IBGM
GIF EVALUATIN - 2017
IRAQI BULLETIN OF GEOLOGY AND MINING
Global Impact Factor
0.936

Iraqi Bulletin of Geology and Mining *Vol.14, No.1, 2018* *p 121 – 130*

PREPARATION OF NANOGAMA ALUMINA FROM IRAQI KAOLIN

Jassim M. Kshash*[1] and Baha'a A. Sabbar[1]**

Received: 01/ 03/ 2016, Accepted: 12/ 10/ 2017
Key words: Sargelu Formation, Basin Model, Jurassic period, Thermal burial history

ABSTRACT

The work reports a procedure for the synthesis of γ-alumina from the Iraqi kaolin. Kaolin was transformed to metakaolin by calcination at 750 °C for 45 minute. γ-alumina powder was synthesized through extracting alumina from metakaolin via H_2SO_4 treatment and precipitation by ethanol, which produces aluminum sulfate of 99% purity. The precipitated aluminum sulfate was dried and calcined at 800, 850, 900 and 1000 °C to study the thermal decomposition of aluminum sulfate. The crystallinity and phase of the synthesized for the assignment of calcined samples was characterized by X-ray diffraction measurements, paving the temperature at which the aluminum sulfate is converted to γ-alumina nano particles. Pure alumina nanoparticle 98.81% was prepared by calcination of aluminum sulfate at 1000 °C for 2 hour. The specific surface area, pore volume and pore size for γ-alumina nano particles were determined by BET measurement i.e. 117 m^2/gm, 1.1 cm^3/g and 337.6 Å respectively. The size of the particles obtained were also calculated from BET analysis to be around 13 nm. The study revealed that the kaolin could be a promising material for the preparation of γ-alumina.

تحضير نانو كاما الومينا من الكاؤولين العراقي

جاسم محمد كشاش و بهاء عبد المجيد صبار

المستخلص

يتضمن هذا البحث دراسة تحضير مادة النانو كاما الومينا من الكاؤولين العراقي. إن عملية التحضير تتضمن تحويل الكاؤولين الى ميتا كاؤولين بواسطة عملية الكلسنة عند درجة حرارة (750 °م) ولمدة (45 دقيقة) ومن ثم الإذابة بواسطة حامض الكبريتيك (30%) بالتالي ترسيب كبريتات الألمنيوم باستخدام الإيثانول.

بعد ذلك يتم تحويل الكبريتات المحضرة الى كاما الومينا بعملية الكلسنة بدرجة حرارة (1000 °م) ولمدة (2 ساعة). تم تحديد الخصائص الفيزياوية مثل التبلور بواسطة فحوصات الأشعة السينية الحائدة (XRD) وكذلك المساحة السطحية (117 m^2/g)، الحجم الحبيبي (13 nm)، والتوزيع المسامي الحجمي (pore volume 1.1 cm^3/g و pore size 337.6 Å) لمادة كاما الومينا المحضرة وبنقاوة (98.81%) باستخدام طريقة (BET).

[1] Assist Chief Engeneer, Iraq Geological Survey, (GEOSURV) P.O. Box 986, Baghdad, Iraq,
*e-mail: Jkshash@yahoo.com
**e-mail: Bahaaalmajeed@yahoo.com

INTRODUCTION

Alumina has enormous technological and industrial applications. It exists in a variety of meta-stable structures including γ-, *η*-, *δ*-, *θ*-, *κ*- and χ-aluminas, as well as its stable *α*-alumina phase (Wang *et al*., 2009). Bauxites have been widely used in industry to produce alumina via Bayer process. On the other hand, nonbauxitic materials, which are more abundant in many countries than bauxite resources, also have been processed in attempts to develop alternative technologies for producing alumina (Gitzen, 1970; McColm, 1983 and Murray, 2000).

Some examples of nonbauxitic raw materials are alunite, sillimanite, andalusite, kyanite, kaolin, mica, and fly ash. Significant advances in alumina purity have been achieved using materials such as sulfates, nitrates, and chlorides as alumina precursors, to obtain high purity alumina (Zaho, 2006; Kato *et al.*, 1981; Blendell *et al.*, 1984 and Dynys, 1982).

