

Preparation of γ -Alumina from Kankara Kaolin in Nigeria by Acid Leaching Using Hydrochloric Acid

A. Aliyu*

Physics Department, Ahmadu Bello University, Zaria, Nigeria

U. Ahmadu

Physics Department, Federal University of technology, Minna, Nigeria

A. A. Abdelmalik

Physics Department, Ahmadu Bello University, Zaria, Nigeria

U. Sadiq

Physics Department, Ahmadu Bello University, Zaria, Nigeria

Abstract: Investigation has been done concerning Kaolin based alumina prepared by acid leaching method. This was initially fired at 600°C for 4 hours to increase its reactivity. For better yield Hydrochloric Acid (HCl) was used for the digestion as against the conventional Sulphuric acid (H₂SO₄). The gelatinous precipitate of the hydrated alumina was further filtered under vacuum 400°C for 2h, which resulted the formation of γ -alumina. The structure of γ -alumina was confirmed by XRD and its corresponding diffractogram parameters and SEM and the mean particles size of γ -alumina was determined by SEM to be 3 - 9 μ m. Foamy agglomerates at low magnification and the presence of larger voids in their structures at high magnification were visible from the SEM images. The study revealed that kaolin could be promising material for preparation of γ -alumina

Keywords: kaolin; Acid leaching; XRD; Nanoscale; Digestion.

1. Introduction

Kaolin synthesis leading to the production of alumina either in industrial scale or otherwise has been carried out by various researcher in various ways. This is because of enormous technological and industrial application of alumina. It exists in a variety of meta-stable states among which are γ -, β -, and α -aluminas. Aluminas are commonly produced in industries through the Bayer process using Bauxites. γ -alumina has become the most important of the nano sized clays in that it can be used as a catalyst and catalyst substrate in automotive and petroleum industries, structural composites for spacecraft, and abrasive and thermal wear coatings [1].

Recent studies have revealed that γ -alumina is thermo dynamically stable compared to α -alumina when a critical surface area is achieved [2], and that nano γ -alumina powder can promote the sintering behaviour of alumina and silicon carbide fibbers [3]. These and other uses like its ability to enhance the electrical properties [4, 5] of insulators and other polymeric insulating materials makes its fabrication and study very important

Kaolinite is a clay mineral, part of the group of industrial minerals, with the chemical composition Al₂Si₂O₅(OH)₄. It is a layered silicate mineral, with one tetrahedral sheet linked through oxygen atoms to one octahedral sheet of alumina octahedral [6]. Kaolin contains 20 - 26 percent by weight of alumina. Therefore, it can be suitable material for production of γ -alumina because of its abundance and having considerable content of alumina in kaolin structure [7].

2. Materials and Synthesis

2.1. Materials

2. 5L of HCl of M. W., 36.48 and purity 35.38% was supplied by BDH Chemical Ltd, Poole England, Ethanol Absoluten (99.7 – 100%) was gotten from Johnson Solomom (Export) Ltd, London, England. NaOH of M. W. 40.0g/mol was also supplied by BDH. Polyvinyl Alcohol (PVA) of 98% purity was supplied by BDH Raw kaolintic clay sample (commercial grade)

2.2. Synthesis

The processes leading to the formation of the alumina is outlined as follows; digestion, precipitation, peptization/gelling/capping and drying

2.2.1. Digestion

The raw Kaolin has earlier been beneficiated and calcined initially for 4 hours at 600°C using a furnace to increase its reactivity by affecting dehydration transformation of the kaolinite to amorphous metakaolin (Al_2SiO_7), which is known to be more reactive and render alumina easily extracted by acid or alkali. The thermal treatment in the temperature range of (500-900)°C is necessary to render alumina soluble [8].

150g of calcined Kaolin was digested with 250g HCl using a KDM Style Control Mantle under reflux at the boiling point of HCl for 70 mins. HCl gives the highest yield among all the other acids like Nitric and sulphuric acids that could also be used. At the end of which alumina will be produced with iron(Fe) contaminant. But if NaOH were used for digestion, it would have been silicate contaminant which is more difficult to handle than iron. The mixture will now be precipitated.

2.2.2. Precipitation

The digested Kaolin was allowed to sediment by ageing it in the refrigerator for 18 hours. The sedimented solution which was decanted and then using filter paper filtered to yield a clear solution. The filtrate was precipitated by the addition 25g of NaOH while keeping the temperature at about 10°C. NaOH was added to the clear solution to neutralize it leading to the formation of aluminium hydroxide precipitate in the basic medium. The gelatinous precipitate of the hydrated alumina was further filtered under vacuum using a vacuum pump, washed repeatedly five times with distilled water and finally with absolute ethanol. The precipitate was then dried, ashed at 400°C for one hour in a muffle furnace to burn any carbonaceous materials. The crude nanokaolin formed was stored in a desiccator. The yield was calculated to be 39.25g based on the drying weight of alumina.

