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Characterization of Kono-Boue Clay as Possible Catalyst for Biodiesel Production

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Abstract: ***The Kono-Boue clay in Rivers State, Nigeria, which is currently applied locally for pottery, building bricks, and as medicine, had been characterized to determine its mineral structure using X-ray crystallography. Its surface morphology and elemental composition were determined using scanning electron microscopy (SEM) and energy dispersive X-ray (EDX) respectively. The X-ray crystallography identified the clay as aluminium silicate with similar structure as kaolinite, which matched with berlinite crystal structure. The SEM image showed smaller particle sizes below 5µm as well as larger particles of range 10-15µm respectively while the EDX result showed ~ 50 % counts of Si/Al (ratio of 4:1); ~ 40 % for O, S, Mg, K, and Fe while the remaining ~10 % were shared by Ti, Zr, W, Hg and Au.***

Keywords: Kono Boue Clay, XRD, SEM, Catalyst, Characterisation, and Biodiesel.

1. Introduction

The inevitability of global warming, the greenhouse effects and criticisms of fossil fuels for their depletion, environmental hazards and lack of sustainability have put many researchers to study in biodiesel production as a viable and promising alternative energy source [1,2]. Presently, both homogeneous and heterogeneous catalysts are being employed to catalyze transesterification reaction for biodiesel productions. Homogeneous catalysts used include some acids and bases such as tetraoxosulphate (VI) acid, phosphoric acid, etc and sodium hydroxide, potassium hydroxide, etc., respectively [3]. However, these have been found to be expensive and environmentally unfriendly. On the other hand, heterogeneous catalysts such as zeolites or clays have the advantage of easy separation from products over the homogeneous and the spent catalysts also ecofriendly.

Clays are natural, earthy, fine-grained materials, <2µm, which develop plasticity when mixed with a limited quantity of water and harden when dried or fired [4]. Clays are collectively called alumino-silicates. This is because the universal minerals contained mainly aluminium and silicon oxides while water often with iron, alkaline and alkaline earth metals are minor components [5]. Clays have special features to be used as catalysts. These features include availability, versatility, selectivity, low cost as well as ease of use and preparation. Besides, it possessed bronsted-lowry basic and acidic sites, porosity and ability to be pillared with exchangeable cations amongst others. Clay catalysts are environmentally benign, recyclable and economical. Therefore both natural as well as numerous modified forms are used as good catalyst for transesterification in biodiesel synthesis and diverse chemical reactions [6].

Biodiesel is one of the pioneering forms of alternative energy. It is a renewable, highly biodegradable, non-toxic and environmentally friendly bioenergy, which can be utilized in engines without any modification [1,7,8,9].

Many clay catalysts have been characterized and studied for the production of biodiesel in recent times. For example, the use of some Brazillian natural clays (smectite, atapulgite and vermicu-lite), without pre-treatment or activation, was demonstrated by Silva and coworkers [10] to act as good catalysts for transesterification of ethyl acetoacetate and ethyl benzoylacetate by six carbohydrate acetonides. In a related study, acid activated Indian bentonite was shown to be a good catalyst, in some cases better than zeolites, for the preparation of aryl and alkyl esters of fourteen different aromatic and aliphatic carboxylic acids [11]. Similarly, Villegas and Coworkers characterized natural Brazillian clays such as F-101 clay, a smectite, F-117, which has an interstratified structure with smectite, kaoline and mica as clay minerals and kaoline and used them as catalysts in the co-iodination reactions of styrene and cyclohexene with water and alcohol [12]. Gao and Xu reported Clay as catalyst support where they used vanadium oxide catalyst supported on clay (chlorite, illite, and atapulgite from inner Mongolia) for the oxidation of benzene to phenol using hydrogen peroxide as co-oxidant [13]. The use of natural zeolite - supported on KOH has also been reported as heterogeneous catalyst or catalyst supports in biodiesel production [14].

