Characterization of Kaolin Clay from Kutigi and Its De-Aluminated form for Catalysts Development towards Economic growth of Nigeria

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Abstract

Kaolin, a product of natural hydrated aluminium silicate which has undergone refinement is a type of clay material which is usually in powder form and is whitish in colour. It is a soft sedimentary rock which has light weight and a chalk-like appearance. The chemical analysis of the kaolin obtained from Kutigi in Niger State by X-ray fluorescence shows that the clay is mainly composed of silica and alumina which are 50.94% and 32.93% respectively. The de-alumination of the clay by action of H_2SO_4 shows that a large percentage of the silica in the clay was removed. X-ray fluorescence of the de-aluminated clay shows a higher alumina content (76.236%) and silica (1.095%) indicating its removal.

Keywords: Kaolin, alumina, silica, sulphuric acid

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1. Introduction

Kaolin $\{Al_2Si_2O_5(OH)_4\}$ was firstly mined in China. Its name was adopted from the word "Kau-Ling", which implies high ridge, the name of a hill near Jau-chau Fu in China. It is sometimes referred to as China clay (Adamis and Williams, 2005; Bu et al., 2017). Comparatively kaolin is pure clay predominantly consisting of about 85 – 95% kaolinite ($Al_2O_3.2SiO_2.2H_2O$). Other constituents usually found in kaolin in addition to kaolinite include quartz and mica and also, less often include feldspar, illite, montmorillonite, ilmenite, anastase, haematite, bauxite, zircon, rutile, kyanite, silliminate, graphite, attapulgite, and halloysite (Adamis and Williams, 2005; Bu et al., 2017). Kaolin is a product of natural hydrated aluminium silicate which has undergone refinement. It is usually in powder form and is whitish \in colour. It is a soft sedimentary rock which has light weight and a chalk-like appearance (Varga, 2007).

The SiO_2/Al_2O_3 ratio is 1.18 which is important for geology, engineering, agriculture, process industries and environmental application (Bu et al., 2017). It is of economic importance for most industries owing to its properties such as high brightness, very fine particle size, inertness and non-toxicity thus giving it versatility and wide spread applications (Bu et al., 2017). Kaolin can be found commercially as sedimentary deposits where weathering of rocks containing high compositions of alumino-silicate minerals is located. It is classified as a clay mineral containing atoms of silicon, aluminium, oxygen, iron, and hydroxyl groups as the main elements. It also contains other elements such as calcium, potassium, phosphorus, sodium and magnesium in very minute quantities. The members of the kaolin family include dickite, nacrite, allophone, and hallosite (Badmus and Olatinsu, 2009). The colour of each type of kaolin is determined from its iron content. It is mostly white or near white in appearance. Impurities in the kaolin material can change the colour to purple or pale brown. Deposits of kaolin are wide spread throughout Nigeria with each state having at least one known deposit (Badmus and Olatinsu, 2009). For instance, the Ozubulu deposit in Anambra state, Darazo deposit in Bauchi, Akpene-Obom deposit in Cross-River state, Kankara deposit in Kaduna state, just to mention a few (Badmus and Olatinsu, 2009).

Kaolinite has a tetrahedral structure of silica sheet alternating with an octahedral structure of alumina sheet. The arrangement of the sheets is such that the tips of silica tetrahedrons and the adjacent layers of the alumina octahedral sheets form a common layer. Two-thirds of the oxygen atoms found in the common layer of the tetrahedral groups and the octahedral groups are shared by aluminium and silicon. They therefore become O instead of OH and the charges within the structural unit are balanced. Analyses of many samples of kaolinite minerals have shown that there is very little substitution in the lattice (Adamis and Williams, 2005).

