

Preparation and characterization of metakaolin from Nigeria Okpella kaolin for zeolite synthesis

O. A. Olafadehan^{*1}, I. J. Okolie² and A. J. Kehinde¹

¹Department of Chemical and Petroleum Engineering, University of Lagos, Akoka-Yaba, Lagos, Nigeria

²Department of Chemical Engineering, Federal University of Technology, Owerri, Imo State, Nigeria
Email: oolafadehan@unilag.edu.ng

Abstract

The suitability of Nigeria Okpella kaolin (NOK) and metakaolin for the synthesis of zeolite has been investigated. Refined kaolin of <14 μm particle size and an estimated kaolinite content of 90.23 % were obtained. The optimal calcination parameters were 750 °C and exposure time of 15 minutes. The conversion of the kaolinite to metakaolinite was confirmed through XRD and TGA/DTA and BET analyses of the raw and thermally treated kaolin samples. The NOK and thermally treated metakaolin samples produced straight lines for the BET plots between relative pressure regions of 0.05 to 0.30 with BET surface areas of (14.5773 ± 0.0894) m²g⁻¹, (11.7811 ± 0.1245) m²g⁻¹ and (11.8714 ± 0.1197) m²g⁻¹ respectively with the respective coefficient of determination, R²=0.9998, 0.9995 and 0.9996. The BET surface area of NOK is within the reported acceptable range for kaolinite. The results obtained for kaolin and metakaolin showed that NOK is a good precursor for zeolite synthesis with minimal impurity.

Keywords: Kaolin, Characterization, Refining, Dehydroxylation, Metakaolin.

1.0 INTRODUCTION

Kaolin (or China clay) is a versatile industrial mineral with numerous technological applications and is abundantly available in Nigeria. Nigeria is blessed with 3 billion metric tons of high quality kaolin clay, with almost every state having at least one known deposit of kaolin (Onwualu and Ibrahim, 2010). Kaolin deposits, their various locations in Nigeria and extent of exploitation have been reported in the work of Onwualu and Ibrahim (2010). Presently, there are few kaolin processing plants in Nigeria, such as in Katsina, Edo and Plateau States. The largest user of kaolin in Nigeria is the paper industry, where it is utilized as a filler and coating agent; it also finds extensive use in the pharmaceuticals and wastewater treatment. However, there is a growing interest in the use of kaolin as a combined source of silica and alumina for zeolite synthesis (Xu *et al.*, 2007). The use of different kaolin deposits around the globe to synthesize zeolite has gained much attention. There has not been any major or reported work in the literature on the use of Okpella kaolin deposits in Etsako East, Edo State, Nigeria, (hitherto referred to as Nigeria Okpella kaolin, NOK), to synthesize zeolite.

Kaolin composition varies with location (Bergaya and Lagaly, 2006, Osabor *et al.*, 2009), and is crystalline natural aluminosilicate in which the molar ratio of silicon (IV) oxide, SiO₂, to aluminum (III) oxide, Al₂O₃, is 2.0-2.3. Kaolin has stratified structure formed with repeated layers of silicon-oxygen tetrahedrons and aluminum-oxygen octahedrons (Pavlov *et al.*, 2012). The common ancillary or impurity minerals occurring with kaolin include parent rocks like feldspar and mica, quartz, ferruginous, titaniferous and carbonaceous materials. The most deleterious impurities in kaolin are iron minerals, which impart colour to the white kaolin. Iron exists as oxides, hydroxides, oxy-hydroxides, sulphides and carbonates along with iron-stained quartz or anatase and mica in kaolin (Richerson, 2005; Ramaswamy and Raghavan, 2011; Hassan and Abdu, 2014). These impurities lacking in plasticity are called non-clay or accessory

minerals (Bergaya and Lagaly, 2006). The associated minerals require removal or reduction because they generally reduce the commercial value of the clay mineral hence purification of the raw material is very important before any industrial usage.

More importantly, kaolin is viewed industrially as a term that means clay, which is composed mainly of mineral called kaolinite, a layered structure, with molecular formula, $\text{Al}_2\text{O}_3 \cdot 2\text{SiO}_2 \cdot 2\text{H}_2\text{O}$ (Brigatti *et al.*, 2006; Rytwo, 2008; Ramaswamy and Raghavan, 2011), or $\text{Al}_2\text{Si}_2\text{O}_5(\text{OH})_4$ (Pavlov *et al.*, 2012), and is amenable to property variation, thereby making it useful for the production of series of industrial products (Murray, 1980). Kaolinite structural layers have been investigated mostly from crystallographic studies, X-ray analysis, thermal analysis and infrared spectral analysis (Kotoky *et al.*, 2006). Kaolinite can be viewed as a continuous two-dimensional structure containing a silica tetrahedral sheet with central cation usually octahedral aluminium, which is linked to four shared oxygen atoms (Kovo, 2010).

The position of Si, Al and O in the kaolinite structure is well documented but the location of the OH is in some doubt. However, the bonding system of OH in the interlayer has been explained by Benco *et al.* (2001). Four different OH groups were identified and two were part of weak bond formation and the remainder did not participate in H-bonding.

The surface of clay mineral generally can be thought of to be hydrophobic; however, in kaolinite, the presence of hydroxyl group and defect sites at the surface introduces hydrophilicity. The defect sites can easily be detected with the aid of XRD. The patterns of ordered kaolin are sharp and narrow in their peaks while the disordered kaolin patterns show broad and asymmetric peaks (Bergaya and Lagaly, 2006). However, two tests are normally performed to identify the degree of order in a kaolin sample: Hinckley index range and Weiss index (Bergaya and Lagaly, 2006).

