ORGANIC TEMPLATE FREE SYNTHESIS OF ZSM11 FROM KAOLINITE CLAY

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ABSTRACT
Synthesis of zeolitic materials from mineral ores, encounter serious challenges due to the presence of inherent impurities with the tendencies of inhibiting formation of desired products. Structure directing agent (SDA) though helps to mitigate this effect, but impact negatively on the environment. Zeolite ZSM11 is a promising catalyst that finds application in area not limited to benzene alkylation, gasoline formation from methanol, conversion of low density polyethene into hydrocarbon, etc. Accordingly, this work present successful synthesis of zeolite ZSM11 from kaolinite clay, seeded with NaY type zeolite and aged for 3-11 days, in an organic template free condition. The used kaolinite clays were sourced from two different mines in Nigeria, namely; Kankara and Onibode. They were both subjected to beneficiation, calcinations, dealumination and the gels formed, had molar composition of $9Na_2O_X30SiO_{2X}Al_2O_{3X}225H_2O$. The raw, intermediate and final products were fully characterized using XRD, XRF, BET and SEM/EDX. The prominent XRD peaks for ZSM11 were noticed for Kankara based sample aged for 11 days with seeding/dealuminatedmetakaolin ratio of 0.2wt% having increased crystallinity and purity as crystallization time increases. Seeding/metakaolin ratios of 0.1, 0.15, 0.25 and 0.3 wt% led to formation of composite material, excluding ZSM11. The morphological analysis gave the shape attributed to ZSM11 and the specific surface area was determined to be 412 and 450m²/g, for Kankara and Onibode based products, respectively.

Keywords— seeding, Kankara, Onibode, ZSM11, organic template free, dealumination

1. INTRODUCTION
Increasing demand for processing heavy petroleum feedstock and stringent environmental requirement has increased the necessity for developing new catalyst system, on one hand. This has also provided incentives to refiners to further reduce sulphur and aromatic levels of the finished products, aside reduction of refinery residues [1-2]. Zeolitic materials of different types are constantly being developed to answer and meet these ever-changing requirements [3].

Zeolite ZSM11 is a shape selective catalyst which has unique channel structures with 10-membered ring openings and rather unusual catalytic properties [4-5], having similar structure of ZSM5 [5], finding important values in the petrochemical industry. Unlike ZSM5 that has intersecting straight and sinusoidal channels, ZSM11 has only straight channels taking full advantage of less diffusion assistance and tortuosity, as depicted in Figure 1. Hongyuan and others [6] attempted the use of two step method for separate control of nuclei generation and crystal growth in ZSM11. Guo and co-workers [7], reported on the synthesis of ultra-fine ZSM11 at low temperature and Wu and others [8] reported same, but using co-templates. The use of zeolite EU as heterogeneous crystal seed was reported by Chenchen and others [9], while Robledo-Muñiz and others [10] reported the synthesis of zeolite ZSM11 from coal fly ash. Shen *et al.,* [11] studied the thermodynamics of ZSM11 zeolite synthesis, while Fyfe [12] reported the effect of using very dense gel for synthesis of ZSM11 at lower temperature. There are several patents on the subject matter, namely; Rollmann *et al* [13], Valyocsik [14], Beck and Schlenker [15] and Nakagawa [16].

To obtain highly crystalline zeolites, particular organic templates or structural directing agents (SDA) are used most often. However, there are obvious disadvantages for the organic template synthesis route, such as relatively high cost [17], environmental pollution due to their negative impact upon their release during post synthesis calcination [18] and development of micro

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cracks (deformity) of the formed products upon thermal treatment [19]. To solve these problems, many efforts have been made, such as reducing the template amount, adopting cheap templates [20], recycling the unused reagents [21], using combustion-free method [22] and application of seeding [23].
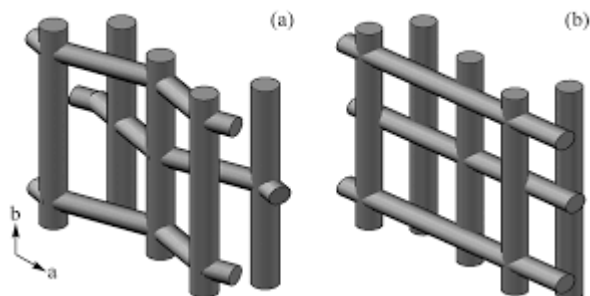

