Synthesis and Characterization of NaA Zeolite Using Natural Kaolinite Clays from Nigeria by Low Temperature Hydrothermal Method

Ifedayo Joshua Akinruli[1], Seun Samuel Owoeye[2], Segun Michael Abegunde[3*], Ayodeji E. Onipede[4], Ukoba Kingsley[5]

[1,2]*Department of Glass and Ceramics, Federal Polytechnic, Ado-Ekiti, Nigeria*
[3,4]*Department of Science Technology, Federal Polytechnic, Ado-Ekiti, Nigeria*
[5]*University of Kwazulu Natal, Durban, South Africa*

Abstract: **Zeolites NaA is one of the most valuable synthetic zeolites widely used as ion-exchange material, catalysts, and adsorbents in industry. There is therefore need to adopt a more energy-efficient route for its synthesis from low-cost and sustainable raw materials. In this present work, zeolites Na-A was synthesized from natural kaolinite clays obtained from three selected regions (Ikere, Okpella and Kankara) in Nigeria. The as-received kaolinite clays (IK$_{clay}$, OK$_{clay}$ and KA$_{clay}$) were initially beneficiated thoroughly to obtain pure powders (<75 µm). The processed kaolinite clay powders were then subjected to heating in a muffle furnace at 850ºC for 3 h at a heating rate of 10ºC/min to convert the kaolinite clays to their respective metakaolins. The obtained metakaolins were then reacted with NaOH solutions at varying concentrations of 3.0 and 4.0M respectively using a low temperature hydrothermal transformation to obtained Zeolites Na-A powders. The obtained zeolites were then analyzed by scanning electron microscopy (FESEM), energy dispersive spectroscopy (EDS) and Fourier-transform infrared spectroscopy (FT-IR). The results showed that zeolite NaA is produced with mixture of hydroxysodalite (HS) while the EDS revealed the presence of Si, Al, O and Na indicating chemical constituents of typical zeolite NaA. All the tested kaolinite clays are therefore suitable for preparation of zeolite NaA as cheaper source of silica and aluminum.**

Keywords: **Na-A zeolites, kaolinite clays, hydroxysodalite, hydrothermal transformation.**

1. Introduction

Zeolites are one of a large group of microporous, crystalline and hydrous aluminosilicates of alkali and alkaline earth metals with a unique 3D structural framework comprising of $[SiO_4]^{4-}$ and $[AlO_4]^{5-}$ tetrahedral units connected through shared oxygen [1], [2]. Zeolites find relevance in several industrial applications such as catalytic cracking of petroleum, treatment of wastewaters, ion exchangers, drying of gases and liquids, purification of industrial effluents and emissions etc. thereby making its synthesis in forms suitable for industrial applications of great relevance [1]–[4]. At present, there are about 50 identified naturally occurring zeolites and more than 150 known synthetic zeolites [5], [6]. In previous times, only natural zeolites were used, but more recently synthetic zeolites are often preferred commercially due to the purity of crystalline products and particle sizes uniformity thereby resulting to tailor-made zeolites which are extremely replicable [2], [7]. Out of these lots, Zeolite NaA finds a major industrial prominence due to its excellent molecular sieving, ion exchange and adsorption attributes [1]. The preparation of synthetic zeolites using chemically pure sources of silica and alumina as starting materials is known to be quite expensive; as a result, cheaper sources of silica and alumina such as clay minerals, industrial slag, incineration ashes, municipal solid wastes etc. are being continuously investigated as starting materials with promising results [8], [9]. The crucial factors influencing the synthesis of zeolite-type are the Si/Al ratio, temperature, hydrodynamics, reaction time and alkalinity [2]. With Si/Al molar ratio almost equal to 1, kaolinite clay is a suitable raw material for preparation of zeolite NaA and having the advantage of being relatively cheaper, highly abundant and readily available [10]. The utilization of kaolin as a precursor of silica and alumina in the preparation of zeolite NaA was started in the 1970s [2], [11] by the reaction of dehydroxylated kaolin (metakaolin) with NaOH solution and since then, several attempts are still ongoing with regard to the use of kaolinite clay and metakaolin (dehydroxylated kaolin) from various countries of the world for synthesis of zeolite Type A, NaA, Y, X, 4A, P, hydroxysodalite, faujasite etc. giving rise to an extensive literature [7], [12]-[18]. However, no attempt has been previously made to synthesize zeolite NaA using natural kaolinite clays from Nigeria.

In this work, zeolite NaA was synthesized by conventional hydrothermal method using kaolinite clays obtained from three prominent deposits (Ikere, Opkella and Kankara) in Nigeria and sodium hydroxide solutions at varying concentration. The synthesized zeolite products were analyzed using scanning electron microscopy with attached energy dispersive spectroscopy (SEM/EDS), Fourier transform infrared spectroscopy (FT-IR) and X-ray diffraction (XRD).

