RESEARCH ARTICLE

SYNTHESIS OF ALUMINA FROM KAOLIN FOUND IN AJEBO, OGUN STATE, NIGERIA

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ABSTRACT

This study proposes the utilization of kaolin as an alternate resource for alumina production due to the decreasing availability of bauxite ores in Nigeria. This project covers the procedures and operations required to produce a high surface area γ-alumina using kaolin, a refractory material. The kaolin used in this study was sourced from Ajebo in Ogun State, Nigeria. The mineral processing of kaolin was the initial step involving removing inherent impurities from the clay. Subsequently, calcination was performed to eliminate crystallised water and impurities and activate the kaolin's limited alumina content. This activation process facilitated the subsequent acid-leaching reactions. At 90ºC, 5M HCl acid was used to leach meta-kaolin, which was then filtered. The filtrate was mixed with 5M NaOH at 900ºC and was transformed into sodium aluminate. This reaction also facilitated the removal of magnesium and iron hydroxides. Subsequently, HCl was introduced to adjust the pH of the solution. The resulting aluminium hydroxide was then calcined at temperatures of 700ºC and 900ºC for 2 hours each to produce γ-alumina. Ultimately, the calcined material was cooled to ambient temperature inside the furnace. The produced γ-alumina was further characterised using X-ray Fluorescence (XRF), Fourier Transform Infrared spectrometer (FTIR), and Scanning Electron Microscopy (SEM).

Keywords: Alumina, Calcination, Kaolin, Leaching, Synthesis

1. INTRODUCTION

The growing global demand for alumina has raised interest in exploring alternate technologies for its production from low-grade ores. Certain low-cost minerals have been identified as viable and economically feasible resources for aluminium, making them suitable for alumina production by synthesis. Several minerals in this category include kaolin, mica, bauxite, sillimanite, fly ash, andalusite, alunite, and kyanite. Among the several minerals examined, it is worth noting that bauxite emerges as a notable source of alumina, albeit with a marked scarcity [1]. Bauxite, the primary raw material used in the Bayer process to produce alumina, is found in limited quantities globally, including Nigeria. The scarcity of bauxite implies a significant demand for kaolin as a viable substitute for the manufacturing of alumina [2]. Kaolin emerges as a particularly appealing option for the manufacture of alumina compared to other types of clays, primarily owing to its higher aluminum concentration. Kaolin is mainly composed of kaolinite, which has a chemical composition of $Al_2O_3.2SiO_2.2H_2O$ and is characterised by its two-layer silicate structure [3]. Kaolin is a low-cost, naturally occurring substance with a high silica and alumina concentration, making it a suitable substitute for bauxite ore. However, because kaolin is inert and inactive, it must be activated to become active kaolin, which is accomplished by calcination [4].

Aluminium oxide, or alumina (Al_2O_3), can occur in several intermediate phases, contingent upon the specific precursor and procedures employed during processing [5]. The most thermodynamically stable form of alumina is known as α-alumina, which is commonly utilized as a ceramic material. The term "transitional aluminas" is used to refer to other phases of alumina, of which gamma(γ)-alumina is a

crucial example [6]. Gamma-alumina has exceptional characteristics such as high purity, excellent dispersion, and a specific surface area. It possesses resilience to elevated temperatures and inert properties, making it highly suitable for many applications [7]. Wang *et al.* [8] conducted a study that found γ-alumina to have more excellent thermodynamic stability than α-alumina, mainly when a critical surface area is achieved. Due to its porous nature and remarkable activity, γ-alumina is commonly employed as an adsorbent and catalyst support [9].