Ojo and others investigated the sedimentological and geochemical studies of Maastrichtian clays in Bida basin of Nigeria. The results obtained from the physical and geochemical features confirmed it to be kaolinitic clay and could be utilized as catalysts, amongst other industrial purposes [15]. Montmorillonite clay from Udi in Nigeria has also been acid-activated and used as a catalyst in liguid-phase esterification of acetic acid with ethanol [16]. Clay obtained from Suleja and Shabu, Nigeria has also been used as catalyst for the esterification of propan-1-ol with propanoic acid [17].

Although, other researchers have investigated and characterized clay obtained from other parts of the country as catalysts for biodiesel production, there is no report on the characterization of Kono-Boue clay. Therefore, this research

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seeks to characterize Kono-Boue clay using techniques like powder x-ray diffraction (PXRD), to confirm its mineral structure; scanning electron microscopy (SEM), its surface morphology and energy dispersive X-ray for its elemental composition and other relevant properties. The study will help to mitigate the environmental effect of the currently used catalysts (NaOH or HCl) with a re-useable solid catalyst. The success of this will provide a new source of cheap and easily available heterogeneous catalyst for our local industries and the world at large.

2. Materials and Methods

2.1 Materials

Kono-Boue clay was taken from Kono-Boue town situated on Latitude 4° 42' North of the equator and Longitude 7° 22' East of Greenwich meridian in the Khana Local Government Area of Rivers State, Nigeria (See **Figure 1** below for the location of Kono Boue Town in Ogoni land of Nigeria). Other materials used include weighing balance, British Standard Sieve (BSS) 100mm mesh, oven, pot, spatula, mortar and pestle.

Map of Ogoniland Showing sampling town of KONO BOUE, www.unep.org/nigeria.

• KONO BOUE (Latitude 4°42' N, Longitude 7°22' E)

Figure 1: Map of Ogoniland showing Kono Boue Town (courtesy, July 2011 UNEP Report).

2.2 Methods

2.2.1 Clay collection and preparation

The raw clay sample was dug and collected from a clay mine at Kono-Boue town, Rivers State Nigeria, manually with a shovel at a depth of about 50 cm, and placed in a clean polythene bag. The clay sample was then oven dried at 110°C for 4 hours to ensure complete evaporation of the moisture content. The dried clay was milled and sieved through a British Standard Sieve (BSS) 100mm mesh.

2.2.2 Characterization of clay

The dried, milled clay sample was characterized to determine its mineral structure using X-ray diffraction (XRD) on an EMMA GBC diffractometer at the NASENI centre, Akure, Ondo, Nigeria. The instrument used the monochromatic CuKα1 radiation source. The settings used included scan angles of 2θ, 20-70° with step size of 0.05 and dwell time of 0.025 s. The SEM was ASPEX 3020 model equipped with an Oxford EDX detector.

3. Results and Discussion

3.1 X-ray Diffraction (XRD)

The major x-ray reflections of Kono-Boue clay matched with berlinite ($AlPO_4$) crystal structure. The pattern was indexed to the Joint Committee on Powder Diffraction and Standards (JCPDS) file number, 003-0447 (**Figure 2**) while the 2-theta angles, d-spacing and relative intensities are shown in **Table 1**. The major peaks as labeled also matched with Kaolinite clay phase as reported in literature [5]. Therefore it was necessary to confirm its elemental composition using energy dispersive X-ray (EDX) analysis.