Natural kaolin is usually fractionated to enrich the kaolinite content and reduce other unwanted clay mineral before being used in manufacturing materials such as zeolites (Chipera and Bish, 2001; Elton, 1994). The most common and simplest method of enriching the kaolinite content of raw (natural) kaolin sample is fractionation by sedimentation (Bergaya and Lagaly, 2006). The refining process of kaolin is chiefly divided into two groups: removal of foreign material by chemical method and refinement by sedimentation to remove larger impurities especially quartz which is trapped within the mineral aggregates. However, addition of chemicals in the treatment process can impair the properties of the parent material; therefore, the use of chemical treatment should be a last resort (Chipera and Bish, 2001). Even though there are several other methods such as selective flocculation, flotation and ultrasonic treatment that can be used to process raw kaolin, fractionation by sedimentation is the most common procedure used for kaolin processing to obtain highly pure kaolin at laboratory level (Duane and Robert, 1997; Chipera and Bish, 2001). Sedimentation is based on the principle that particles with different masses and densities will settle at different terminal velocities in a given viscous medium (Pabst *et al.*, 1999). Stokes' law enables the separation based on the clay particle size, which is assumed to have a spherical shape (Bergaya and Lagaly, 2006).

Although commercial exploitation of NOK has been carried on for a couple of years, there seems to be a lack of proper characterization of this mineral. The detailed structure and characteristics of this mineral are not yet known. Hence, this work attempts to fill the gaps in the exploitation of this material as the kaolin deposits in all parts of Edo State are yet to be exploited, so that non-traditional uses may be found for the NOK. The analytical verification of

the suitability of NOK for zeolite synthesis is of value to the industrial aspirations of Nigeria to facilitate or enhance the realisation of its vision in the near future.

2.0 MATERIALS AND METHOD

This section highlights the characterization and refining of pulverized raw NOK, dehydroxylation/metakaolinization of refined dried NOK, and dehydroxylation/metakaolinization of refined dried NOK

2.1 Characterization and refining of pulverized raw NOK

Natural NOK was collected from Okpella in Etsako East, Edo State, Nigeria. The NOK was pulverized in the Freedom Group Pulverisation plant in Okpella and the fine particles of NOK were collected in 50 kg bags. The raw pulverized sample was characterized using XRD, SEM, XRF, TGA/DTA, BET and SEM-EDS. The pulverized raw NOK was then refined to purify the kaolin and enhance size separation.

Three measuring cylinders, each of 40 cm high and 2000 mL by volume were used as settling tanks. A portion of the measured deionised water was introduced into a beaker and 92 g of raw kaolin was poured into it and stirred to obtain slurry. The kaolin slurry was then poured into the second portion of the deionised water in the measuring cylinder used as settling tanks. The size separation was achieved by allowing free settling of clay suspension in the settling tanks for about 26-29 min. The settling time of heavier component (quartz) and larger size particles ($\geq 15 \mu\text{m}$) was determined from Stokes' law based on the density of particle and water, the viscosity of water, particle size, the temperature of the surrounding environment and height of the settling tanks. The supernatant was carefully decanted into a white transparent plastic bucket, covered and allowed to settle for 24 hr. A settled fine NOK sample ($\leq 14 \mu\text{m}$ particle) was obtained after decanting the suspended deionised water. The process was repeated several times in order to obtain enough samples of the refined NOK. The settled fine NOK was dried in an oven for 48 hr at 45°C. The product obtained was characterized using XRD and packed into sample bottles for the next experimental stage. The Stokes' equation of sedimentation for the calculation of settling time, t_s , is given by Eq. (1):

$$t_s = \frac{18\eta h}{(\rho_p - \rho_0)d_p^2 g} \quad (1)$$

where η is the viscosity of solvent at 30 °C (Nsm^{-3}), h the height of settling tank (m), ρ_p and ρ_0 the respective densities of particle and solvent (kg/m^{-3}), d_p the diameter of particle (m), and g the gravitational acceleration (ms^{-2}).

2.2 Dehydroxylation/metakaolinization of refined dried NOK

The refined NOK was processed to metakaolin using a muffle furnace. 10 g of refined dried NOK in a crucible was heat-treated for 5 min in a muffle furnace pre-heated to a temperature of 550 °C. The sample was removed and cooled, and the weight loss was recorded. This dehydroxylation process was repeated for 10, 15, 30, 60 and 90 min at 550 °C independently. The dehydroxylation process was also carried out at 600 °C, 650 °C, 700 °C, 750 °C for the six different exposure times respectively. The percentage weight losses of NOK at different dehydroxylation temperatures, T , and exposure times are depicted in **Figure 1**.

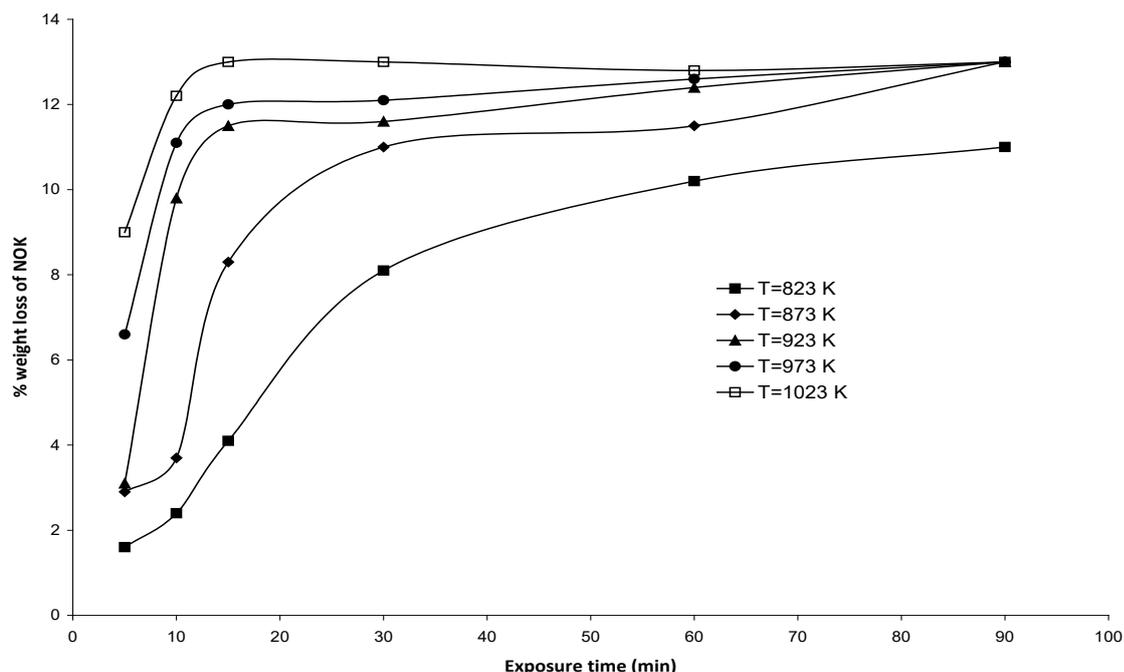


Figure 1: % weight loss of NOK against exposure time at different temperatures

The degree of dehydroxylation, DDH , was obtained using Eq. (2) on the data from weight loss during dehydroxylation:

$$DDH = M/M_{\max} \quad (2)$$

where M is the percentage weight loss (%) and M_{\max} the weight loss on ignition (%).