Among various structures for alumina, γ-alumina is one kind of extremely important nano sized materials. It is used as a catalyst and catalyst substrate in automotive and petroleum industries, structural composites for spacecraft, abrasive and thermal wear coatings (Paglia *et al.*, 2004). Recent studies have shown that γ-alumina is thermodynamically stable relative to *α*-alumina when a critical surface area is achieved (Wang *et al.*, 2009). Nano γ-alumina powder can promote the sintering behaviour of alumina and silicon carbide fibbers (Parida *et al.*, 2009), moreover, the use of single phase of γ-alumina powders makes the densification temperature shift to lower temperature as compared with the sample consisting of *γ*- and *χ*-alumina (Yajima *et al.*, 2003). Those outcomes can open up endless possibilities for the applications of *γ*-alumina, paving for the significance to investigate the preparation of γ-alumina. Until now, various methods have been used to prepare γ-alumina such as sol-gel synthesis from calcination of boehmite (Paglia *et al.*, 2004), poly hydroxo aluminum-polyvinyl alcohol (Wang *et al.*, 2009), laser ablation of an aluminum target in an oxygen atmosphere (Johnston *et al.*, 1992), hydrolysis of alumina alkoxide (Ogihara *et al.*, 1991), thermal decomposition of aluminum sulfate (Kato *et al.*, 1981), metal organic chemical vapor deposition with $Al(CH_3)_3$ (Noda *et al.*, 2003).

Kaolinite is a clay mineral, part of the group of industrial minerals, with the chemical composition $Al_2Si_2O_5(OH)_4$. It is a layered silicate mineral, with one tetrahedral sheet linked through oxygen atoms to one octahedral sheet of alumina octahedral (Deer *et al.*, 1992), Kaolin contains 30 – 35 percent by weight of alumina. Therefore, it can be a suitable material for production of γ-alumina because of its abundance and having considerable content of alumina in kaolin structure. In this study we report the production of γ-alumina from kaolin using a simple and commercial method. All materials used in this methods, are relatively cheap and are found on industrial scale.

- **Objective**

The aim of the current work is to use a simpler and feasible method for preparing nano sized gamma alumina.

- **Location**

The Kaolin used as starting material was supplied from Dwaikla mine which is located in the Western Desert area about 80 Km to the north of Rutba city.

EXPERIMENTAL WORK

- **Materials**

The kaolin used came from Al-Anbar province, west of Iraq. The chemical and mineralogical compositions of kaolin are given in Table (1).

Table 1: Chemical and Mineralogical Composition of kaolin clay

Chemical Composition (wt.%)	**SiO_2**	**Fe_2O_3**	**Al_2O_3**	**CaO**	**MgO**	**L.O.I**	**Na_2O**	**K_2O**	**Total**
	48.6	1.2	35.45	0.17	0.08	12.62	0.07	0.49	98.68
Mineralogical Composition	Kaolinite, Quartz								

Chemical materials: {sulphuric acid, 95 – 98 %} (J.T. Baker) and {ethanol, 100%} (Hayman)

- **Experimental Procedure**

After extracting from mine the kaolin was crushed by laboratory jaw crusher and ground in ball mill to particles below (0.6 mm) in size. The powdered kaolin was calcined into meta kaolin at (750 °C) for (45 minute) in rotary furnace to loosen the alumina components. Then, the meta kaolin powder was leached with (30%) sulphuric acid. The mixture of kaolin powder and acid was contained in a (500 ml) round flask. The reaction flask fitted with a reflux condenser and the mixture was mixed with magnetic stirrer. Heating was achieved by using a heating mantel to maintain and control the desired temperature.

During leaching of metakaolin in sulphuric acid, the alumina in metakaolin is extracted and dissolvesd in H_2SO_4 which leads to formation of aluminum sulfate according to the following reaction (Equation 1).

$$Al_2O_3\,(\text{in metakaolin}) + 3H_2SO_4 \rightarrow 2Al^{3+} + 3SO_4^{2-} + 3H_2O \quad \ldots\ldots\ldots\ldots 1$$

After the mixture of kaolin and acid had been leached, it was cooled to room temperature and filtered to remove the leached residue, which mainly consisted of silica. The filtered leached liquor was then added slowly into ethanol while the ethanol was stirred with a magnetic stirrer. Ethanol was used as a precipitating agent because aluminum sulfate can be selectively precipitated by ethanol from the ionic solution (Wang *et al.*, 2009) as shown in Equation (2).

$$Al^{3+} + 3SO_4^{2-} + 3H_2O \rightarrow Al_2(SO_4)_3 .3H_2O \quad \ldots\ldots\ldots\ldots\ldots 2$$

The precipitate is washed again with the ethanol and with distilled water and then dried at (70 °C) for (24 hr). Finally, the precipitates are calcined in an electric furnace to transform aluminum sulfate to γ-alumina; Equation (3).

$$Al_2(SO_4)_3 .3H_2O \xrightarrow{\Delta\ (900\ ^\circ C)} \gamma\text{-}Al_2O_3 + 3\,SO_3\uparrow \quad \ldots\ldots\ldots\ldots 3$$

A flow chart of this process is presented in Fig. (1).

