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SYNTHESIS AND CHARACTERIZATION OF ZEOLITE Y FROM UKPOR CLAY FROM ANAMBRA STATE, NIGERIA

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Abstract: The present study involved the processing of raw Ukpor clay from Anambra State, Nigeria to kaolin as a precursor for the development of Y-type zeolite. The clay was first subjected to pretreatment by separating the foreign bodies from it using deflocculant (Sodium hexametaphosphate and Sodium hydrogen carbonate). Subsequently, the pretreated clay was calcined at 850^0C for 6 hours at atmospheric pressure. The calcined clay was formulated by adding sodium hydroxide and sodium metasilicate to produce a gel aged at room temperature for 12 hours. The gel was subsequently heated in a laboratory oven at 100^0C for 9*hrs* to produce the Y-type zeolite in a process called crystallization and a product with Si/Al molar ratio of 4.07 was achieved which is suiting for a typical Zeolite Y. The formulated samples were characterized using X-ray Fluorescence (XRF), Fourier Transform Infrared Spectroscopy (FTIR), and Scanning Electron Microscope (SEM). The results showed possible synthesis of Y-type zeolite from Ukpor kaolinite having a molar ratio of $15Na_2O:Al_2O_3:15SiO_2:450H_2O$. The synthesized product with Si/Al ratio of 4.07, an agglomerated euhedral morphology, and FTIR spectra peak at wavelengths of 719cm^{-1} and 3424cm^{-1}, are the basis upon which the conclusion of possible development of Y-type zeolite is drawn.

Keywords: XRF, FTIR, SEM, y-type zeolite, deflocculant

INTRODUCTION

Currently, there is need to improve hydrocarbon fuels both qualitatively and quantitatively, and to effectively use them. Hydrocarbon fuels have been essential to the growth of transportation, industry, and the agricultural sector [1], and also of immense importance in domestic lightening and heating. Energy consumption growth is projected at 28% between 2015 and 2040 worldwide. And petroleum consumption to take 31% of this cumulative increase [2]. The rising energy demand have instigated the need for the further processing of heavy petroleum feedstock. Residue content of heavier petroleum feedstock is about 40% and needs to be further processed into more valuable product to find use. This requires new catalytic systems, and improvement of already existing ones [1].

Catalytic cracking of heavy molecular weight hydrocarbon is required to meet the increased demand of energy consumption [1]. Catalytic cracking in petroleum refining is a process of converting or breaking large hydrocarbon molecules into smaller molecules by the action of catalyst [3]. Zeolite catalyst ensures higher yield of desired product in catalytic cracking compared to other catalyst systems such as acidified clay, alumina, silica, etc. They have high stability to thermal shocks, loading and physical impact, and have strong resistance to poisoning caused by carbon dioxide, nitrogen compounds, air and steam [4]. Zeolites are hydrated aluminosilicate minerals made from interlinked tetrahedral of alumina (AlO_4) and silica (SiO_4). Zeolite X and Y are known as faujasites and serve as catalysts in catalytic cracking [5]. The use of natural materials for the production of zeolite has economic advantage over conventional commercial chemicals [6]. Previously, only zeolites from natural sources were used, but presently tangible achievements have been made to synthesize them on industrial scale which have aided replication [7]. Kaolin is a well-placed material and is regarded as the next generation material because it is more abundant and environmentally friendly than precursors used in zeolite production, hence their application in the synthesis of zeolite has continued to receive tremendous research interest [8].

Several studies indicating development of faujasite type zeolite has been carried out. These works includes; that of Adeoje, J.B *et al.*, titled "Synthesis of Zeolite Y from Kaolin using Novel Dealumination Method". In the study Zeolite Y of silica/alumina molar ratio of 3.46was successfully synthesized and modified to its hydrogen form through the process of ion exchange with ammonium chloride (NH_4Cl) from local kaolin from Ado-odo Ota, Ogun State [9], The work of Atta, A. Y. *et al.*, titled "Synthesis of Faujasite Zeolites from Kankara Kaolin Clay", where X type faujasite zeolite was developed. The X-ray diffraction analysis revealed a composite crystalline phase consisting zeolite X (32-36%) and zeolite Y (21-25%), unnamed zeolite (<1%), quartz (2-5%) and anatase (2-5%). In addition an amorphous phase (>20%) was found in the synthesized zeolite. He attributed the formation of zeolite X and Y in the same reaction to lack of proper mixing, and the presence of high level of quartz (4%) and anatase (4%) are speculated to be as a result of lower number of days in which aging was done. Previous attempts to produce Y zeolite from Kankara resulted in D-type zeolite being formed predominantly, and this was attributed to presence of potassium ion in the clay, reagents and leaching of glass wares used which hindered successful synthesis of the targeted zeolite[10], and the work of Ajayi, A. O *et al.* on *Novel Method of Metakaolin Dealumination-Preliminary Investigation.* He indicated that the silica-alumina ratio using the novel method increased with increase in strength of sulfuric acid and was found to be good enough for the synthesis of faujasite type of zeolites. Although, the quantity of heat released by the heat of sulphonation was found to be sufficient to effect the dealumination reaction, it was not determined [11].

