

Preparation and Characterization of Zeolite type 4A using Kaolin from Ajebo, Nigeria

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ABSTRACT

This work investigates the hydrothermal synthesis and characterization of zeolite-4A from kaolin found in Ajebo, Nigeria calcined at 700 and 900°C respectively. The synthesized zeolite-4A was further characterised using X-ray Fluorescence (XRF), Fourier Transform Infrared spectrometer (FTIR), Scanning Electron Microscopy (SEM), X-Ray diffraction (XRD), Brunauer-Emmet-Teller (BET) surface area analysis as well as Differential Thermal Analysis/Thermo-gravimetric (TG). Water adsorption capacity tests were also carried out on the synthesized zeolite-4A. The results from the XRF measurements indicated that the amount of Al₂O₃ and SiO₂ in the studied kaolin was similar to the standard kaolin composition making it a perfect candidate for zeolite-4A synthesis. FTIR showed the characteristic zeolite peaks while XRD confirmed the crystalline nature of the synthesized zeolite-4A. TG studies showed that the zeolite-4A samples were stable up to temperatures of 700°C. This stability as well as the surface area and pore size of 7 Å makes it potentially suitable for use in water treatment applications. The SEM showed cubic crystals which were

typical of the morphology of zeolite-4A with water adsorption capacity of approximately 29%. These results indicate that zeolite-4A can be synthesized from kaolin found in Ajebo as an inexpensive alternative to traditionally sourced materials and also is suitable for use as adsorption agent.

Keywords: Adsorption agent, Ajebo kaolin, hydrothermal, metakaolin, zeolite-4A

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INTRODUCTION

Zeolites are commonly synthesized via hydrothermal methods with commercial chemicals as the primary sources of silica (SiO_2) and alumina (Al_2O_3) (Barrer, 1982). Chemicals such as sodium metasilicate, sodium aluminate, silica gel, tetraethylorthosilicate (TEOS) and aluminium hydroxide are used as precursor materials resulting in high purity, smaller pore sized zeolites. However, this pathway of production is complex and expensive thereby restricting the use of these materials in many industrial applications (Barrer, 1982; Breck, 1974; Chiang & Chao, 2001). As an example, a cost comparison of obtaining SiO_2 and Al_2O_3 sourced from a chemical feedstock of kaolin shows that by using kaolin as the precursor material, a cost advantage of about 15% over commercial chemical can be achieved (Vaculikova et al., 2011). The use of raw materials such as readily available and relatively cheap kaolin in zeolite synthesis is highly desirable as they contain SiO_2 and Al_2O_3 in the correct stoichiometry (Atta et al., 2007; Chandrasekhar, 1996; Chandrasekhar & Pramada, 1999; Yaping et al., 2008).

According to the report by Ugal et al. (2010) and the database of zeolite structures, zeolite type A or the Linde Type A (LTA), zeolites can be classified into three different grades, 3A, 4A and 5A, all of which possess the same general formula but with different structural cation types. When 75% of the Na^+ in type 4A is replaced by K^+ , it is referred to as type 3A zeolite, alternatively replacing the Na^+ in type 4A by Ca^{2+} gives rise to zeolite type 5A.

Kaolin composition varies with location and the presence of impurities has an effect on the conversion to the final zeolite products (Bergaya et al., 2006). Therefore, it is important to source the material from a reliable region, hence, the significance of studying Ajebo kaolin as an inexpensive alternative with regards to the major zeolite properties such as adsorption.

The aim of this study was to synthesize and characterize zeolite-4A using kaolin from Ajebo as the precursor material and also to examine the effect of calcining at different temperatures.