The results are shown in **Table 1**. The dehydroxylated samples were characterized using XRD, TGA/DTA and BET analyses to confirm production of metakaolin (MK), as presented in **Table 2**.

Table 1. Thermal properties of NOK and metakaolin.

Temperature of calcination (°C)	Time, min	Weight loss % (TGA)	% of total hydroxyls remaining in MK
0		13.04	-
650	60	2.63	20.2
750	15	2.28	17.5

Table 2. BET analysis of NOK, MK650 and MK750.

Parameters	NOK	MK650	MK750
SURFACE AREA (m²g⁻¹)			
BET surface area	14.577	11.781	11.871
Single point surface area at $p/p_0=0.2997$	14.251	11.639	11.708
t-plot micropore area	1.198	2.776	2.506
BJH adsorption cumulative surface area of pores	12.655	9.477	9.695
BJH desorption cumulative surface area of pores	12.630	9.461	9.612
PORE VOLUME (cm³g⁻¹)			
t-plot micropore volume	0.0005	0.0014	0.0013
BJH adsorption cumulative volume of pore	0.0312	0.0283	0.0288
BJH desorption cumulative volume of pore	0.0313	0.0284	0.0289
PORE SIZE (Å)			
BJH adsorption cumulative average pore width (4V/A)	98.748	119.344	118.813
BJH desorption cumulative average pore width (4V/A)	98.970	119.874	120.108

Where, p is the total pressure of the adsorption (mm Hg), p^0 the vapour (or saturation) pressure of nitrogen gas at the temperature of adsorption experiment (mm Hg), and BET and BJH for Brunauer-Emmett-Teller and Barrett-Joyner-Halenda respectively.

The surface area, pore volume and sizes of the NOK and metakaolin samples were determined by the corresponding nitrogen adsorption isotherms at 77.3 K, obtained from Micrometric Analyser. The BET method was used for the corresponding calculations.

3.0 RESULTS AND DISCUSSION

This section presents the experimental results for the raw and refined kaolin, analyses as well as succinct discussion pertaining to the suitability of Nigerian Okpella kaolin for zeolite synthesis.

3.1 Proximate analysis of raw NOK sample

The proximate analysis of the raw NOK sample is presented in **Table 3**.

Table 3. Proximate analysis of the raw NOK sample.

	NOK		Kaolinite	
Elements	Weight (%)	Oxides	Weight (%)	
O	58.6	-	-	
Si	22.9	SiO ₂	55.3	
Al	16.5	Al ₂ O ₃	39.9	
Ti	1.0	TiO ₂	2.4	
Ca	0.5	CaO	1.2	
Fe	0.5	Fe ₂ O ₃	1.2	
Total	100	Total	100	

Loss on ignition, $LOI=13.2(XRF)$

The SEM-EDS and XRF analyses of the raw NOK are shown in **Table 3**. These reveal that NOK is a high quality kaolin with its kaolinite composition: 55.3 % SiO₂, 39.9 % Al₂O₃, and 13.2 % H₂O, thereby comparing favourably with the theoretical composition of kaolinite in terms of oxides given as follows: 46.54 % SiO₂, 39.5 % Al₂O₃, 13.96 %; H₂O. The high composition of silicon (IV) oxide in the raw NOK is due to the presence of the secondary mineral, quartz. The silicon to aluminum molar ratio of NOK is 1.32 while the silicon to aluminum oxide ratio is 2.35. The percentage impurities of titanium, calcium and iron in the raw kaolin are very low as well as low percentage impurities of TiO₂, CaO and Fe₂O₃ in kaolinite.

3.2 Characterization of raw and refined NOK

The raw NOK was characterized using XRD, SEM, EDS and XRF. **Figures 2(a)-(c)** show the SEM-EDS analysis and SEM micrograph of raw NOK. These figures confirm the crystalline structure of the NOK.

