

## **Synthesis and characterisation of zeolite a for adsorption refrigeration application**

**\*N. O. Omisanya<sup>1</sup>, C. O. Folayan<sup>2</sup>, S. Y. Aku<sup>2</sup> and S. S. Adefila<sup>3</sup>**

<sup>1</sup>*Centre for Automotive Design and Development ABU, Zaria, Nigeria*

<sup>2</sup>*Mechanical Engineering Department, ABU, Zaria, Nigeria*

<sup>3</sup>*Chemical Engineering Department, ABU, Zaria, Nigeria*

---

### **ABSTRACT**

*The use of Kankara (Nigeria) kaolin as an alternative cheap raw material for the synthesis of Zeolite 4A for solar adsorption refrigeration application in developing countries especially Africa, using microwave oven was carried out by hydrothermal treatment of metakaolin with aqueous alkali Sodium hydroxide (NaOH). The study highlighted the preparation of Zeolite from metakaolin of quality Kankara kaolin and their characterization by XRF, XRD and FTIR spectrometer. The morphology was examined using SEM. Thermal analysis was followed by performing a TGA/DTA. Similar analysis was performed on the commercial Zeolite 4A sample thus confirming the production of Zeolite A with relative percentage of quartz.*

**Keywords;** Zeolite A, Refrigeration, adsorption, XRF, XRD, FTIR, SEM, TGA/DTA.

---

### **INTRODUCTION**

Alumina  $Al_2O_3$  and silica  $SiO_2$  are two most abundant minerals of the earth crust. Zeolite materials are micro porous aluminosilicate with crystalline structure within which there are large number of small cavities which are interconnected. These cavities and channels are precisely uniform in size. The material is known as molecular sieve since the dimension of the pore is to accept for adsorption molecules of certain dimension while rejecting those of larger dimension. Clay minerals have been used as a combined source for  $Al_2O_3$  and  $SiO_2$  for the synthesis of Zeolite [4]. However the production of Zeolite from cheap raw material is of economic importance. Kaolinite is a clay mineral of chemical formula  $Al_2O_3 \cdot 2SiO_2 \cdot 2H_2O$  with a 1:1 uncharged dioctahedral layer structure where each layer consist of single silica tetrahedral sheet and single alumina octahedral sheet. It is conveniently used as a starting material for Zeolite A synthesis since its Si/Al ratio is near unity. Zeolite A is one of the synthetic molecular sieves that have various applications such as adsorption, separation, ion-exchange etc. Zeolite A with a pore opening of about 5A and high sorptive and ion exchange capacities, [4]. It is widely employed as molecular sieve and adsorbent of refrigerants, purification and water softening. Usually, Zeolites are synthesized under hydrothermal condition in a period ranging from hours to few days depending on the nature of Zeolite mixture and temperature of synthesis [12]. Zeolites are conveniently syntheses from sodium aluminosilicate gel prepared from pure chemical in air oven or autoclave. The synthesis involves the treatment of the clay with sodium hydroxide solution in an autoclave at elevated temperature. This conventional way of synthesis of Zeolite required very high temperature to reduce the reaction time. Thus a decrease in processing temperature is desirable for energy savings and low production cost. The aim of this investigation was the production of Zeolite A from Kankara kaolin under the microwave conditions and the characterization of the starting materials (kaolin, metakaolin) and the product (Zeolite) to serve as adsorbent in a Solar CPC Refrigerator. Towards ascertaining its production the synthesized sample were characterized by X-ray diffraction (XRD), Scanning electron microscopy (SEM), X-ray Fluorescence (XRF), and Fourier Transformation Infrared (FTIR) spectroscopy and Thermal gravimeter analysis/ Differential thermal analysis

(TGA/DTA). In particular Zeolite 4A has high adsorptive capacity [11] for water which is the envisage refrigerant. The pore size is 4A and the surface area is  $22\text{m}^2/\text{g}$ , [5].

## MATERIALS AND METHODS

### 2.1 Material

White kaolinite clay used in the course of the synthesis was procured from Kankara village in Katsina state. The material was beneficiated as prescribed by [2 & 1] to remove impurities as stated below. Used in the synthesis was the analytical grade sodium hydroxide NaOH product of KEM light laboratories PVT Ltd.

### 2.2 Production Procedure;

#### 2.2.1 Beneficiation of Kankara Kaolin Clay

In achieving the objective, 4kg of clay was measured and soaked with 10litres of water. The mixture was allowed to age for four days with constant stirring. At each stage of sedimentation the water on top was decanted and replaced with fresh one. On the fourth day, 60 and 250micromesh sieve were each used to sieve the mixture and obtain fine particles of kaolin clay. After sieving, the mixture was allowed to settle (the silica being denser than the alumina settled at the base of the container) and the water was decanted. Then the kaolin clay on top was removed and centrifuged to remove the remaining water. After centrifuging the kaolin clay was sun/air dried (while spreading it on a polythene material in form of a small size lump) for 2days. After drying, the lumped kaolin clay was milled and later the sample was sieved using 75microns sieve followed by calcinations. The beneficiation was to remove most of the impurities (quartz, pebbles, plants remain and grits) from the clay.

