

2. X-Ray Diffraction for nano powders

X- ray diffraction is used for the analysis of prepared powder, to insure its compound, purity and the size of particles. Under measure condition target (Cu) , wave (1.54 A°), voltage (40 Kv), current (30 mA) and scan mode (continuous scan) with 2θ range (20-70)º. Fig. 1 shows the results of X- ray diffraction. This figure shows the X-ray diffraction patterns for nano powders of alumina with different concentrations (0.03, 0.05, and 0.07) gm/L of glucose surfactant, and different percentages (5%, and 7%) of surfactant, and without surfactant after calcination at 700℃ for 2 hrs respectively.

Table (4) compares the broad peaks at 2θ from Fig. (1), with intensity (I). The table indicates the type of alumina is γ–alumina.

Fig.(1) shows the XRD pattern of synthesized nano γ–alumina powder. The three main reflections of nano γ-Al_2O_3 phase are obviously observed as broad peaks at 2θ angles around (37.6º, 45.8º, and 66.7º), respectively. The peaks in the pattern significantly indicate the formation of pure nano sized γ-AL_2O_3 crystallites.

It is clear from these figures, the homogeneity of particles are nearer to amorphous than crystalline samples except a small broad peak at about $2\theta=66.76^{\circ}$. This may be due to the prepared fine particles size of nano powders. Furthermore, it is shown later that the X-ray diffraction patterns, give sharp peaks for all samples. This satisfies that the crystallization is obtained at suitable temperature with time.

Using the Scherrer's, the crystallite sizes were measured as 1 nm for 700 ºC treated samples. It is obvious that crystallite sizes of γ-AL_2O_3 in the presence of glucose were smaller than those of γ-AL_2O_3 obtained without glucose.

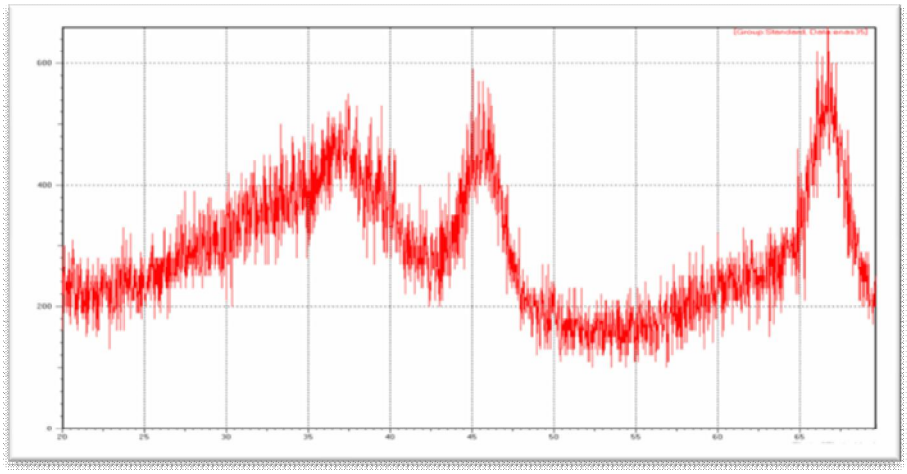

Fig. 1: XRD patterns for nano powder AL_2O_3 with 5% glucose of concentration 0.03gm/L.

AL_2O_3Table (4): Broad beaks of 2θ for

00-029-0063 Apr 12, 2015 11:01 PM (SHIMADZU XRD-6000)

Status Primary **QM:** Blank (B) **Pressure/Temperature:** Ambient **Chemical Formula:** Al2 O3
Weight %: Al52.93 O47.07 **Atomic %:** Al40.00 O60.00 **Compound Name:** Aluminum Oxide
Common Name: γ-Al2 O3

Radiation: CuKα **λ:** 1.5418Å **Reference:** Rooksby. X-Ray Identification and Crystal Structures of Clay 264 (1951).

SYS: Cubic **SPGR:** Fd-3m (227) **AuthCellVol:** 497.55 **Z:** 10.90
Author's Cell [AuthCell-a: 7.924Å **AuthCellVol:** 497.55Å³ **]** **Dcalc:** 3.709g/cm³ **SS/FOM:** F(7) = 8.4(0.092, 9)
Reference: Ibid.

