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Research paper

# Synthesis of gamma alumina from Kankara kaolin using a novel technique

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ABSTRACT

Synthesis of gamma alumina from Kankara kaolin using simple novel dealumination, precipitation and calcination steps and the product characterization have been presented. The raw clay was wet beneficiated, metakaolinized and dealuminated. Amorphous aluminum hydroxide was precipitated from the aluminum sulfate produced, using sodium hydroxide solution as the precipitating agent. Chemical, mineralogical, physiochemical, morphological and thermal analyses of the products were carried out using XRF, XRD, BET, FTIR, SEM, TEM and TGA/DTA. The aluminum hydroxide produced was subjected to thermal treatment at variable calcination temperatures in the range of 300 to 900°C, gradual phase transformation was observed, a fully formed gamma alumina phase was observed at 900°C. XRF analysis of the various materials at each stage of processing showed a progressive trend of increase in $Al_2O_3$ content, at calcination of 900°C the $Al_2O_3$ content was 91.02 wt.%. The XRD pattern of the alumina obtained at 900°C was similar to that of commercial gamma alumina. The BET surface area, pore volume and pore diameter of the as-synthesized gamma alumina were 102.6 $m^2/g$, 0.0305 $cm^3/g$ and 11.89 Å respectively and the crystal size was 10 nm. This novel process is an industrially feasible alternative to the conventional Bayer process, and it offers a solution to the environmental hazards posed by the wastes generated by the Bayer process.

## 1. Introduction

Alumina is the technical name used for oxide of aluminum ($Al_2O_3$). It is also referred to as aloxide, aloxite or alundum, although these other names are not as commonly used as the famous name, alumina. Alumina exists in different thermodynamically stable phases depending on the method and/or extent of processing applied to its source material. The thermodynamically stable transitional phases of alumina include gamma, delta, kappa, theta and alpha phase (Lee et al., 2013). When it exists in these phases, the material is referred as gamma-alumina, delta-lumina, kappa-alumina, theta-alumina and alpha-alumina respectively. Virtually in all its possible phases alumina possesses high economic viability owing to its versatile technological applications which cut across a wide range of fields. These include its use as high quality insulators (Chang et al., 2009; Miney et al., 2003; Ueki et al., 2010) semiconductors (Lee et al., 2013) and microelectronics (Kerness et al., 1997) in electrical, electronic and computer engineering. It is used for the production of high strength materials (Lee et al., 2009) in the construction industry. It is used in the materials and metallurgy industry for the production of varieties of ceramics, alloys and refractories (Andrews et al., 2014). Alumina is also used as a highly potent processing material and as a catalyst in biofuel and cell-fuel processing. Alumina remains a very important catalyst support for metal supported and zeolite catalysts used for processing petroleum, gas, and petrochemicals and for other applications in the chemical processing industry (Phung et al., 2014; Syngiridis et al., 2013; Takbiri et al., 2013; Zhang et al., 2014). Other industrial applications of alumina include its use as fire retardant in production of plastics (Lee et al., 2009), production of high grade polishes (Lei et al., 2012), and for sapphire crystal growth (Lee et al., 2013).

Kaolinite is planar hydrous phyllosilicate clay, belonging to an interlayer structural class referred to as 1:1. Kaolinite possesses a dioctahedral 1:1 (TO) structure having structural dimension in the nanometer range; the thickness of a 1:1 (TO) layer is about 0.7 nm (Bergaya and Lagaly, 2013). Kaolin also consists of non-phyllosilicate minerals such as carbonates, feldspars and quartz together with the (hydr)oxides of iron and aluminum which are referred to as 'non-clay constituent' or 'accessory minerals' (Bergaya and Lagaly, 2013; Hughes et al., 2009). Kaolinite is one of the most abundant minerals in soils and sediments, it is a common weathering product of many tropical and sub-tropical soils (Hughes et al., 2009; Miranda-Trevino and

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Coles, 2003). Kaolin has been a very useful and versatile domestic and industrial material dating back to before the industrial revolution. The oldest known use of the kaolin is as a ceramic raw material (Saikia et al., 2003). Other uses of kaolin include application in medicine, coated paper, paint and construction.

Many researches in the past have looked into making the conventional method of producing alumina from bauxite via the Bayer process more efficient. Some researchers made different attempts to modify the conventional approach such as precipitating gibbsite from sodium aluminates or other aluminum complexes by employing different precipitating agents and techniques. Zeng et al., 2007 synthesized gibbsite using a seeding technique; a solution of commercial aluminum hydroxide and 15-crown-5-ether was used as the seeding agent. The precipitation reaction involved heating at 75°C. Zhang et al., 2009 synthesized gibbsite by preparing synthetic Bayer liquor using commercial sodium aluminate and sodium hydroxide. Methanol was used as the precipitating agent in this work and the precipitation reaction was carried out at 110–120°C. Li et al., 2011 synthesized gibbsite with a seeding technique; commercial aluminum trihydroxide and sodium hydroxide solution was used as the seeding agent. Rajendran et al., 2011 synthesized gibbsite by preparing synthetic Bayer liquor via fusing commercial raw bauxite with sodium hydroxide at 600°C. $H_2SO_4$, HCl and $HNO_3$ were used as the precipitating agent. The gibbsite obtained was calcined at 500°C to obtain gamma alumina.