Figure 1: Structure of (a) ZSM5 and (b) ZSM11

Previously, we observed a transformation of zeolite X and Y to ZSM3 [24] which was suggested to be in line with the work of Hong-Jian *et al*[25] who produced ZSM2 from NaX seeds. Recently, Goel *et al* [26] discussed the inter-zeolite transformations route without organic structure-directing agents for zeolite synthesis. Encouraged by these findings and previous works, aside with the motivation of decreasing cost and process pollution, we embarked on this project. Zenonos *et al* [27] reported on the direct hydrothermal conversion of high-silica faujasite to ZSM5, while Yu *et al* [28] discussed the effect of seeding on the rate of crystallization of ZSM11. They stated that zeolite Y was responsible for the accelerated rate of crystallization for both ZSM5 and ZSM11. Nevertheless, the most attractive way to overcome the shortcoming is to develop new methods to prepare zeolites in the absence of organic template [29]. There exist reports on organic template free synthesis of selected zeolite materials [30-34], but there is none known to us on organic template free synthesis of ZSM11 using kaolinite clay as monomer.

Hence, this present work reports the synthesis of ZSM11 from kaolinite clay sourced from Onibode and Kankara towns, in Ogun and Katsina State of Nigeria, respectively, without the addition of any organic template or SDA but seeded with commercial grade Y type zeolite.

2. METHODOLOGY

2.1 Materials

Clays of kaolinite origin were selectively mined from Onibode and Kankara villages, in Ogun and KatsinA State, Nigeria. The chemicals used in this work, namely 96% sulphuric acid, NaOH, and commercial type Y zeolite (procured from Zeolyst, Holland) were of laboratory grade.

2.2 Kaolin Treatment and Synthesis of Template-Freezsm11

The beneficiation, calcinations and dealumination of the clay was done as detailed in [24]. The cake formed was grounded to fine powdered of particle size 120microns and preserved for analyses. The batch composition of $9Na_2O_x30SiO_{2x}Al_2O_{3x}225H_2O$ was formed from the Kankara and Onibode based dealuminated samples, NaOH as mineralizer and deionized water. The resulting gels seeded with commercial type Y zeolite in seeding/dealuminated sample ratios of 0.1; 0.15; 0.2; 0.25 and 0.3wt% were aged for 3, 5, 7, 9 and 11days at room temperature. The compounded slurries were crystallized dynamically at 135^0C for 72 hours under autogenous pressure in an electric oven.

2.3 Characterization Technique

The materials obtained at various stages were subjected to analyses, namely XRD, EDX-SEM, XRF and BET. X-Ray Fluorescence mineralogical composition of the samples was determined using a Thermo Fisher ARL9400 XP+ Sequential XRF equipped with a WinXRF software was for analyses. The samples were milled in to achieve particle sizes <75micron, dried at 100°C and roasted at 1000°C to determine Loss on Ignition (LOI) values. 1g Sample was mixed with 6g lithium tetraborate flux (Li2B4O7) and fused at 1050°C to make a stable fused glass bead. The XRF analysis for the clay was conducted following ASTM C114 standard for oxide identification.

X-ray powder diffraction (XRD) patterns were collected on an XPERT-PRO diffractometer (PANalytical BV, Netherlands) with theta/theta geometry, operating a cobalt tube at 35 kV and 50 mA. The goniometer is equipped with automatic divergence Slit and a PW3064 spinner stage. The XRD patterns of all specimens were recorded in the 5.0°- 90° 2θ range with a step size of 0.017° and a counting time of 14 s per step. The XRD analysis was conducted following ASTM 2478, standard for clay identification, while those for ZSM11 were conducted following ASTMD5758 vol. (05.03)

SEM and EDX analysis were recorded by using LEO S430 scanning electron microscope coupled with energy dispersive X-ray analyzer model Oxford LINK ISIS. Samples were prepared by dispersing dry powder on double sided conductive adhesive tape. Samples were coated with carbon by arc discharge method for SEM-EDX. Samples were scanned in secondary electrons (SE) for morphology and back scattered electrons (BSE) mode for compositional image.