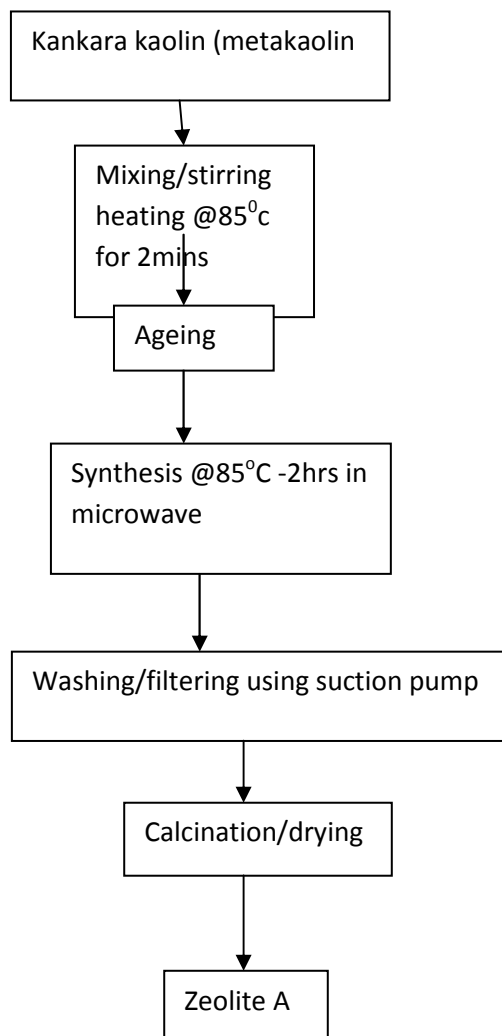


Figure 1; Zeolite A synthesis from Kankara kaolin process flow diagram.

### 2.2.2 Calcination

The beneficiated kaolin clay was converted to metakaolin by thermal treatment in Electric furnace (Nabertherm, GMBH) at a temperature of 700°C for 2hours using ceramic crucible as container. The essence is to dehydroxylate the beneficiated kaolin to form an activated X-ray amorphous material called metakaolin. The calcined clay was later measured into 4g sizes using electronic weighing machine and parking it into polythene bag to ensure air proof in preparation for synthesis. De-ionised water was used as water in the synthesis process. De-ionised water was produced by connecting de-ionising machine hose to water tap and turning it on, while the other hose end was dropped into a container for the collection of the de-ionised water. The de-ionised water collected was then used for the synthesis in a measured quantity.

### 2.2.3 Production of Zeolite A

A MD-6 microwave reactor made in China with thermocouple and programmer for accurate setting and measurement of temperature and pressure was used for the gel synthesis. The gel (Sodium aluminosilicate) was prepared with the molar ratio  $\text{SiO}_2/\text{Al}_2\text{O}_3 = 2$ ,  $\text{Na}_2\text{O}/\text{SiO}_2 = 2.5$ , and  $\text{H}_2\text{O}/\text{Na}_2\text{O} = 40$  by mixing calculated amounts of metakaolin with sodium hydroxide solution. The NaOH (Analytical grade) was dissolved in de-ionised water and metakaolin was slowly added to the alkali and a thorough mixing was done using electrically powered stirrer to achieve uniformity. A series of experiment was performed by varying the alkalinity of the gel (Table 1). The reactant mixture was transferred into 90ml Teflon vessel. The gel was initially exposed to heating at a temperature of 85°C, 1 atmosphere for 2mins in the microwave and later 20hours ageing at room temperature, [6]. The reaction time for the synthesis was 2hours at a temperature of 85°C, 1 Atmosphere in the microwave oven. Ordinary metalkaolin mixed with de-ionised water served as control experiment. The microwave heating was carried out at a frequency of 2450MHz and maximum power of 1200Watt. At each time, the microwave vessel was 50% filled with sample as precaution. After each reaction, samples were immediately filtered using suction pump, washed with de-ionised alkaline water (pH 9-10) and dried in an oven at a temperature of 80°C for 1hr. Zeolite A production process flow chart is presented in Figure 1 above. The experiment was designed as tabulated below in Table 1.

**Table 1; Experiment Reactant quantities**

Samples	A	B	C	D	E
$\text{Na}_2\text{O}/\text{SiO}_2$ (Moles)	1.5	2.0	2.5	3.0	3.5
NaOH Weight (g)	4.063	5.417	6.77	8.106	9.4808
Volume of de-ionised water( $\text{cm}^3$ )	60.74	60.74	60.74	60.74	60.74

### 2.2.4 Experimental Setup: Based on 4g of metakaolin sample

The tabulated data was calculated on the bases of 4g of metakaolin sample. The Microwave flask volume ( $90\text{cm}^3$ ) was used in determining the size of the sample experiment. For effective synthesis, sample volume of  $60\text{cm}^3$  was chosen. This is to ensure appreciable air space above the reactant during synthesis. Equally loss of reactant material was prevented by using Nylon to cover the flask vessel before corking it, thus ensuring a closed system synthesis. Pictures of the produced sample and that of the commercial sample (pelletised Zeolite 4A) are presented in Figure 3 & 4 respectively.