The current study employs an additional silica source, sodium metasilicate to develop Y-type faujasite zeolite rather than the process of dealumination, since much leaching of the alumina from the metakaolin precursor was not necessary. The work highlights the possible development of Y-type zeolite from Ukpor kaolinite from Anambra State, Nigeria to create a more sustainable supply of catalysts for fluid catalytic cracking, and to serve as substitute to their alternative synthesized from uneconomical commercial chemicals which serve as sources of silica and alumina [1].

MATERIALS AND METHODS

— Beneficiation of raw clay

The raw clay mined from Nnewi Local Government Area of Anambra State was beneficiated by deflocculation in order to purify it from physically and chemically combined impurities such as metallic oxide, soluble salts and grits. The raw clay was crushed and ground. 2.75*kg* of crushed clay sample weighing out and poured into a plastic bucket. Then 220*g* of sodium hydrogen carbonate and 880*g* of sodium hexametaphosphate were mixed and 11 liters of distilled water was added to the sample for deflocculation purposes. It was allowed to stand for 8hrs whence three distinct layers were observed namely the supernatant layer, fine and coarse layer after which the supernatant fluid was decanted and thoroughly washed with distilled water to remove excess deflocculant subsequently, the mixture was passed through a 70*μm* sieve to obtain the fine particles, and was allowed to settle and the water decanted before centrifugation. The centrifuge machine was operated at 1500 rpm (revolution per minute) for 10 minutes per run. After 10 minutes, the tubes were removed and the wet lumped clay was scooped out and was collected into a tray. The removed tray was dried overnight in an oven at 120^oC to liberate completely the physical water content and to obtain beneficiated clay (cake). The cake formed was crushed and milled to +70 *μm* particle size using a micro sieve.

— Calcination of refined clay

Calcination was done in a programmable electric furnace (Model no: BF51794C-1) from 25^oC to the calcination temperature (T_{cal}). The sample was held at T_{cal} (850^oC) for 6*hrs* [12]. Calcination was achieved by evenly placing beneficiated kaolin into crucibles to allow for a relative good heat distribution since the specific heat capacity and latent heat of the kaolin is poor. The metakaolin obtained was then cooled in a desiccator before characterization and usage.

— Gelation and synthesis of Y-type zeolite

Synthesis of zeolite Y was carried out according to the method reported by Kovo [13]. In the synthesis of zeolite Y from Ukpor kaolin, the use of external silica source was adopted. [14] The aluminosilicate gel used to synthesize zeolite Y was produced based on the following molar ratio:

$$15Na_2O: Al_2O_3: 15SiO_2: 450H_2O \qquad (1)$$

Sodium hydroxide pellets (97.9% w/w) and anhydrous sodium metasilcate which served as a source of additional silica source were used for gel formation. The Ukpor metakaolin served as a combined source of alumina and silica.

One hundred and fifty nine point nine two decimeter cube ($159.92dm^3$) of distilled water was measured and was divided into two equal parts in separate beakers. One point six five grams (1.65*g*) of sodium hydroxide pellets were measured and were added into the first half of the distilled water and the mixture was stirred until it dissolved completely. Four point four grams (4.4*g*) of Ukpor metakaolin was measured and was also dissolved in the first half of the distilled water. Thirty three grams (33*g*) of sodium metasilicate was measured and dissolved in the second half of the distilled water. After properly stirring and mixing of the two sets of precursors, they were then mixed together to form a homogeneous aluminosilicate gel. The gel was then aged at room temperature at varying ageing time of 12 hours with intermittent stirring. The aged gel was then crystallized using the oven at crystallization temperature and crystallization time of 100^oC and 9 hours respectively. Upon crystallization and/or hydrothermal treatment, the sample was retrieved from oven, allowed to cool and was washed using the distilled water until the pH of the sample was between 7 and 9. This was followed with drying of the sample at 70^oC using the oven for 5 hours.

