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Production and Characterization of Catalysts from Ngbo Clay in Ebonyi State, Nigeria

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ABSTRACT

This work was focused on the development and characterization of clay catalyst from Ngbo clay. The raw clay was crushed, refined, dried, and grinded before activation to produce acid activated clay (AAC), base activated clay (BAC), thermal activated clay (TAC), zinc chloride activated clay (ZAC) and pillared clay (PLC) catalysts respectively. The samples were characterized using Atomic Absorption Spectrophotometry (AAS), X-Ray Flourescence (XRF), Fourier Transform Infrared (FTIR), Scanning Electron Microscopy (SEM) and X-Ray Diffraction (XRD). The AAS result indicates that the raw Ngbo clay has high concentration of Aluminium and low concentration of lead. The results of the XRF analysis on the Ngbo clay and activated Ngbo clays indicate a high content of silicon and aluminium oxides compared to other oxides. The bands at 3697 and 3628cm^{-1} in FTIR results are assigned to the stretching vibration of hydroxyl groups in the clay structure, which indicates that Ngbo activated clay by acid or alkaline treatments, even under strong conditions and thermal treatment below 500 °C, does not change due to its low reactivity. The SEM images of all Ngbo activated clay show retention of kaolinite structure but with noticeably small aggregate particles in between the silica-alumina plate on higher magnification, an indication of impurities on the beneficiated kaolin. The halloysite phase detected in the raw clay SEM image was not in the activated clay SEM image,The X-Ray Diffraction (XRD) of the raw clay sample showed that the physical properties of raw clay are kaolinite clay with a high aluminium to silicon ratio, which is a good characteristic of clay for the production of catalysts and synthetic zeolites. The catalysts produced could be applied in the esterification of carboxylic acids with alcohols and in the production of synthetic zeolites, to avoid the drawbacks of corrosion, loss of catalyst and environmental problems.

KEYWORDS: *Characterization, Clay catalyst Production, Acid Activated catalyst, Base Activated catalyst, Thermal Activated Catalyst, Zinc Chloride Activated Catalyst, Pillared Clay*

1.0 INTRODUCTION

In the past decades, the high demand for catalysts and zeolites for industrial processes has been of serious concern to developing countries like Nigeria considering the industrialization growth. Also insufficient and unsafe quality of drinking water due to effluents or waste-products from textiles, chemicals, mining and metallurgical industries are considered major water contaminants [1]. Several conventional methods such as precipitation [2], ion exchange [3], membrane filtration technology [4], electrochemical processes [5] and adsorption process [6] have been employed to remove these contaminants from wastewaters. The conventional methods are expensive and sometimes ineffective, especially when the contaminant's concentration is higher than 100mg/l [7].

There are increased researches on the development of solid acid catalysts for esterifications, adsorption of contaminants in

wastewater and other various organic transformations. Even though there are sets of regulations established to aid in the substitution of unfriendly and corrosive liquids used in chemical and petrochemical industries, the use of solid acid catalysts for esterificatios and adsorption of water contaminants are important [8]; [9]. The clays as heterogeneous and environmental friendly catalysts are considered as promising adsorbents for corrosive liquid acids currently used in many industries for various organic transformations and water treatment to reduce the amount of waste generated and render the synthetic process more attractive [10]. The uses of clay as catalyst in heterogeneous reaction catalysis are considered economically viable, environmentally friendly, abundant, low cost, high selectivity, thermal stability and reusability [11].

Clays are hydrated aluminum silicate minerals that occur in nature as rocks, consolidated or unconsolidated earthly material [12]. Clays from different locations have different properties making them more reactive than the others [13]. The high surface area, high pore volume and pore sizes of clay increased their potential applications as adsorbent and catalyst [14]. Clay is one of the raw materials in abundance in Nigeria, it is readily available in Nigeria in large deposit yet its potentials have not been fully explored. Different types of clay deposit are found in the world today [15]. In Nigeria, large quantities of clay mineral deposit are found in Udi in Enugu State, Ukpor in Anambra State [16]. The exploitation of clay resources in Nigeria has attracted a lot of attention (Raw Material Research and Development Council, RMRDC). These large clay deposits in Nigeria have been under exploited for use as sources of raw materials [17]. However, there is recent interest in exploring the potentials of clays such in bleaching of palm oil [18]:; [19] in adsorption of dyes [20]; [21] and [22] among others. In a quest to develop green processes, clay is mostly used in the synthesis of catalysts, although use of Nigerian clays from Ngbo, Ohaukwu- Ebonyi State for producing clay catalysts is limited in literature.

This work investigated the development and characterization of local clay from Ngbo in Ohaukwu Local Government Area of Ebonyi State Nigeria for the production of activated catalysts.

2.0 MATERIALS AND METHODS

2.1 Source of Raw Materials

The clay sample was obtained from Ngbo in Ohaukwu L.G.A. of Ebonyi State (N 06°30' 32.8''), (E 007°58'13.7''). The reagents used was purchased from a chemical shop at Ogbete main market, Enugu, Enugu State. Other chemicals such as tetraoxosulphate (vi) acid, sodium hydroxide, zinc chloride, aluminium trichloride ($AlCl_3$), distilled water, etc were of standard grade.

2.2 Physico-Chemical Characterization of Ngbo Clay

The Ngbo clay sample was subjected to some physical analysis in order to obtain their physical properties. The analysis carried out include: Bulk density, Moisture content, pH and Loss on Ignition (LOI).