*Corresponding author: abegundes@gmail.com

2. Materials and Methods

A. Material preparation

The starting materials used in this present study are kaolinite clays and sodium hydroxide pellets. The kaolinite clays used in this present investigation were obtained from three different zones in Nigeria, namely: Ikere Ekiti (7.4991°N, 5.2319°E) in Ekiti State, Okpella (7.272°N, 6.3465°E) in Edo State and Kankara (11.9313°N, 7.4138°E) in Katsina State while sodium hydroxide pellets (purity 98%) was obtained from a reliable chemical vendor.

The kaolinite clays which were obtained in their as-received state were labeled IK_{clay} (Ikere clay), OK_{clay} (Okpella clay) and KA_{clay} (Kankara clay) respectively. These clays were taken through beneficiation route following standard procedures in order to obtain highly pure clay free from organic matter and other attached impurities. The pure clays were further milled and then sieved respectively through a 75 µm sieve. By colour identification after processing, Okpella kaolinite is the most whitish clay among the three different processed clays. The kaolinite clays were then subjected to heating (calcination) inside a muffle furnace at 850°C for 3 h in order to convert the kaolinite clays to their respective metakaolins which are used in the preparation of zeolite. This is done to obtain a more reactive phase (amorphous metakaolin) as previous work has shown that raw kaolin is unstable under high alkaline conditions resulting into formation of different zeolitic materials [1]. The processed kaolinite clays are shown in figures 1 (a-c) respectively.

(a)
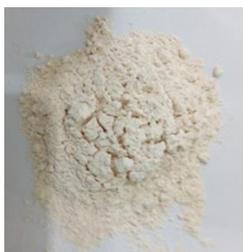
(b)

(c)

Fig. 1. Processed kaolinite clays (a) IK_{clay} (b) OK_{clay} (c) KA_{clay}

B. Synthesis of zeolite NaA (Hydrothermal method)

In this present investigation, the obtained metakaolins from IK_{clay} (Ikere clay), OK_{clay} (Okpella clay) and KA_{clay} (Kankara clay) respectively were not dealuminated as done by some previous studies in order to further reduce cost of preparation. However, the synthesis of zeolite in this work followed the adopted method by Mousa and Buhl [1].

Metakaolins from each kaolinite clay sample were separately mixed with sodium hydroxide (NaOH) solutions of varying concentrations of 3.0 and 4.0 M respectively. The samples were initially stirred gently for about 10 min at room temperature for proper homogenization. The solid/liquid ratio of metakaolins to alkaline solution was 1.0 g/25 ml. The obtained gels from the reacted mixtures were then left to cure for 7 days under room temperature. After the completion of curing, the gels obtained from respective metakaolin were then heated to hydrothermally crystallize at 100°C for 24 h following the adopted method of Adeoye et al. [19]. The synthesized zeolites were then washed with distilled water three times followed by drying at 80°C for 24 h.

C. Characterization of the raw materials and as-synthesized zeolite NaA

Characterization was carried out on the processed kaolinite clays and the synthesized zeolite NaA respectively in order to study their properties using standard procedures. The chemical composition was examined using high performance Energy Dispersive Spectrum (EDS) to quantify the concentrations of the elements present. Phase identifications were determined by X-ray diffractometer using BRUKER AXS with D8 Advanced diffractometer Cu Kα radiation XRD in the range of 2 tetha angle from 5 to 70 scanning range. The morphology features were examined by high performance scanning electron microscope (FESEM, Hitachi S-2460 N) in order to assess their microstructure characteristics. Identification of molecular bonding of the kaolinite clays were evaluated using Fourier-transform infrared spectroscopy (Shimadzu FTIR - 4200).

3. Results and Discussions

A. Characterization of the starting materials

Figure 2 (a) – (c) showed the results of the morphology and chemical composition of the three clays (IK, OK and KA respectively) by SEM/EDS while Figure 3 (a) – (c) revealed the mineralogical constituents of the clays by X-ray diffraction analysis. Figure 4 (a) – (b) displayed the functional bonding existing in the kaolinite clays.