The instrumental analysis of all the samples were carried out using modern equipment/analyzers to study the XRF, SEM and FTIR.

INSTRUMENTAL ANALYSIS

— X-ray fluorescence (XRF) analysis of samples

The XRF of the various samples were carried out using Energy Dispersive X-Ray Fluorescence (EDXRF) spectrometer analyzer of model "Minipal 4". The analyzer was set at the following conditions;

- Elemental composition determination.
- Nature of the samples to analyzed as press powder (pellet)
- The current used as 14*kv* for major oxides
- Selected filters were "kapton" for major oxides

The samples were pulverized (grind to fine powder) using arget pulverizing machine (planetary micro mill pulverisette 7). The ground samples were ensured to pass 150 micro mesh sieves. This was to ensure homogeneity of the samples.

5*g* of the pulverized sample was weighed into a beaker, 1*g* of binding aid (Starch soluble) added. The mixture was thoroughly mixed to ensure homogeneity, which was pressed under high pressure (6 "tone") to produced pellets; labeled and package ready for the analysis.

Time of measurement for each sample was 100 seconds and the medium used was air throughout. The machine was then celebrated by the machines gain control, after which the respective samples were measured by clicking the respective positions of the sample changer.

— Scanning Electron Microscopy (SEM) analysis of the samples

The SEM of the various samples were carried out using SEM analyzer. Samples were coated with an ultrathin coating of electrically conducting material (carbon), which was deposited on the sample by low-vacuum sputter coating. Samples were then mounted rigidly to the sample holder or stub using a conductive adhesive called double sided carbon tape.

The pump icon on the software machine was clicked and the pump attached to machine started automatically and draws out air completely from the Chambal.

The light showed green and the beam icon was clicked. The machine then scans the surface of the sample in the SEM analyzer at set magnifications of x150, x500 and x1000.

— FT-IR analysis of samples

The FT-IR of the various samples were carried out using FT-IR analyzer of model "Bulk scientific M530 FTIR USA". Analysis was done using 0.4g of KBr, weighed and ground to powder. 0.001g of the samples were weighed and poured into the ground KBr and both were thoroughly mixed together and moulded into a disc. The disc was inserted into the sample compartment of the analyzer. The scan button was pressed.

RESULTS AND DISCUSSION

— Elemental Analysis

Table 1 presents the elemental composition of raw Ukpor kaolin, beneficiated kaolin, calcined kaolin, and synthesized zeolite obtained using XRF.

Table 1: composition of raw Ukpor kaolin, beneficiated kaolin, calcined kaolin, and synthesized zeolite

Component	Weight %			
	Raw Kaolin	Beneficiated Kaolin	Calcined Kaolin	Synthesized Zeolite
SiO2	88.70	56.20	58.80	55.60
Al2O3	4.16	20.00	22.70	23.20
K2O	0.24	ND	ND	
Na2O	0.046	ND	ND	
CuO	0.033	0.047	0.019	0.026
Fe2O3	2.08	3.53	1.50	3.32
TiO2	3.63	3.76	2.54	3.32
BaO	0.15	0.10	ND	0.08
CaO	0.14	0.01	0.027	0.05
ZnO	0.002	0.013	0.005	0.003
MnO	0.021	ND	0.005	0.025
LOI	0.48	10.04	12.81	13.0

ND = Not Detected

The results indicate Ukpor kaolinite contained impurities of oxides of potassium, iron, titanium, magnesium etc. The results also indicate the effect of refinement using deflocculant on the raw kaolinite, as value of SiO_2 declined from 88.70% to 56.20% owing to expulsion of free silica (quartz) from raw kaolinite.

The Table also highlight that Ukpor kaolinite is ferric in nature owing to the high iron oxide (Fe_2O_3) content of (2.08) when compared with that of potassium K_2O (0.24). Similarly, the white colour of the raw and beneficiated Ukpor kaolin can be attributed to the significant content of TiO_2.

Pure raw kaolinite clay is expected to have silica/alumina ratio of between 1 to 2 [15]. Table 1 indicate that SiO_2/AlO_2 ratio of 21.32 and 2.81 for the raw and refined kaolinite respectively do not fall within the theoretical value, This shows that Ukpor clay contained so much mineral impurities. It is also observed that Ukpor clay has high silica content making it a good source from which silica can be produced and development of high silica zeolites.