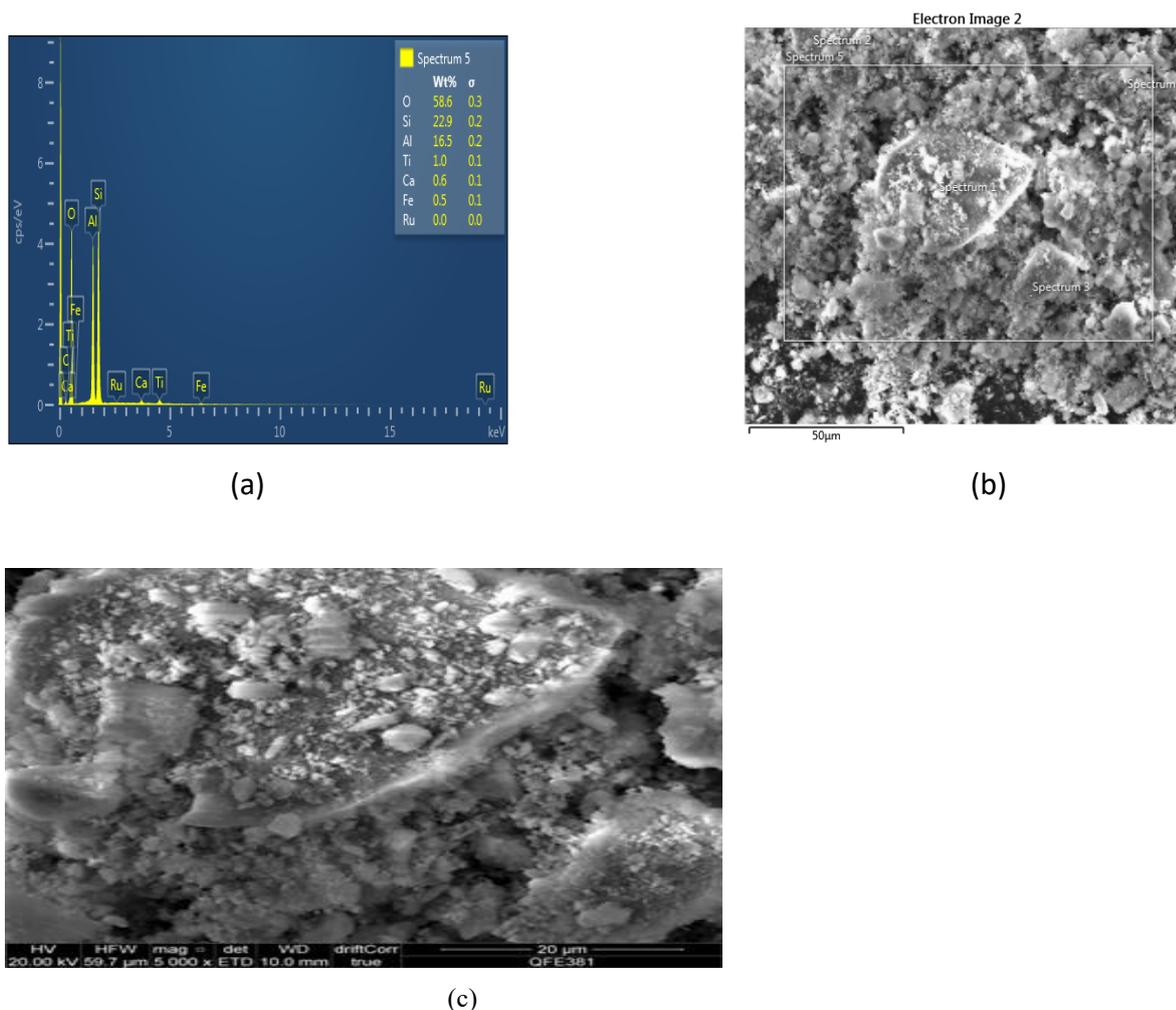


Figure 2: (a) EDS; (b) SEM analysis, and (c) SEM micrograph of raw NOK.

The respective XRD patterns of the raw and refined NOK are shown in **Figures 3(a)** and **3(b)** respectively, with comparative analysis of the XRD pattern of diffractograms in **Figure 3(c)** with the standard XRD pattern of kaolinite clay in literature. The results show that NOK is kaolinite clay with few peaks of the secondary minerals. The sharp peak with high intensity at $2\theta=12.4^\circ$ ($d=7.15 \text{ \AA}$) is the characteristic peak used in the identification of kaolin (Chandrasekhar and Ramaswamy, 2007; Lori, *et al.*, 2007; Kovo, 2010). Further analysis of the diffractograms indicates the reflection of quartz at $d=3.36 \text{ \AA}$. Natural kaolin deposits are predominantly an association of kaolinite and quartz (Eva Mako, 2001) and as such the high concentration of quartz in NOK is not unexpected. Other impurities found with kaolin include anatase, and non-crystalline hydroxide of iron. The level of each impurity in individual kaolinite deposit depends on location and geology of the deposit. However, the diffractogram of the refined kaolin, Fig. 3b, shows that some impurities were removed and the quantity of quartz in the kaolin was reduced through refining, making the kaolin suitable for the synthesis of zeolite.

3.3 Conversion of NOK to metakaolin

Figure 1 shows the degree of dehydroxylation through thermal treatment (calcination) of the refined kaolin at various temperatures and exposure times in a muffle furnace. The region ($0.9 < \text{DTG} < 1$) is generally accepted as the metakaolinite region (Rahier *et al.*, 2000). The optimal calcination parameters for which nearly complete dehydroxylation of the kaolin

occurred were at 750 °C and exposure time of 15 min. This is confirmed in the diffractograms in **Figures 4(a)** and **4(b)**.