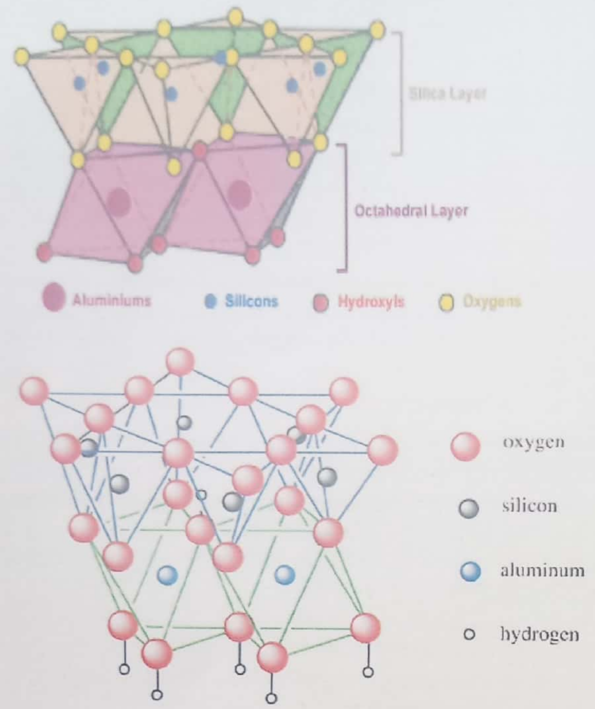


Figure 1: Lattice structure of kaolin

1.1 Physical and Chemical Properties of Kaolin

Kaolinite is composed of small, thin, pseudo-hexagonal, elastic sheets of triclinic crystal having a diameter of 0.2–12 µm. Its density ranges between 2.1–2.6 g/cm3. The cation exchange ability of kaolinite is significantly low, which is dependent on the particle size, but the rate of the exchange reaction is rapid, almost instantaneous (Adamis and Williams, 2005). Kaolinite does not only adsorb small molecular substances such as lecithin, quinoline, paraquat, and diquat, it also absorbs proteins, polyacrylonitrile, bacteria, and viruses. The adsorbed substance can be eliminated easily from the particles owing to the fact that adsorption is limited to the surface of the particles, that is, the planes and edges. Kaolinite loses it water when heated to approximately 400°C, and the process of dehydration reaches completion at approximately 525°C. The dehydration depends on the particle size and crystallinity (Adamis and Williams, 2005).

2. Alumina

Alumina s chemical compound which is found to be extensively distributed in nature. It is mixed with silica, calcium oxide and titanium oxide and is said to occur in clays, feldspars and micas. Alumina is the main constituent of bauxite and occurs in a pure form as corundum (Olarenmu, 2015). It is commercially essential as it is majorly used in the manufacture of aluminum metal (Belver et al., 2002; Olarenmu, 2015). It is also used in ceramics, pigments, in manufacture of chemicals and also for abrasives (corundum and emery). A combination of the physical, chemical and electrical properties of alumina has resulted to its usage as an advanced ceramic material. Alumina has found usage in critical structural applications due to its strength and hardness, good wear and chemical resistance at high temperatures. High demand for alumina comes largely from the electrical and electronic sectors due to its brilliant dielectric and insulating properties. For high technical applications, high purity alumina (more than 95%) with very low sodium and iron content are required. During the processing method of alumina from bauxite, sodium impurity results from the use of sodium hydroxide whereas iron is present in the bauxite mineral (Olarenmu, 2015).

Alumina in its pure form is used in making crucibles and many refractory materials. The hydrated form finds application in the production of lake pigments (mordant dyeing). Its use is also

extended to glassmaking, cosmetics and medicine where it is used as an antacid. Alumina provides a very good support in catalysis particularly when ordered mesoporous alumina (OMA) can be reproduced easily (Olarenmu, 2015; Davis, 2010).

Alumina which is a whitish powder can be produced from clay materials but it is generally produced from bauxite using the Bayer process which accounts for more than 90% of world's commercial production. This process was first developed in 1888 and involves the following stages: grinding of bauxite to obtain fine particles, digestion of bauxite, settling and washing of residues, crystallization of hydrates and the calcinations of the hydrate formed. Other methods of producing alumina involve its extraction from clay using sulphuric acid or hydrochloric acid and also the reaction of bauxite with sodium carbonate and subsequent precipitation of alumina hydrate (Davis, 2010).

Some examples of non-bauxite raw materials which contain alumina include alunite, Laterite, clay alusite fly ash, sillimanite, aluminous shales, mica and kyanite (Olarenmu, 2015). Although, the Bayer process remains the most sought-after method for producing alumina from bauxite, many researchers have sought ways to modify this process to utilize these other non-bauxite raw materials (Olarenmu, 2015). This works explores the leaching of alumina from Kutigi clay through the use of sulphuric acid.

2.1 Properties of Alumina

Fused alumina (the substance produced after being melted and re-crystallized) is identical with natural corundum in terms of chemical and physical properties. According to Davies (2010), it is one of the hardest known substances which are only exceeded by diamond and a few man-made substances such as carborundum and silicon carbide in terms of hardness. This property is what qualifies alumina as an abrasive material. In addition to its hardness, alumina has a high melting point usually above 2000°C, which makes it function as a refractory and linings of special furnaces (Davis, 2010). Table 1 gives the mechanical properties.