2.3 Grain Size Analysis

The clay sample was oven-dried at 105 °C. 100g of the dried clay sample was weighed in a beaker and the weight; recorded on the sieve data sheet. The sample was poured into the beaker and the resulting weight was recorded on the sieve data sheet. The clay samples were placed in a sieve shaker and the weight of the clay material is determined in each size fraction and the proportion of sample that was left during sieving was recorded. The percentage (by weight) for each fraction and cummulative weight (%) for the sample recorded.

2.4 Production of Ngbo Clay Catalysts/Clay Catalyst Preparation

2.4.1 Clay particle size reduction

The method reported by [22] was used. The clay sample was first crushed in the mortar to powdery form, and then introduced into the screen and shaken vigorously. At the end a

sample quantity was obtained at the collecting tray.

2.4.2 Acid Activation

The acid activation method used in this work is as reported by [22]. A 100g of pulverized and screened clay was mixed into slurry with 50ml of diluted water, 30ml of 1M H_2SO_4 was added and stirred vigorously and placed in an oven where it was maintained at a temperature of 100°C. The sample was washed thereafter and left to sediment. Complete removal of all residual acid was achieved by repeating washing and decanting until a pH of six was obtained. The final slurry was filtered and dried at 100°C. The dried, activated and washed clay was then pulverized, screened and stored in desiccators prior to use.

2.4.3 Alkaline Activation

The alkaline activation method used in this work is as reported by [22]. A 100g of pulverized and screened clay was mixed into slurry with 50ml of diluted water, 30ml of 1M NaOH was added and stirred vigorously and placed in an oven where it was maintained at a temperature of 100°C. The sample was washed thereafter and left to sediment. Complete removal of all residual bases was achieved by repeating washing and decanting until a pH of eight was obtained. The final slurry was filtered and dried at 100°C. The dried, activated and washed clay was then pulverized, screened and stored in desiccators prior to use.

2.4.4 Thermal activation

The thermal activation method used in this work is as reported by [22]. A 100g of pulverized, screened clay sample was transferred into a carbolite furnace. The sample was heated at 400°C for three hours after which it was cooled in a desiccator and stored in an airtight container.

2.4.5 $ZnCl_2$Activation

The $ZnCl_2$ activation method used in this work is as reported by [22]. The same procedure for the acid and alkaline activation was used for the activation, that is 1 mole of $ZnCl_2$ (aq) was used instead of 1 mole of H_2SO_4 or NaOH.

2.4.6 Clay Pillarring

The pillared clay was prepared according to the method described by [23] with some modification. The pillaring agent used was an alluminium polioxocation prepared by basic hydrolysis of an aluminium trichloride ($AlCl_3$). A 0.20m/dm^3 of sodium hydroxide (NaOH) solution was poured at 4ml/min over the 0.2m $AlCl_3$ salt solution and stirred vigorously until a molar ratio OH/Al of 2 was reached. The final pH was 3.5 and the solution was kept for 1 hour at 50°C.

100g of clay sample were suspended in distilled water and stirred continuously for 30 min after which the pillaring agent solution was added (4ml/min) over the clay suspension while stirred vigorously. The final Aluminium/clay was 2mol/g. The resulting suspension was kept at 80°C for 4 hours. The solid was recovered by filtration and oven dried at 450°C. The clay sample was pulverized and stored in an airtight container.

2.5 Characterisation of the raw clay and activated clay samples

The Ngbo clay sample was characterised using AAS, XRF, XRD, FTIR, SEM, and TGA/DTA.

2.5.1 Atomic Absorption Spectrophotoscopy (AAS)

The clay sample was examined using Atomic Absorption Spectrophotoscopy (AAS). It makes use of absorption spectrometry to assess the concentration of an analyte in a sample. It therefore relies heavily on the Beer-Lambert Law.

In short, the electrons of the atoms in the atomizer can be promoted to higher orbitals for a short amount of time by absorbing a set quantity of energy (ie light of a given wavelength). This amount of energy (or wavelength) is specific to a particular electron transition in a particular element, and in general, each wavelength corresponds to only one element. This gives the technique its elemental selectivity.

2.5.2 X-Ray Flourescence (XRF) Analysis

The Mini Pal 4 version used is PW 4030 X-ray Spectrometer, which is an energy dispersive microprocessor controlled analytical instrument designed for the detection and measurement of elements in a sample (solids, powders and liquids), from sodium to uranium.

The sample for analysis was weighed and grounded in an agate mortar and a binder (PVC dissolved in toluene) was added to the sample, carefully mixed and pressed in a hydraulic press into a pellet.

The pellet was loaded in the sample chamber of the spectrometer and voltage (30KV maximum) and a current (1mA maximum) is applied to produce the x-rays to excite the sample for a preset time (10 mins in this case). The spectrum from the sample is now analysed to determine the concentration of the elements in the sample.

2.5.3 X –ray diffractometry (X-RD)

The adsorbents were characterized by means of X – ray diffraction using a diffractometer system (EMPYREAN) using radiation Cuα (α_1= 1.540598Å and α_2= 1.544426Å) and a secondary graphite monochromator (No), angle 2θ swept and the scan range (-0.002 – 74.99997°).

2.5.4 Fourier transforms infrared spectroscopy (FTIR) analysis

The structural organization of the adsorbents was investigated to identify the functional groups presents. The adsorbents were examined using SHIMADZU FTIR-8400S spectrophotometer with the range 500 – 4000cm^{-1}. KBr was used as background material in the analysis.