**Figure 2; Microwave oven with flask**

**Figure 3; Produced sample****Figure. 4; Commercial Sample (Pelletised Zeolite 4A)**

As a reference and for comparison purpose commercial pelletized sample was acquired from Grace Davison, USA (SYLOBEAD 513 Molecular sieve). The pore opening is of diameter 4Å, sphere size is a nominal 1/8" diameter, bulk density 44lb./ft<sup>3</sup>, H<sub>2</sub>O Adsorption capacity 23.5wt%. The need for pelletized sample and commercial quantity lead to the procurement of the sample for the purpose of the experiment. Especially that a good binder is required to produce the sample in pellet. The equipment used can only synthesis 4g sample each in each of the five flasks (90ml Teflon vessels) per synthesis. The time spent in synthesizing starting from the metakaolin per set of synthesis is 28hours. From a set of synthesis each flask sample yields average to 2.5g.

### 3.0 CHARACTERISATION

The basic analytical techniques employed in this research work are X-ray fluorescence (XRF) and X-ray diffraction (XRD) coupled with FTIR, SEM, and DTA/TGA due to equipment limitation in with [8, 10].

1 X-Ray Fluorescence (ED-XRF): This is for analyzing the elemental composition of the starting, intermediate and the final product. X-ray fluorescence (XRF) is the emission of characteristic 'secondary' (or fluorescence) X-rays from a material that has been excited while bombarding with high energy X-rays or gamma rays. The method employed in this research is the energy-dispersive analysis (ED-XRF) and the machine model used is the XGT 5000 located at National Metallurgical Development Centre (NMDC), Jos.

2 X-Ray Diffraction (XRD): This gives the crystallographic structural status and phases of the entire component in a material. X-ray Powder diffraction (XRD) is an efficient analytical technique used to identify and characterize unknown crystalline material. Phase characterization of the synthesis Kankara clay mineral was carried out at National Steel Raw Materials Exploration Agency, (NSRMEA) Malali Kaduna with X-ray diffraction (XRD) using Schmalz model XRD 6000 automated with Ni-Filtered Cu K $\alpha$  radiation operating at 40.0(kV) and 30.0(mA) with a graphite monochromator ( $\lambda=1.5418$ )

3 Fourier Transform Infra red Spectra (FTIR): The infrared spectra deal with complex organic molecules [3, 9]. Information about the nature of a compound can be extracted not only from the frequencies that are present but also by peak shape and intensity. The FTIR machine employed in this research is that of National Research Institute for Chemical Technology, (NARICT) Zaria.

4 Scanning Electronic Micrograph (SEM): This gives the pictorial description of the material and sometime the particle size distribution. A scanning electron microscope (SEM) is used to study the surface of solids and give information about their morphology and topological presentations. Such presentations may provide possible explanations about the solid's behavior. The SEM analysis was carried out at PANanalytical South Africa.

5 Differential Thermal Analyses/ Thermogravimetrics Analysis (DTA/TGA): The thermal analysis is used to determine the phase diagram, heat change measurement and desorption in various atmosphere. It provides mass loss and thermal information. The thermal analysis (DTA/TGA) was carried out at PAN analytical South Africa.

## RESULTS AND DISCUSSION

### 1 XRF Result

The elemental analysis of the Kankara clay is presented in Table 2. The analysis was conducted using energy dispersion X-ray fluorescence ED-XRF. Table 2 shows the elemental analysis for Raw, Calcine and beneficiated sample. The Kankara kaolin contains SiO<sub>2</sub>, Al<sub>2</sub>O<sub>3</sub> and some oxides of Fe, Mg, Ca, P, Ti etc. The main constituents are silica and alumina as shown in Table 4.2.