In order to determine the specific surface area, automated gas adsorption analyzer, AUTOSORB-1 (Quanta Chrome Instruments, USA) was used with adsorption-desorption isotherms of nitrogen at -196^{0}C. For each analysis, 0.2g of sample were degassed at 300^{0}C

under nitrogen for at least 3h. The specific surface areas of sample was calculated by the BET (Brunauer, Emmett, and Teller) method while volume of micropore was estimated using the Dubinin Radushkevich (DR) equation. For pore volume, it was directly calculated from the volume of nitrogen held at the highest relative pressure (P/Po = 0.99). The Specific surface area were determined following the standard method of ASTM C1274.

3. RESULTS AND DISCUSSION
3.1 Kaolin beneficiation
The compositional analysis conducted on raw and beneficiated kaolin (Kankara and Onibode) indicated presence of impurities in the raw clay as depicted in Table 1. The silica content was observed to reduce with beneficiation while alumina increases for Kankara but almost constant for Onibode. The potassium and ferric content were observed to reduce for both clays, which further reduces during dealumination.

The XRD patterns shown in Figure 2 for the parent clay shows well defined characteristic peaks of kaolinite clay. The Kankara kaolinite clay (Figure 2a) was found to contain anatase, potassium iron oxide and for sterite, while Onibode (Figure 2b) was observed to be purer though having some inherent impure phases, namely ilmenite and halloysite and less crystalline in nature.

The SEM in Figure 3(a) shows the card- like or platy morphology of kaolinite material [35] and presence of rod or tubular material attributed to halloysite and clinochlore and micelles- to mica and muscovites, which

corroborates the XRD findings. The average particle size was estimated as 2.0 μm for both the raw and beneficiated kaolin. The kaolin EDX spectrum for both kaolins (as shown in Figures 3 a and b) were characterized by nearly equal peak height of Al and Si, another means to confirms the predominance of kaolinite. The closely parked flaky particle is stacked together in agglomerates and seems to be widely distributed in the sample analyzed as depicted in Figure 3(b). Noticeable small aggregate particles found in between the silica-alumina plates, are indicative of inherent impurities. In total agreement with the diffractograms shown in Figures 2 (a and b), and the XRF result in Table 1 further buttress the level of crystallinity and purity of the two kaolin.
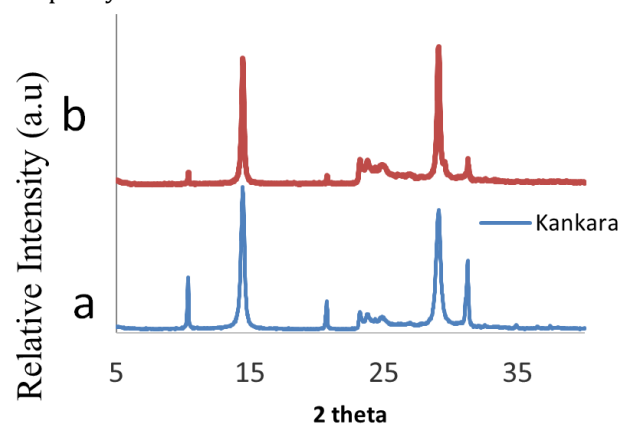

Figure 2: XRD patterns of raw kaolinite clays (a) Kankara (b) Onibode

Table 1: Compositional analysis for the samples

Oxides	A	B	C	D	E	F	G	H
SiO$_2$	48.3	49.04	46.5	47.1	47.79	47.6	76.2	77.6
Al$_2$O$_3$	32.2	40.1	35.2	39.6	36.65	44.1	5.5	7.4
CaO	0.15	0.21	0.14	0.06	0.49	0.03	0.33	0.26
Fe$_2$O$_3$	3.16	2.95	2.28	1.58	2.1	1.77	0.24	0.31
K$_2$O	1.26	0.25	0.68	0.23	0.4	0.13	1.53	1.22
MgO	1.04	0.91	0.64	0.9	1.02	0.76	0.87	nd
MnO	0.09	0.02	0.04	0.006	0.07	0.01	nd	nd
Na$_2$O	0.12	0.08	0.07	0.04	0.11	nd	nd	nd
TiO$_2$	0.84	3.97	0.34	2.89	0.07	2.55	0.32	0.19
SO$_3$	0.09	Nd	0.089	0.06	0.03	0.04	10.3	8.01
LOI	12.57	11.67	11.48	10.36	7.21	9.78	9.89	10.75
Si/Al	2.55	2.08	2.25	1.99	2.22	1.83	23.55	17.83