2.5.5 Scan electron microscopy analysis (SEM)

The surface morphology of the solid adsorbents was inspected using a scanning electron microscope (SEM) PHENOMWORLD operating at 25kV. Micro-particles for SEM studies were mounted on metal stubs with double – side adhesive, and coated with gold in vacuum using an IB – 3ion coater. The analysis also includes the micro pore volume, and diameter of the various adsorbents. The energy dispersive x-ray (E – DX) was used to determine the elemental compositions of the adsorbents.

2.5.6 Thermogravimetric Analysis (TGA)/ Derivative Thermal Analysis (DTA)

The materials were analyzed by thermogravimetry on a Mettler Toledo TG 50 thermobalance between 25-700 °C, using a heating rate of 10 °C min^{-1} under flowing air. The ground sample is directly filled into the crucible for TG testing. The amount was normally 15-20 mg to minimize background noise. This analytical technique was very useful to estimate the thermal stability of the clay.

3.0 RESULTS AND DISCUSSIONS

3.1 Physical properties of the raw clay

The result of the physical properties of raw Ngbo clay is presented in table 3. The result showed that the clay has a moisture content of 3.3 % and bulk density of 1.25 g/ml, which are in agreement with the previous research of [24 – 26] that reported the moisture content of kaolinite clay is between 3.0 – 4.0% and the bulk density is 1.2 – 1.4 g/ml.

Table 1: Results of Bulk density, Moisture content, pH, and LOI

Clay type	Bulk density (g/ml)	% moisture content	pH	LOI (%)
Ngbo clay	1.25	3.33	7.5	10.52

3.2 Characterization of Raw Clay and Activated Ngbo clay

The chemical properties of the raw Ngbo clay was analysed using AAS, TGA, XRF, FTIR, SEM and XRD.

The result of the AAS analysis of raw Ngbo clay is presented in Table 2. The result showed that the raw Ngbo clay has elemental composition of Al, Ca, Pb, Co, Mn, K, Na, Cr, Zn, Cd, Fe, Ni, Cu and Mg respectively. The result indicates that the raw Ngbo clay has high

concentration of Aluminium and low concentration of lead.

Table 2: Results of AAS analysis of raw Ngbo clay

Element	Actual Concentration (ppm)	Absorbance (Å)
Al	61.0645	0.1893
Ca	15.0090	0.1213
Pb	0.3114	0.0021
Co	0.4246	0.0071
Mn	2.9949	0.5965
K	15.2574	1.2480
Na	1.5641	0.2444
Cr	0.2339	0.0093
Zn	1.4662	0.2701
Cd	0.0296	0.0043
Fe	24.7391	0.6671
Ni	0.0500	0.0048
Cu	0.0362	0.0048
Mg	0.9289	0.2929

The result of thermogravimetric analysis (TGA) of raw Ngbo clay is presented in figure 1. The result showed the mass loss and the transition of kaolinite to metakaolinite. The results describe the regular mass loss change and structural transformations of kaolinite, and indicate the main changes pointed out by TGA during the heating of the Ngbo kaolinite sample from 30-1000ºC. In the first stage, when the kaolinite was heated, the dehydration process took place. The adsorbed water was liberated below 400°C and the weakest part of the chemical bond was broken or perturbed. Then dehydroxylation took place in the range 450– 600 °C. At this stage of the transformation, the kaolinite was transformed to the metakaolinite phase with the loss of structural hydroxyl groups.

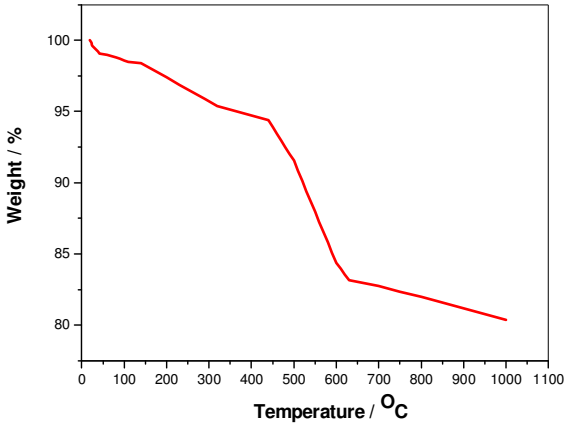


Figure 1: Thermogravimetric analysis (TGA) of Raw Ngbo Clay

The result of the XRF composition analysis of raw Ngbo clay and activated Ngbo clays (AAC, BAC, TAC, ZAC and PLC) is presented in Table 3. The result showed that raw and activated clays have contaminations of oxides and other impurities, but the clay minerals compositions are not meaningfully affected by acid or alkaline treatments even under strong conditions and thermal treatment below 500 ℃ as reported in literature by [27 – 30].. This shows that improvements on the properties of the clay by chemical methods or thermal treatment below 500 ℃ are difficult due to its low reactivity. This result of the XRF on the Ngbo clay and activated Ngbo clays as shown in table 3 also indicates high content of silicon and aluimium oxides when compared to other oxides.