This work investigates the production of gamma alumina from kaolinite by employing a novel three step method: (i) Dealumination of kaolinite to produce aluminum sulfate solution (alum), (ii) precipitation of aluminum hydroxide from the aluminum sulfate obtained using caustic soda solution and (iii) calcination of the aluminum hydroxide obtained at various temperatures to produce gamma alumina. Unlike previous works, this work offers an alternative technique to the conventional Bayer process. The waste product generated by the Bayer process known as the “red mud” is a hazardous material; its annual production by the alumina industry is 77 million tonnes (Ayres et al., 2001). This constitutes a serious environmental concern. This novel process is a complete deviation from the Bayer process; it offers the advantage of using abundantly available clay, kaolinite, as the raw material for production of alumina without generating hazardous wastes. The by-product of this process is silica, an economically viable product. The chemical reactions involved in the proposed steps are as presented in Eqs. (1)–(3) respectively.

Dealumination step:

$$Al_2O_3 \cdot 2SiO_2 \cdot 2H_2O_{(s)} + 3H_2SO_{4(l)} \rightarrow Al_2(SO_4)_{3(l)} + 2SiO_{2(s)} + 5H_2O_{(l)}. \tag{1}$$

Precipitation step:

$$Al_2(SO_4)_{3(l)} + 6NaOH_{(l)} \rightarrow 2Al(OH)_{3(s)} + 3Na_2SO_{4(l)}. \tag{2}$$

Calcination step:

$$2Al(OH)_{3(s)} \rightarrow Al_2O_{3(s)} + 3H_2O_{(g)}. \tag{3}$$

## 2. Materials and methods

### 2.1. Materials

Analar grade gamma alumina was purchased from Merck KGaA, Germany. This commercial sample is henceforth referred to as CAL in the subsequent discussion. Laboratory grade sodium hydroxide pellets (≥98%) and concentrated sulfuric acid (≥98%) were purchased from Lobal Chemie, India. Raw kaolin was mined from Kankara Local Government Area of Katsina State, Nigeria.

### 2.2. Clay beneficiation

The raw clay was crushed and ground using wooden mortar and pestle. The ground clay was wet-beneficiated using 0.1 kg/L clay to water ratio, settling time of 24 h. After soaking for 24 h the mixture was stirred at 200 rpm (Silverson, L2R) for 3 h. The fine clay slurry was sieved using Tyler sieve, mesh 200. The resulting clay slurry was dewatered until a solid clay cake was obtained. The clay cake was oven dried at 200°C overnight then ball milled (Pascal Engineering 21947) for 4 h. The resulting sample is henceforth referred to as BK in the subsequent discussion.

### 2.3. Metakaolinization

The beneficiated clay was calcined at 750°C for 2 h in an electric chamber furnace (Nabertherm; 30–1400°C) for processing into metakaolin. The resulting sample is henceforth referred to as MK in the subsequent discussion.

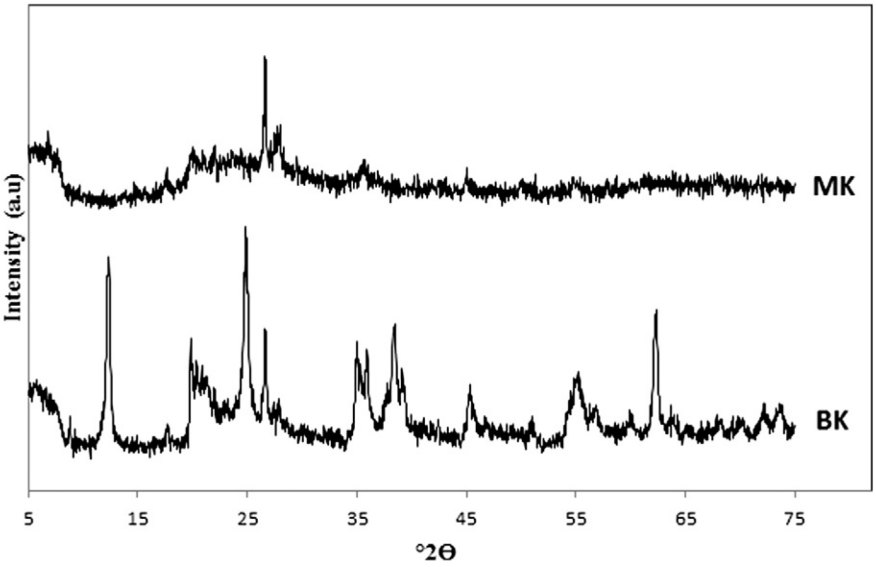

**Fig. 1.** XRD patterns for the starting and calcined clay.