2.2.3. Peptization/Gelling

A small amount of the crude nanokaolin was weighed into a crucible and dried further for 1 hour at 400°C. 10ml of 70% nitric acid was then added to 18.100g of the hydrated alumina in a 500ml beaker. This was done with constant and vigorously stirring until it turned almost translucent. More distilled water was then added to make it up to 100ml. In a separate beaker, 5g of polyvinyl alcohol (PVA) was dissolved in 100ml of water and boiled with stirring to dissolve it. This was allowed for sometimes until the colloids completely dissolves. The PVA acts as **surfactant** to control hydrolysis. After the dissolution, it was kept in the refrigerator in order to get chilled and then the two were mixed together and stirred for 40 minutes. This process of adding PVA and mixing is called **capping**. The reason why we used Poly vinyl alcohol in the absence of commonly used silane is that PVA is a non-toxic, water-soluble synthetic polymer that has good film forming ability. It has a large number of hydroxyl groups which allows it to react with many types of functional groups [9].

After which ammonia was added to make the pH to 8. At this point the solution turns into a thick gel due to condensation. Again the mixture was finally stirred for 40 minutes to age the sample and poured on a filter paper and allowed to dry at 60°C in a hot oven.

2.2.4. Drying

The dried sample is broken to pieces and calcined in a furnace at 600°C to burn out the remaining carbonaceous materials such as PVA and volatile ammonium nitrate contaminants. The process also helps to crystallize the alumina (Nanokaolin). The schematic diagram is below.

3. Results and Discussions

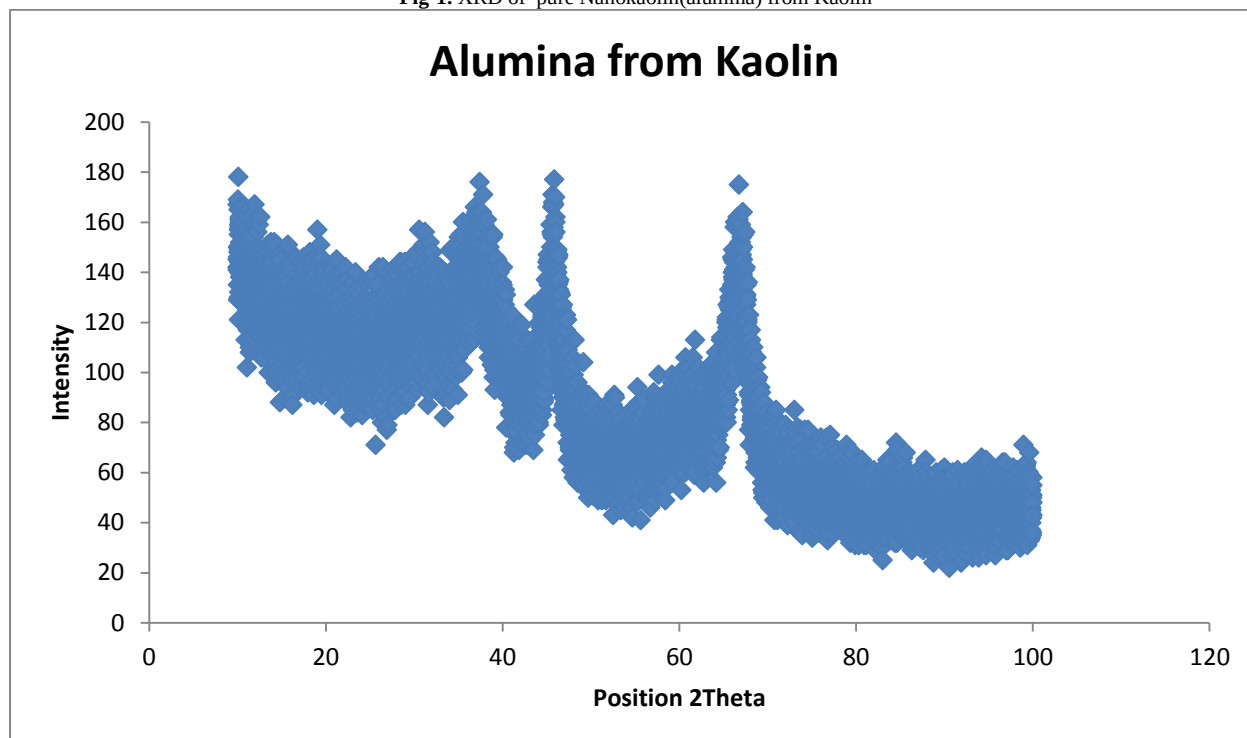
3.1. X-Ray Diffraction (Xrd)