In Figure 2(a) – (c), it is observed that three kaolinite clays displayed a similar somewhat platy morphology with hexagonal outlines characteristics of kaolinite, though with few agglomerations. This feature has also been reported by previous works [1, 20]. However, the chemical composition by the EDS showed the presence of predominant peaks of Si, Al and O indicating typical elements of kaolinite clays. In Figure 3 (a) – (c) shown by the XRD pattern, it is observed that kaolinite is the predominant mineral phase in all the three clays which can be recognized by their distinctive reflections at 12.34° and

$24.64°$ of 2 tetha as stated by Zhao et al. (2004). However, the presence of quartz is also confirmed by the XRD patterns for all the three clays, while minor impurity like muscovite is observed for KA_{clay} sample (Fig. 3c). In Figure 4 (a) – (b) indicated by the FT-IR spectra, it is observed that all the three clays exhibited somewhat similar pattern and bonding values. The peaks observed at 3687.9, 3618.46, 3647.39, 1114.86, 1028.06, 912.33 and 750.31 cm^{-1} are characteristics of kaolinite [21]. The absorption bands observed between $3566.38 – 3687.90\ cm^{-1}$ might be attributed to Al – O – H stretching while peaks at 1028.06 and 1114.86 cm^{-1} are attributed to Si – O stretching [22]. Also the bands appearing at 750.31, 910.4 and 912.33 cm^{-1} respectively can be attributed to –OH deformation [23]. However, the bands observed at 530.42 and 534. 28 cm^{-1} respectively might be attributed to Si – O – Al stretching [23]. The bands appearing at $1417.68 – 1489.05\ cm^{-1}$ might indicate the presence of carbonate bearing minerals which is confirmed by their EDS spectra [21].

(b)

(a)

(c)
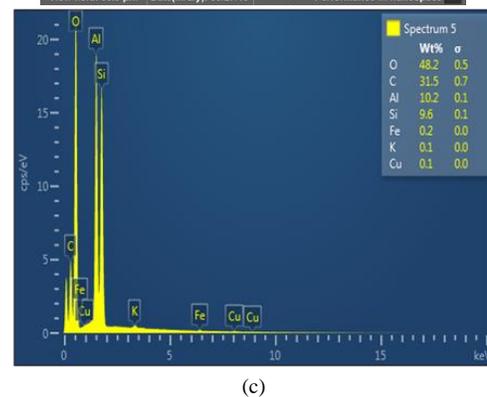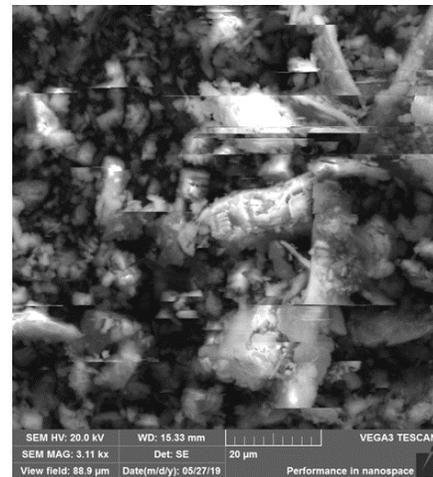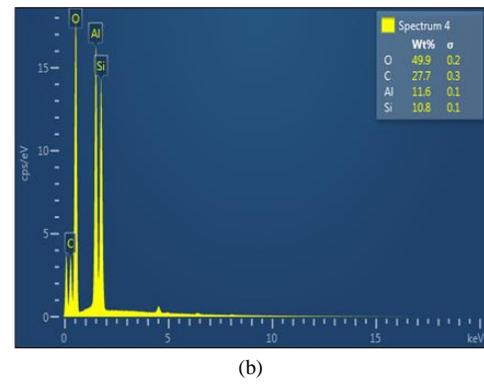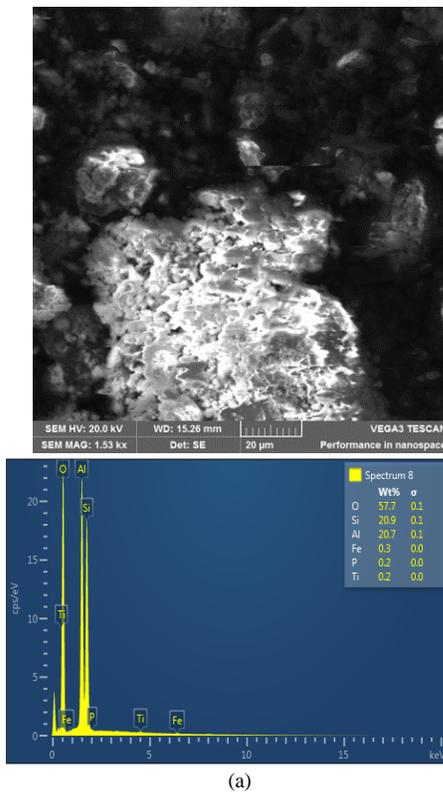
Fig. 2. Morphology and chemical composition of (a) Ikere clay (b) Okpella clay (c) Kankara clay

(a)

(b)

(c)

K – Kaolinite (blue, green), Q – Quartz (red), M – Muscovite (purple)
Fig. 3. X-ray diffraction analysis of (a) Ikere clay (b) Okpella clay (c) Kankara clay

(a)

(b)