Space Group: Fd-3m (227) **Z:** 10.90 **Molecular Weight:** 101.96
Crystal Data [XtlCell-a: 7.924Å **XtlCell-b:** 7.924Å **XtlCell-c:** 7.924Å **XtlCell.α:** 90.00° **XtlCell.β:** 90.00°
XtlCell.γ: 90.00° **XtlCellVol:** 497.55Å³ **]**
Reduced Cell [RedCell-a: 5.603Å **RedCell-b:** 5.603Å **RedCell-c:** 5.603Å **RedCell.α:** 60.00°
RedCell.β: 60.00° **RedCell.γ:** 60.00° **RedCellVol:** 124.39Å³ **]**

Crystal (Symmetry Allowed): Centrosymmetric

Pearson: cF54.50 **Prototype Structure:** Mg Al2 O4 **Prototype Structure (Alpha Order):** Al2 Mg O4

Subfile(s): Cement and Hydration Product, Common Phase, Forensic, Inorganic, Metals & Alloys, Primary Pattern, Superconducting Material (Superconductor Reaction Product)

Last Modification Date: 01/29/2008
Cross-Ref PDF #'s: 04-007-2478, 04-007-2615, 04-007-2479, 04-007-2867, 04-003-3818

Database Comments: Footnotes for D-spacings and Intensities: 1 Revised from 4.33. Unit Cell Data Source: Powder Diffraction.

00-029-0063 (Fixed Slit Intensity) - CuKα1 1.54056Å

2θ	d(Å)	I	h	k	l	*	2θ	d(Å)	I	h	k	l	*	2θ	d(Å)	I	h	k	l	*
19.5803	4.530000	35	1	1	1	1	39.4909	2.280000	40	2	2	2		66.7616	**1.400000**	100	4	4	0	
31.9359	2.800000	45	2	2	0		45.7883	**1.980000**	80	4	0	0								
37.6033	**2.390000**	65	3	1	1		60.4574	1.530000	10	5	1	1								

3. Scanning Electron Microscopy (SEM)

To study the morphology of the prepared nano activated alumina by using Scanning Electron Microscope (SEM) with HV 20Kv and magnifier 14716X. Fig. (2.a) shows the maximum size 500 µm and Fig. (2.b) show the maximum size 5 µm without glucose. These figures show uniform distributions, size, shape of particles and the low agglomeration of particles due to Vander vales forces.

Figs.(2 and 3) show that the maximum size of the nano particles of the synthesized γ-AL_2O_3 sample after calcination is (5 µm). The crystals of the sample reached a porous form, and the morphology of the crystals is regular pores and of a volume suitable for reaction and an increase surface area. SEM of synthesized catalyst shows low bulk density and high bulk pores, these structures are made of evaporation of ethanol. The surface area, pore size distribution and pore volume data obtained for nano size synthesized γ-AL_2O_3 catalyst using ammonia agent are obtained by its calcination at 700 °C for 2 hr.

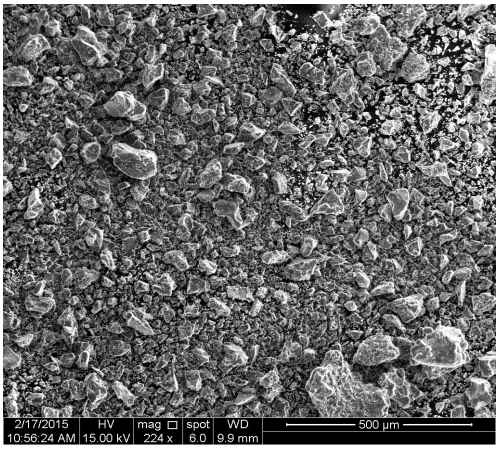

Fig. (2): (a) SEM image for nano composite powder Al_2O_3 of 0% with 0gm/L glucose.

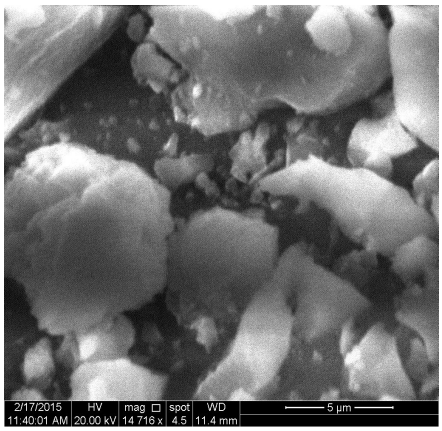

Fig. (2): (b) SEM image for nano composite powder Al_2O_3 of 0% with 0gm/L glucose.

