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Synthesis of γ- alumina nanoparticle from Agar Ashatti kaolin

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Abstract

This paper reports a process for the production of γ-alumina from Agar Ashatti kaolin, kaolin was calcined at 900°C for 2h to obtain meta-kaolin. Extracting process was used to synthesise Gamma alumina powder by meta-kaolin via H_2SO_4 and aluminium sulphate was formed, the precipitated aluminium sulphate was dried at 70 C and calcined at 900°C for 2h, which resulted in the formation of γ-alumina with purity 98%. The structure of γ- alumina was confirmed by XRF and XRD, and the mean particle size of γ- alumina was determined by SEM to be 0.5 – 0.9 µm. The study revealed the kaolin of Agar Ashatti could be a promising material for preparing γ- alumina.

Keywords: synthesis, Agar Ashatti Kaolin, γ- alumina, Calcination.

* Introduction

Clay ores are available in abundance in southern Libya, especially in the areas around the city of Sebha, such as the Agar-Shatti area, where previous studies by the Industrial Research Centre (IRC) confirmed that these ores are considered a mineral wealth that requires exploitation in strategic industries and supporting the national economy [3,4].Studies also showed that the chemical composition of the clays extracted from the southern regions of Libya and the Agar Al-Shatti clay block, the subject of the study, is that their chemical composition conforms to the standard specifications specified by the American Society for Testing Materials ASTM (618-03) through chemical analysis by X-ray flash

(XRF)[1]. The kaolin content in beach Agar clays is more than 50% of the clay content, and the percentage of silica and alumina is appropriate compared to standard specifications (618-03). The map in Figure No (1) shows the location of the Agar Al-Shatti area near the city of Sebha in southern Libya.

Figure (1): The location of the Agar Al-shatti-Libya

Alumina has many technological and industrial applications. It exists in a variety of meta-stable structures including γ- δ- θ- κ- and χ- alumina, as well as its stable α- alumina phase [2]. Kaolin has been widely used in industry to produce alumina. Additionally, many studies have been explained that Agar Ashatti kaolin contains high purity of alumina [3-5], γ-alumina is more important nano-sized than other various structures for alumina, it used as a catalyst in petroleum industries and catalyst substrate, thermal wear coatings and structural composites for spacecraft [5-7]. Recent studies have shown that γ-alumina is good thermodynamically relative to α-alumina when a critical surface area is done [8], and sintering behaviour and densification temperature of alumina can be promoted with nano γ-alumina powder compared with χ-alumina sample [9], γ-alumina has been prepared by variety methods such as hydrolysis of alumina alkoxide [10], sol-gel synthesis from calcination of Boehmite [11], laser ablation of an aluminium target in an oxygen atmosphere [12], thermal decomposition of aluminium sulphate [13]. Agar Ashatti kaolin was investigated as a magnificent clay mineral containing 30-36 percent by weight of alumina and had layers of silicate mineral $Al_2Si_2O_5(OH)_4$. The geometric shape of kaolin as a tetrahedral sheet linked through oxygen atoms to one octahedral sheet of alumina octahedral [14]. The literature survey explained that researchers [15-23] studied the production and characterisation of γ-alumina from kaolin in different areas. In this study, Agar Ashatti kaolin can be a suitable material for preparing γ-alumina using a simple and feasible method. The materials used in this work are relatively cheap and industrial.

* **Experimental**

*** Materials**

Chemical materials were used in this work sulphonic acid 98% from Sigma Aldrich, ethanol 100% from Sci-Chem, distilled water and kaolin clay from the stone-pit of Agar Ashatti /Libya.

*** Instrumentation**

X-ray diffraction (XRD) studies were carried out on a Siemens D5000 X-ray powder diffractometer using a Cu anode with 70 % intensity. Measurement of samples was carried out in the range 2θ of 0°-60°, at a scanning rate of 1°/ min. SEM characterization of γ- alumina was carried out with scanning electron microscopy (Hochschule). The chemical composition of Agar Ashatti kaolin was analysed by X-ray fluorescence spectroscopy (EDXRF). All of the examinations were done at Central Metallurgical Research institute-Egypt.