Fig. 4. Representative FT-IR spectra of (a) Ikere clay (b) Okpella clay
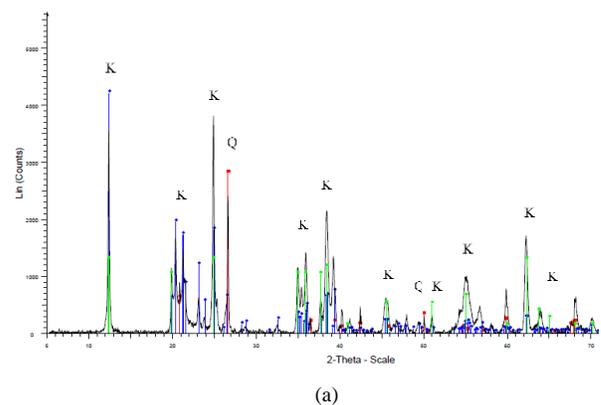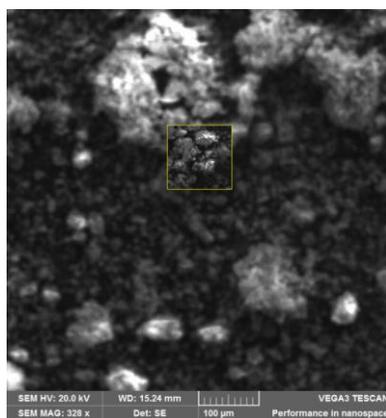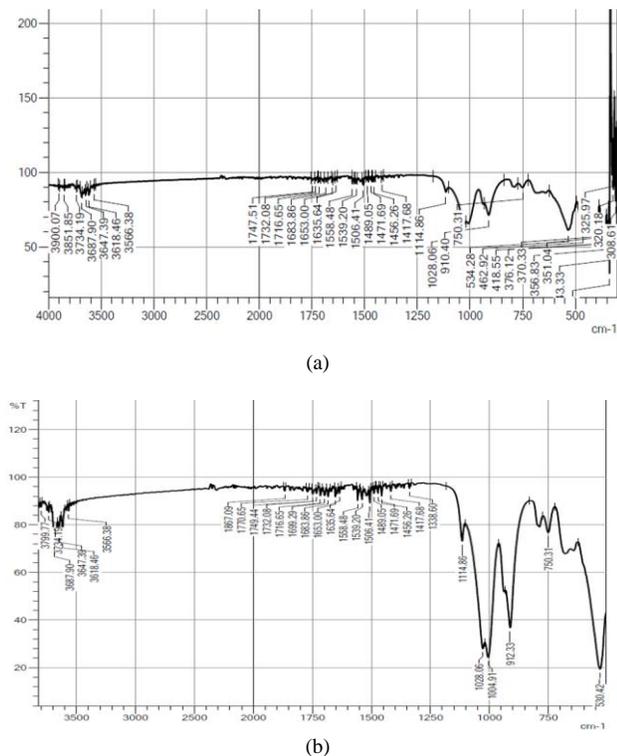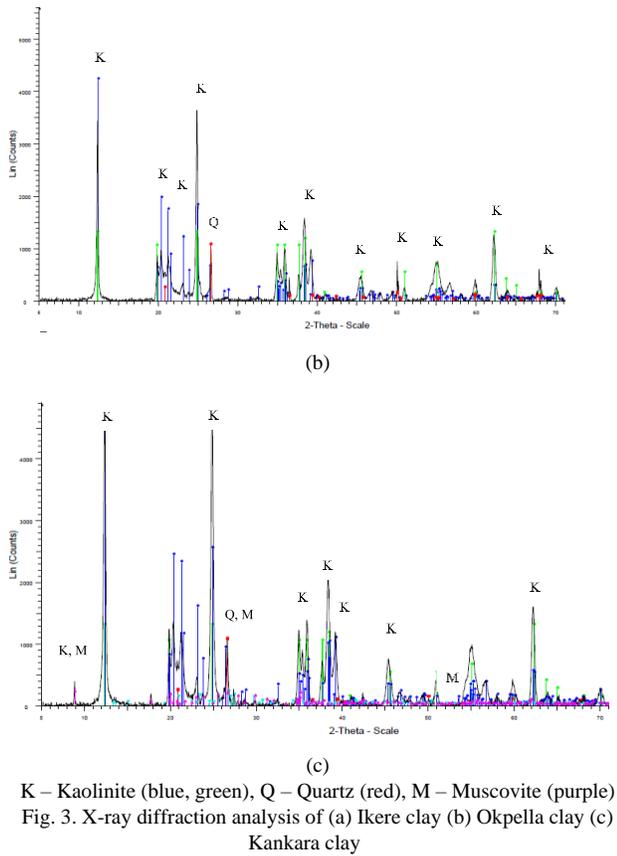
B. *Characterization of the synthesized NaA Zeolite*