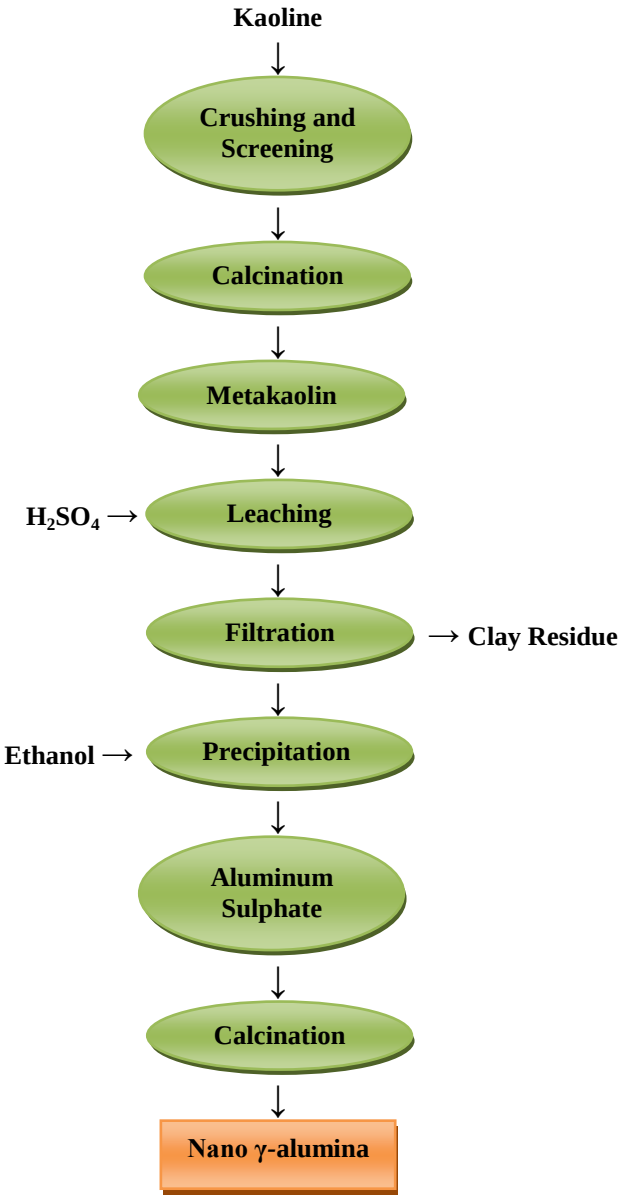

Fig.1: Schematic flow diagram of the Nano-gama Alumina production

RESULTS AND DISCUSSION

- **Phase Analysis**

The crystallinity and phase identification of the prepared samples were determined using 7000 shimadzu X-Ray diffractometer with Cu-Kα as the radiation source and Ni filter.

Figures (2 and 3) show the XRD pattern of kaolin and calcined kaolin at (750 °C). It is observed that the kaolin shows all the characteristic peaks of kaolinite. On calcination, these peaks disappear giving a featureless band of X-ray amorphous metakaolin. Kaolin type clays undergo a series of phase transformations upon thermal treatment in air at atmospheric pressure. Endothermic dehydroxylation (or alternatively, dehydration) begins at (550 – 600) °C to produce disordered meta-kaolin, $Al_2Si_2O_7$; continuous hydroxyl loss (-OH) is observed up to (900 °C) and is attributed to gradual oxolation of the metakaolin (Bellotto

et al., 1995). In this study, calcination of kaolin at (750 °C) led to form the meta-kaolin, which is transient and more active and reacts easier than kaolin. Equation (4) shows the changes during calcination and formation of metakaolin. During the calcination the structure of kaolin was degraded and two molecules of water are released.

$$Si_2O_5(OH)_4Al_2 \rightarrow Al_2Si_2O_7 + 2H_2O \quad \ldots\ldots\ldots\ldots\ldots\ldots 4$$