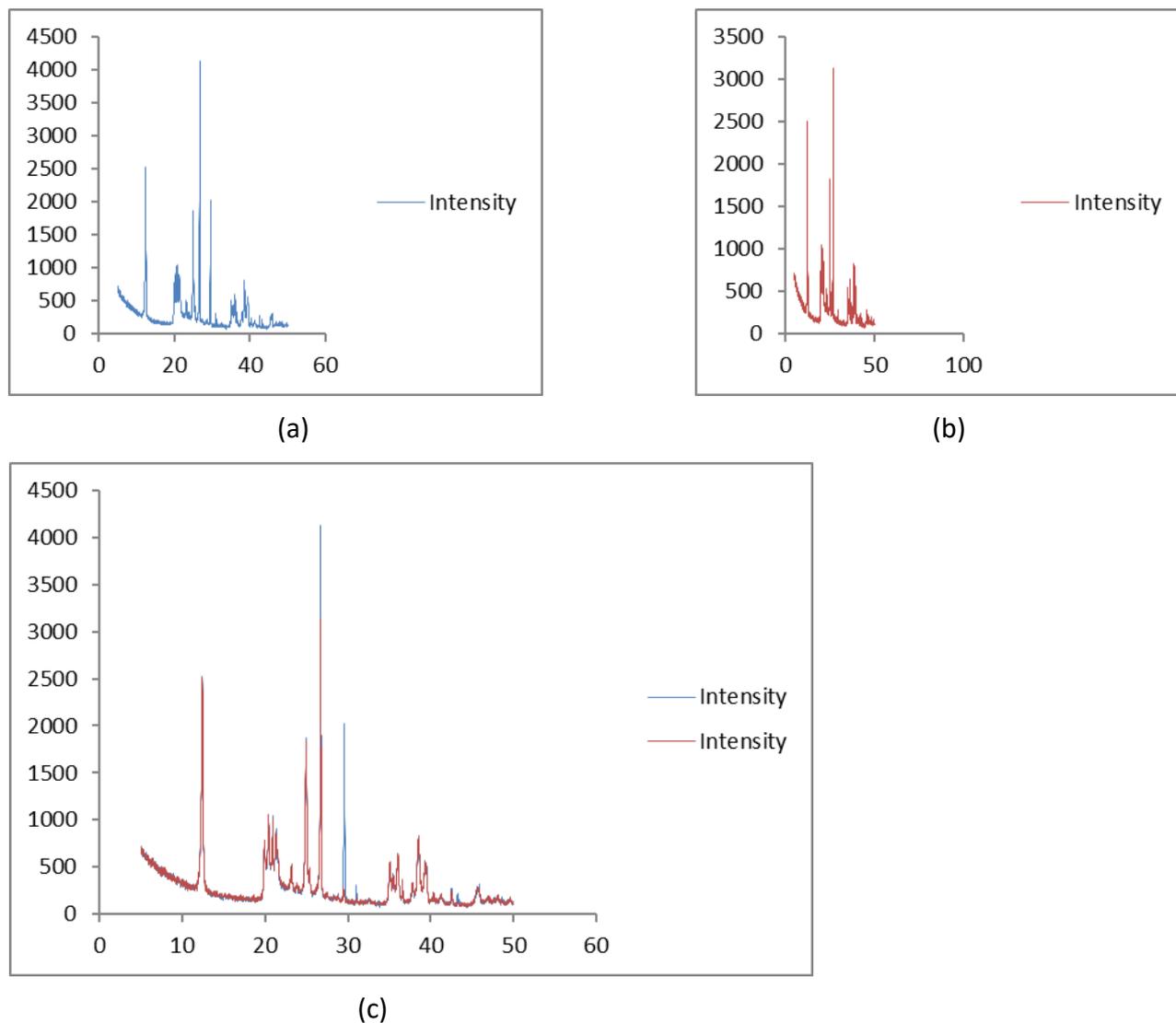


Figure 3: XRD pattern of (a) raw NOK, (b) refined NOK and (c) raw and refined NOK at 2 theta degree where the ordinate and abscissa represent intensity and 2θ (°C).

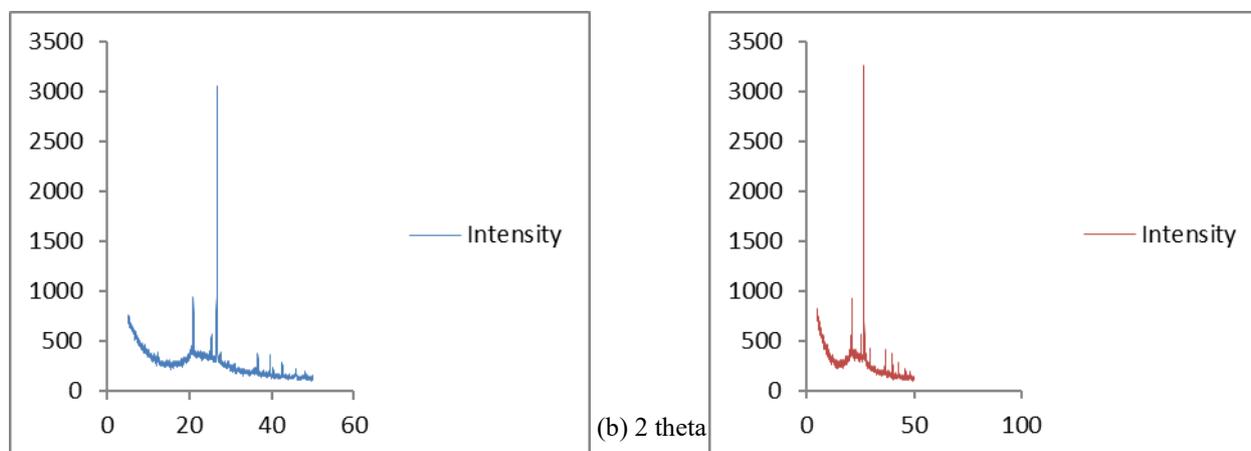
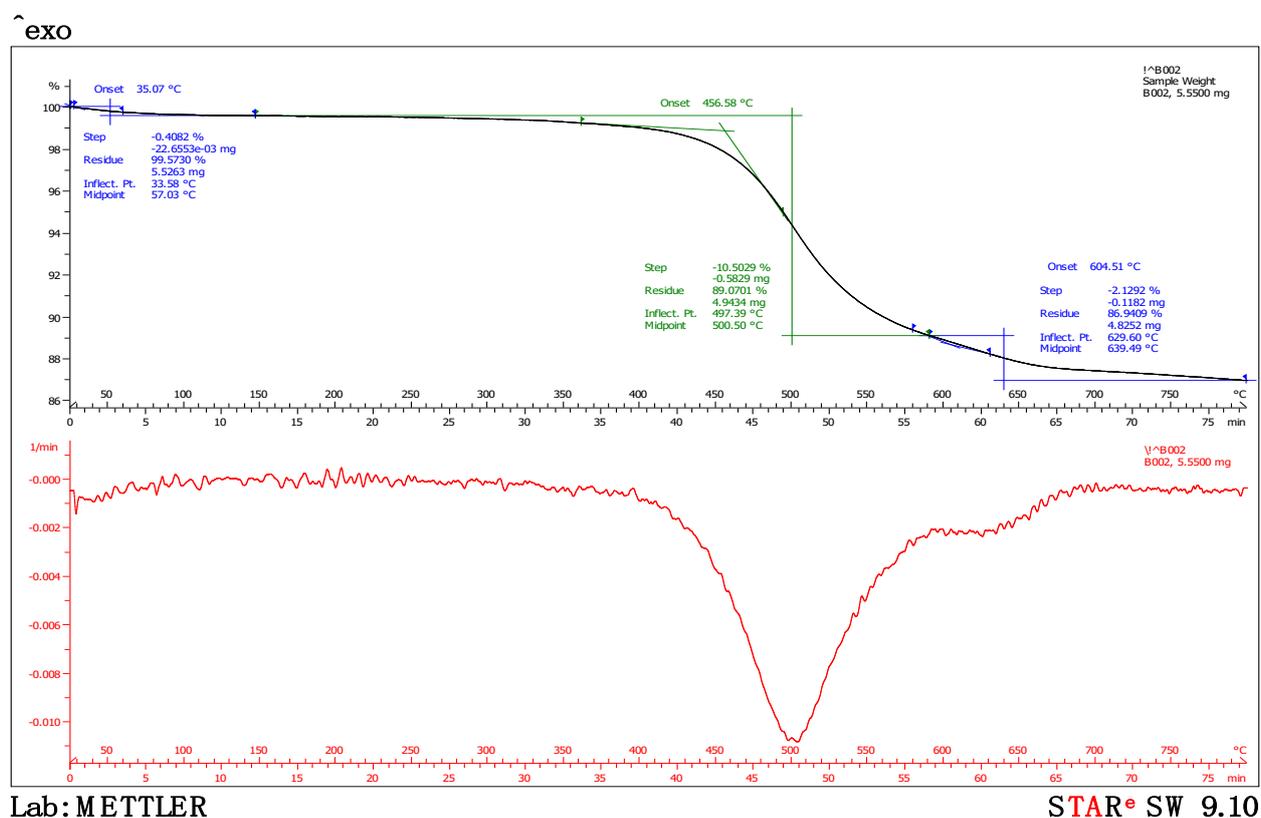