Table 1: Mechanical Properties of Alumina

Properties	Conditions	Units	Values
Bulk Density	20°C	g/cm^3	3.96
Tensile Strength	20°C	Mpa	220
Bending Strength	20°C	> Mpa	410
Elastic Modulus	20°C	Gpa	375
Hardness	20°C	Kg/mm2	14
Fracture Toughness	20°C	Mpa.m2	4-5
Porosity	20°C	%	0

Source: Davis, 2010

Table 2 shows the thermal properties of alumina (99.7% purity) as often used in the ceramic industry.

Table 2: Thermal properties of alumina

Properties	Conditions	Units	Values
Max. Working temperature	-	°C	1700
Coefficient Thermal Expansion	25-300°C	10-6/oC	7.8
Coefficient Thermal Expansion	25-1000°C	10-6/oC	8.1
Thermal Conductivity	20°C	W/moK	28

Source: Davis, 2010

3. EXPERIMENTAL METHOD

3.1 Preparation of alumina from kaolin

The alumina used for this experiment was obtained from kaolin clay sourced from Kutigi in Niger State. The clay was crushed to very fine powder in a mortar and sieved using a 125-μm mesh sieve. The kaolin was calcined in an electric furnace at 800oC for 3 hours to form meta-kaolin. This is to loosen the alumina component in the clay. 18 g of Meta-kaolin was reacted with 300 ml of a 2.0 M H2SO4 solution. The mixture of kaolin powder and acid was contained in a 500ml round flask. The mixture was stirred for 4 hours at a temperature of 80oC in a water bath. This is a leaching process which enables the alumina component to be leached into the acid solution. The leached mixture was cooled to room temperature and filtered to remove leached residue, largely consisting of silica.

The leached filtrate was added drop wise into 600 ml of ethanol while the ethanol was stirred with a magnetic stirrer. Ethanol was used as a precipitating agent because aluminium sulphate can be selectively precipitated by ethanol from ionic solution. The precipitates were again washed with the ethanol and then dried at 100oC for 6 hours in an electric oven. Finally, the precipitates were calcined at 900oC for 2 hours in an electric furnace. This method is in accordance with the work reported by (Olarenmu, 2015).

3.2 X-Ray Flouresence Analysis for Raw and De-Aluminated Kaolin

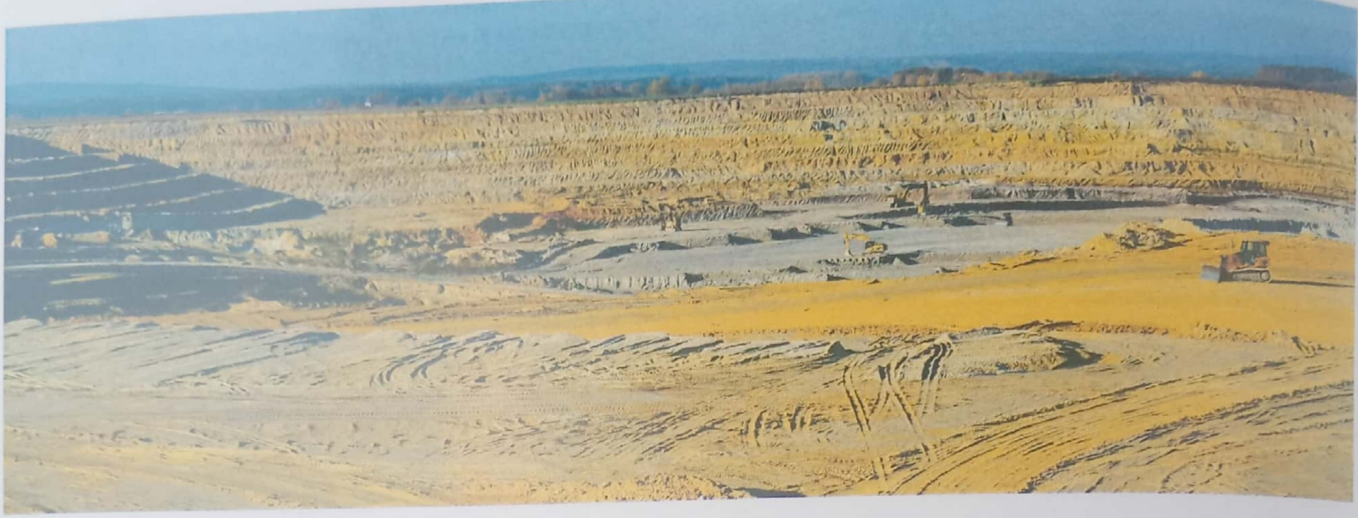
The X-Ray Fluorescence study was carried out to identify the chemical compositions of the clay. Table 3 illustrates the results of chemical analysis of the raw and de-aluminated kaolin clay. The raw clay contains 50.938 % and 32.929 % of silica and alumina respectively which is the major constituent meanwhile other oxides of metals such as iron, calcium, zinc and titanium are present in trace amounts.