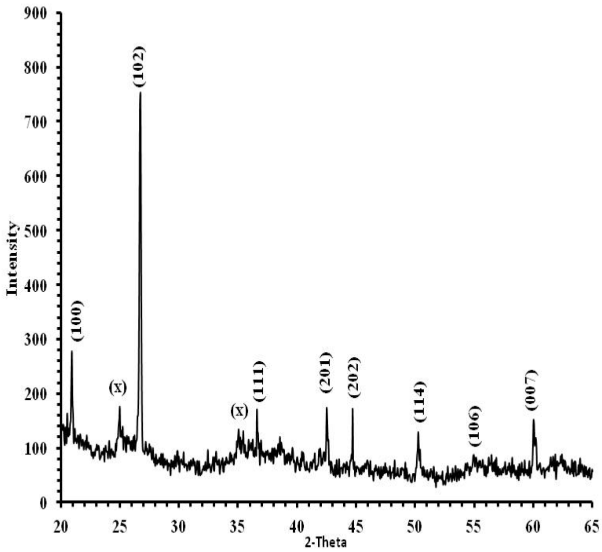

Figure 2: XRD analysis of Kono-Boue Clay showing reflections of Aluminium Silicate (Clay) which crystallized with $AlPO_4$ Crystal Structure (JCPDS file number: 003 – 0447). X= Minor oxide phases.

Table 1: Showing the d-spacing, relative intensities and hkl of Kono Boue clay powder

2-Theta	*d(Å)*	*Intensity*	*hkl*
21.0344	4.22	66	100
26.8311	3.32	100	102
36.8048	2.44	52	111
39.4909	2.28	56	104
42.6109	2.12	45	201
45.7884	1.98	29	202
50.0775	1.82	86	114
54.9350	1.67	53	106
60.0241	1.54	75	007
63.6854	1.46	23	116
67.8592	1.38	96	206

The EDX (**Figure 3**) showed absence of Phosphorus and as such Kono Boue clay would not contain $AlPO_4$ rather it should be aluminium silicates (Kaolinite) due to its composition. Kaolinite minerals, $Al_2Si_2O_5(OH)_4$ or $Al_2O_3.2SiO_2.2H_2O$ consist of silica (tetrahedral) and aluminium (octahedral) sheets separated by small singly and doubly charged metals like K, Mg and Fe [5]. However, Kono Boue clay also contained S. Peaks of only the major elements appeared on the EDX spectrum of Figure 3 while the data sheet contained all of them (See **Table 2** for the elemental compositions).

Table 2: Elemental composition of Kono-Boue clay as analyzed by EDX

Elements	*Counts*
Al	10.0
Si	41.4
S	1.0
K	3.3
Mg	3.3
Fe	3.9
O	30.8
Ti	1.3
Zr	1.7
W	2.7
Hg	2.2
Au	1.7

The presence of other important elements like Ti, Zr, W, Hg and Au in Kono Boue clay would enhance its catalytic activity and commercial value. The result also indicates the possibility of larger occurrence of these elements in other minerals around the same geographical location. This report would also inform the users of the clay for medicinal purposes presence of the presence of toxic elements like mercury in Kono Boue clay.

3.2 Energy Dispersive X-ray (EDX)

The EDX spectrum showed counts of major components with Silicon being the highest (Figure 3) followed by oxygen and aluminium while others were of approximately the same count rate. This EDX result confirmed that Kono-Boue clay is of the alumino-silicate (Kaolinite) type clay. Kono-Boue clay like any other naturally occurring clay such as kaolinite, hectorite and montmorillonite, have layer structures of octahedral and tetrahedral units. Aluminum occupies the octahedral site while silicon, the tetrahedral site. The crystal structure of Kono Boue clay compared closely with other clays found in Nigeria.