Figure 4: XRD pattern of metakaolin at (a) 750°C for 15 minutes (MK750) (b) 650°C for 60 minutes (MK650), where the ordinate and abscissa represent intensity and 2θ (°C).

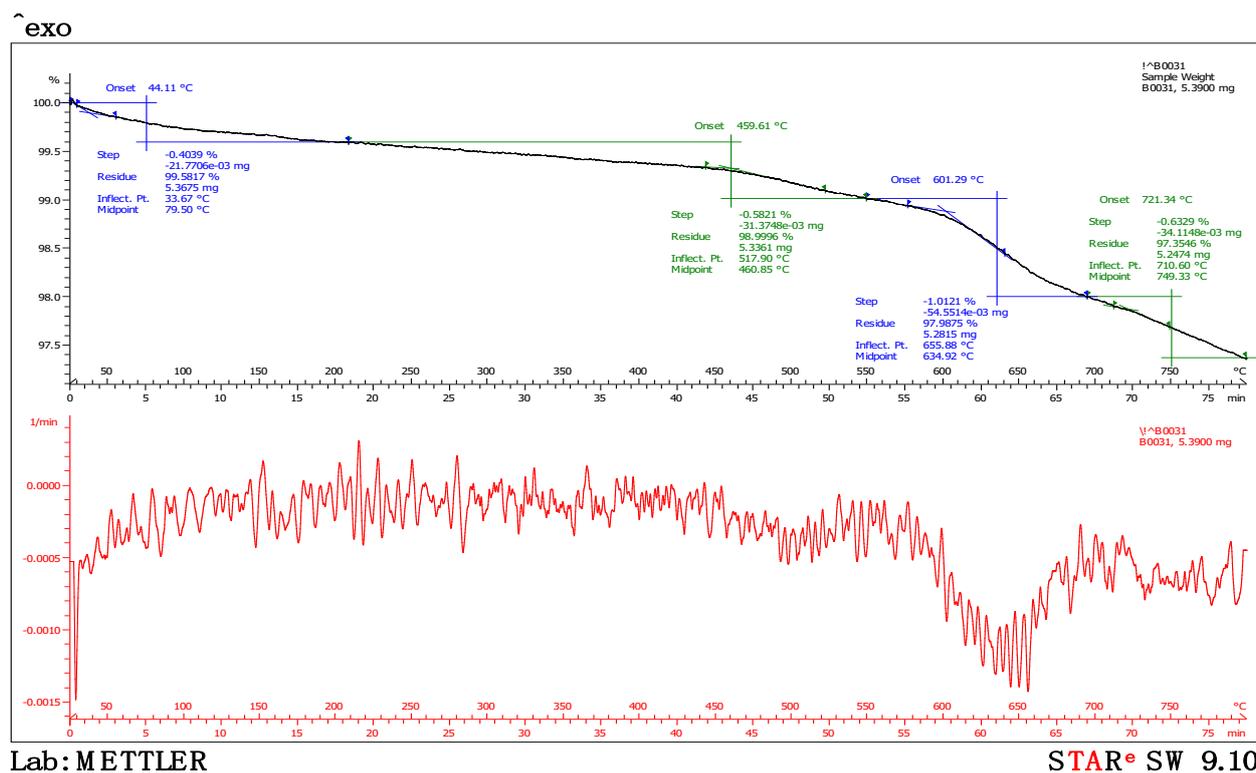
Figure 4(a) presents a broad featureless hump extending between 2θ of 12 to 37.9° indicating the transformation of kaolinite to an amorphous phase, metakaolin. A sharp peak of very low intensity of anatase impurity could be seen at 2θ of 24.95° and sharp peaks of quartz at 2θ of 20.9° , 26.73° , 37.9° and 42.5° . The appearance of quartz peaks indicates the presence of some of the silica in the form of free quartz. In the same trend, the anatase presence is a common feature of most calcined kaolin as a reflection of the TiO_2 crystallization at the high temperature of calcinations (Alkan *et al.*, 2005; Mostafa *et al.*, 2011). The presence of both secondary minerals (quartz and anatase) and the low iron content does not significantly affect the crystallization of zeolite, notwithstanding a slight decrease in the conversion degree (Basaldella, 1998; Alkan, *et al.*, 2005; Mostafa, *et al.*, 2011). The calcined NOK sample at $750^\circ C$ for 15 min is therefore a good precursor for zeolite synthesis.

3.4 DTA/TGA analysis

The Differential thermal analysis (DTA) and Thermogravimetric analysis (TGA) of raw NOK, thermally treated NOK at $650^\circ C$ for 60 min and thermally treated NOK at $750^\circ C$ for 15 min are shown in **Figures 5(a)-(c)** respectively. These analyses reveal the thermal properties of the Nigerian Okpella kaolin and metakaolin. The characteristic endothermic peak of kaolinite was observed at around $500^\circ C$, which is consistent with kaolinite (Robert and White, 1966; Bloodworth *et al.*, 1993; Foldvari, 2011). The total weight loss on heating NOK is about 13.04 % (TGA) within the range of 500 to $650^\circ C$. About 20 % of this water remains in the sample MK650 and only about 17 % of it in MK750. It is reported that metakaolin has a structure containing approximately 11 % of the total hydroxyls in the clay over most of its stability range (Brown *et al.*, 1985; Bloodworth *et al.*, 1993; Chandrasekhar, 1996). The MK750 sample therefore gives a structure closer to the ideal metakaolin structure. The refined kaolin has an estimated kaolinite content of about 90.23 % (Bloodworth *et al.*, 1993).