Table 3: Results of XRF analysis of raw Ngbo Clay and activated Ngbo clays

Chemical constituent	Raw clay (Wt. %)	Acid activated (AAC), (Wt. %)	Base activated (BAC), (Wt. %)	Thermal Activated (TAC), (Wt. %)	ZnCl Activated (ZAC), (Wt. %)	Pillard clay Activated (PLC), (Wt. %)
SiO_2	62.70	67.030	73.100	61.822	65.743	65.395
TiO_2	1.52	1.285	1.468	1.528	1.386	1.354
Al_2O_3	19.70	23.924	18.155	25.981	23.457	24.562
Fe_2O_3	2.06	4.968	4.521	7.223	5.855	5.667
P_2O_3	_	0.149	0.167	0.057	0.000	0.000
CaO	0.789	0.143	0.479	0.810	0.232	0.359
MgO	0.026	0.646	0.490	0.726	0.522	0.586

Na_2O	0.20	0.057	0.101	0.000	0.256	0.261
K_2O	0.85	1.109	0.943	1.402	1.149	1.196
Mn_2O_3	_	0.079	0.208	0.160	0.135	0.148
V_2O_5	0.071	_	_	_	_	_
Cr_2O_3	0.035	0.012	0.006	0.012	0.011	0.011
CuO	0.044	_	_	_	_	_
BaO	0.19	_	_	_	_	_
L.O.I	11.82	_	_	_	_	_
SO_3	_	0.573	0.329	0.220	0.181	0.220
Cl	_	0.008	0.017	0.024	0.131	0.217
ZnO	_	0.013	0.011	0.023	0.936	0.016
SrO	_	0.006	0.007	0.009	0.007	0.007

The result of the FTIR spectra over the range 600 - 4000 cm^{-1} of Ngbo raw clay and activated clays ((a) AAC (b) BAC, (c) TAC, (d) ZAC, (e) PLC) is presented in figure 2 and 3. The bands at 3697 and 3628 $cm^{-1}$are assigned to the stretching vibration of hydroxyl groups in the clay structure as reported in literature by [31 – 33]. This indicates that Ngbo activated clay by acid or alkaline treatments even under strong conditions and thermal treatment below 500 ℃ does not change due to its low reactivity. The result collaborates with the XRF result of the Ngbo activated clays.

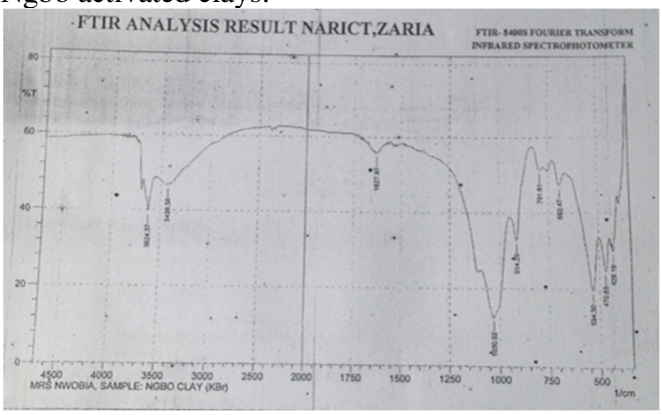
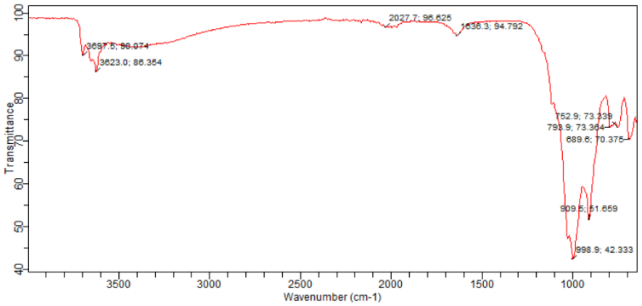
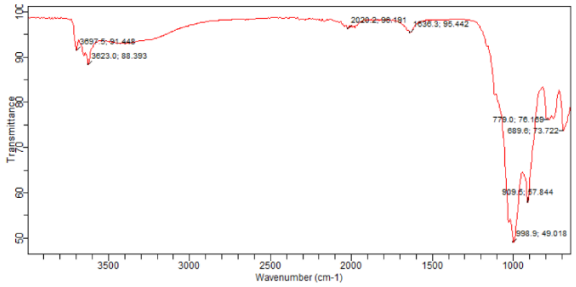


Figure 2: Results of FTIR analysis of raw Ngbo Clay

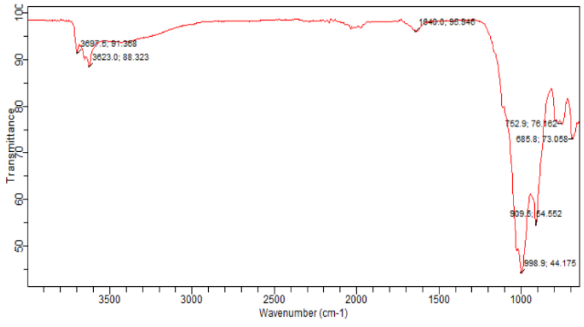
(a) AAC



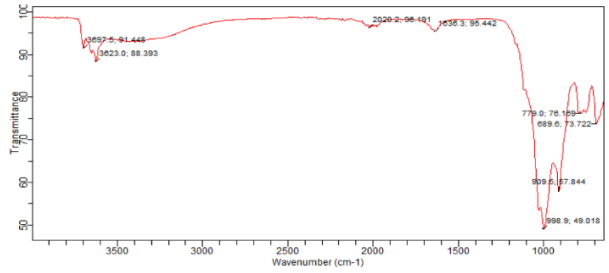
(b) BAC



(c) TAC



(d) ZAC



(e) PLC

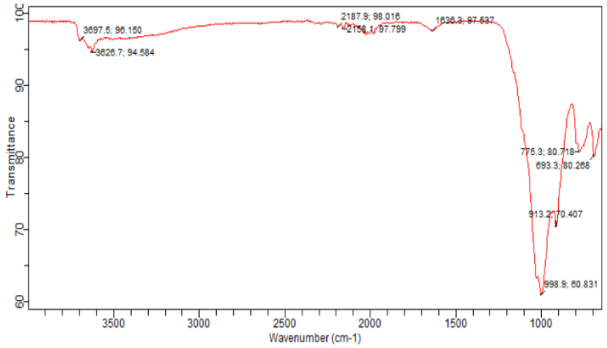


Figure 3: Results of FTIR analysis of Ngbo activated clay, (a) AAC (b) BAC, (c) TAC, (d) ZAC, (e) PLC