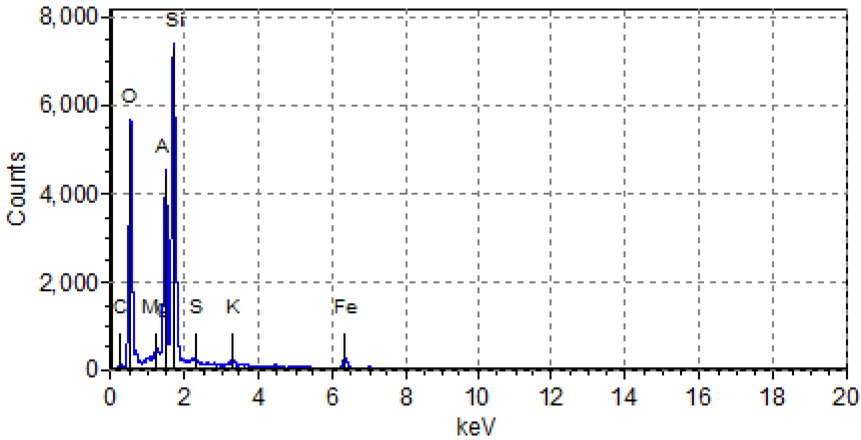

Figure 3: EDX spectrum of Kono-Boue Clay showing counts of major components (Si, O, Al, etc)

Forinstance, the Ibere and Oboro clay deposits in Abia State, a neighbouring State to Rivers State in Nigeria are largely kaolinite, chemically composed of mainly silica (52.06% and 60.21% respectively) and alumina (27.87% and 19.05% respectively) [18]. In a related study of sedimentological and geochemical characteristics of Maastrichtian clay in Bida Basin Nigeria, geochemical data showed that the clay stone at Share composed of SiO_2 ranging from 45.2% to 64.8% (average of 58.1%) while at Agbeja, the values ranged from 48.5% to 74.7% (average of 63.3%) [15]. The Al_2O_3 value for the clay at Share ranged from 20.3% to 37.9% (averaging 26.9%) while, the Agbeja samples was between 15.61% and 34.23% with an average of 24.6%. The findings indicated that the clays were essentially hydrated siliceous aluminosilicates. Similar high percentage of SiO_2 (F-101, 66.19%; F-117, 59.57% and kaoline, 53.09%) and low percentage of Al_2O_3 (F-101, 17.0%; F-117, 22.28% and kaoline, 42.47%) was reported for Brazilian clay [12].

3.4 Scanning Electron Microscopy (SEM)

The surface morphology of Kono-Boue clay was studied by using the SEM technique. The SEM micrograph shown in **Figure 4** showed varying distribution of aggregate crystallites. The smaller particle sizes were largely below 5µm while the larger ones were of the 10-15µm ranges, respectively. Thus indicating non-uniformity and inherent porosity. This could offer or act as micro catalytic sites or channels when applied as catalysts.

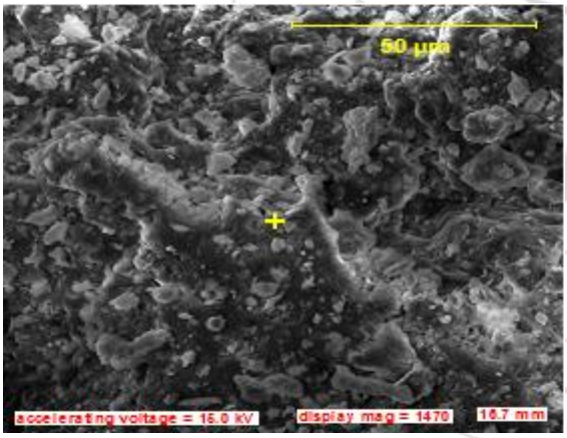

Figure 4: SEM image showing surface morphology of Kono-Boue Clay

4. Conclusion

The characterization of Kono-Boue clay using XRD has been reported for the first time. The reflections matched those of $AlPO_4$ and Kaolinite crystal structures. However, the EDX analysis confirmed that it consists largely of Kaolinite clay structure with silicon to aluminum ratio of 4:1. The EDX spectrum also indicated the presence of S, Mg, K, and Fe. Other elements found on the EDX analysis data included those of Ti, Zr, W, Hg and Au. Therefore Kono-Boue clay with the aluminum silicate structure mixed with the above listed elements would be a promising zeolite or clay catalyst for biodiesel production and heterogeneous catalysis in general.

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