Kaolin has been used to synthesize alumina in various studies. Ibrahim *et al.* [10] used a low-cost kaolin to extract γ-alumina by employing a combination approach for producing alumina particles from local kaolin. The method consisted of a two-step process: calcination at 700°C using sodium chloride and leaching using sulfuric and hydrochloric acids, yielding 79.28% pure alumina. In a study conducted by Hosseini *et al.* [11], synthesizing γ-alumina from kaolin was achieved by subjecting kaolin to a calcination process at 800°C for 2 hours, resulting in the transformation of kaolin into meta-kaolin. The synthesis of γ-alumina powder then involved the extraction of alumina from meta-kaolin via a reaction with H_2SO_4. Subsequently, the resulting aluminium sulfate precipitated in ethanol. The aluminium sulfate was dried and subsequently subjected to calcination at 900°C for 2 hours, which led to the formation of γ-alumina. A similar procedure was reported by Kshash and Baha'a [12]. Bawa *et al.* [13] and Salahudeen *et al.* [14] described the synthesis of γ-alumina from Kankara kaolin. The hydrothermal process was used by Bawa *et al.* [13] to synthesize γ-alumina from kaolin. The alumina was obtained through the thermal processing of ammonium alum produced from the filtrate of dealuminated metakaolin. At 800°C calcination temperature and 3 hours soaking, crystalline aluminium sulfate with 39 wt. % Al_2O_3 was produced, while γ-alumina was produced after 3 hours of soaking at 850°C. However, Salahudeen *et al.* [14] used a simple three-step dealumination, precipitation, and calcination method. The kaolin underwent a wet beneficiation process, followed by metakaolinization and dealumination. The precipitation of amorphous aluminium hydroxide from aluminium sulfate was achieved by utilizing a sodium hydroxide solution. The generated aluminum hydroxide underwent thermal processing at various calcination temperatures ranging from 300°C to 900°C. Subsequently, at 900°C, a complete formation of the γ-alumina phase was identified.

Tantawy and Alomari [15] describe using hydrochloric and sulfuric acids to produce alumina from kaolin through acid leaching. The kaolin sample underwent calcination at 850°C. Subsequently, it was subjected to leaching using a 6 M acid solution at 90°C. This was followed by adding 5.0 M NaOH and HCl solutions to the leaching solution. The resulting precipitated aluminium hydroxide was then transformed into alumina through calcination at a temperature of 900°C. However, Yang *et al.* [16] describe synthesizing nanosized γ-Al_2O_3 using acid-leachates from calcined kaolin. The precipitation of Aluminium (hydro)oxide occurred with the addition of ammonia to the leachate, facilitated by its inclusion of polyethylene glycol. After calcination, a fine white powder consisting of nanosized γ-Al_2O_3 particles was successfully produced. On the other hand, Park *et al.* [17] synthesized alumina powders from kaolin with 1.0 M H_2SO_4 solution via alumina extraction processes with and without ultrasound and found that the utilization of ultrasound during the synthesis of Al_2O_3 powders proved to be an effective method for reducing the required synthesis time.

This current study utilized kaolin, a readily available and cost-effective mineral in Nigeria, as the primary material for the synthesis of alumina. This study aims to synthesize γ-alumina with a high surface area using kaolin sourced from Ajebo in Ogun State, Nigeria.

2. MATERIALS AND METHODS

Figure 1 describes the methodology involved in the production of alumina from kaolin.
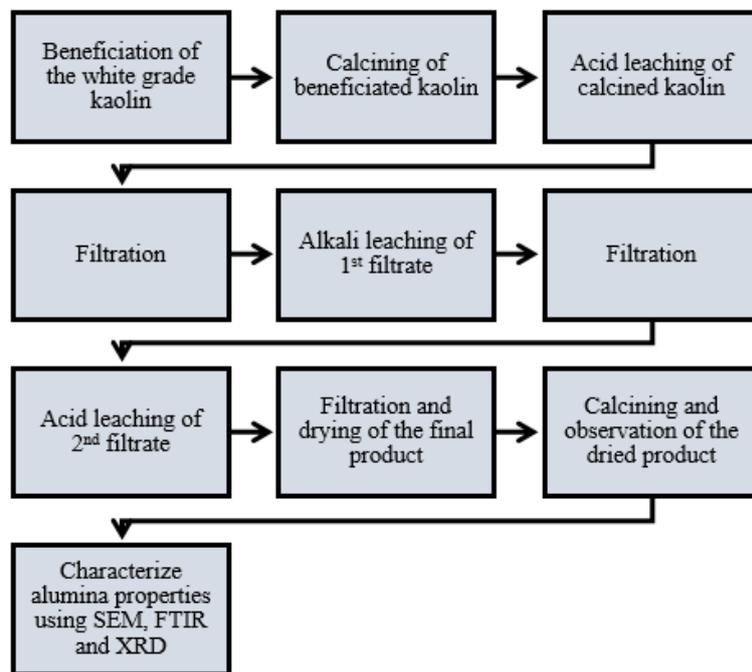
Figure 1. A schematic representation illustrating the sequential steps involved in the production of alumina from kaolin.