The SEM image results of the raw clay at 80μm, 20μm and 8μm magnifications are presented in figure 4. The SEM image results of Ngbo raw clay showed cracking or peeling morphology and presence of tubular or rod material attributed to halloysite, clinochlore, mica and muscovites as reported in literature by [34]. The results are in agreement with the XRD results.

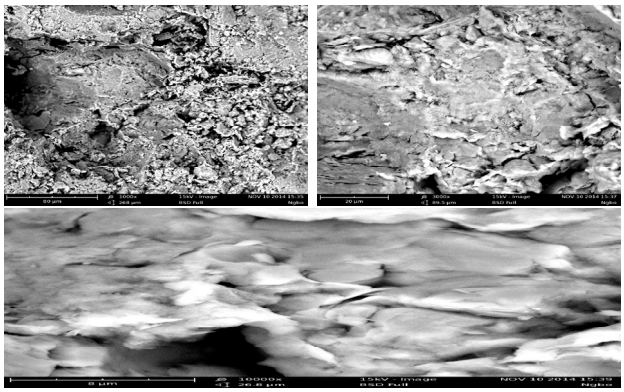
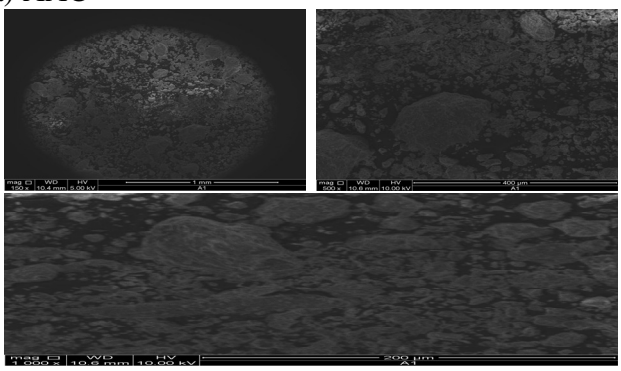


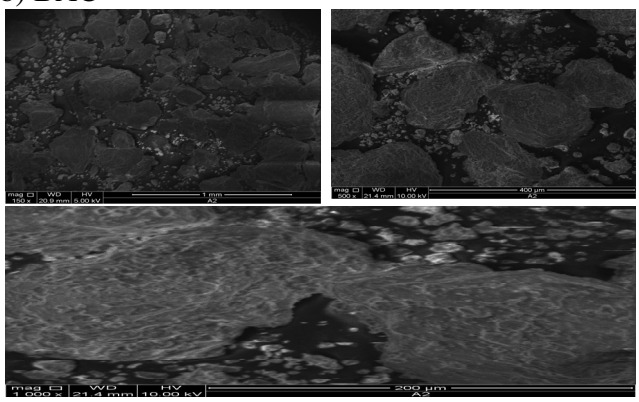
Fig 4: Results of SEM analysis of Ngbo Raw Clay

The SEM image results of Ngbo activated clay at 80μm, 20μm and 8μm magnifications are presented in figure 5. The SEM images results of all Ngbo activated clay shows retention of kaolinite structure but with noticeable small aggregate particles in between the silica-alumina plate on higher magnification, an indication of impurities on the beneficiated kaolin [34]. The halloysite phase detected in the raw clay SEM image was not in the activated clay SEM image, which are in agreement with both the XRD and XRF results. The dark and bright patches witnessed in the image were attributed to the presence of imbedded chemicals and completely dried portion of the samples respectively.

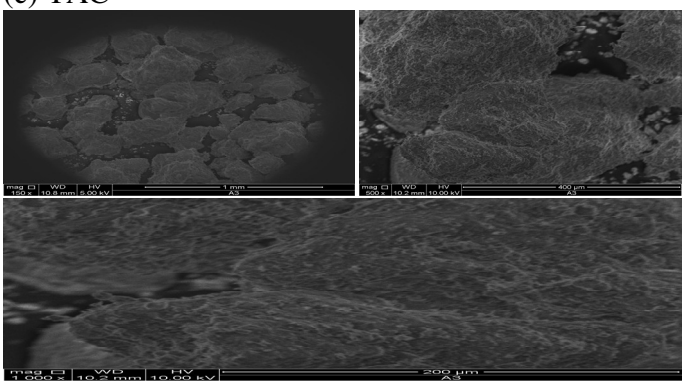
(a) AAC



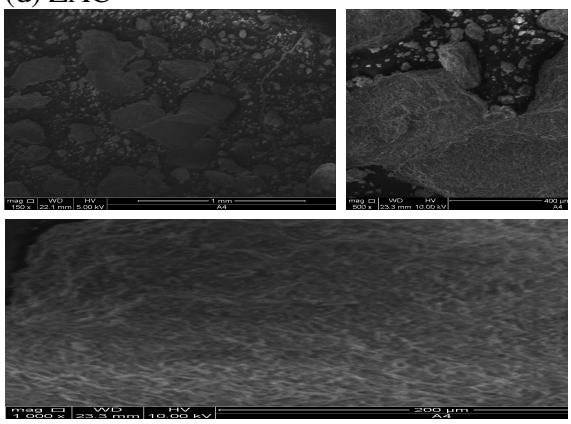
(b) BAC



(c) TAC



(d) ZAC



(e) PLC

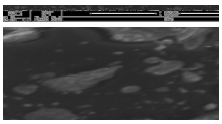


Figure 5: Results of SEM analysis of Ngbo activated clay, (a) AAC (b) BAC, (c) TAC, (d) ZAC, (e) PLC