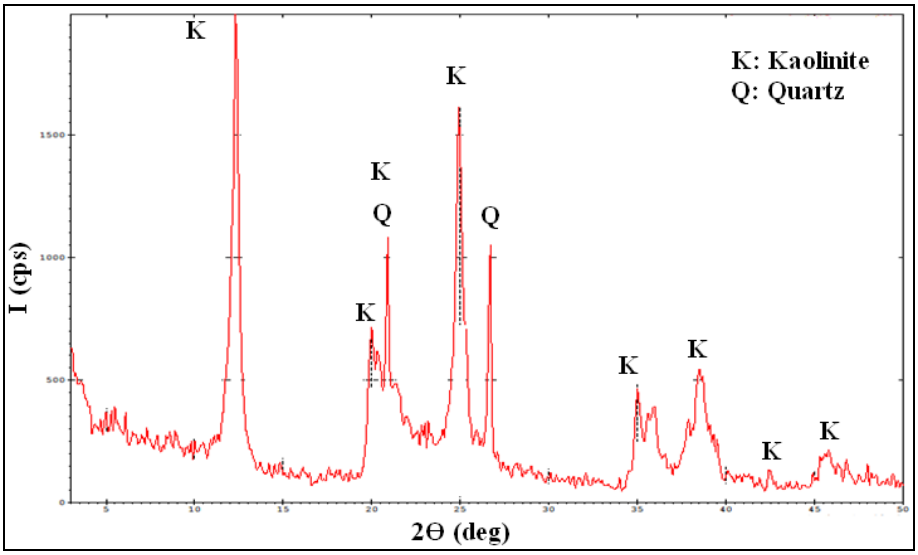

Fig.2: XRD pattern of Kaolin Clay

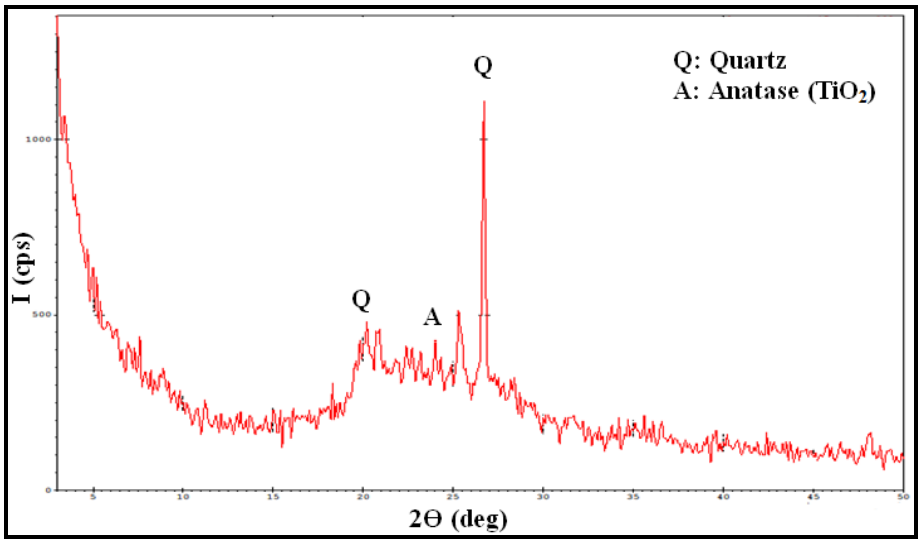

Fig.3: XRD pattern of Meta Kaolin

- **Effect of Leaching Time**

A mixture of (83 ml) of sulfuric acid (30%) is mixed with (25 gm) of (600 µ) of metakaolin at varying time of (30 to 60 minutes) at (75 °C).

As shown in Fig. (4) the optimum leaching time for alumina extraction is found to be (60 minutes).

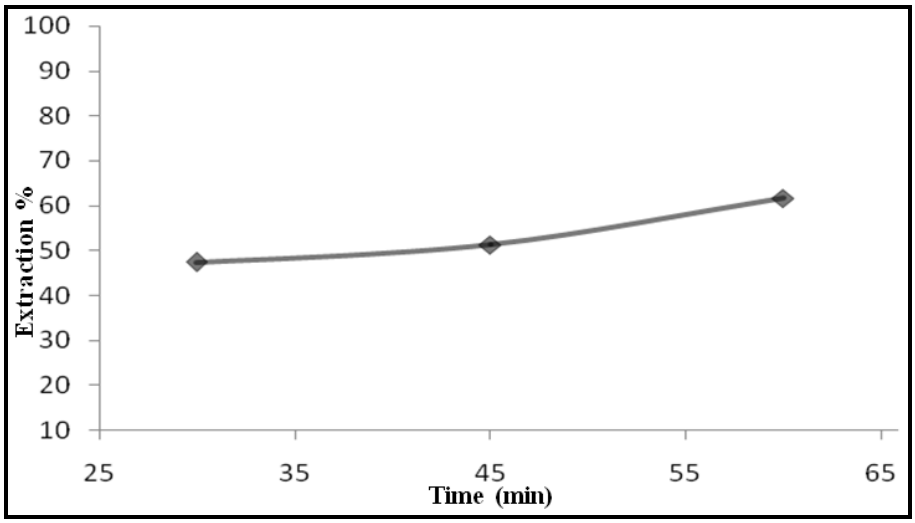

Fig.4: Effect of time on alumina extraction %

- **Effect of Reaction Temperature**

(25 g) of (600 µ) metakaolin samples were leached with (83 ml) of (30%) sulfuric acid at varying temperatures from 75 – 105 °C for 1 hour. The results of extraction of alumina from meta kaolin are illustrated in Fig. (5). The rate of leaching increases with increase in temperature because the rate of diffusion of aluminum ions in solution increases and the solution becomes less viscous. At (105 °C), (90%), alumina was extracted.