XRD was carried out using a PANalytical XPERT-PRO diffractometer system with a Reflection-Transmission Spinner configuration on a PW3064/60 sample stage for powder diffraction. A Goni scan axis with a start position of 5.0464 (2θ) and end position of 99.9184 was employed using a step size (2θ) and scan time (s) of 0.067 and 29.8450 respectively. The scan mode was continuous with a specimen length of 10mm ray-length and measurement was conducted at room temperature of 25°C. The generator setting employed was 30 mA and 40 kV with K-Alpha 1 (Å) wavelength of 1.54060 using Copper (Cu) as the anode material. In cases where the scan time and setting differs, it will be stated.

The XRD results and interpretation as obtained from PANalytical XPERT-PRO diffractometer system was done with a view of deriving the structural phases from samples prepared. Before doping the low density polyethylene with the alumina that gives the various samples at varying composition, the nanosize of the alumina was confirmed by the use of the well-known Scherrer formula.

The XRD result is expected to give the lattice parameters like phase identity, phase purity crystallinity, crystal structure and percent phase composition as following information required from the samples.

Fig-1. XRD of pure Nanokaolin(alumina) from Kaolin



In this work, the $[2\theta]$ peaks are visible at 36, 46 and 66 respectively. From [fig 1](#), the pure alumina sample was matched with a reference code of 01 – 075 – 0921, compound formula and name of γ - (Al_2O_3)1.33 and aluminum oxide. The sample had a cubic crystal system, Fm-3m space group. The $[hkl]$ value was calculated to be $[200]$ from ICDD using POWD-12++ (1997).

The other two peaks shows the presence of the intermediate product (aluminium Chloride) from the concentrated hydrochloric acid used [\[10\]](#). The sample had a cubic crystal system, Fm-3m space group and 225 space group number. The $[hkl]$ value was calculated to be $[200]$ from ICDD using POWD-12++ (1997) and classified as an inorganic alloy with metal or intermetallic ICDD pattern.

The analysis of the diffractogram from [fig 1](#) revealed a crystalline material though with relatively three average peaks which were quite pronounced with various intensities. These peaks which appeared at 36, 46 and 66° are the characteristic peaks of all γ -alumina. This is in conformity with the work of [Seyed, et al. \[7\]](#) where their $[2\theta]$ peaks appeared at 37, 46 and 67°. The nanosized alumina was calculated to be 24.91 nm using the Sherrer's equation. The well-known Debbay Scherrer equation as follows:

$$D = 0.9\lambda / (B \cos\theta) \quad 1$$

Where D is crystallite size in nm, λ the wavelength of the radiation, B is the FWHMs observed for the sample, θ is the Bragg's angle. The comparison of the obtained XRD result with previous work confirmed the formation of γ -alumina [\[7\]](#).

3.2. Scanning Electron Microscopy (Sem)

The SEM measurement was carried out using MODEL -PHENOM ProX Scanning Element Microscope Before putting the sample in the SEM for measurement; some quantities of sample were placed on a double adhesive sticker placed in a sputter coater machine for 5sec to give the sample a conductive property. This might not affect the quality of the images formed. Sample stub was fixed on a charge reduction sample holder, and then was changed into the machine column thereafter the doors of the SEM was closed. The parameters to be used were set immediately after the machine was allowed to stabilize for some seconds. 15kv was used in imaging the sample set at 1000x magnification and was focused using a rotary knob until a clear and proper image was produced in a NavCam mode then this was transferred to an electron imaging mode, the image was then transferred to Phenom suite software where, fibermetric/pore measurements were carried out; after contrasting/ brighten , after the spots where all analyzed then a report was generated by the machine and was saved in a folder using the name of the sample used. Same was used in determining the pore measurement and fiber present in the sample.