**Table 2; Chemical ED-XRF elemental analyses (in wt %)**

Sample	WBK	WKC	WKR
Al <sub>2</sub> O <sub>3</sub>	37.80	38.65	36.06
SiO <sub>2</sub>	50.86	50.79	51.10
K <sub>2</sub> O	4.06	4.40	6.40
CaO	0.55	0.49	0.20
TiO <sub>2</sub>	0.05	0.07	0.04
MnO	0.07	0.07	0.14
Fe <sub>2</sub> O <sub>3</sub>	1.08	1.10	0.72
NiO	0.01	0.01	0.01
CuO	0.06	0.05	0.03
ZnO	0.03	0.03	0.01
Na <sub>2</sub> O	0.07	0.11	0.08
MgO	0.96	1.02	0.94

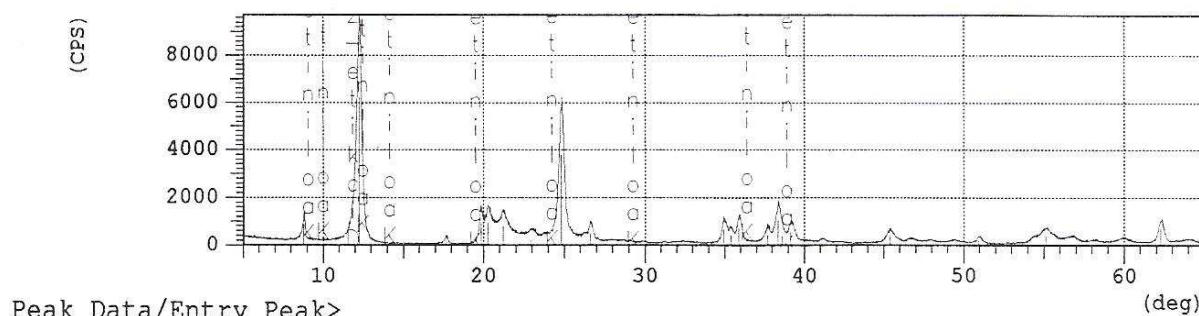
Note – Loss on ignition was not determined

Wt% - weight in percentage

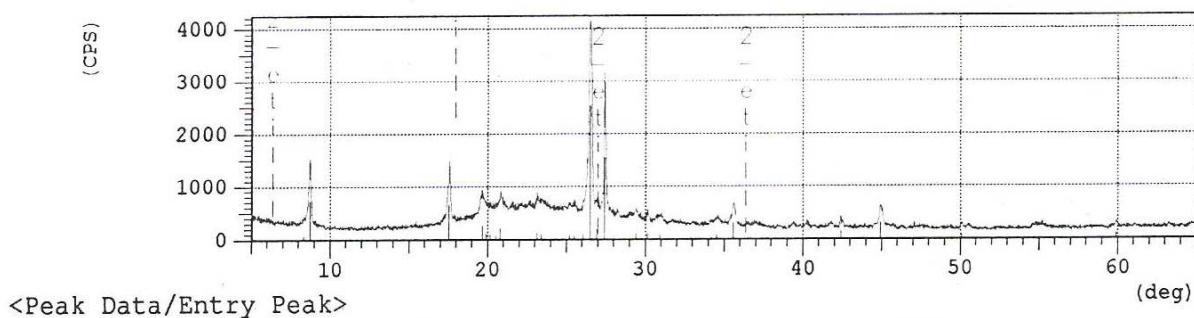
WBK – Beneficiated white

WKC – Calcined white (metakaolin)

WKR – Raw white

**Figure 5; Powder XRD diffraction pattern of Kankara Kaolin clay**

<Raw Data>

**Figure 6; XRD Pattern of the Calcined sample (Metakaolin)**

#### 2XRD results

The XRD pattern of the Kankara kaolin clay (beneficiated) is presented in Figure 5. Various crystalline peaks present in the sample were identified with the aid of collections of simulated XRD power pattern for Zeolite by [14]. In the course of matching the samples, the first five 2-Theta peaks in the diffractogram correspond to peaks pattern of kaolin as presented in the XRD pattern from Literature [5] showing all the characteristic peaks of kaolinite. However, the XRD pattern of the beneficiated clay shows the presence of some quartz peaks. The crystallinity of the kaolin was obvious in the pattern. The quartz which is on the 2-Theta peak 26° is very small relative to the Kaolin peaks. On Calcinations, these peaks disappear leaving a featureless band of X-ray amorphous metakaolin as shown in Figure 6. Metakaolin has a pattern with a broad hump having maximum at 2-theta ≈ 22°.