Legend: A-Raw Kankara Kaolin,   B-Raw Onibode Kaolin   C-Beneficiated Kankara Kaolin, D-Beneficiated Onibode Kaolin,
         E-Calcined Kankara Kaolin, F-Calcined Onibode Kaolin, G-DealuminatedKankaraMetakaolin,
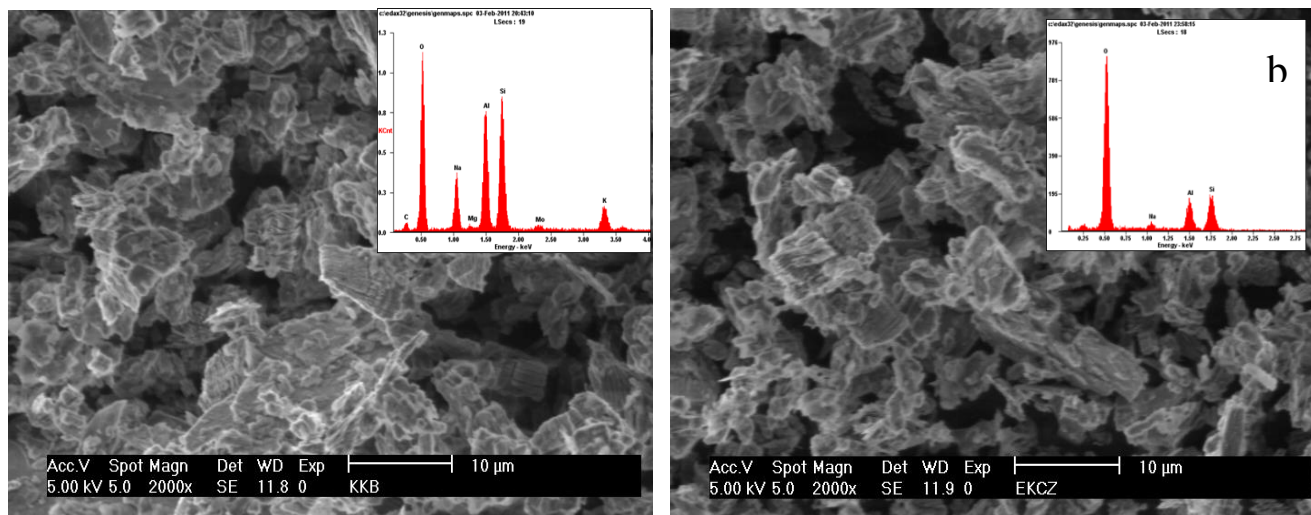   H-Dealuminated Onibode Metakaolin, nd-Not detected

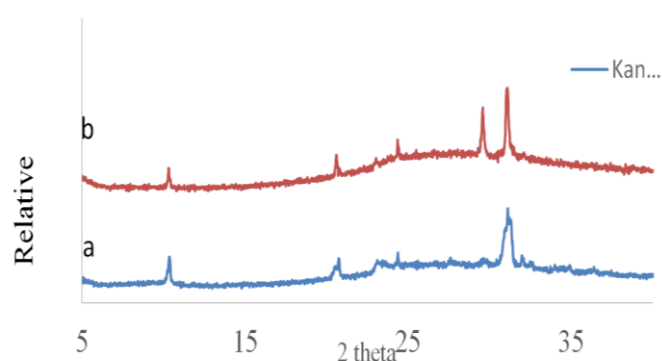Figure 3: SEM/EDX for raw kaolin (a) Kankara (b) Onibode

Figure 4: XRD patterns of beneficiated kaolinite clays: (a) Kankara (b) Onibode

The XRD pattern shown in Figure 4, was dominated by the kaolinite peaks after beneficiation of the kaolin, with the peak attributed to quartz, a confirmation that this material (especially the chemically combined form of it) was not removed via wet method of beneficiation.

The SEM image of beneficiated kaolin (Figure 5)shows retainment of kaolinite structure with small aggregate particles of silica-alumina plate. Halloysite phase noticed in the raw kaolin was not observed in the SEM for the beneficiated clays. It was observed that the SEM for beneficiated kaolin was lean in the earlier identified fibrous materials, pointing to removal or reductions in the inherent impurities. Additionally, the silica-alumina plate for kaolinite clay sourced from Kankara was observed to be better arranged with little or no broken edges as compared with the one from Onibode. The EDX showed less silica retainment in Kankara which conforms with the XRF result.