2.1. Sample Preparation and Characterisation

The kaolin clay was collected in lumps from Ajebo in Ogun State, Nigeria. Afterward, it was crushed and pulverised to smaller sizes using a milling machine. The powdered clay was soaked in water for forty-eight hours. This enabled easy separation of the fine clay particles that are physically bonded and may not disintegrate by mere vibration. The decantation process was carried out to reduce water content before wet sieving. Wet sieving was done to optimize the properties with a sieve of finer mesh size (100 μm) to avoid near misses of impurities in the clay. Wet sieving aims to separate fine clay particles still bonded to the surfaces of sand particles and other impurities in the batch. A suspension of clay and water was the result of wet sieving. The clay particles, which were initially dispersed, were allowed to settle, after which the water left above was decanted. After the decantation of water, the leftover clay slurry was dried and pulverised. The dried kaolin was calcined in the Vecstar heat treatment furnace, Model LF3, at a temperature of $750^{\circ}C$ for 2 hours. It was cooled to room temperature in the furnace to obtain the metakaolin phase. Calcination was performed to eliminate the presence of crystallized water and impurities and to activate the small amount of alumina in the kaolin, activating this layer for the leaching with acid reactions.

The calcined kaolin 20 g was mixed with 200 ml of 5M hydrochloric acid in a 250 ml round bottom flask. The mixture in a round bottom flask attached to a reflux condenser was heated to $90^{\circ}C$ and stirred at 500 rpm for 3 hours using a Stuart Hot Plate and Stirrer Model No. UC152. The reflux condenser was used to minimize the acid loss; stirring was done to have a homogenous mixture and speed up the kaolin bond's breaking. The slurry produced was diluted with 200 ml distilled water and filtered using a funnel and Whatman filter paper of Cat No. 1001125. The filtrate was a golden yellow solution, while the residue was cream-like powder. Distilled water was used to wash the dealuminated residue and dried at $100^{\circ}C$ in the laboratory oven. A second leaching stage was done by heating the filtrate to $90^{\circ}C$ in an Electrotherm EM 250 heating mantle. Afterward, the filtrate was mixed with an excess 5M Sodium hydroxide solution at $900^{\circ}C$. It was transformed into sodium aluminate to aid the separation of the hydroxides of magnesium and iron. A cloudy solution was formed with the addition of excess sodium hydroxide. The resulting mixture, when filtered, yielded a colourless solution, and the residue was

brownish. After filtration, 5M HCl was mixed with the sodium aluminate while stirring to bring the pH to 7 using pH Meter Model PHS – 25. The aluminium hydroxide produced was filtered and dried at 120ºC in the laboratory oven for 24 hours. The aluminium hydroxide produced was divided into two portions, calcined at temperatures of 700ºC and 900ºC for 2 hours, and cooled to room temperature inside the furnace to obtain alumina. The samples were characterised using Scanning Electron Microscope (SEM), X-ray Fluorescence (XRF), X-ray Diffractometry (XRD), and Fourier Transform Infrared (FTIR).

3. RESULTS AND DISCUSSION

3.1. Compositional Analysis

Table 1 presents the chemical analysis by XRF of raw kaolin and processed alumina at temperatures of 700ºC and 900ºC, illustrating the amounts and types of constituents. Based on the data presented in the table, a substantial amount of the gangue in the kaolin sample was eliminated during the calcination process and subsequent acid leaching. This resulted in the production of the final alumina product, which underwent calcination at temperatures of 700ºC and 900ºC. Alumina had a purity of 82.32% and 82.91% after the final calcination at 700°C and 900°C, respectively. These values are roughly comparable to the chemical composition of commercial gamma-alumina, which is 89.80% [7]. However, they are higher than the 79.28% alumina extraction observed by Ibrahim *et al.* [10] and comparable to the 85.02% value obtained by Bawa *et al.* [12] for alumina synthesized from kankara kaolin.