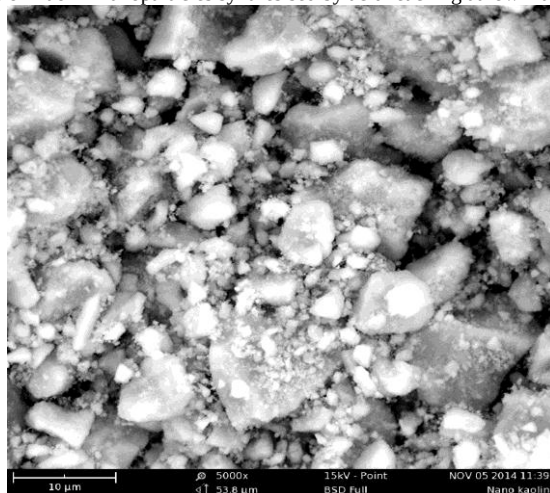
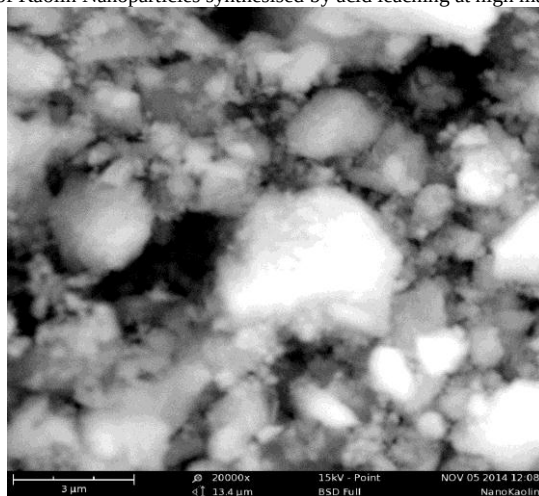
Fig-2. SEM image of Kaolin Nanoparticles synthesised by acid leaching at low magnification (5000x)**Fig-3.** SEM image of Kaolin Nanoparticles synthesised by acid leaching at high magnification (20000x)

Fig 2 and fig 3 are the SEM images (morphology) of the solid phase at nanoscale of local kaolin from kankara by acid leaching, after filtration and drying at low and high magnifications. It also shows the formation of foamy agglomerates at low magnification and the presence of larger voids in their structures at high magnification. [11] posit that formation of these features is attributed to the evolution of a larger amount of gas during combustion/firing.

4. Conclusion

Foamy-like and nanocrystalline γ -alumina powder have been synthesized by acid leaching via sintering. XRD reveal that we got a crystalline material of $24.91nm$ using the Sherrer's equation. The calcinations of kaolin at $600^{\circ}C$ for 4 hours did actually help reaction during digestion in HCl.

5. References

- [1] 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, p. 220.
- [2] 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, pp. 405-412.
- [3] 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, pp. 244-248.
- [4] Yong, S., Jong, M., and Dong, W., 2008. "Microstructure and electrical conductivity of NiO-YSZ nanopowder synthesized by aerosol flame deposition." *Journal of Ceramics International*, vol. 34, pp. 873-876.
- [5] Dima, A., Corteb, D., and Williamsa, F., 2008. "Silicon nano-particles in SiO₂ sol-gel film for nano-crystal memory device applications." *Journal of Microelectronics*, vol. 39, pp. 768-770.
- [6] Deer, W. A., Howie, R. A., and Zussman, J., 1992. *An Introduction to the rock-forming minerals*. 2nd ed. Harlow: Longman.

- [7] Seyed, A. H., Aligholi, N., and Dariush, S., 2011. "Production of γ -Al₂O₃ from Kaolin." *Open Journal of Physical Chemistry*, vol. 1, pp. 23-27.
- [8] Abdulwahab, A., Al-Ajeel, and Al-Sindy, S. I., 2006. "Alumina recovery from iraqi kaolinitic clay by hydrochloric acid ruote." *Iraqi Bulletin of Geology and Mining*, vol. 2, pp. 67-76.
- [9] El-Hefian, E. A., Nasef, M. N., and Yahaya, A. H., 2010. "The preparation and characterization of chitosan poly (vinyl alcohol) blended films." *E Journal of Chemistry*, vol. 7, pp. 1212-1219.
- [10] Lai-shi, L., Yu-sheng, W., Ying-ying, L., and Yu-chun, Z., 2011. "Extraction of alumina from coal fly ash with sulphuric acid leaching method." *The Chinese Journal of Process Engineering*, vol. 11, pp. 254-258.
- [11] Sharma, A., Modi, O. P., and Gaurav, K. G., 2012. "Effect of fuel to oxidizer ratio on synthesis of alumina powder using solution combustion technique-aluminium nitrate & glycine combination." *Advances in Applied Science Research*, vol. 3, pp. 2151-2158.