*** Synthesis**

The kaolin was collected from the Agar Ashatti region in south Libya and used as a starting material. The chemical composition of used kaolin is given in Table 1. The kaolin sample was ground and sieved to particles below 0.5 mm in size. After mechanical processes, kaolin powder was calcined at 800°C for 2 h in an electronic furnace, the calcined kaolin is called Meta kaolin. After calcination, the alumina components became easier to react, and 2.0 N of the sulphonic acid solution was prepared to dissolve the powder of meta kaolin at a ratio of 20 gm meta kaolin and 80 ml of acid. The total volume of a mixture of kaolin and acid (250 ml) was kept in a 500 ml round flask. The reaction flask was fitted on a magnetic stirrer to mix the mixture for 3-6 h, the mixture temperature was set at 70°C using a heating mantel to control the desired temperature, and a reflex condenser was fitted with the flask. After the mixing process was completed, the mixture of kaolin and acid was leached, cooled at room temperature and filtered to remove the rest While 550 ml of ethanol was going on a stirrer, the filtered leach was added drop by drop at a rate of 5ml\min. Ethanol was used as a precipitating agent to precipitate aluminium sulphate from the ionic solution [15, 16]. The residue was washed again with distilled water and dried at 70°C for 1 h. The final precipitate was calcined at 900°C for two hours in an electric furnace.

According to the literature survey [17, 18], the main parameters that affected the synthesis process are the effect of leaching time, reaction temperature, particle size of meta

kaolin and calcination temperature. So that the optimum leaching time for alumina extraction is 6 h, the reaction temperature is 70°C, the particle size of meta kaolin powder is 0.5 mm in size and the applied calcination temperature is 900°C.

Table 1: Chemical and mineralogical composition of Agar Ashatti kaolin

Compound Formula	Na_2O	TiO_2	Al_2O_3	SiO_2	Fe_2O_3	K_2O	CaO	L.O.I	Total
Concentration	**0.11**	1.38	33.53	48.01	2.15	0.98	0.98	12.91	**98.63**
Mineralogical Composition	**Kaolinite, Quartz, Anatase**								

* Results and discussion

XRD analysis was used to investigate the crystalline structure of the synthesis nano-gamma alumina Figure 1 shows the XRD pattern of kaolin containing 62.9 % kaolinite, 31.1 % silica and 6% TiO_2. After the calcination process of kaolin at 800 °C converted to meta kaolin, it observed that meta kaolin shows only the characteristic peaks of kaolinite and silica, all other peaks disappear giving a featureless band of X-ray amorphous meta-kaolin. Kaolin undergoes a series of transformations thermal in the air at atmospheric pressure. Endothermic dihydroxylation (dehydration) begins at 500 °C-750 °C to produce disordered meta-kaolin, $Al_2Si_2O_7$, but continuous hydroxyl loss (-OH) is observed up to 900 °C to gradual oxidation of meta-kaolin [17, 18]. In this study, calcination of kaolin at 900 °C led to form meta-kaolin which is transient and easier to react than kaolin. As shown in the XRD of kaolin Figure (1) Equation (1) shows the changes during calcination and formation of meta-kaolin. During the calcination, the structure of kaolin was degraded and two water molecules were excepted.

$Si_2O_5(OH)_4Al_2 \rightarrow Al_2Si_2O_7 + 2H_2O$ (1)

Aluminium sulphate was formed during the leaching of meta-kaolin in sulphonic acid, due to the alumina in meta-kaolin being extracted and dissolved in H_2SO_4 as shown in (Equation 2).

Al_2O_3 (in meta-kaolin) + $3H_2SO_4 \rightarrow 2Al^{+3} + 3SO_4^{-2}$ (2).

The precipitate of aluminium sulphate was obtained after the addition of aluminium sulphate in ethanol, as shown in Equation (3).

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

$Al_2(SO_4).3H_2O \xrightarrow{(\Delta\ 900°C)} \gamma\text{-}Al_2O_3$ (4)

Evaporating ethanol first, followed by calcination at 900°C, resulted in the conversion of aluminium sulphate to γ-alumina (Equation 4).

The XRF analysis of Agar Ashatti kaolin revealed the high purity of γ-alumina (98% by weight) along with other metal oxides and Sio_2. Various studies [1-19] have indicated that aluminium sulphate decomposes within the temperature range of 700°C to 1030°C. The XRD analysis of the sample after being subjected to calcination at 900°C showed the presence of γ-alumina, which was confirmed by comparing it with the XRD pattern of kaolin and meta-kaolin, as illustrated in Figures (2, 3). The Figures showed the presence many of oxides which disappeared in Figure (4) confirming the presence of only the characteristic peaks of γ-alumina. The Gama alumina peaks were confirmed by SEM analysis. Scanning electron microscopy was used to evaluate the surface morphology and measure the particle sizes of synthesized gamma alumina. Figure (5) displays the SEM images of meta-kaolin and synthesized Gamma alumina kaolin; it was observed the difference between the two images in particle size and structure of meta-kaolin and synthesized nano γ-Al_2O_3 which means transforming meta kaolin to nano kaolin. The particles obtained fall within the range of 0.5 - 0.9 micrometres.