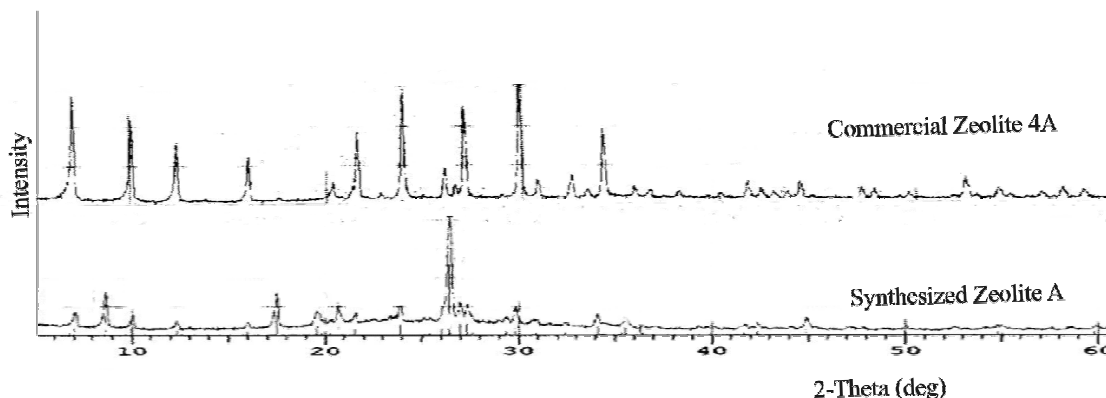
The diffractogram of synthesised samples with 1.5M, 2.0M, 2.5M, 3.0M and 3.5M NaOH alkalinity revealed different peak intensity/count. Peaks in the diffractograms confirmed the presence of Zeolite A, Sodalite and Quartz [14]. In contrast the metakaolin sample treated with 1.0 and 2.0M NaOH and heated under the same previously mentioned condition show no Zeolite A peaks. This implies the importance of alkalinity as the main contributory factor for Zeolite A crystallization. The synthesised samples with 2.5M, 3.0M and 3.5M NaOH alkalinity showed relative presences of Zeolite A peaks with that of 2.5M NaOH exhibiting the most peaks where the first five peaks are



distinct. The prominent peaks of Zeolite A, 2-theta values with their corresponding relative intensity are tabulated in Table 3. The commercial Zeolite 4A diffractogram were cascaded with the synthesized 2.5M NaOH sample as shown in Figure 7. The cascaded diffractogram further revealed the presence of Zeolite A peaks with relatively low intensity.

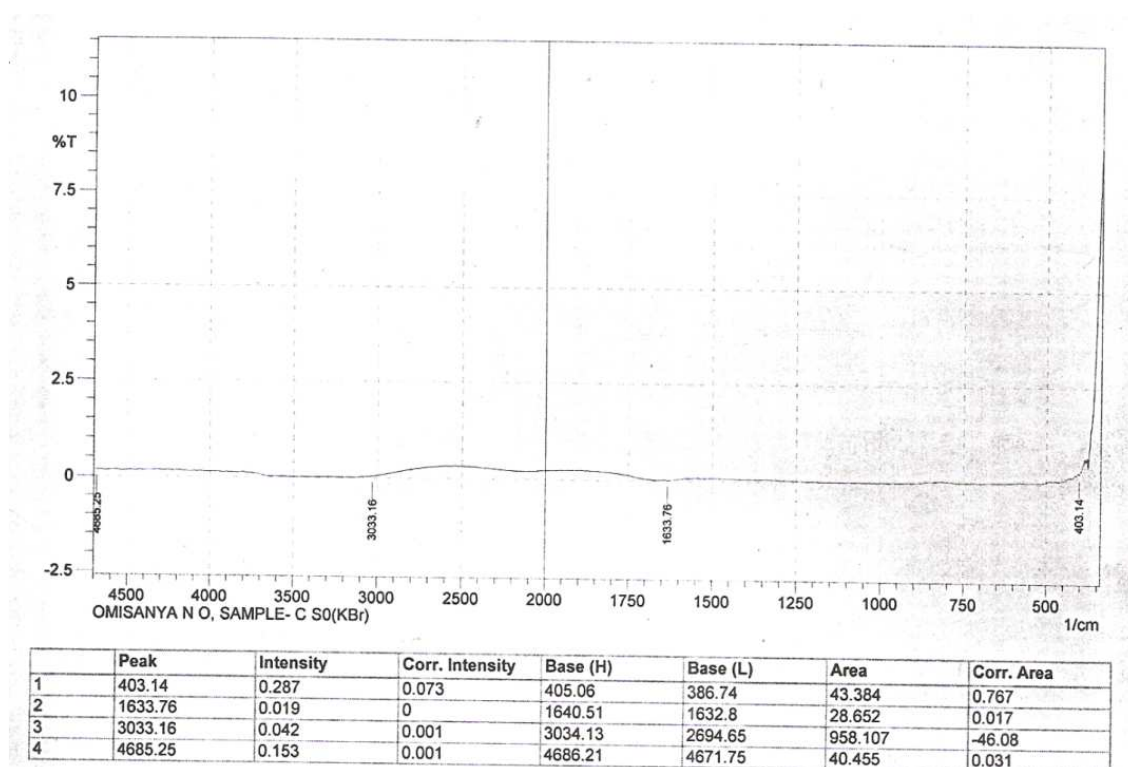
**Table 3; Major 2-Theta peaks in the Zeolite A XRD Diffractogram**

Peaks	2-Theta(deg)	Intensity (counts)
1	7.20	195
2	10.19	158
3	12.49	104
4	16.14	81
5	24.04	223



**Figure 7; XRD Pattern of Synthesized Zeolite A and Commercial Zeolite 4A**

The XRD analyses support the fact that when reaction mixture is subjected to a Microwave exposure for 2mins, ageing for 20hours and heating at 85°C for 2hours Zeolite A of maximum crystallinity is formed.