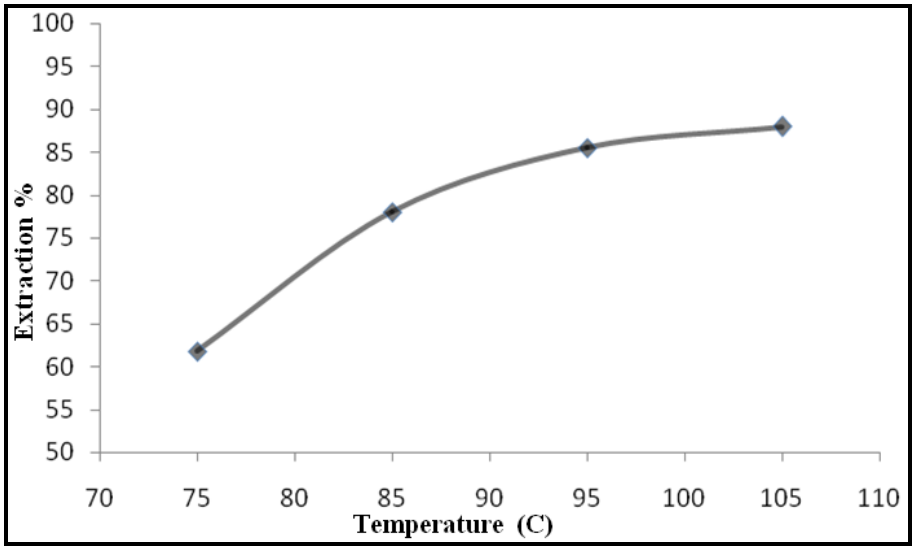

Fig.5: Effect of temperature on alumina extraction %

- **Effect of Meta Kaolin Particle Size**

Different particle size of metakaolin (30, 50, 100) mesh were used. The experiments were carried out at the conditions of (30 wt.%) H_2SO_4, (60 min) reaction time, and (95 °C) reaction temperature). Fig. (6) shows the results of alumina extraction from the ore, both (50 and 100) mesh particle size has reflected extraction of almost (90%), lower extraction is obtained at the particle size of 30 mesh. However, the results gained from the particle size of 30 mesh can be considered as optimum, and due to some energy saving as a finer grinding would result in a high power consuming operation.

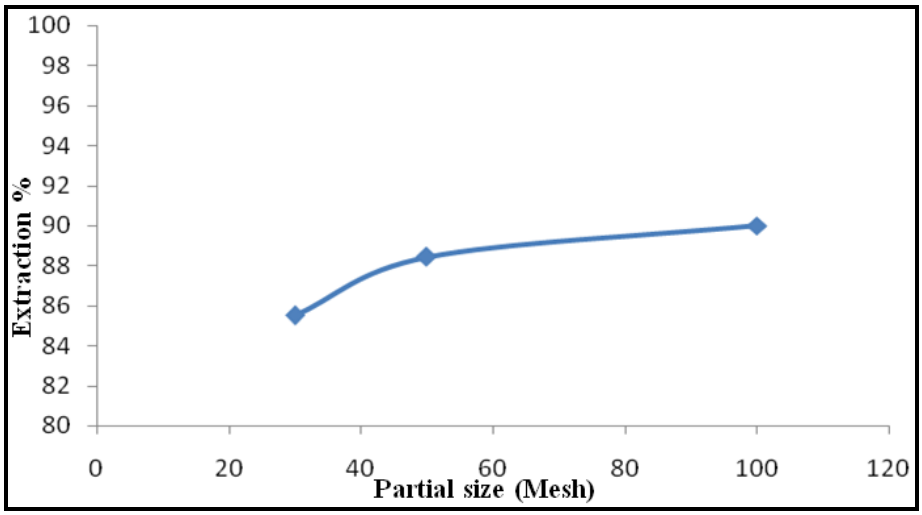

Fig.6: Effect of particle size on alumina extraction %

- **Effect of Aluminum sulfate Calcination Temperature**

The prepared Aluminum Sulfate was studied by X-Ray, it is found that the produced compound correspond to $\{Al_2(SO_4)_3.12H_2O\}$ as shown in Fig. (7). The chemical composition is presented in Table (2).