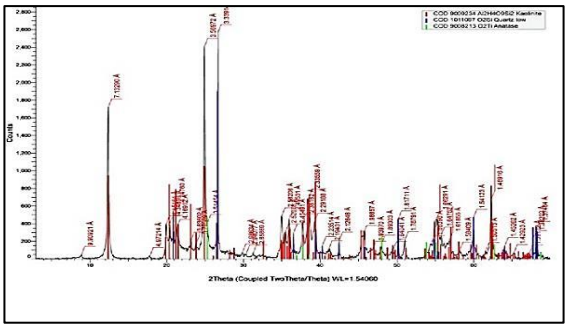

Figure (2): XRD pattern of kaolin Agar Ashatti Clay.

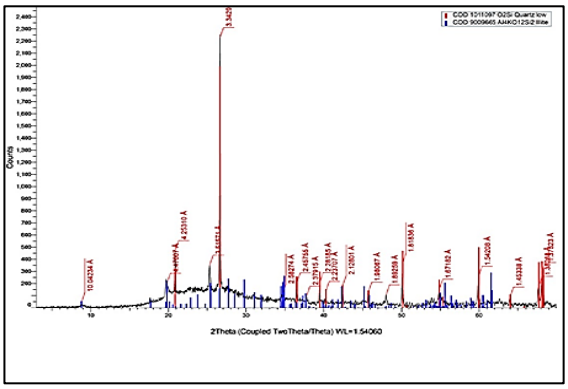

Figure (3): XRD pattern of meta kaolin Agar Ashatti Clay.

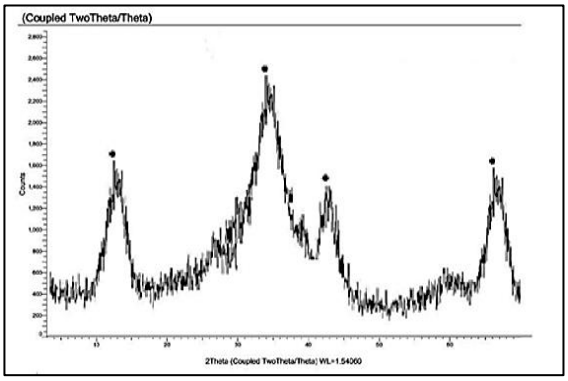

Figure (4): XRD pattern of synthesized nano γ-Al_2O_3

Gamma alumina is utilized as both a catalyst and catalyst support due to its increased specific surface area and thermal stability. Gamma alumina remains stable up to 1030°C. Studies suggest that the addition of alkaline-earth ions, rare-earth ions, silicon, phosphor, or a combination of these can improve its thermal

stability [21, 22, 24]. Silicon supports the stabilizing alumina more than other elements and also acts as an effective inhibitor in the transformation of γ-alumina to α-alumina [23, 25, 26, 27].

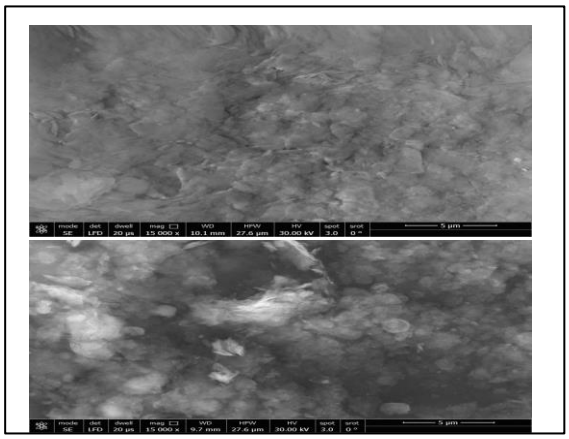

Figure (5): SEM image of Meta kaolin

The chemical analysis and mineralogical composition of nano Gama alumina were supported with the XRF technique which confirmed the formation of nano Gama alumina in a high percentage (98.46) with a few impurities as explained in Table 2.