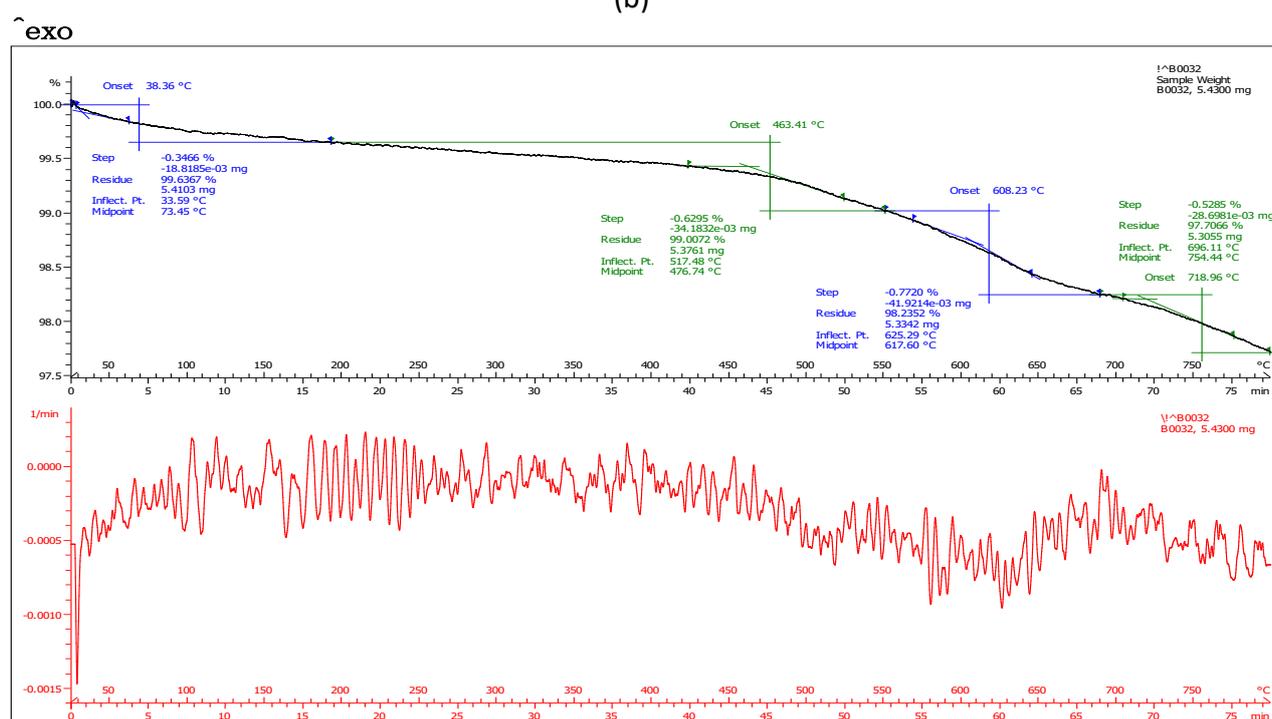
(a)



Lab: METTLER

STAR[®] SW 9.10

(b)



Lab: METTLER

STAR[®] SW 9.10

(c)

Figure 5: TG/DTG of (a) raw NOK, (b) thermally treated NOK at 650 °C for 60 minutes, (c) thermally treated NOK at 750 °C for 15 minutes.

3.5 BET surface area and BJH pore size/volume

The nitrogen adsorption-desorption isotherms for the NOK, MK650 and MK750 samples were typical type IV isotherms according to the BET classification (Liew *et al.*, 1985; Olaremu, 2015). The three isotherms are of sigmoid shape with an inflexion point at low relative pressure region, a gentle slope at intermediate pressure region (figure not shown). Small hystereses

were observed for the three samples at relative pressure above 0.45. According to the de Boer classification (1968), these are type A hystereses which are characterised by steep and narrow hysteresis loops. This type of hysteresis is usually obtained with cylindrical pores. This is consistent with the computer prediction performed for kaolinite by Christian *et al.* (1981), who showed that cylindrical pore model provides a reasonable fit for both branches of the isotherms of MK650 and MK750.

The NOK and metakaolin samples produced straight lines for the BET plots between relative pressure regions of 0.05 to 0.30 as shown in **Figures 6 and 7**, where Q is the volume of nitrogen gas adsorbed (cm^3). From these plots, the BET surface areas of the NOK, MK650 and MK750 were determined to be $(14.5773 \pm 0.0894) \text{ m}^2\text{g}^{-1}$, $(11.7811 \pm 0.1245) \text{ m}^2\text{g}^{-1}$ and $(11.8714 \pm 0.1197) \text{ m}^2\text{g}^{-1}$ respectively with the respective coefficient of determination, $R^2 = 0.9998, 0.9995$ and 0.9996 . The volume of nitrogen gas required to cover the surface of the adsorbent with a unimolecular layer was found to be $3.3486, 2.7063$ and $2.7271 \text{ cm}^3\text{gmol}^{-1}$ at STP. The BET surface area of NOK is within the reported acceptable range for kaolinite (Liew *et al.*, 1985; Bloodworth *et al.*, 1993). There is a little decrease in the BJH adsorption-desorption cumulative volume of pore of the NOK and the metakaolin (MK650 and MK750) showing the refractoriness of the kaolin because as temperature increases during calcination, the pore volume and porosity decrease (Bloodworth *et al.*, 1993).