1) *Morphology characteristics*

Figures 5 (a–c) and Figures 6 (a–c) represent the morphologies of the as-synthesized zeolite products at NaOH concentration of 3.0 and 4.0 M respectively. The morphologies showed a pronounced change from the morphologies of the stating materials (kaolinite clays) used. It is observed that the morphologies of the synthesized zeolite NaA at both NaOH concentrations (3.0 and 4.0 M) is somewhat similar. Zeolite NaA can be identified in its characteristics cubic morphology, however, the morphology obtained in this work reveals irregular but somewhat spherical aggregates of Zeolite NaA crystals. The cubic crystals probably developed before emergence of hydroxysodalite (HS) growing at the surface of zeolite NaA. The occurrence of hydroxysodalite alongside zeolite NaA has been attributed to be dependent on the concentration of NaOH solution [1]. Hydroxysodalite occurs at high concentration of NaOH solution as observed in this work. At 4.0 M NaOH, it is observed that lephispheric morphologies similar to hydroxysodalite grew out at the surface of the cubic crystals of zeolite NaA, showing interpenetrating twining (Fig. 6a, b, c). This has also been reported by Mousa and Buhl [1] and also similar to morphology obtained by Zahra and Habibollah [24]. Usually, it is proper to observe the following phenomenon between phases of hydroxysodalite and zeolite NaA: crystals of hydroxysodalite growing on the surface of cubic crystals of zeolite NaA, and aggregates of cotton ball-like spheroidal structure of hydroxysodalite occurring with cubic crystals of zeolite NaA [1]. It is also observed that when concentration of NaOH is increased from 3.0 to 4.0 M, the lephispheric morphology indicated by the spheroidal cotton-ball like morphologies increased which might be due to increase in sodium (sodalite) as confirmed by the EDS spectra. The results of the chemical composition shown by the EDS indicates the peaks of Si, O, Al and Na as major elements thereby confirmed that the synthesized products are zeolite NaA. It can also be observed that the sodium (Na) content increases with increase in NaOH concentration used which is actually expected thus resulting into growing of hydroxysodalite phase in the Zeolite NaA matrix. However, zeolite NaA synthesized from Okpella kaolinite clay (OK$_{clay}$) exhibited less hydroxysodalite phase.
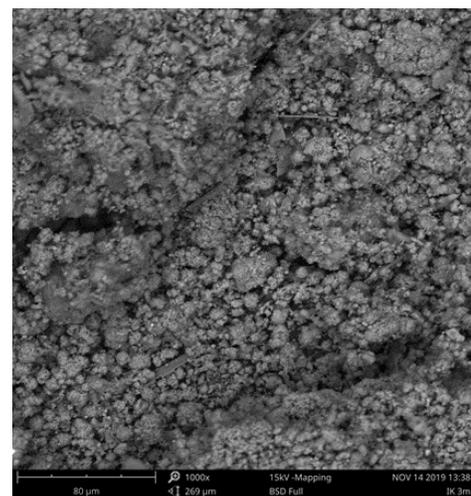
Element Symbol	Element Name	Atomic Conc.	Weight Conc.
O	Oxygen	37.62	28.45
Si	Silicon	20.78	27.59
Al	Aluminum	15.14	19.31
Na	Sodium	10.92	11.87
Fe	Iron	0.34	0.90
K	Potassium	0.29	0.53
P	Phosphorus	0.28	0.41
Cl	Chlorine	0.13	0.22