Table 2: Chemical composition of synthesized nano γ-AlO_3

Al_2O_3 %	TiO_2 %	Fe_2O_3 %	Description
98.06	0.15	0.25	$^{\gamma}$-Al_2O_3

* Conclusion

It is concluded that Agar Ashatti kaolin was a very good starting material for synthesising γ-alumina powder in pure (98%) successfully, the synthesising processes was done by alumina extraction through the reaction of meta kaolin with H_2SO_4 solution. The most important step for the production of gamma alumina was direct precipitation in ethanol. In conformity with other searches, it resulted that calcination temperature is the main factor to get hold of various alumina phases. Calcination temperatures were applied in this work at 700 °C – 900° C, techniques were used in this work X-ray fluorescence (XRF), X-ray diffractometer (XRD) and scanning electronic microscope (SEM).

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* Declaration of Conflicting Interest

There are no conflicts of interest.

* Funding

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* Data Availability

There are no more data.

* Author Contribution

Dr. Fathyah Omar: a main author how design the experiments, analysis and explain of results.

Sumaya Mehriz: co-author who does the experiments.

Fatima Ali: reviewing.

*** References**

Y. Cao, Y. Wang, Z. Zhang, Y. Ma, and H. Wang, " Recent progress of utilization of activated kaolinitic clay in cementitious construction materials" Composites B. Engineering, 211, (2021), 108636. https://doi.org/10.1016/j.compositesb.2021.108636.

K. Kaunisto, J. Lagerbom, M. Honkanen, T. Varis, A.Lambai, G. Mohanty, E. Levanen, P. Kiviky-Reponen, E. Frankberg, "Evolution of alumina phase structure in thermal plasma processing" Ceramics International, A 49, 21346-21354 (2023) doi: https://doi.org/10.1016/j.ceramint.2023.03.263.

R. Borg, A. Hamed, R. Edreis, A. Mansor, "Characterization of Libyan metakaolin and its effects on the mechanical properties of mortar", Materials Science and Engineering, A 442, 012005 (2018) doi: 10.1088/1757-899X/442/1/012005.

A. Shebani, W. Elhrari, A. Klash, A. Aswei, K. Omran, A. Rhab, "Effects of Libyan Kaolin Clay on the Impact Strength Properties of High Density Polyethylene/Clay Nanocomposites" International Journal of Composite Materials, A 6, 152-158, (2016).

R. Yassin, F. Abd EL-Rahiem "Some Characterization & Beneficiation Methods of Kaolin Ore", International Journal of Innovative Science, Engineering & Technology, A 9, 2348-7968, (2022) doi: https://www.ijiset.com

R. Prins, "On the structure of γ-Al_2O_3," Journal of Catalysis, A 392, 336-346 (2020) doi: https://doi.org/10.1016/j.jcat.2020.10.010.

M. Abbaspour, M. Makarem, T. Roostaei, E. Rahimpour, M. Bonyadi", Synthesis and Characterization Studies of γ-Alumina Catalyst Prepared by Orange Peels as a Template" Topics in Catalysis, A10, 1007 (2022) https://doi.org/10.1007/s11244-022-01578-6

K. Ishaq, A. Saka, A. Kamardeen, A. Abdulrahman, I. K. Adekunle, A. Afolabi, "Application of γ-alumina as catalyst support for the synthesis of CNTs in a

CVD reactor" Advances in Natural Sciences: Nanoscience and Nanotechnology, A 9, 035012(2018) doi: 10.1088/2043-6254/aad5bb.

S. Wang, X. Li, S. Wang, Y. Li, and Y. Zhai, "Synthesis of γ-alumina via precipitation in ethanol," Materials Letters,A 62, 3552-3554 (2008) doi: https://doi.org/10.1016/j.matlet.2008.03.048.

M. Boldin, A. Popov, E. Lantsev, A. Nokhrin, V. Chuvil'deev, "Investigation of the Densification Behavior of Alumina during Spark Plasma Sintering," Materials, A 15, doi: 10.3390/ma15062167.

S. Siahpoosh, E. Salahi, F. Hessari, and I. Mobasherpour, "Synthesis of γ-Alumina Nanoparticles with High-Surface-Area via Sol-Gel Method and their Performance for the Removal of Nickel from Aqueous Solution," Bulletin de la Société Royale des Sciences de Liège, A10, 812-934 (2016), doi: 10.25518/0037-9565.5748.