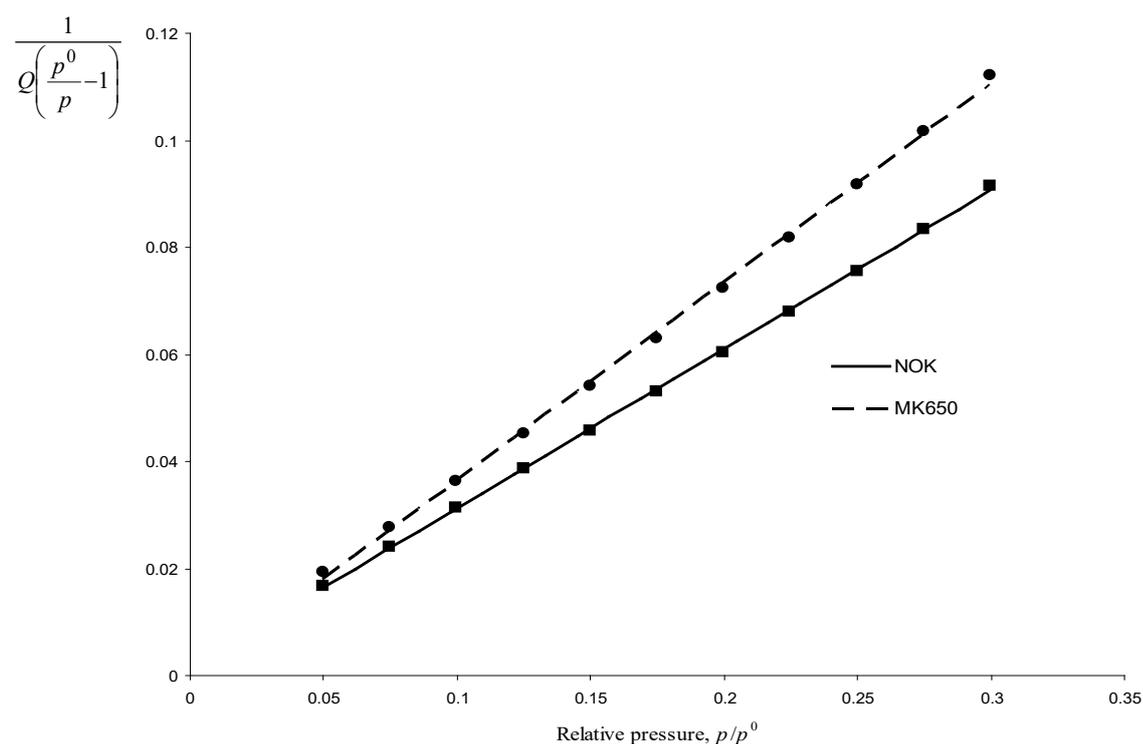


Figure 6: BET surface area plots for NOK and MK650.

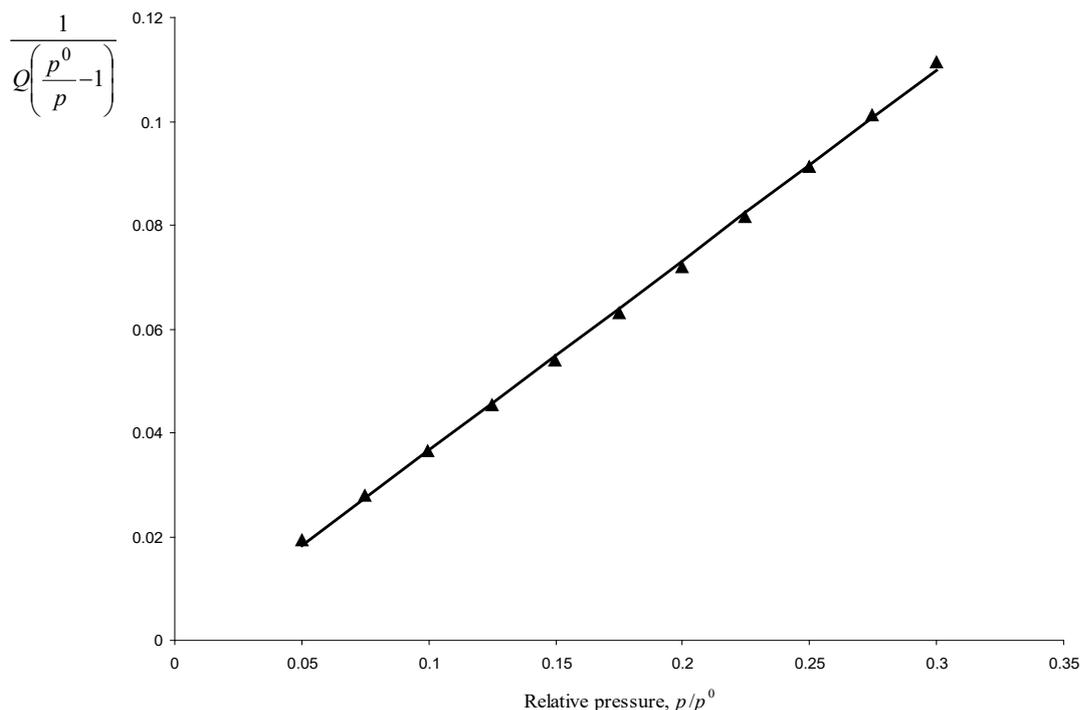


Figure 7: BET surface area plot for MK750.

4. CONCLUSIONS

The characterization and evaluation of Nigerian Okpella kaolin and metakaolin have been carried out. The XRD and SEM-EDS analyses confirmed that Nigerian Okpella clay is kaolinite clay with few peaks of the secondary minerals like quartz. Impurities and secondary clay minerals were eliminated or reduced by beneficiation of the NOK. The XRD and TGA/DTA confirmed that 750 °C and exposure time of 15 minutes were the optimal calcination parameters, for which nearly complete dehydroxylation of the kaolin was achieved to obtain metakaolin. The BET surface areas of NOK, MK650 and MK750 were determined to be $(14.5773 \pm 0.0894) \text{ m}^2\text{g}^{-1}$, $(11.7811 \pm 0.1245) \text{ m}^2\text{g}^{-1}$ and $(11.8714 \pm 0.1197) \text{ m}^2\text{g}^{-1}$ respectively with $R^2 = 0.9998$, 0.9995 and 0.9996. The BET surface area of NOK was within the reported acceptable range for kaolinite. Hence, Nigerian Okpella kaolin or metakaolin is a good precursor for zeolite synthesis.

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