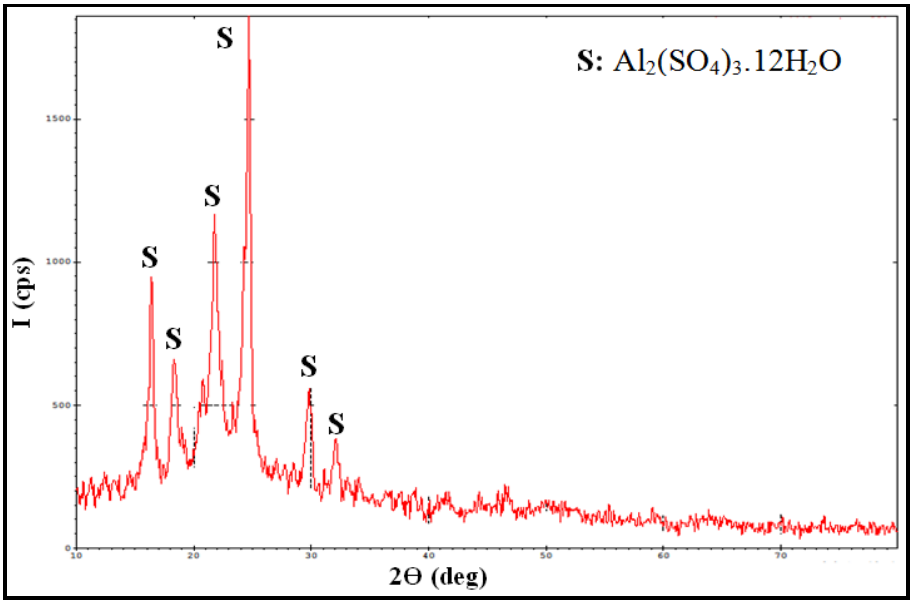

Fig.7: XRD pattern of Prepared Aluminum Sulfate

Table 2: Chemical composition of prepared Aluminum sulphate

Fe_2O_3%	Al_2O_3	SO_3%	Description
0.15	17.90	43.08	$Al_2(SO_4)_3.12H_2O$
-	18.3	43.01	theoretical

In order to remove the sulfate, aluminum sulfate was first dried at (70 °C) and then calcined at different temperatures for (2 hour) in an electric furnace. It has been reported in literature that decomposition of aluminum sulfate occur at temperature range of

(680 – 1030) °C (Wang *et al.*, 2009 and Park *et al.*, 2002), thus a calcination temperature ranging from (800 °C) to (1000 °C) for a duration of (2 hour) was operated in order to study the effect of such factor on the alumina obtained from aluminum sulfate. Fig. (8) shows the effect of Calcination temperature on the γ-alumina purity.

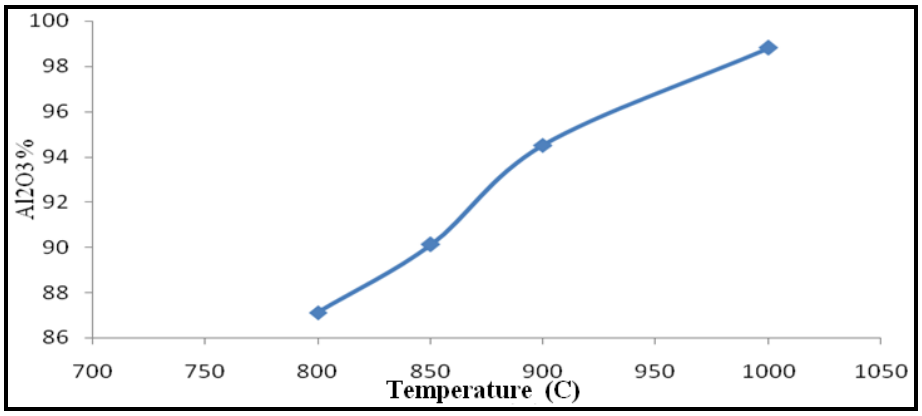

Fig.8: Effect of calcination Temperature on γ-alumina purity

CHARACTRAZATION OF Nano γ-alumina

- **X-Ray Analysis**

The chemical analysis and mineralogical composition of nano γ-alumina were carried out by X-Ray Fluorescence (XRF) type Shimadzo (1800) and X-ray diffractometer (XRD) type Shimadzo 700 in the central laboratories of the Iraq Geological Survey (GEOSURV) are shown in Table (3) and Fig.(9).