Table 1. Chemical composition of kaolin, processed alumina at 700ºC and 900ºC.

Compound	Concentration Weight %		
	kaolin	alumina (700^{0}C)	alumina (900^{0}C)
Al_2O_3	36.11	82.32	82.91
SiO_2	57.492	15.63	15.07
CaO	2.043	0.24	0.29
TiO_2	2.246	0.09	0.09
Fe_2O_3	0.519	0.21	0.13
P_2O_5	0.385	1.07	1.39
LOI	1.040		

3.2. X-Ray Diffraction

XRD analysis was conducted to characterise the sample's phase and crystal structure. Different peaks at various crystallite sizes indicate alumina phases or crystal shape anisotropy (e.g., preferred development in particular directions). Using the Debye-Scherrer formula, the average crystallite size (D, nm) of the alumina sample was calculated;

$$D = \frac{0.9\lambda}{\beta\cos\theta} \tag{1}$$

Where 0.9 is Scherrer's constant, λ is the wavelength of X-ray radiation, β is the full width at half maximum (FWHM) of the diffraction peak, and θ is the Bragg diffraction angle.

At 700°C, the average crystallite size of calcined alumina is estimated to be 1.18 nm, while at 900°C, it is estimated to be 1.46 nm. This may be attributed to a high temperature of calcination, which increased atomic mobility, causing grain growth and consequently yielding improved crystallinity.

The XRD patterns for alumina powder made by calcination at 700^{0}C and 900^{0}C are displayed in Figure 2. As the calcination temperature increased, it was observed that the diffraction patterns became slightly

clearer and had higher peak intensities. Additionally, the diffraction pattern of the alumina powder at 900°C shows narrow peaks, indicating a high degree of crystallinity. An increase in calcination temperature would also cause a change in some diffraction peaks from γ- to α-alumina. The XRD pattern seen below reveals the presence of several amorphous phases that are distinguished by low peaks.

The JCPDS file exhibited a congruence with the X-ray diffractogram provided by [11], confirming the presence of γ-alumina at low and high calcination temperatures. The characteristic peaks of γ-alumina are $2\Theta = 716.67°$, $2\Theta = 550°$, $2\Theta = 433.33°$, $2\Theta = 400°$, and $2\Theta = 283.33°$. The findings of the analysis are depicted in Figure 2.
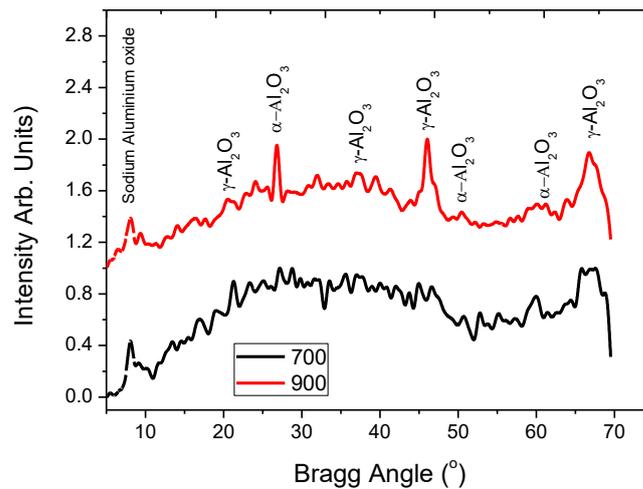
Figure 2. The XRD patterns for the gamma-alumina processed at 700^{0}C and 900^{0}C.