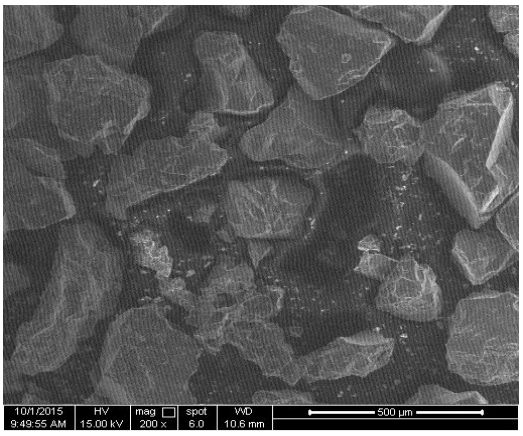

Fig. (3): (a) SEM image for nano composite powder Al_2O_3 of 7% with 0.05gm/L glucose.

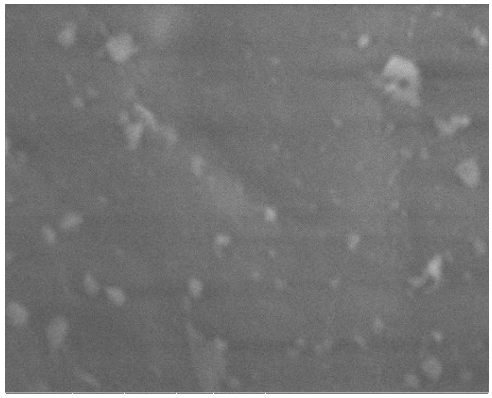

Fig. (3): (b) SEM image for nano composite powder Al_2O_3 of 5% with 0.05gm/L glucose.

4. High Resolution Transmission Electron Microscope (HRTEM) Results

Fig. (4) show the HRTEM bright field micrographs for alumina powders at calcination temperature at 700℃ for two hrs. Using different concentration (0.03, 0.05, and 0.07) gm/L and different percent of glucose (5%, and 7%) from each concentration as surfactant agent (glucose) prevents the agglomeration of powder and also prevent the grain growth of the materials. The lower percentages of the of the surfactant agent (3%, and 5%) do not dispersed the particles as shown in Fig. 6 which clearly show the agglomeration. In these figures HRTEM illustrates the size and shape of the composites particles extracted from the powder reduced at 700℃ for two hrs. These figures show the particle size up to (20) nm.

All particles resulting from the route of powder preparation have show regular and nearly rounded shape appearance and all particles are in good contact to each other. Some appreciable formation of heavy agglomerated powders are present and this is attributed to the large surface of these nanoparticles. The agglomeration refers to the adhesion of the particles to each other because of Vander vales force of attraction which is significantly higher in nanoparticles.

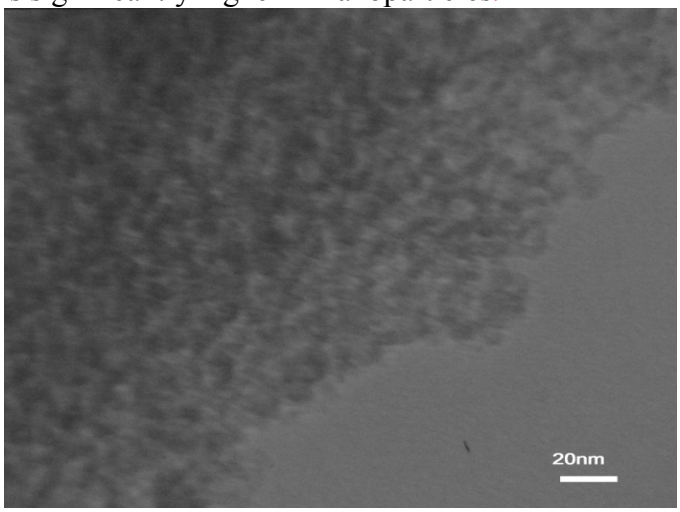

Fig. 4: TEM image for prepared nano powder calcination at 700℃ for 2 hrs and with 5% surfactant of 0.03 gm/L concentration.

5. Brunauer–Emmett–Teller (BET)

The N_2 adsorption and desorption isotherm at a relative pressure range of P/P_0 =0.6–0.95, indicate a broad pore size distribution with uniform size and shape.

It is also to be noted that the BET surface area of γ-AL_2O_3 found in the presence of glucose at 700 ºC is even smaller than that of γ-AL_2O_3obtained in the absence of glucose at same temperature degree. In the present case, the average particle size (D) of alumina calcined at 700 ºC is calculated by the BET method as in Eq.5:[Omid *et. al.*, 2012]

$$D = {}^{6}/_{pS} \qquad \text{.....(5)}$$

where *p* is the theoretical density and S the BET surface area. Assuming the particles to be spherical in nature and the theoretical density of alumina as $3.98*10^6$ gm/m^3, the particle sizes of alumina are calculated and showed in table (5) for the temperatures of 700 ºC. It is noticed that there is a large discrepancy in crystallite sizes calculated by the XRD method (Scherrer's formula) and the BET surface area data. It is to be pointed out that Scherrer's equation measures the crystallite size (primary particle size) whereas, the BET method determines the secondary particle size, which is comprised of many crystallites (primary particles). The agglomeration of nano-crystalline materials due to the high surface energy of the ultrafine particles results in larger values of particle sizes calculated by the BET method. It is to be mentioned that for the nonspherical nature of particles obtained in the absence of glucose, the measurement of particle sizes by BET and XRD methods becomes impossible, [Milan, 2010].