The results of XRD pattern analysis of raw Ngbo clay is presented in figure 6. The results of XRD pattern results showed several characteristic peaks due to minerals compositions present. The peak obtained at position corresponding to 2Θ = 22.64° indicated the presence of large quantities of quartz. Minor impurities, such as illite, muscovite, haloysite, quartz hydrated mica, non-christalline hydroxide iron and halloysite present. The presence of these minor impurities and quartz content of Ngbo clay needs to be reduced to minimum before its usage for industrial purpose especially in zeolites development in line with researches of [35 – 36]. The XRD analysis corroborates with the results obtained with the XRF analysis.

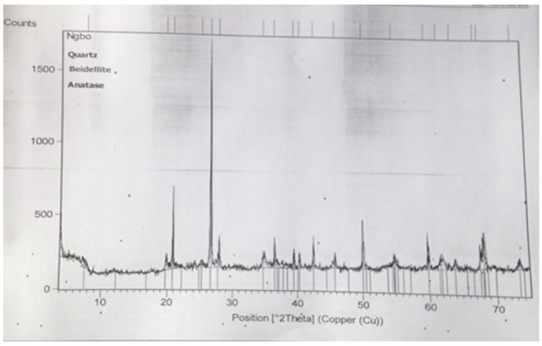
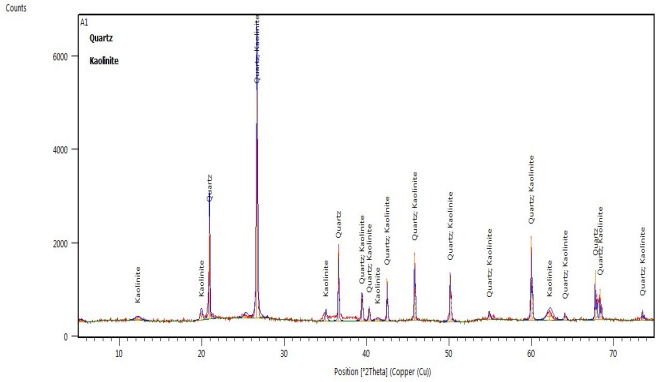


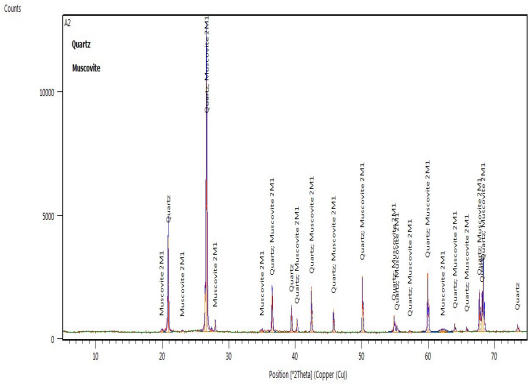
Figure 6: Results of XRD of raw Ngbo Clay

The results of XRD pattern analysis of Ngbo activated clay, (a) AAC (b) BAC, (c) TAC, (d) ZAC, (e) PLC are presented in figure 7. The results of XRD pattern results showed several characteristic peaks due to minerals compositions present. The analysis of the peaks showed sharp peaks with low intensity at $2\theta = 11.30^0$, which is the main peak used in the identification of kaolinte clay as reported in literature by [37].