3.3. Fourier Transform Infrared Spectroscopy (FTIR)
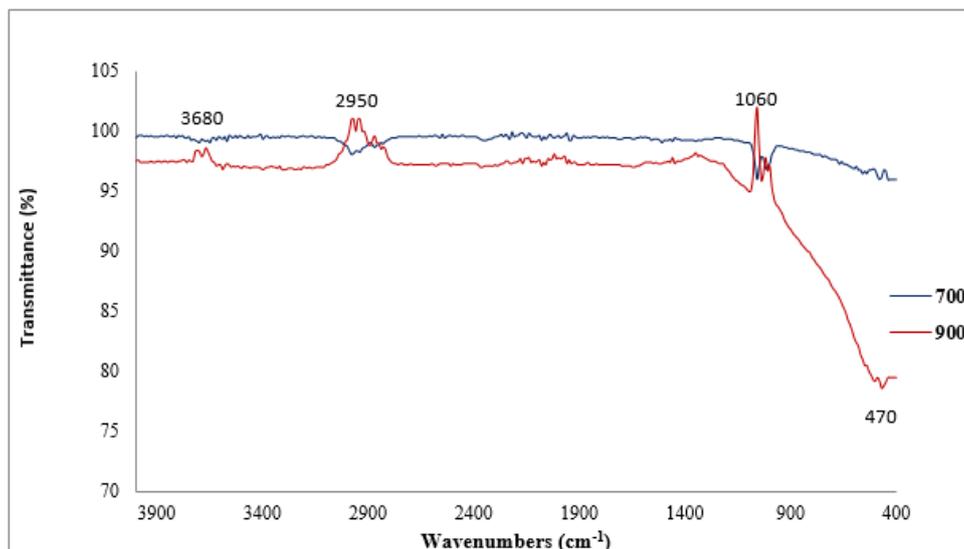
Figure 3. The FTIR spectra of gamma-alumina processed at 700^{0}C and 900^{0}C.

The observed result demonstrates the presence of an absorption peak within the mid-infrared (mid-IR) region spanning from 400 cm^{-1} to 4000 cm^{-1}. This peak identifies the chemical bonds and functional

groups within the compound. The spectra region involves a lot of essential stretch modes. An FTIR spectrum alumina's Figure 3 showed the distinctive peak at 470 cm^{-1} wavenumber, which can be attributed to the stretching vibration of the Al-O band in alumina. The absorption peak within the 1060 cm^{-1} wavenumber increased when the calcination temperature was raised from 700^{0}C to 900^{0}C, as can be seen. This wavenumber corresponds to the symmetric bending of the Al-O-H bond [18]. The wavenumber around 2950 cm^{-1} could be associated with C-H bonds from organic remains observed in the calcined samples. The O-H vibrational mode is found around 3680 cm^{-1}. This could be ascribed to the rapid adsorption of water molecules in the environment. Generally, it was observed that raising the calcination temperature from 700^{0}C to 900^{0}C decreases the absorption peak except for the peaks at 1060 cm^{-1} and 2950 cm^{-1} corresponding to the alumina produced at the calcination temperature of 900^{0}C.