3.2 Calcination and Dealumination

The XRD patterns for Kankara and Onibode kaolin subjected to thermal treatment are depicted in Figure 6, showing a typical semi-amorphous nature of metakaolin phase formed. Figure 6 shows that the XRD pattern for the metakaolin obtained from both kaolinite clays have retained peaks at 2theta between 30 and 35, responsible for the presence of quartz, anatase, nepheline and hematite (Fe_2O_3). These minerals were observed not to be affected by thermal treatment despite the elevated temperature of calcinations.
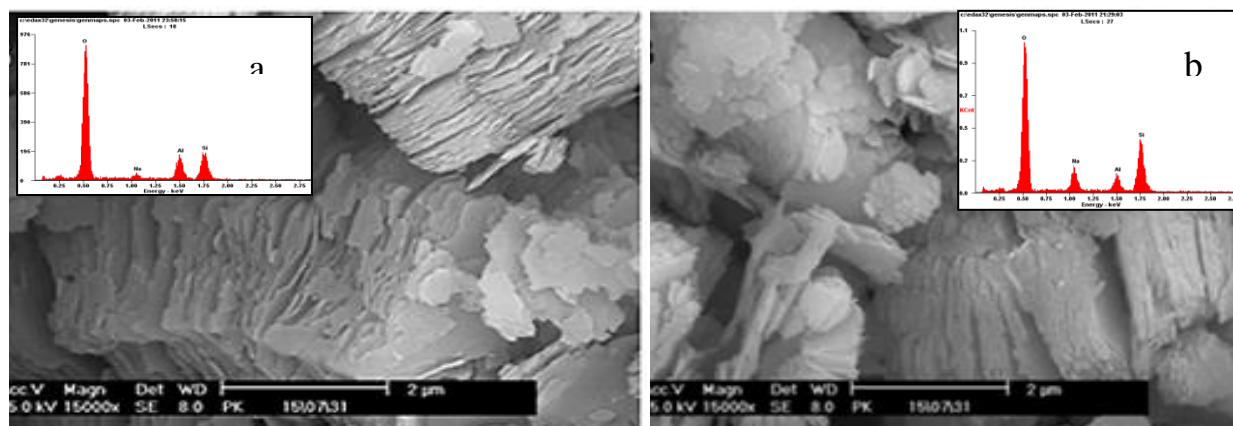

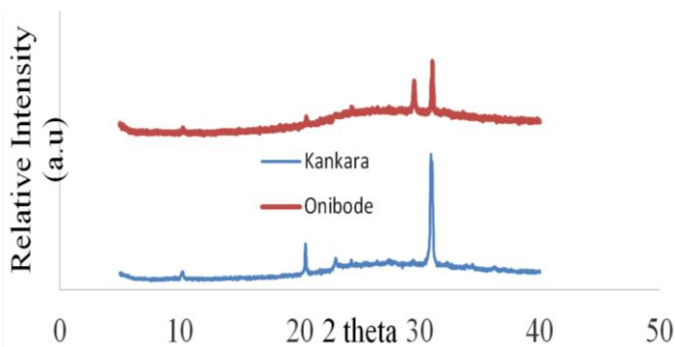Figure 5: SEM/EDX for beneficiated kaolin (a) Kankara (b) Onibode

Figure 6: XRD patterns for thermally treated kaolinite clays (a) Kankara (b) Onibode.
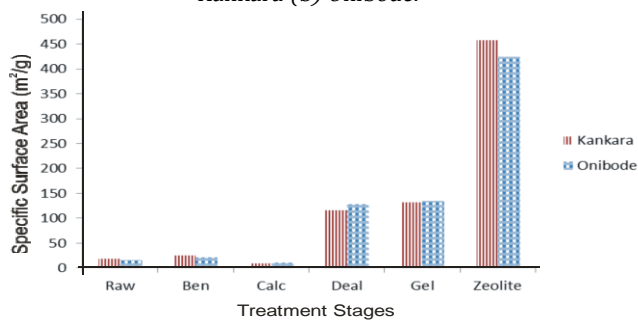

Figure 7: Specific surface area for kaolin treatment and zeolitization stages.