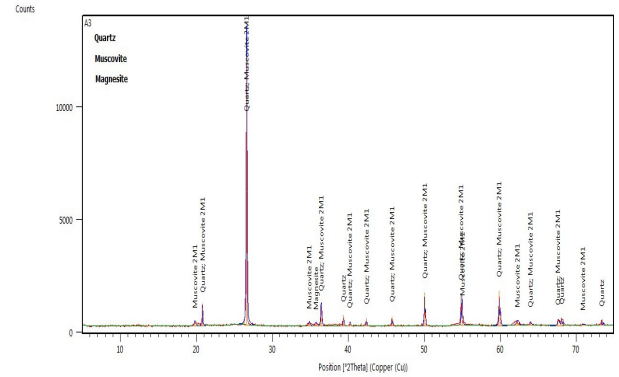
(a) AAC



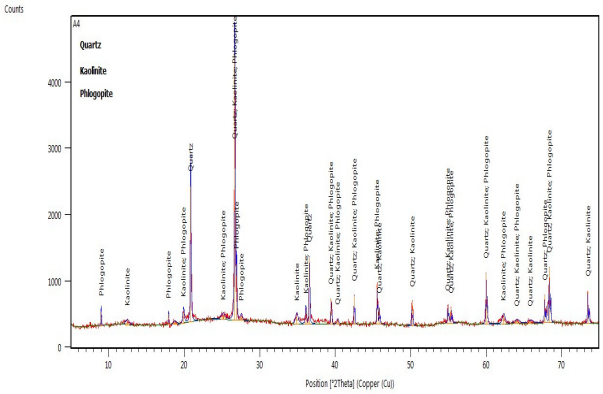
(b) BAC



(c) TAC



(d)ZAC



(e) PLC

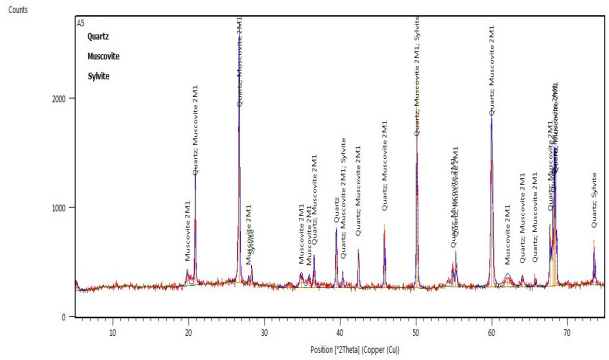


Figure 7: Results of XRD analysis of Ngbo activated clay, (a) AAC (b) BAC, (c) TAC, (d) ZAC, (e) PLC

CONCLUSION

This research work investigated the development and characterization of Ngbo raw clay and Ngbo activated clay catalyst. From the study, the physical properties of raw Ngbo clay showed that it is a kaolinite clay with high aluminium to silicon ratio, which are good characteristics of clay for the production of catalysts and synthetic zeolite. The characterization of the clay revealed the major constituents of the clay are aluminium, silicon and iron with crystalline nature suitable for adsorption of particulates. The activated clay catalyst of acid, base, thermal, zinc chloride and pillared will all be suitable for catalyzing liquid – phase esterification reaction of carboxilic acid and alcohol.

COMPETING INTERESTS

Authors have declared that no competing interests exist.

REFERENCES

1. Gómez-Álvarez, A.; Valenzuela-García, J.L.; Meza-Figueroa, D.; De, M.; O-Villanueva, L.A.; Ramírez-Hernández, J.; Almendariz-Tapia, J.; Pérez-Segura E. Impact of mining activities on sediments in a semi-arid environment: San Pedro River, Sonora, Mexico. *Appl. J. Geochem*. **2011**, 26, 2101-2112.
2. Martins, A.; Mata, T.M.; Gallios, G.P.; Vaclavikova, M.; Stefusova, K.(2010) Modeling and simulation of heavy metals removal from drinking water by magnetic zeolite. *Water Treatment Technologies for the Removal of High-Toxicity Pollutants.Project*; No. APVT 51, 017104, 61-84. Available at: https://link.springer.com/book/10.1007/978-90-481- 3497-7
3. Yuan, P.; Liu, D.; Fan, M.; Yang, D.; Zhu, R.; Ge, F.; Zhu, J.X.; He, H (2010).“Removal of hexavalent chromium [Cr(VI)] from aqueous solutions by the diatomite supported/unsupported magnetite nanoparticles”*Journal of. Hazard Mater*, 173, 614-621.
4. Song, J.; Oh, H.; Kong, H.; Jang, J. Polyrhodanine modified anodic aluminum oxide membrane for heavy metal ions removal. *J. Hazard. Mater*.**2011**, 187, 311-317.
5. Karami, H.(2013).“Heavy metal removal from water by magnetite nanorods”.*Journal of Chemical Engineering,* 219, 209-216.
6. Chiban, M.; Soudani, A.; Sinan, F.; Persin, M. Single, binary and multi-component

adsorption of some anions and heavy metals on environmentally friendly *Carpobrotusedulis* plant. *Colloids Surf. B* **2011**, B 82, 267-276.