**Figure 8; FT-IR result of the commercial sample**

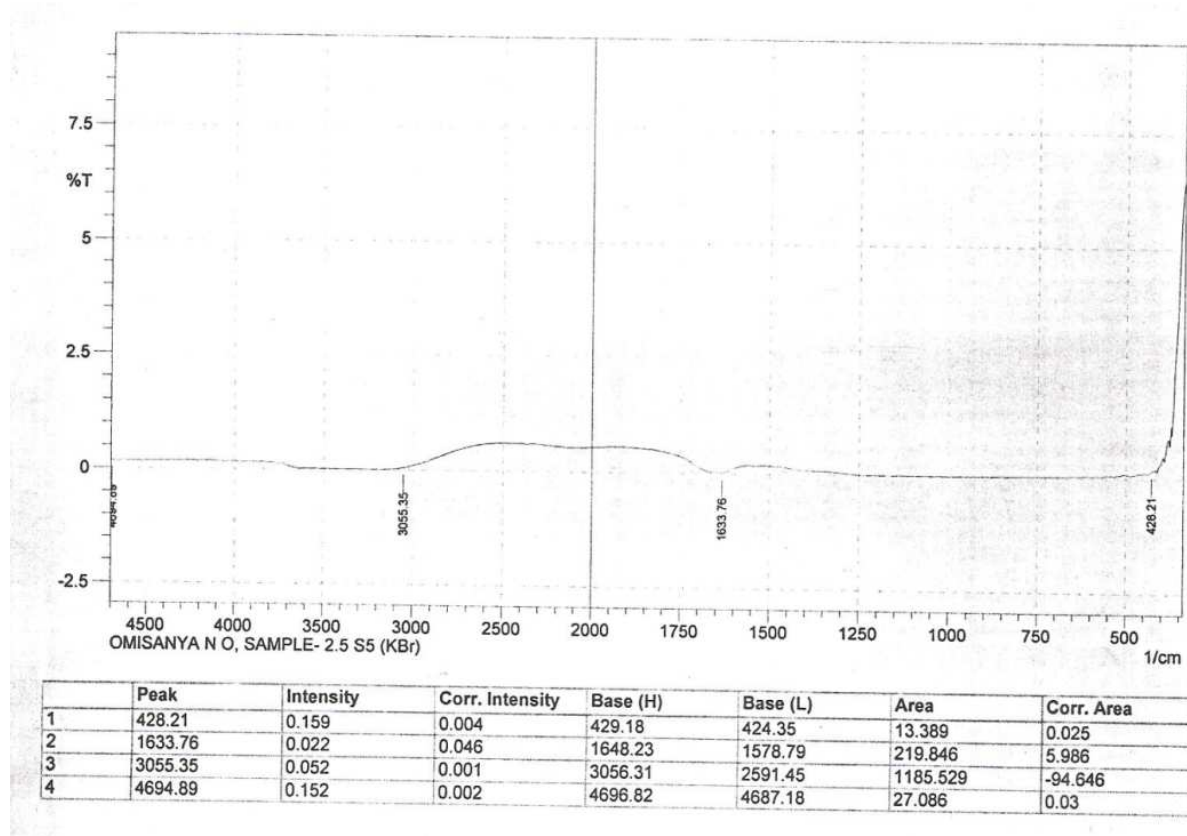


Figure 9; FT-IR result of the synthesis sample

### 3 FTIR results

The FTIR spectra of the 2.5M synthesis sample formed are presented in Figure 9. That of the commercial Zeolite 4A was also presented in Figure 8. The typical bands of Zeolite A representing the asymmetrical and symmetrical stretch are observed in the sample Figure 8 and 9. The FTIR spectra analyses is found to substantiate the XRD results. The position, height and width of each of the peaks are nearly identical. The peaks at  $403.14\text{cm}^{-1}$  is assigned to the structure insensitive internal ( $\text{TO}_4$ ) tetrahedral bending peaks of zeolite A in literature. Peaks  $1633.75\text{cm}^{-1}$  and  $3033.16\text{cm}^{-1}$  are assigned to the external linkage asymmetrical stretching and internal tetrahedral symmetrical stretching respectively. The peaks  $4685.25\text{cm}^{-1}$  is assigned to the external linkage asymmetrical stretching.