Figures 6 points to the disappearance of peaks attributed to kaolin, while the LOI in Table 1 shows the extent of moisture loss, escape of volatiles and other combustible materials find in the starting kaolin. The specific surface area (s.s.a), for all the samples and product determined by BET method depicted in Figure 7, shows the effect of various treatment on kaolin, which agrees with [36-38].

The SEM shown in Figure 8 for both metakaolin, testifies to partial destruction of the kaolinite structure. It is worth mentioning, that the extent of metakaolinization differs for sources of kaolin. The specific surface area

(s.s.a) shown in Figure 7, for the calcined Kankara and Onibode kaolinite samples reduces in value due to aggregation of particles when the inherent structural water molecules and fibrous materials were removed. Apparently, the s.s.a for dealuminated products resulting from Kankara and Onibode, were observed to increase, testifying to the role of the dominant amorphous silica in the residue (Table 1), which is in line with the report of Belver [39].

3.3 Zeolitization Process

Figure 9 showed the XRD patterns for the as-synthesized zeolite ZSM11 from both Kankara and Onibode resulting from gel seeded with commercial Y type zeolite, aged for 3-11 days at room temperature. The typical peaks at 2 theta values of 7.92, 8.78, 23.14, 23.98 and 45.2 were attributed to ZSM11 using the reference code 01-074-1787 and 01-087-1591. Traces of ZSM5 were identified by the peaks at 2 theta values of 7.96, 8.91, 14.00, 14.87, 20.92, 23.28, 23.97 and 24.52. The XRD patterns were satisfactorily confirmed from the atlas for ZSM11 [40] and ZSM5 [41].

The Onibode based product gave a spike for the characteristic peak of ZSM11 only after 7 days, which diminishes with ageing period. The speculated reasons were; state of alumina and silica in the gel, the Si/Al ratio and presence of sulphatic salts. Aside these, it is likely that the alumina in the gel could be of $Al_2(SO_4)_3$ and partly $Al(OH)_3$, leading to low intensity of the as-synthesized product. Confirmatory peak at around 2 theta-18 and 30-34 indicated the presence of $Al(OH)_3$ and $Al_2(SO_4)_3$ in the system, respectively.
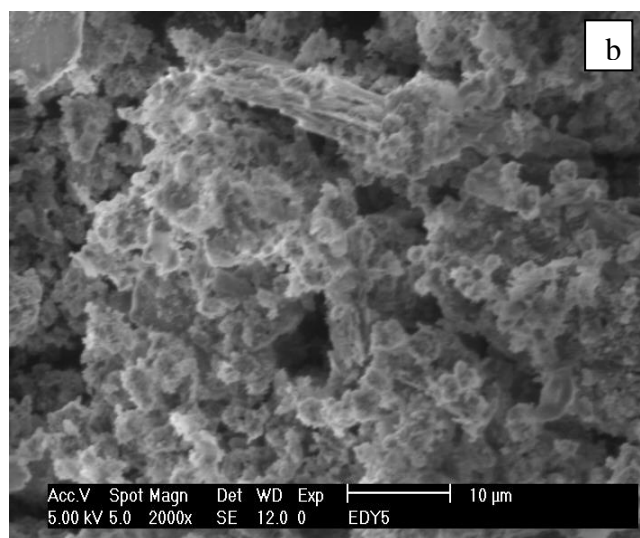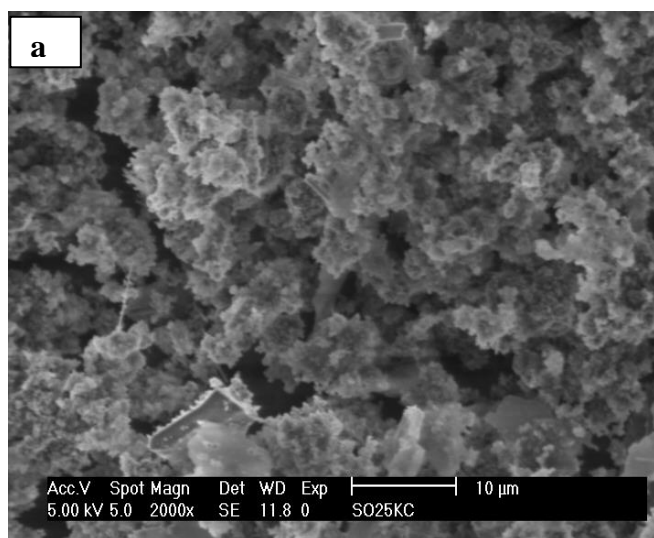