7. Miretzky, P.; Saralegui, A.; Cirelli, A.F. Simultaneous heavy metal removal mechanism by deadmacrophytes. *Chemosphere* 2006, 62, 247-254
8. Igbokwe, P.K., and Ogbuagu, J.O., Effects of Process parameters on the Yield of Alumina from Indigenous Kaolinitic Clay Deposit, *Nigerian Journal of Engineering Research and development*, vol. 2, no.2, pp.23 – 26, 2003.
9. Shanmugan S; Viswanathan B.; and Varadarajan T. K. (2004).''Esterification by solid acid catalysts – a comparison''.*Journal of molecular catalysis A: Chemical* 223, 143 – 147.
10. Dillip K Pradhan, RNP Choudhary, BK Samantaray (2008). Studies of dielectric relaxation and AC conductivity behavior of plasticized polymer nanocomposite electrolytes. *Int. J. Electrochem. Sci* 3 (5), 597-608
11. Ravindra Reddy, C; Lyengar, P; Nagendrappa, G; Jai Prakash, B.S (2005).'' Esterification of dicarboxylic acids to diesters over Mn^{+}-montmorillonite clay catalysts'' *Catalyst Letter*, 101, 87 – 91.
12. Adamis Z. (2005) Bentonite, Kaolin and Selected Clay Minerals, Geneva pp 11- 12
13. Igbokwe P. K, and Ogbuagu J. O (2003), 'Effects of process parameters on the extraction of alumina from indigenous kaolinitic clay deposit' *NJERD*, 2, 2.
14. SoumayaBouguerraNeji, Mahmoud Trabelsi and Mohamed H. Frikha (2009).''Esterification of fatty acids with short-chain alcohols over commercial acid clays in a semi-continous reactor'' *Energies Journal*, 2, 1107 – 1117.
15. Nwajagu C. O and Aneke L. E. (1986).''Characteristics of Ukpor Clay Deposits''.*Journal of Nigerian Society of Chemical Engineers,* 5, 1.
16. Igbokwe P.K., Ogbuagu, J.O. and Nwokolo, S.O., Catalytic Esterification of Stearic Acid using a Local Kaolinitic Clay Mineral, *Nigerian Journal of Engineering Research and development*, vol. 4, no. 1, pp. 22 – 27, 2004.
17. Nwabanne, Joseph T., Onu, Chijioke E. and Nwankwoukwu, Okwudili C. (2018) Equilibrium, Kinetics and Thermodynamics of the Bleaching of Palm Oil Using Activated Nando Clay. Journal of Engineering Research and Reports 1(3): 1-13. DOI: 10.9734/JERR/2018/42699
18. Ajemba R.O, Onukwuli O.D (2012) Process optimization of sulphuric acid leaching of alumina from Nteje clay using central composite rotatable design. International Journal of Multidisciplinary Sciences and Engineering. 2012;3(5):1–6.
19. Onu, C. E. and Nwabanne, J. T. (2014) "Application of Response Surface Methodology in Malachite green adsorption using Nteje clay". Open Journal of Chemical Engineering and Science. 1 (2) 19 – 33.
20. Nwobasi Veronica Nnenna, Igbokwe Philomena K., and Onu Chijioke Elijah (2020) Removal of Methylene Blue Dye from Aqueous Solution Using Modified Ngbo Clay. Journal of Materials Science Research and Reviews, 5(2): 33-46. May 2020
21. Elijah, C. O. and Nwabanne, J. T. (2014). "Adsorption kinetics for Malachite green removal from aqueous solution using Nteje clay". Journal of Environment and Human. 1 (2) 133 – 150. doi: :10.15764/EH.2014.02015
22. Igbokwe P. K, Nwokolo S. O, and Ogbuagu J. O, (2005).Catalytic esterification of stearic acid using a local kaolinitic clay mineral. *NJERD*, 4, 1.
23. Huan-Yan Xu-, Zhuo Zheng, Gui-Jie Mao (2009). Enhanced photocatalytic discoloration of acid fuchsine wastewater by TiO2/schorl composite catalyst. .*Journal of hazardous material,* .2009.10.059. Epub 2009 Oct 27.

24. Igbokwe P. K and Olebunne F. L,(2011). On the catalytic esterification of acetic acid with ethanol, using Nigerian montmorillonite clay: effect of reaction variables on catalyst efficiency. *Journal of the University of Chemical Technology and Metallurgy*, 46, 6, 389-394.
25. Igbokwe P. K, Ugonabo V. I, Obarandiku E, Ochili A, (2008) ''Characterization and use of catalyst produced from local clay resources'' *Journal of Applied Sciences (JAS)*, 2, 2.
26. Igbokwe, P.K., Olebunne, F.L., and Nwakaudu, M.S (2011)., Effect of Activation Parameters on Conversion in Clay – Catalysed Esterification of Acetic Acid, *International Journal of Basic and Applied Sciences*, 11,.5, 1 – 8,
27. Murat, M., A. Amokrane, J.P. Bastide, and L. Montanaro,(1992). "Synthesis of zeolites from thermally activated kaolinite. Some observations on nucleation and growth".*Clay Minerals*, 27, 1, 119.
28. Akolekar, D., A. Chaffee, and R.F. Howe (1997), "The transformation of kaolin to low-silica X zeolite". *Zeolites*, 19, 5–6, 359–365.
29. Demortier A., Golbeltz N., Letlieur J.P., Duhayon C.(1999). Infrared evidence for the formation of an Intermediate compound, during the synthesis of Zeolite Na – A from metakaolin. International Journal of Inorganic materials. Volume 1, issue 2, August 1999, pages 129 – 134
30. Yi Xu, (1999). Effects of tone and focus on the formation and alignment of f0 contours.. *Journal of Phonetics* (1999) 27, 55}105.
31. Liu, Q., Spears, D.A. and Liu, Q. (2001) MAS NMR study of surface-modified calcined kaolin. Applied Clay Science, 19, pp.89-94.
32. Zhao, G. ; Wang, A. ; Tang, Y. ; Hu, Z., 2004. Research on the nutrient constituents and medicinal values of *Fagopyrum cymosum* seeds. Proc. 9th Int. Symp. Buckwheat, Prague 2004, 669-673
33. Alkan, M., Hopa, C., Yilmaz, Z., Guler, H (2005). The effect of alkali concentration and solid/liquid ratio on the hydrothermal synthesis of zeolite NaA from natural kaolinite. *MicroporousMesoporous Materials*, 86, 176–184.
34. Davies J, Haq S, Hawke T, Sarjent J.P (2009). A practical approach to the development of a synthetic Gecko tape. International journal of Adhesion and Adhesives. Volume 29, issue-4, June 2009, pages 380 – 390.
35. Tracy, M.M.J. and J.B. Higgins,(2001) "Collection of simulated XRD powder patterns of Zeolites" Fourth revised edition ed. 2001, Amsterdam Elsevier 379.
36. .Evamako O. Yusuf, Efeovbokhan V.E, and Babalola R. (2001). Development and characterization of zeolite – A from Elefun kaolin. *Journal of physics conference,* series 1378 – 032016.
37. Ramirez J.H, Maidonaldo – Hedar F.J, Ferez A.F, Moremo C., Costa C.A. Madeira L.M. (2007). Azo-dye orange II degradation by heterogeneous Fenton-like reaction using carbón – Fe catalysts. Applied catalysis B: Environmental. Volume 75, issue 3 – 4,26 September 2007, pages 312 – 323.