Table 3: Chemical composition of prepared Nano γ-alumina

Al_2O_3%	Fe_2O_3%	Description
98.81	0.17	γ-alumina

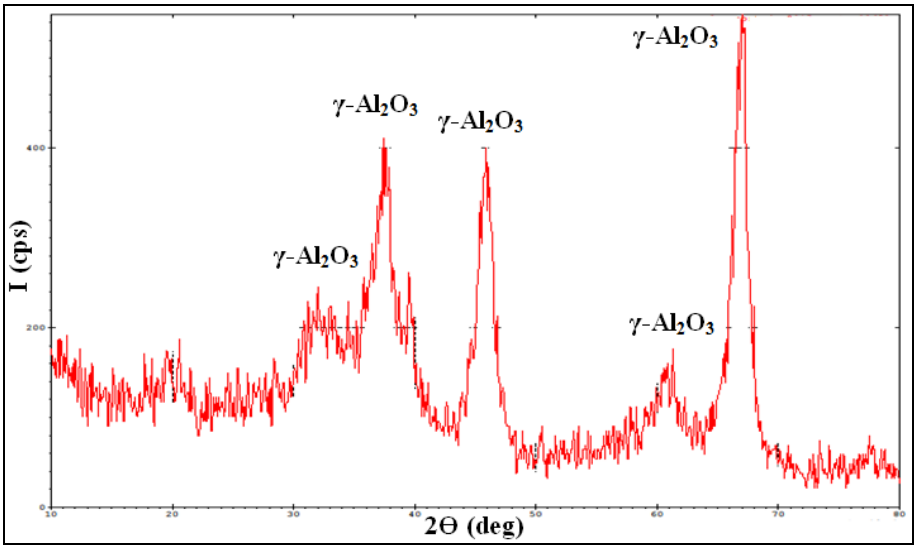

Fig.9: XRD pattern of synthesized nano-gama alumina

The results of XRD analysis of resulted sample confirmed the formation of γ-alumina through comparing with JCPDS 29 – 63. The characteristic peaks of γ-alumina are 2Θ = 37.37, 2Θ = 45.86° and 2Θ = 66.84°.

- **BET Analysis**

The surface area, pore size and pore volume of the pure nano-gama alumina obtained using N_2 adsorption-desorption isotherm were accomplished in the Petroleum Research and Development Centre as shown in Table (4).

Table 4: BET analysis results for the synthesized nano-gama alumina

Surface area (m^2/g)	Pore volume (cm^3/g)	Pore size (Å)
117	1.1	337.64

The specific surface area is one of the most important characteristics of the alumina powder.

Most of the industries need powders with high specific surface area. Therefore, this sample is suitable for use as catalyst, catalytic support, support and adsorbent.

The measured specific surface area can be converted to equivalent particle size according to the following equation:

$$D_{BET} = \frac{6000}{\rho * S_{BET}} \quad \ldots\ldots\ldots\ldots\ldots\ldots 4$$

Where D_{BET} (nm) is the average particle size, S_{BET} is the specific surface area expressed in ($m^2.g^{-1}$) and ρ is the theoretical density of gamma alumina expressed in $g.cm^{-3}$ (ρ Al_2O_3 = 3.9 $g.cm^{-3}$) (Contreras *et al*., 2006).

The average particle size calculated from BET was found to be (13.2 nm).

CONCLUSIONS

γ-alumina powders were successfully synthesized by alumina extraction processes through reaction of meta kaolin with H_2SO_4 solution. Pure aluminum sulfate (99%) was obtained by direct precipitation in ethanol. Pure alumina nano particle (98.81%) was prepared by calcination of aluminum sulfate at 1000 °C for 2 hr. particle size about 13 nm, specific surface area of 117 $m^2.g^{-1}$, pore volume 1.1 cm^3/g and pore size 337.6 Å. It is concluded that kaolin can be used as promising material for the preparation of γ-alumina by a simple, rapid and economical method.

REFERENCES

Bellotto, M., Gualtieri, A., Artioli G. and Clark, S.M., 1995. Kinetic Study of the Kaolinite-Mullite Reaction Sequence. Part I: Kaolinite Dehydroxylation, Physics and Chemistry of Minerals, Vol.22, No.4, p. 207 – 214.

Blendell, J.E., Bowen, H.K. and Coble, R.L., 1984. Effects of Particle Distribution on Transformation-Induced Toughening in an MgO-PSZ, American Ceramic Society Bulletin, Vol.63, p. 799 – 804.