(a)
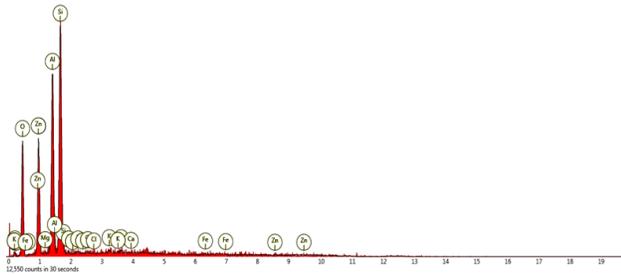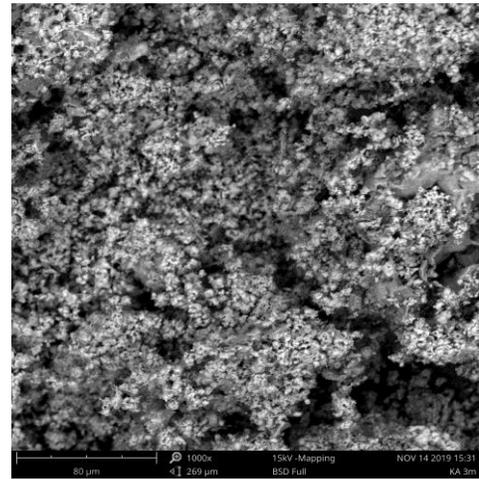
Element Symbol	Element Name	Atomic Conc.	Weight Conc.
Si	Silicon	27.20	32.60
Al	Aluminum	18.33	21.10
O	Oxygen	22.84	15.59
Na	Sodium	12.41	12.17
K	Potassium	0.60	0.99
P	Phosphorus	0.46	0.61
Cl	Chlorine	0.39	0.58
Fe	Iron	0.18	0.43
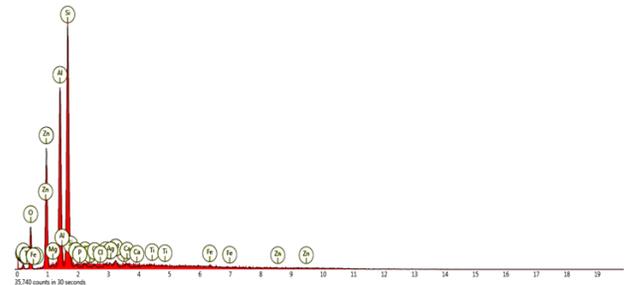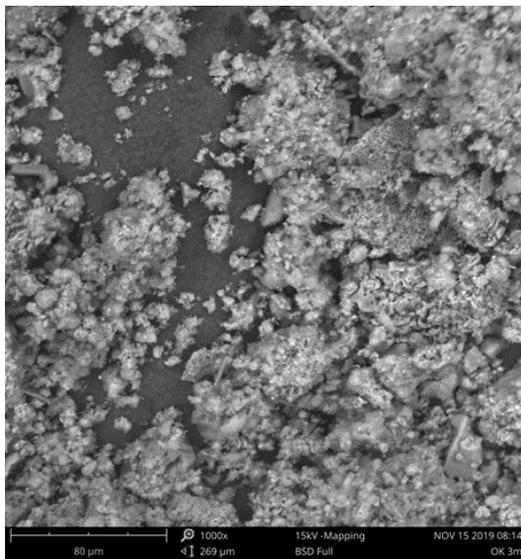
(c)

Fig. 5. SEM/EDS of the synthesized zeolite NaA at 3.0M NaOH from (a) IK_{clay} (b) OK_{clay} (c) KA_{clay}

Element Symbol	Element Name	Atomic Conc.	Weight Conc.
Si	Silicon	34.68	38.42
Al	Aluminum	22.19	23.62
O	Oxygen	24.34	15.36
Na	Sodium	11.56	10.48
Fe	Iron	0.81	1.79
K	Potassium	0.87	1.34
Cl	Chlorine	0.64	0.89
P	Phosphorus	0.67	0.81

(b)
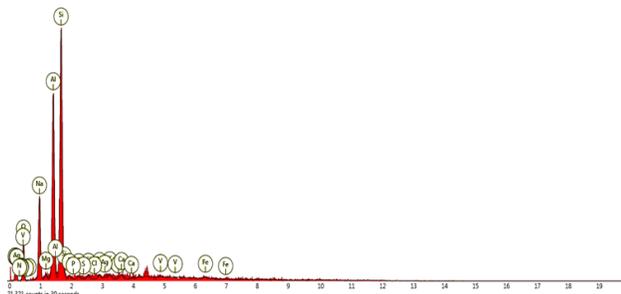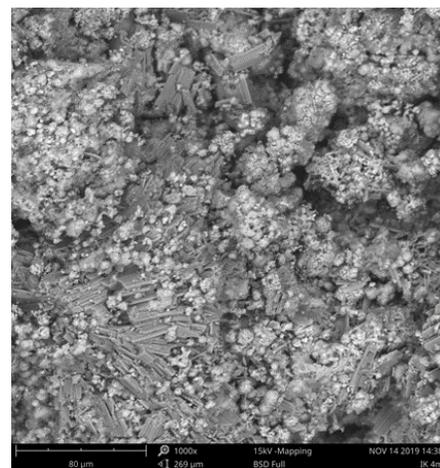
Element Symbol	Element Name	Atomic Conc.	Weight Conc.
Si	Silicon	22.13	29.09
O	Oxygen	30.02	22.48
Al	Aluminum	14.29	18.05
Na	Sodium	13.52	14.54
P	Phosphorus	0.35	0.51
Cl	Chlorine	0.27	0.45
Ca	Calcium	0.20	0.37
K	Potassium	0.00	0.00

(a)

Element Symbol	Element Name	Atomic Conc.	Weight Conc.
Si	Silicon	18.79	24.72
O	Oxygen	32.23	24.15
Al	Aluminum	14.15	17.89
Na	Sodium	12.61	13.57
K	Potassium	0.46	0.84
Cl	Chlorine	0.48	0.79
P	Phosphorus	0.42	0.60
Fe	Iron	0.23	0.60
Zn	Zinc	0.00	0.00