The compositional analysis of the refined kaolininite clay indicates a reduction in the amount of its free silica, potassium and other impurities, were as there was record increase in both alumina and iron content. All of these follow a proportionate decline in the content of silica. It is expected that the refining of raw kaolin will help improve kaolinite content.

The XRF analysis indicated little or no difference in chemical composition of samples of both the beneficiated and metakaolinized Ukpor kaolin. The obvious variation is captured in the values of the loss on ignition (LOI) which had increase from 10.04% to 12.81% for beneficiated and metakaolinized samples respectively. This may be attributed to the combustion of impurities such as the iron content during calcination.

The compositional analysis of the final synthesized material indicates a silica to alumina molar ratio of 4.07, hence suggesting successful synthesis of Y-type zeolite. The silica to alumina ratio is between 2 and 3 for X-type zeolites, while it is 3 or higher for Y-type zeolites [16].

— Shape Analysis

≡ SEM analysis of Raw Clay

The platelet structure of kaolinite clay reported in the literature [17-19] which normally portrays pseudo-hexagonal platelet morphology could be clearly observed. Each of the images showed a pseudo-hexagonal morphology consisting of platelet sheets of kaolinite mineral as reported in the literature, the pseudo-hexagonal morphology became clearer as the magnification increased.

≡ SEM analysis of calcined Ukpor clay

From Figure 2, it can be observed that the pseudo-hexagonal platelet morphology that was earlier obvious in the SEM image of the raw and beneficiated kaolin samples has been lost. Even though the metakaolin SEM image still possessed some relatively low platelet morphology, the morphology of the metakaolin was lump-like.

The lump-like morphology could be attributed to the highly amorphous nature of the material as a result of the crumbling of the kaolinite structure. The relatively low platelet morphology observed in the material could be as a result of the crystalline silica contained in the clay even after the metakaolinization.

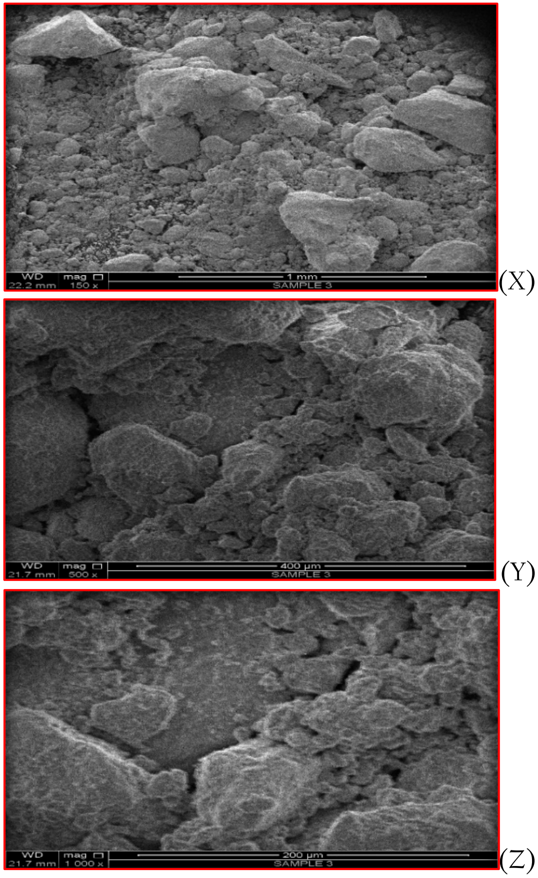

Figure 1: SEM Analysis of Beneficiation Kaolin with magnification of 150x(X), 500x(Y), 1000x (Z)