Figure 8: SEM/EDS patterns for thermally treated kaolinite clays (a) Kankara (b) Onibode.
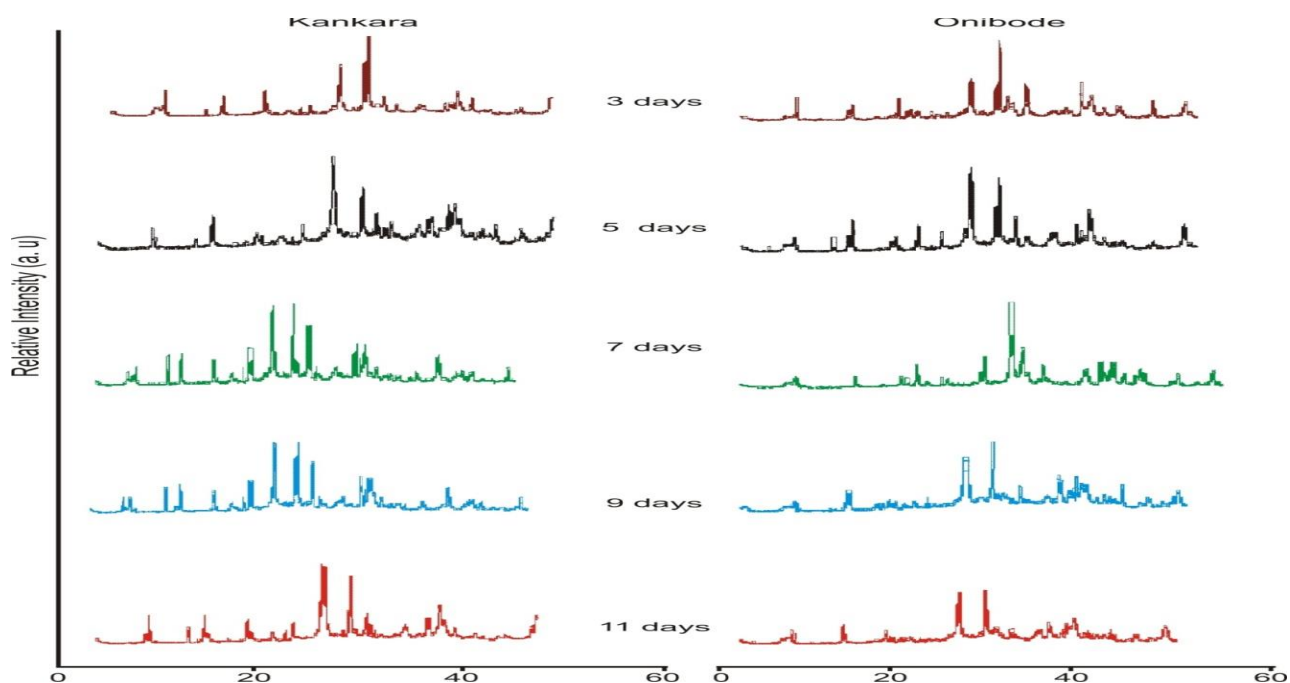
Figure 9. XRD patterns for as-synthesized zeolite ZSM11 from both Onibode and Kankara
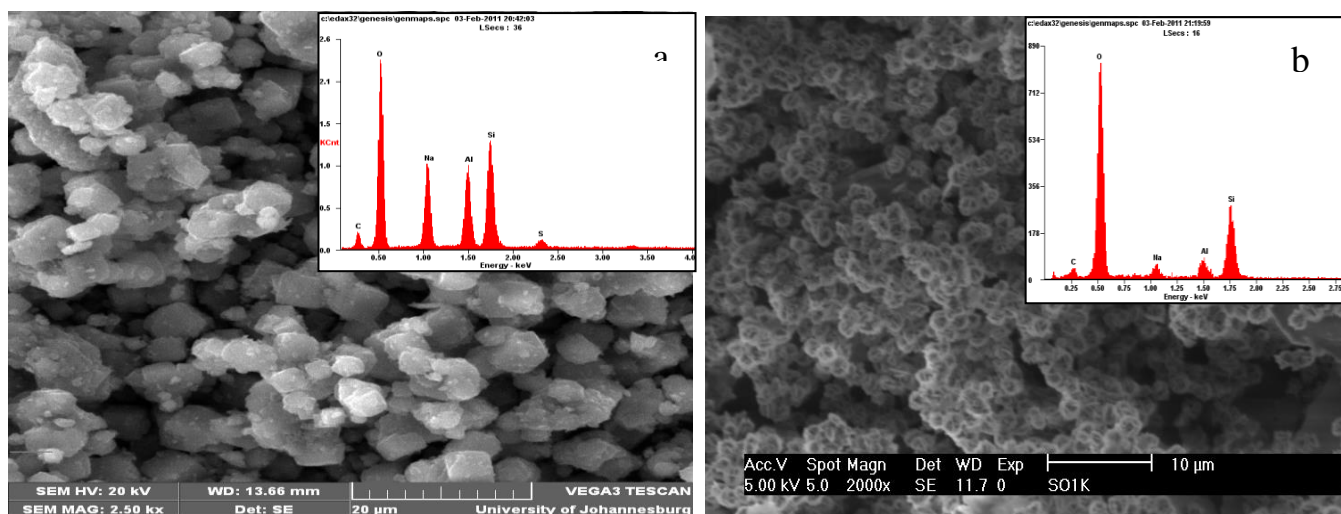