Summary of surface area and pore volume of synthesized AL_2O_3 result test made by Brunauer–Emmett–Teller BET type (ASAP 2020) is shown in table (5).

Table (5): summary of surface area and pore volume of synthesized AL_2O_3.

Surfactant, (gm/L)	0.03			0.05		0.07		0
Surfactant percent, (%)	5	7	16	5	7	5	7	0
Surface Area, (m^2/gm)	200.5	204.5	212.7	194.9	210.5	207.4	208.9	211.3
Average pore hydraulic radius, (nm)	1.02	1.02	0.97	1.05	0.97	0.96	0.92	1.01
Pore Volume, (cm^3/gm)	0.31	0.33	0.31	0.29	0.31	0.29	0.26	0.32
D, (nm)	7.51	7.36	7.08	7.73	7.15	7.26	7.21	7.13

weight losses

The prepared gel after drying for 3 days in oven we get aluminum hydroxide and noticeable shrinkage in volume of the gel and it becomes hard, crystal, and black in color for all samples except the one without surfactant kept his white color. That means during drying the sugar (glucose) with chemical form $C_6H_{12}O_6$ will cause the change in color because the carbon get burn.

After that the drying gel will undergo hand crashing to convert aluminum hydroxide to powder with gray color and it will be weighted by using sensitive four digits balance type (Denver, Germany) then aluminum hydroxide will be calcinated in furnace type (Lindberg , Germany) at 700 °C for 2 hours to convert it to aluminum oxide AL_2O_3 (Alumina). Then we let alumina to cool slowly inside the furnace to the next day, then we see the color turns to pure white with rough powder. Finally we also apply hand crashing to the powder which becomes a nano-active alumina. At last we weight the final powder after crashing see table (6). To predicate the percent of weight losses by using Eq. (6):

$$W_L = \frac{w_b - w_a}{w_b} * 100\% \qquad \text{..... (6)}$$

which is $W_L$weight losses, (w_b, w_a) weight before and after drying, respectively. The total percentage weight losses is 70.7%. This percent is important to know and

predicate the quantity of alumina need to be prepared in the future and to have an idea about how much it cost to prepare one gram of alumina.

The loss in weight is due to water evaporating from $AL_2(OH)_3 + H_2O$ by heating it at 700°C for 2 hrs to convert it to alumina AL_2O_3 .

Table (6): Sample weight after and before draying

Sample Code	Glucose cons.	Glucose percent	Weight			Percent of losses
			Before drying	After drying	Losses	
A1	0 gm/L	0%	10.44	3.10	7.33	70.2%
A2	0.03 gm/L	5%	7.00	2.16	4.84	69%
A3		7%	10.03	2.87	7.15	71.3%
A4	0.05 gm/L	5%	10.92	2.90	8.02	73.4
A5		7%	10.12	3.02	7.10	70.1%
A6	0.07 gm/L	5%	8.35	2.52	5.82	69.7%
A7		7%	10.12	2.91	7.21	71.2%
Average weight losses						70.7%

Conclusions

Based on the results, conclusions may be drawn:-

1. Sol-gel technique proves to be an efficient method for the synthesis of nano powder alumina especially when glucose is used as starting materials.
2. The addition of 0.05 gm/L with 7 % glucose is used as surfactant to prevent grain growth showing that the average particles size is (7) nm.
3. X-ray Diffraction technique, used to identify phases, shows that sintering at 700°C for 2 hrs, γ- alumina phase only is obtained because of solid solution from alumina formation, and the crystal size about (20)nm.
4. High Resolution Transmission Electron Microscope (HRTEM) results showed all particles resulted from the route of powder preparation showed regular and nearly round shape appearance and all particles were in good contact with each other.
5. The BET surface area of γ- Al_2O_3found in the presence of glucose at 700 ºC was even smaller than that of γ- Al_2O_3obtained in the absence of glucose at same temperature degree, with particle diameter 7.15nm.
6. The losses in weight was duo to water evaporation from$AL_2(OH)_3$+H_2O by heating 70.7%.

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