Contreras, C.A., Sugita, S., Ramos, E.L., Torres, M. and Serrato, J., 2006. J. of Materials Azojomo, Satoshi Sutoshi Sugita. 2

Deer, W.A., Howie, R.A. and Zussman, J., 1992. An Introduction to the Rock-Forming Minerals, 2 Edition, Longman, Harlow.

Dynys, F.W. and Halloran, J.W., 1982. Alpha Alumina Formation in Alum-Derived Gamma Alumina, Journal of the American Ceramic Society, Vol.65, No.9, p. 442 – 448.

Gitzen, W., 1970. Alumina as Ceramic Material, American Ceramic Society, Columbus

Johnston, G.P., Muenchausen, R., Smith, D.M., Fahrenholtz, W. and Foltyn, S., 1992. Reactive Laser Ablation Synthesis of Nanosize Alumina Powder, Journal of the American Ceramic Society, Vol.75, No.12, p. 3293 – 3298.

Kato, E. Diamon, K., Nanbu M., 1981. Decomposition of Two Aluminum Sulfates and Characterization of the Resultant Alumina, Journal of the American Ceramic Society, Vol.64, No.8, p. 436 – 443.

McColm, J., 1983. Ceramic Science for Materials Technologist. Chapman and Hall, New York.

Murray, H.H., 2000. Traditional and Newapplications for Kaolin, Smectite, and Palygorskite: A General Overview, Applied Clay Science, Vol.17, No.5 – 6, p. 207 – 211.

Noda, H., Muramoto, K. and Kim, H., 2003. Preparation of Nano-Structured Ceramics Using Nano-sized Al2O3 Particles, Journal of Materials Science, Vol.38, No.9, p. 2043 – 2047.

Ogihara, T., Nakagawa, H., Yanagawa, T., Ogata, N. and Yoshida, K., 1991. Preparation of Monodisperse, Spherical Alumina Powders from Alkoxides, Journal of the American Ceramic Society, Vol.74, 2263pp.

Paglia, G., Buckley, C.E., Rohl, A.L., Hart, R.D., Winter, K. and Studer, A.J., 2004. Boehmite Derived γ-Alumina System 1. Structural Evolution with Temperature, with the Identification and Structural Determination of a New Transition Phase, γ'-Alumina," Chemistry of Materials, Vol.16, No.2, 220pp.

Parida, K.M., Pradhan, A.C., Das, J. and Sahu, N., 2009. Synthesis and Characterization of Nano-Sized Porous Gamma-Alumina by Control Precipitation Method, Materials Chemistry and Physics, Vol.113, No.1, p. 244 – 248.

Park, J.H., Kim, S.W., Lee, S.H., Kim, H.S., Park S.S. and Park, H.C., 2002. Synthesis of Alumina Powders from Kaolin with and without Ultrasounds, Journal of Materials Synthesis and Processing, Vol.10, No.5, p. 289 – 293.

Wang, Y.H., Wang, J., Shen, M.Q. and Wang, W.L., 2009. Synthesis and Properties of Thermostable γ-Alumina Prepared by Hydrolysis of Phosphide Aluminum, Journal of Alloys and Compounds, Vol.467, No.1 – 2, p. 405 – 412.

Wang, S., Li, X., Li Y. and Zhai, Y., 2009. Synthesis of Gamma-Alumina via Precipitation in Ethanol, Materials Letters, Vol.62, No.20, p. 3552 – 3554.

Yajima, Y., Hida, M., Taruta, S. and Kitajima, K., 2003. Pulse Electric Current Sintering and Strength of Sintered Alumina Using γ-Alumina Powders Prepared by the Sol-Gel Method, Journal of the Ceramic Society of Japan, Vol.111, No.1294, p. 419 – 425.

Zhao, R.H., Guo, F., Hu, Y.Q. and Zhao, H.Q., 2006. Self-Assembly Synthesis of Organized Mesoporous Alumina by Precipitation Method in Aqueous Solution, Micro-porous and Mesoporous Materials, Vol.93, No.1 – 3, p. 212 – 216.

About the authors

Mr. Jassim Mohammed Kshash, is a Chemical Engineer. He is working in the Geological Survey of Iraq (GEOSURV) Research and Development Department. He holds a B.Sc. degree in Chemical engineer (1992) and in Environmental engineering (2008) from the University of Baghdad.

e-mail: Jkshash@yahoo.com

Mr. Baha'a Abdul Majeed Sabbar, is a Chemical Engineer. He is working in the Geological Survey of Iraq (GEOSURV) Research and Development Department. He holds a B.Sc. degree in Chemical engineer (1997) from the University of Baghdad.

e-mail: Bahaaalmajeed@yahoo.com