Figure 10. SEM/EDX for as-synthesized zeolite ZSM11 (a) Kankara and (b) Onibode

Some silicon-rich species [42] with their peaks at 2theta of 24-29, were observed to have reduced intensity with post seeded-ageing period. The SEM image shown in Figure 10 (a and B) have some hexagonal-shaped crystals of ZSM11 along with irregular shaped crystal clusters of impurities, side-products or unconverted materials, with Figure 10a recording better morphology attributed to ZSM11.

The characteristic peaks for zeolite ZSM11 noticed in Figure 9 for Kankara, gave a better crystalline product. The reason for this was attributed to Si/Al of 24, good enough for ZSM11 synthesis [43]. All other silicon-rich impurities observed in Onibode were also noticed in Kankara, though with increased peak intensities. Despite seeding with NaY zeolite, it took 7 days of ageing for the appearance of ZSM11 peaks, which was retained for yet another 2 days and later, disappeared. Apparently, the intensity of ZSM5 tends to reduce with days of aging for Onibode while it was prominent for 7 and 9 days for Kankara which dropped at the 11th days, having density of 2.08g/cm³ and a cubic shape as suggested by the XRD and confirmed in the micrograph.

This could only point to the rigidity of the silica polymorphs in Kankara, which depolymerised and reconstituted to form phases like cristobalite, potassium magnesium silicate and others on the 11th day. The SEM shown in Figure 10 depicted irregular shapes of crystalline materials overshadowing the spherical and hexagonal shapes of ZSM11. The morphology of zeolite ZSM11 shown in Figure 10, was similar to that of [29, 34].

The SEM clearly show that the material is in matrix form, resulting from the presence of other morphological shapes in the SEM. The BET surface area for ZSM11from

the two kaolinite clays from Kankara and Onibode were determined to be 412m^2/g and 450m^2/g, respectively, as represented in Figure 7, which is relatively higher than the ones reported by Yua *et al* [38], probably due to the presence of undepolymerized quartz.

4. CONCLUSIONS

A fully characterized ZSM11 was successfully synsezized from Kankara and Onibode kaolinite clay via organic template-free and environmentally friendly route. The results here presented puts Kankara clay ahead Onibode, in terms of its response to all the treatments, as well as, the products obtained. This is probably due to its Si/Al ratio, less quartz content after calcinations and state of ingredient in it. It is likely that the intensity of the ZSM11 obtained was less due to the known effect of potassium on rate of nucleation and effects of other unwanted materials. Onibode had less Si/Al ratio compared to required, which is responsible for the low crystalline product after 7 days of seed-ageing with NaY. It was suggested that for the seeded samples (Kankara and Onibode), the NaY zeolites used served as activator and also provided the increased number of nucleation sites on the NaY-dealuminated sample surface, thereby accelerating the rate of zeolitization.

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