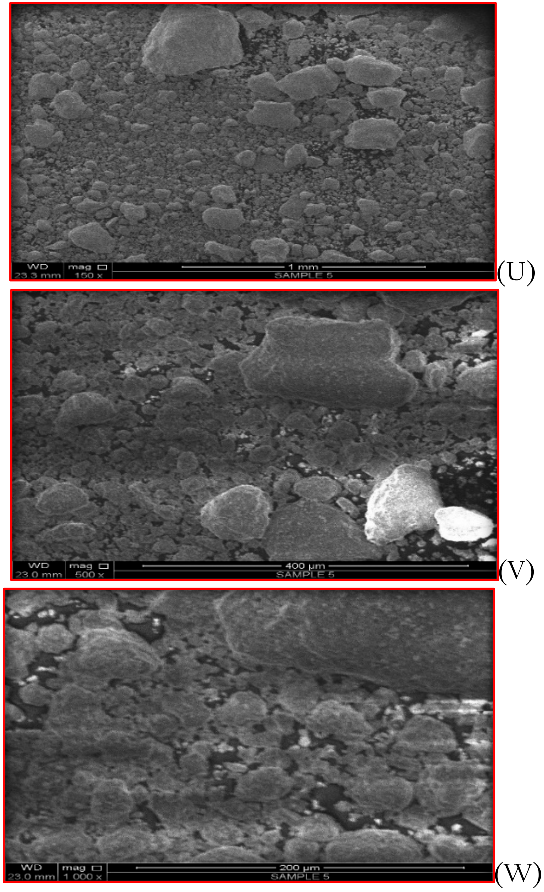

Figure 2: SEM Analysis of Metakaolin with magnification of 150x (U), 500x (V), 1000x (W)

≡ SEM analysis of attributed synthesized zeolite Y

Figure 3 Shows the SEM micrograph scanned at various magnifications. The SEM micrograph scan of Zeolite Y shows images at magnification of 150 (I), 500 (J) and 1000(K). Irrespective of the various magnification, the zeolite Y particles appeared densely agglomerated. At the high magnification, the micrograph appeared densely agglomerated revealing the definite shape of the particles, although the micrograph was not clear enough to show the actual shape clearly. It could be obtained from the images therefore that the Zeolite Y has an agglomerated euhedral morphology. This is similar to that reported by Salahudeen N. in his work "Development of Zeolite Y and ZSM5 composite catalyst from Kankara kaolin".

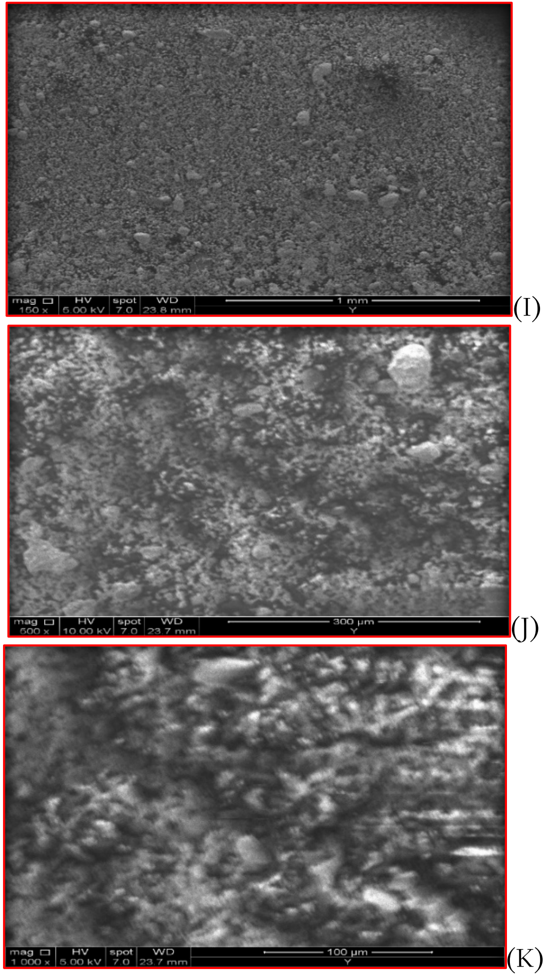

Figure 3. SEM Analysis of Zeolite Y with magnification of 150x (I), 500x (J), 1000x (K)

— Absorbance Analysis

≡ FTIR analysis of raw and calcined Ukpor clay

Figure 4 shows FTIR spectra of raw Ukpor kaolin (A) and calcined kaolin (B).For a kaolinite clay mineral, the –OH hydroxyl group is identified at wave number (cm^{-1}) of either 3696, 3671 or 3650 [21]. Therefor the peak at 3696.034818 cm^{-1} for Fig. 4 (A) shows the presence of an –OH group. Also in Fig. 4.4(A), the peak at 2729.8723 cm^{-1} shows the presence of an –OH cabonyl group confirmed by the peak which it overlaps at 2987.863 cm^{-1} representing a C-H single bond. The peak at 3530.21736 cm^{-1} in Fig. 4 (A) signifies an alcohol –OH which is confirmed by the peak at 1054.27961 cm^{-1}

signifying a C-O single bond. In Fig. 4 (B) due to metakaolinization which involves removal of hydrogen and framework oxygen, the FTIR spectra reveals dissapearance of the various –OH peaks indentifed in the raw clay.