(b)
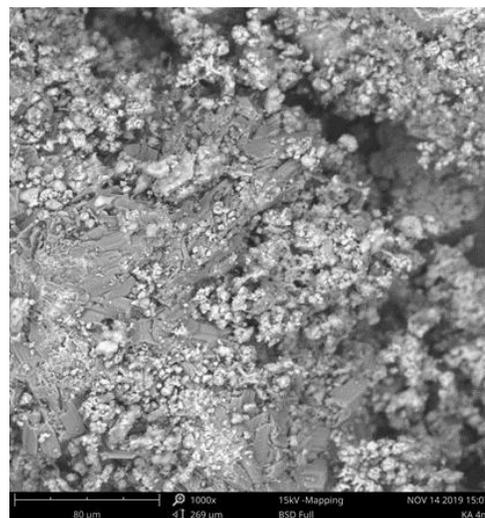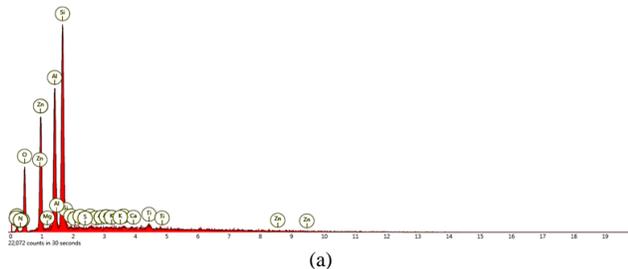
Element Symbol	Element Name	Atomic Conc.	Weight Conc.
Si	Silicon	27.50	31.65
Al	Aluminum	19.00	21.00
O	Oxygen	31.66	20.76
Na	Sodium	16.25	15.31
K	Potassium	0.71	1.13
P	Phosphorus	0.64	0.81
Cl	Chlorine	0.48	0.70
Zn	Zinc	0.00	0.00

(c)
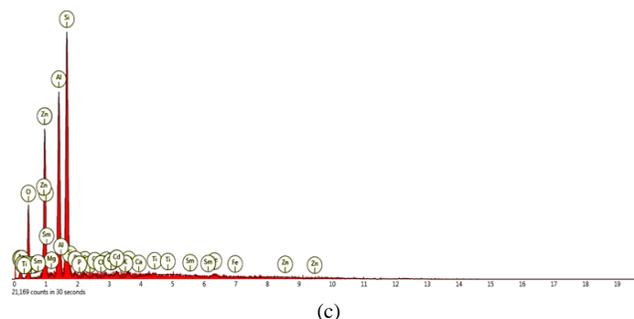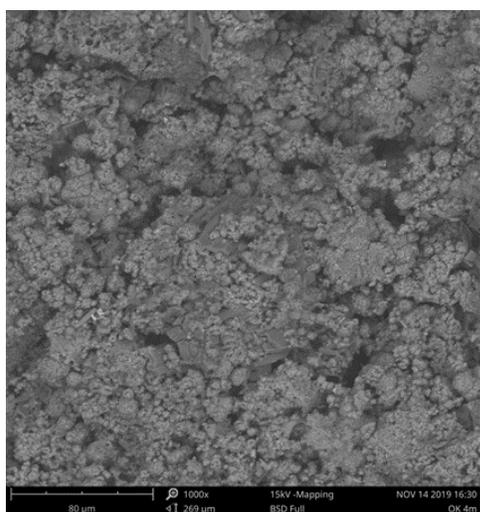
Fig. 6. SEM/EDS of the synthesized zeolite NaA at 4.0M NaOH from (a) IK$_{clay}$ (b) OK$_{clay}$ (c) KA$_{clay}$
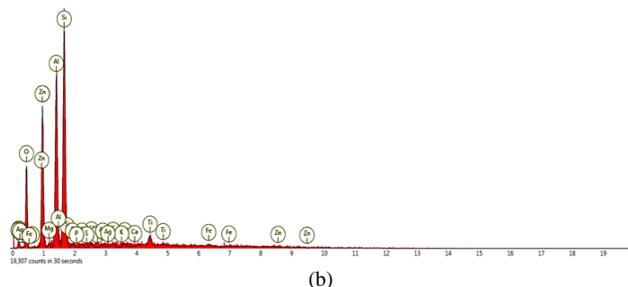
2) FT-IR analysis