Table 3: Chemical composition of raw and de-aluminated kaolin

Composition	Raw Kaolin (%)	De-aluminated Kaolin (%)
SiO2	50.938	1.095
Al2O3	32.929	76.236
Fe2O3	1.019	-
CaO	0.225	0.889
TiO2	0.03	0.008
ZnO	0.005	-
L.O.I	14.854	21.772
Total	85.146	78.228

The composition of the de-aluminated clay shows that the percentage of Al2O3 increased to 76.236 % while that of silica reduced to 1.095 %. The result clearly shows that the silica content which was highly present in the raw clay have been removed via leaching with sulphuric acid. Iron (II) oxide which was present in the raw kaolin was also removed showing no trace in the de-aluminated sample.

Zahrani and Abdul-Majid (2009) researched on kaolin from Riyadh area of Saudi Arabia. The chemical compositions of the kaolinitic clay were determined from X-ray fluorescence. The major constituents in the clay are SiO2 having 47.25% and Al2O3 having 29.4%. The sample is found to be rich in silica and alumina but poor in Fe2O3 (2.87%) and TiO2 (1.17%). Other components



present such as CaO, MgO and MnO are in negligible amounts. This is closely related to the work of Varga (2007) who studied the chemical position of kaolin and found the clay to be rich in SiO2 (46.3%) and alumina (39.8%). Bu et al., (2017) investigated the removal of fine quarts from coal-series kaolin sourced from Xuzhou, Jiangsu Province of Eastern China. The X-ray fluorescence analysis showed the silica and alumina content to be 56.72% and 21.67% respectively. Other constituents such as CaO, MgO, Fe2O3 and TiO2 are present in trace amounts.

Table 4: Comparison of the chemical compositions for different kaolin

	Amount (%)				
A	B	C	D	E	F
SiO2	50.94	56.72	61.50	47.25	57.85
Al2O3	32.93	21.67	24.50	29.40	28.15
Fe2O3	1.02	1.78	0.55	2.87	2.91
TiO2	0.03	0.87	-	1.17	-
MgO	-	0.32	0.60	0.35	-
CaO	0.23	0.28	1.55	0.59	0.4
K2O	-	1.80	-	0.17	-
Na2O	-	0.37	0.80	2.11	-
MnO	-	-	-	< 0.05	< 0.2
SO3	-	0.45	-	< 0.05	-
ZnO	0.01	-	-	-	-
P2O5	-	-	-	< 0.05	0.9
L.O.I	14.85	14.13	10	16.02	13.14

A: Composition

B: This Work (Kutigi, Nigeria)

C: Bu et al., (2017) (Xuzhou, China)

D: Hosseni et al., (2011) (Marand, Iran)

E: Zahrani and Abdul-Maji (2009) (Riyadh, Saudi)

F: Eterigho and Olutoye, (2007) (Ukpor and Ahoko, Nigeria)

The loss on ignition (L.O.I) value gives information about the organic matter content in a sample. It calculates the percentage organic matter by comparing the weight of a sample before and after the sample has been ignited (Robertson, 2011). The L.O.I value for the Kitigi clay (14.85%) was found to be closely related to that obtained by Bu et al., (2017) which was 14.13%. Although these were a little higher than the values reported by Hosseni et al., (2011) and lower than that reported by Zahrani and Abdul-Majid (2009) which were 10% and 16.02 % respectively. This is an indication that there is low organic matter present in these clay materials.

Conclusion

The chemical composition of Kaolin from Kutigi clay as revealed by the X-ray fluorescence analysis shows that the clay is majorly composed of silica (50.94%) and alumina (32.94%). The de-alumination of the clay was achieved through the use of sulphuric acid and analysis shows that the percentage of silica was greatly reduced to 1.095%. Iron (II) oxide which was present in kaolin although in small amounts was completely removed through de-alumination.

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