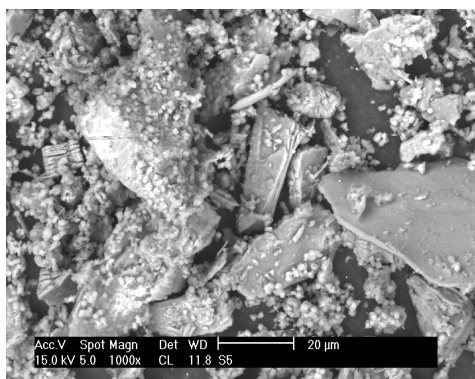


Figure 10; SEM of Synthesis Zeolite

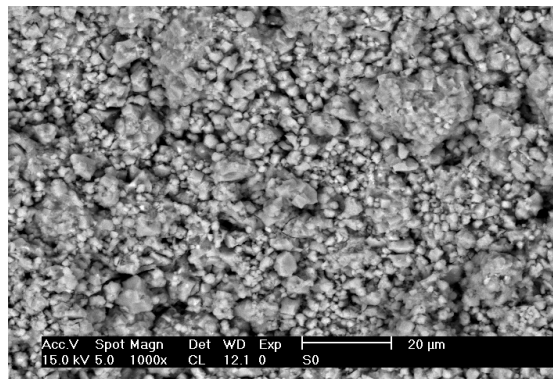


Figure 11; SEM of commercial sample

### 4 SEM results

The morphology of commercial sample and 2.5M NaOH synthesis product as examined under an electronic microscope. The micrograph are presented in Figure 10 and Figure 11 respectively. In comparison, the sample revealed the presence of some cubic crystal of zeolite A along with the gel are observed in the sample. The micrograph indicated a plate like structure for the kaolinite clay which is an indication that the silica and alumina are sliding over one another. Some partial destruction of the plate like structure were observed in the synthesised and commercial sample. The SEM image revealed a uniform particule size of the sample with a regular shape. The

commercial and synthesis SEM results give a narrow distribution of particle size with average crystal size of  $<20\mu\text{m}$ .

### 5 TGA/DTA results

The charts Figure 12 and Figure 13 below represent the corresponding sample TGA/DTA (commercial and the 2.5M NaOH synthesis respectively) thermal analysis. The curve in color red stands for the TGA while the one in colour Blue stand for DTA. With the application of heat sample desorption commenced at temperature  $25^{\circ}\text{C}$  to  $200^{\circ}\text{C}$  continuously for the commercial sample as shown in Figure 12 & 13.

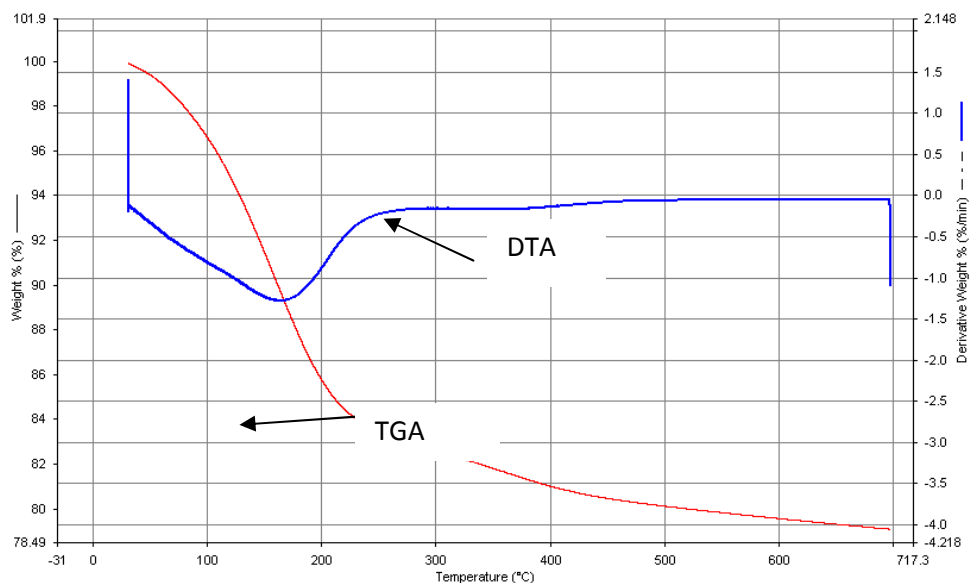


Figure 12; Commercial Sample TGA/DTA @ $10^{\circ}\text{C}/\text{mins}$  to  $700^{\circ}\text{C}$