Figures 7 (a – c) illustrate the representative IR spectra of the synthesized zeolite products at NaOH concentrations of 3.0 and 4.0 M respectively. The IR spectra were recorded a wavenumber 4000 – 500 cm^{-1}. Representative diagrams are used because all the samples showed similar IR pattern and values. It is observed from the IR spectra that the band observed between 750 – 650 cm^{-1} is attributed to symmetric T – O – T vibration (where T = Si or Al) which is on agreement with values reported for NaA zeolite in previous work [25]. The broad band between 4000 – 3000 cm^{-1} might be attributed to the vibration stretching of hydroxyl group of water molecules and amines present in the pores of the zeolites [26, 27] while the band observed at 957 cm^{-1} is related to HS [25]. However, the band observed at 1650 cm^{-1} might be attributed to zeolitic water [1,] while the peaks observed at 1450 cm^{-1} might be due to excess alumina present in the pore has also reported by Byrappa and Suresh Kumar [26]. The initial weak peak observed at about 550 cm^{-1} can be attributed to external linkages, is characteristics

of zeolite NaA [25]. The IR peak also observed at about 850 cm^{-1} is also characteristic of zeolite NaA as reported by Markovic et al. [28].

(a)

(b)

(c)
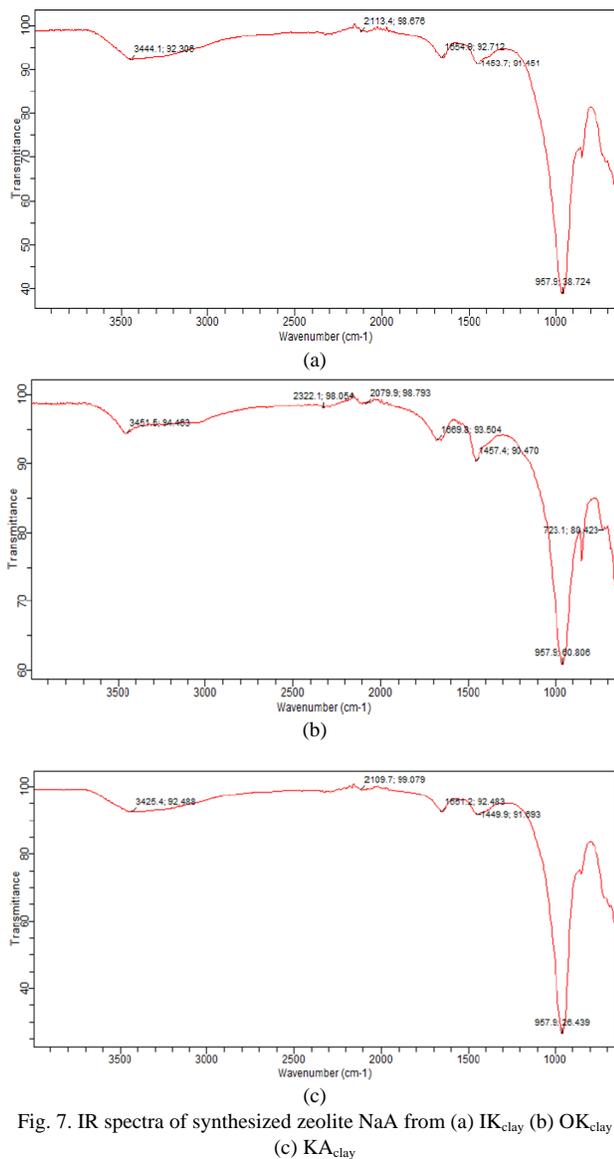
Fig. 7. IR spectra of synthesized zeolite NaA from (a) IK$_{clay}$ (b) OK$_{clay}$ (c) KA$_{clay}$

4. Conclusion

In this work, investigations have been successfully carried out on the synthesis and characterization of Zeolite NaA using natural kaolinite clays from Nigeria by low temperature hydrothermal method. The following conclusions were drawn based on the results of SEM/EDS and IR of the produced zeolite NaA by reacting activated metakaolins obtained from respective kaolinite clays with various concentrations of NaOH solution at 100ºC:

- Kaolinite clays obtained from Nigeria are suitable raw materials for precursors in the hydrothermal synthesis of zeolite NaA thus justifying their feasibility and economical for the industrial production of Zeolite NaA instead of using chemical grade materials.
- The morphology evaluation showed the presence of

hydroxysodalite (HS) growing on the surface of the zeolite NaA matrix while the chemical composition revealed by the EDS spectra indicate major elements such as Si, Al, O, Na confirming the synthesized products are zeolite NaA while the presence of Cl confirms HS phase.

- The sodalite content increased with the increase in NaOH concentration resulting into increased HS phase identified by spheroidal cotton-ball like morphology which could account for reduction in Zeolite NaA phase thus affecting the conspicuousness of the cubic crystal morphology known with NaA zeolite.
- In order to prevent the occurrence or prevalence of HS phase in Zeolite NaA matrix, NaOH concentrations must not be high.
- The results of the IR spectra showed that the peaks and wavenumber obtained are characteristics of Zeolite NaA as also supported by previous works.
- For future work, the efficiency of the synthesized zeolite products as cation exchangers and adsorbents shall be evaluated.

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