B. Huang, C. Bartholomew, B. Woodfield, "Facile synthesis of mesoporous γ-alumina with tunable pore size: The effects of water to aluminum molar ratio in hydrolysis of aluminum alkoxides," Microporous and Mesoporous Materials, A 183, 37-47(2014) doi: https://doi.org/10.1016/j.micromeso.2013.09.007.

N. Tanaka, M. Watanabe, K. Komurasaki, H. Sekine, and H. Koizumi, "Aluminum precipitation on oxygen-deficient alumina in laser alumina reduction," Vacuum, vol. 217, p. 112289, 2023/11/01/ 2023, doi: https://doi.org/10.1016/j.vacuum.2023.112289.

G. K. Çılgı and H. Cetişli, "Thermal decomposition kinetics of aluminum sulfate hydrate" Journal of Thermal Analysis and Calorimetry,A 98, 855-861(2009) doi: 10.1007/s10973-009-0389-5.

K. Neeraj, M. Chandra, "Basics of Clay Minerals and Their Characteristic Properties" in Clay and Clay Minerals, N. Gustavo Morari Do Ed. Rijeka: IntechOpen, p. Ch. 2(2021).

H. Potdar, K.. Jun, J. Bae, S. Kim, Y. Lee, "Synthesis of nano-sized porous γ-alumina powder via a precipitation/digestion route," Applied Catalysis A: General, A321, 109-116(2007), doi:

https://doi.org/10.1016/j.apcata.2007.01.055.

S. Hosseini, A. Niaei, D. Salari, "Production of γ-Al_2O_3 from Kaolin," Open Journal of Physical Chemistry, A 01, 23-27,(2011), doi: 10.4236/ojpc.2011.12004.

M. Kshash, B. Sabbar, "Preparation of Nano-gamma Alumina from Iraqi Kaolin," Iraqi Bulletin of Geology and Mining A 14, 121130(2018).

H. Mgbemere , C. Oluigbo, "Synthesis of Alumina from Kaolin Found in Ajebo, Ogun State, Nigeria," Eskişehir Technical University Journal of Science and Technology A - Applied Sciences and Engineering, A 25, (2024) doi: 10.18038/estubtda.1375497.

P. Song, J. Mahy, C. Calberg, A. Farcy "Influence of thermal and acidic treatments on the morphology of a natural kaolinitic clay mineral," Results in Surfaces and Interfaces, A 12, 100131 (2023) doi: https://doi.org/10.1016/j.rsurfi.2023.100131.

S. Zhang, Z. Wu, J. Chen, R. Xu, M. Wang, W. Ni, "Study on the Hydration Reaction of Typical Clay Minerals under Alkali and Sulfate Compound Activation," Gels,A 8 564(2022),doi: https://www.mdpi.com/2310-2861/8/9/564.

S. Said, S. Mikhail, M. Riad, "Recent processes for the production of alumina nano-particles," Materials Science for Energy Technologies,A3 344-363 (2020), doi: https://doi.org/10.1016/j.mset.2020.02.001.

N. Stuart K. Sohlberg, "Investigation of γ-Alumina Particle Size: The Role of Hydrogen Defects on Size Constraint," The Journal of Physical Chemistry C, A 128, 8803-8811, (2024), doi: 10.1021/acs.jpcc.4c01070.

H. Muñoz, S. Korili, A. Gil, "Progress and Recent Strategies in the Synthesis and Catalytic Applications of Perovskites Based on Lanthanum and Aluminum", Materials (Basel),A 15, 9, (2022), doi: 10.3390/ma15093288.

A. Al-Abbasi F.Almahdi, M. Almaky, R. Irzriq, A. Milad, S. Salim, A. Najar "BaO as a heterogeneous nanoparticle catalyst in oil transesterification for the

production of FAME fuel," Inorganic Chemistry Communications A 158 111620, (2023) doi: https://doi.org/10.1016/j.inoche.2023.111620.

S. Jang,D. Gunoh, H. Kim, K. Kim "Controlling the Phase Transformation of Alumina for Enhanced Stability and Catalytic Properties," Angewandte Chemie International Edition,A 63, 15 (2024), doi: https://doi.org/10.1002/anie.202400270.

S. Khanmohammadi, E. Taheri-Nassaj, M. Farrokhi-Rad, "Synthesis of meso-porous gamma-alumina membrane: effect of yttria addition on the thermal stability," Surfaces and Interfaces, A 21, 100683(2020), doi: https://doi.org/10.1016/j.surfin.2020.100683.