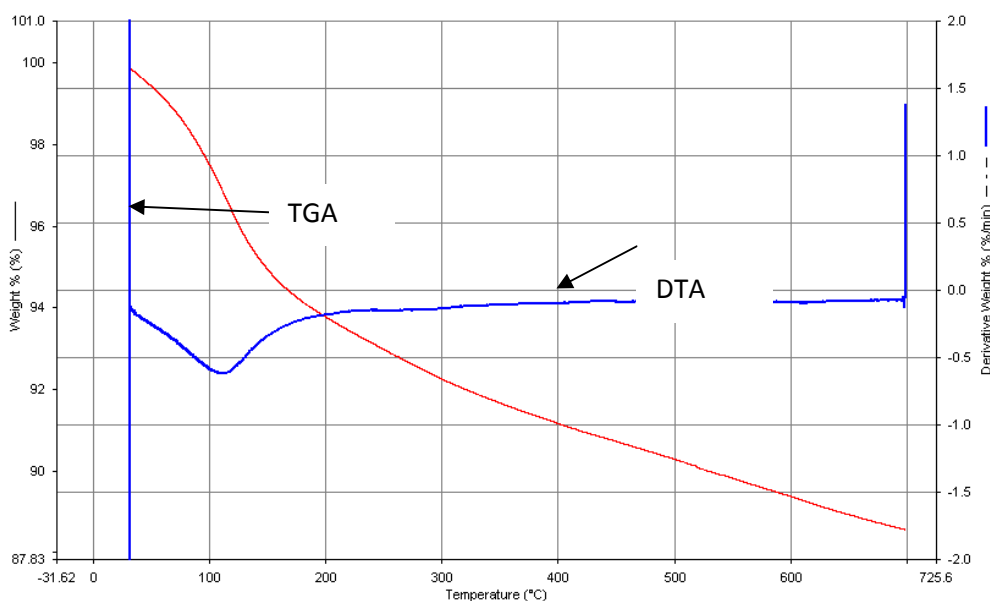


Figure 13; Synthesis sample TGA/DTA @ $10^{\circ}\text{C}/\text{mins}$  to  $700^{\circ}\text{C}$

In the case of the Synthesis sample, with the application of heat desorption started at about  $30^{\circ}\text{C}$  and increase continuously to about  $150^{\circ}\text{C}$ .

### CONCLUSION

These studies highlighted the literatures on Zeolite synthesis, production processes starting from Kankara kaolin, Calcination, synthesis and characterization. Results of analyses were also presented with proper interpretation given. Zeolite A formation was found to depend on the alkalinity of the reactants. The crystallinity of NaX zeolite sample with 2.5M NaOH obtained gives the most peaks compared with other sample based on result from XRD and FTIR.



A pure phase of Zeolite A with high crystallinity has been synthesis using microwave and comparison has been made with commercial sample. The reduced crystallization time was achieved with the use of microwave as compared to the conventional method (Autoclave). Some percentage of quartz was noticed but further work is on to completely reduce the presence of quartz in the product. Towards ascertaining its production the synthesized sample were characterized by X-ray diffraction (XRD), Scanning electron microscopy (SEM), X-ray Fluorescence (XRF), and Fourier Transformation Infrared(FTIR) spectroscopy and Thermal gravimeter analysis/ Differential thermal analysis (TGA/DTA).

#### **Acknowledgement**

The authors are grateful to the Petroleum Technology Development Fund (PTDF) Chair in Chemical Engineering, Ahmadu Bello University, Zaria, for using their facilities in the course of the research work. Assistance rendered by these individuals; Aigbodion V. S, Ajayi A. O, Iliyasu J. are highly appreciated. The authors are also grateful to NMDC Jos, NSRMEA Kaduna and Pan-analytical South Africa for analyzing the samples in this research work.

#### **REFERENCES**

- [1] Aderemi B. O., *Nigerian Journal of Engineering ABU Zaria, Nigeria*. **2003**, 11: 2-3
- [2] Ahmed, *Properties of Kaolin and method of Beneficiation*, Proceedings of PTDF on zeolite Development in Nigeria workshop **2008**, 1:1-17
- [3] Arup Dutta and A Sarker, *Adv. Appl. Sci. Res.*, **2011**, **2(1):125-128**
- [4] Barren R M, *Hydrothermal Chemistry of Zeolite* Academia Press, London, **1978**
- [5] Breck D. W, *Zeolite Molecular Sieve structure and use*, John Wiley and son U. S Pat. **1974**, 3, 130, 007.
- [6] Chandrasekhar S and P. N. Pramada, *Elsevier Science Direct Microporous and Mesoporous Material* **2008**, 108: 152-161.
- [7] Chandrasekhar S, *Clay mineral* **1996** 31: 253-261
- [8] Hemant Mittal, Balbir Singh Kaith and Rajeev Jindal, *Adv. Appl. Sci. Res.*, **2010**,**1(3): 56-66**.
- [9] Prabu K and Natarajan E, *Adv. Appl. Sci. Res.*, **2012**, 3(3):1870-1875.
- [10] Ramaswamy V, Vimalathithan R. M. and Ponnusamy V, *Adv. Appl. Sci. Res.*, **2010**,**1(3):197-204**
- [11] Sayyed Hussain, Sayyed Abed and Mazahar Farouqui, *Adv. Appl. Sci. Res.*, **2010**, **1(3):147-152**.
- [12] S. Sang, Z. Liu, P. Tian, Z. Liu, L. Qu, Y. Zhang, *Mater. Lett.* **2006**, 60: 11
- [13] Slangen P. M, Jansen J.C, H. Van Beckkum, *Microporous material* **1997**, 9:259 -265.
- [14] Treacy M. M. J, and Higgins J. B, **2007** Collections of simulated XRD powered patterns for zeolites. *Commission of the international zeolite Association*. Linde Type A dehydrated pp 250-251.