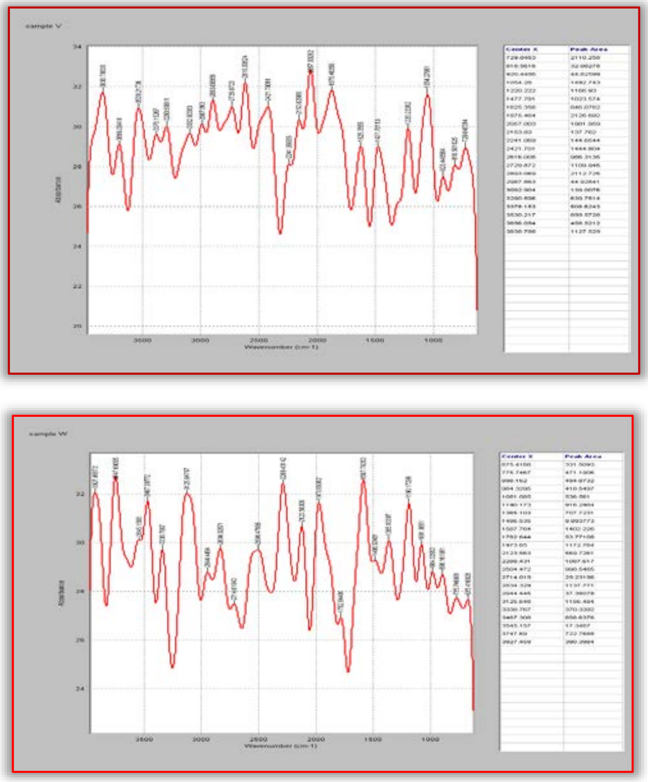

Figure 4: FTIR spectra of raw (A) and calcined Ukpor clay (B)

≡ FTIR result for attributed synthesized Y-type zeolite

Figure 5 shows FTIR spectra of attributed synthesized Y-type zeolite. Prior studies reported that the characteristic FTIR bands for zeolitic lattice are in the wavelength range of 460–1200 cm^{-1} [22] and the bands in these range of wavelength indicate the crystallinity of the material [23]. Particularly the characteristic FTIR bands for zeolite Y are located around 1025, 790 and 715 cm^{-1} [24].

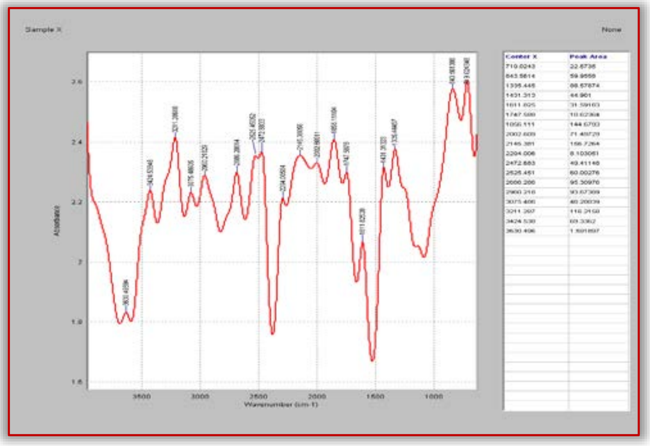

Figure 5: FTIR Spectra of Attributed Synthesized Zeolite Y

The vibrational bands at 760–710 cm^{-1} correspond to the vibration of Al-O fragment. The band at 719.024348 cm^{-1} was attributed to Si–O–Al in-plane bending. The band at 3500 - 3200 cm^{-1} was attributed to O-H bond stretching vibration [20]. These observations confirm the possible formation of zeolite Y.

CONCLUSION

The authors concludes that the various analysis; XRF, SEM and FTIR conducted in the study affirms successful synthesis of Y-type zeolite. Hence, Y-type zeolite was successfully synthesized from kaolinite deposit located in Ukpor in Anambra State. The synthesis involved beneficiation by deffloculantion, calcinations at 850^0C, ageing for 12 hours, crystallization at temperature of 100^0C for 9 hours and drying for 9 hours. This will go a long way to ensure an economical and sustainable supply of Y-type zeolites in addition to those synthesized from different kaolin deposits in Nigeria. In the current study XRD analysis is recommended to ascertain the purity of the synthesized y-type zeolite. Also, each process should be subjected to varying conditions to obtain optimum process parameters.

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