3.4. Scanning Electron Microscopy (SEM)

The SEM micrographs for the 700^{0}C and 900^{0}C processed alumina is shown in Figure 4.
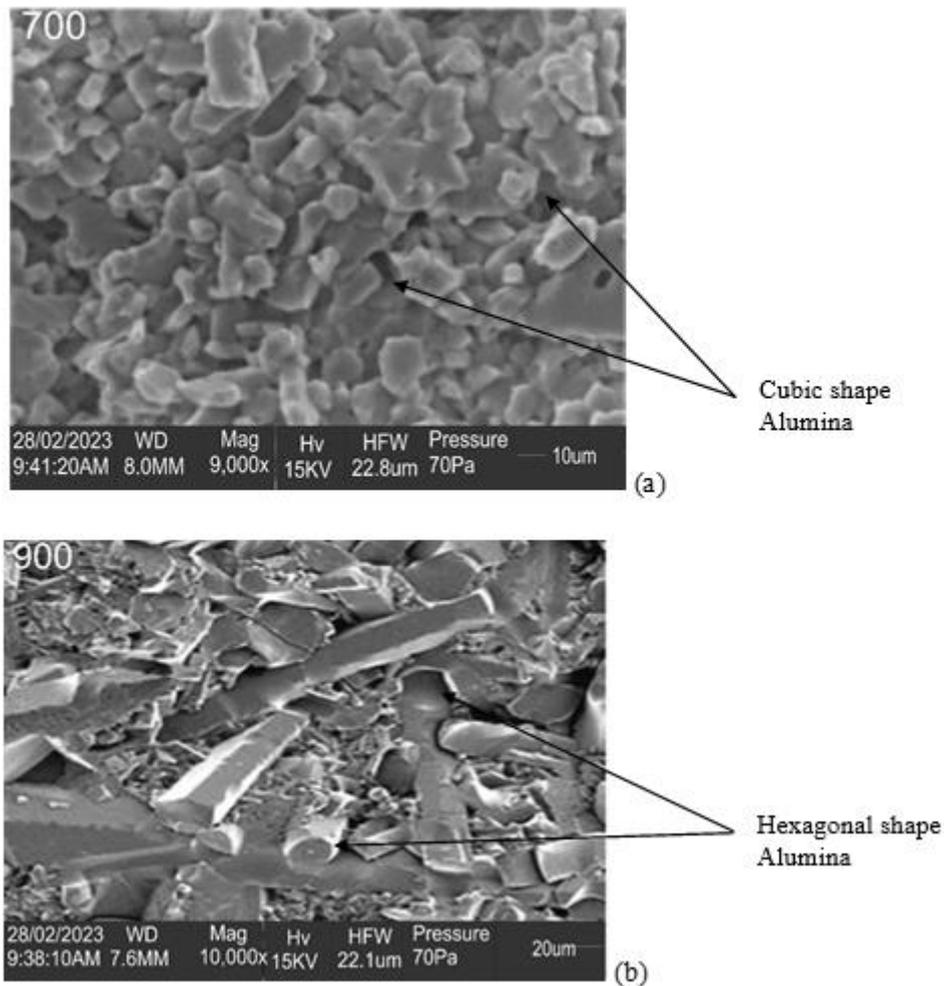
Figure 4. SEM images of gamma-alumina (a) calcined at 700^{0}C (b) calcined at 900^{0}C.

The SEM was employed to analyze and characterise the morphology of the material. The morphology of the alumina changes as the temperature increases from 700^{0}C to 900^{0}C during calcination. The Figure 4(b) micrograph of processed γ-alumina reveals the presence of rod-like hexagonal structures in the sample that underwent calcination at 900^{0}C. This is in contrast to Figure 4(a), which shows the cubic-

shaped γ-alumina sample that was calcined at 700^0C. A lesser fraction of tubular crystals is also observed at 700^0C. The SEM image further indicates the presence of tiny amorphous particles alongside the crystalline ones in Figure 4(b).

4. CONCLUSION

This study extracted alumina from kaolin by leaching with hydrochloric acid and sodium hydroxide. The alumina hydroxide produced underwent calcination at temperatures of 700^0C and 900^0C, and the final γ-alumina produced was characterised using FTIR, XRD, and SEM. Based on the findings above and analysis, it can be established that:

- There is a considerable increase in the proportion of the alumina obtained from 36.11 wt. % to 82.32 wt. % and 82.91 wt. % at temperatures of 700^oC and 900^oC, respectively, which are suitable for the production of aluminum metal.
- The morphology of the alumina changes as the calcination temperature changes from 700^0C to 900^0C with a small number of amorphous particles alongside the crystalline ones.
- As displayed in the FTIR, the absorption peak decreases except for the peaks at 1060 cm^{-1} and 2950 cm^{-1} corresponding to the alumina produced during the calcination process at a temperature of 900^0C when the calcination temperature is increased from 700^0C to 900^0C.
- At higher temperatures, the crystallite sizes were bigger, indicating a higher degree of crystallinity.

CONFLICT OF INTEREST

The authors stated that there are no conflicts of interest regarding the publication of this article.

AUTHORSHIP CONTRIBUTIONS

Henry Ekene Mgbemere: Conceptualization, Original draft data analysis, Graphing and Review.
Chiedozie Valentine Oluigbo: Investigation, Formal analysis, Graphing, Writing – review and editing.

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