MATERIALS AND METHODS

Sample Preparation

The base materials used in this research were kaolin from Ajebo (located in Ogun state, Nigeria with GPS coordinate 7.1229° N, 3.6585° E), NaOH and de-ionised water. The zeolite-4A was prepared according to the following procedure: The kaolin was initially crushed, ground and wet beneficiated to improve overall purity. After allowing the kaolin to soak for 24 hours, the top water and kaolin were separated by decantation. The slurry was sieved using a Tyler mesh sieve of mesh size 200 (75 μm aperture opening), allowed to

settle and the supernatant water layer decanted in regular intervals until the slurry became thick. The thick slurry was then poured into a fabric sieve to drain off all the remaining liquid and pressure was applied until a cake like mass is formed. Finally, the solid cake was broken into smaller pieces and dried for 3 days after which it was milled in a ball milling machine made of steel cylinder, lined with ceramics to prevent contamination and loaded with ceramics ball with a ball to powder ratio (BPR) of 10:1 for 6 hours at a speed of 60 rpm. The calcination of the kaolin was done by controlled heating at a rate of 5°C/min in a muffle furnace at 700 and 900°C respectively and held at these temperatures for 2 hours followed by cooling in air. This process helps in the conversion of the unreactive and highly stable kaolin to a more reactive and less stable metakaolin which easily accepts and exchanges ions in its lattice.

The metakaolin was mixed with NaOH and deionised water in the ratio 0.6:0.8:12. The mixture was aged for 24 hours with intermittent mechanical stirring. Crystallization was achieved by heating the mixture in an oven operating at a temperature of 100°C for 6 hours. After crystallization the synthesized zeolite-4A was washed three times with distilled water to remove any excess unreacted NaOH. The synthesized zeolite-4A was placed into a centrifuge rotating at a speed of 20 rpm for 20 minutes to separate the zeolite from the water. After the water has been decanted, the residual zeolite-4A was dried in an oven at 110°C for 6 hours.

Sample Characterization

The composition of the kaolin and the as-synthesized zeolite-4A were analysed using an XRF (AXIOS, PANalytical, Netherlands). The samples were pressed into 6 mm thickness pellets using wax as a binder with a pellet to wax ratio of 11:3. The thermal analyses (Differential Thermal Analysis/Thermogravimetric (DTA/TG, Netzsch STA 409 C, Germany) were carried out in 50 mL/min argon flow from 20 to 800°C at a heating and cooling rate of 5°C/min respectively.

Synchrotron X-Ray diffraction measurements were done at the Deutsches Elektronen Synchrotron (DESY) radiation facility in Hamburg at the beamline P02.1 of PETRA III at a photon energy of 60 KeV ($\lambda = 0.20716 \text{ \AA}$). The data were collected with a Perkins Elmer 2D detector and radially integrated in 5° steps (Dippel et al., 2015; Herklotz et al., 2013). The Fourier Transform Infrared spectroscopy was carried out with a Shimadzu IR Affinity-1S (Shimadzu Corporation, Japan). The powder samples were pressed into pellets by mixing with dried KBr and placing them in a pre-heated die under a heat lamp. The pellets were degassed at 120°C for 1 hour prior to obtaining the spectra. The spectra typically had an average of 128 scans with 1 cm⁻¹ resolution. The infrared spectra were acquired in transmission mode while the recorded peaks were based on percentage transmittance to the given wavelengths.

The morphology of the samples was acquired using SEM (ASPEX 3020, Aspex Corporation, USA). The samples were coated with 10 nm of gold to inhibit charging and improve the secondary electron signals. The Brunauer-Emmett-Teller (BET) nitrogen adsorption and surface area analysis were carried out using a Micromeritics ASAP 2020 porosity analyzer (USA). The samples were initially degassed at 80°C under vacuum for 40 hours while the cold and warm free space values were determined using Helium. The samples were subsequently degassed again at 350°C for 8 hours under vacuum and N₂ sorption determined using the previously measured free space values. The water adsorption capacity of the zeolite-4A was measured using a custom-built apparatus where high humidity air flow was introduced to a sample of the zeolite-4A. The increase in weight of the zeolite-4A with adsorbed water was then measured after 24 hours.

RESULTS AND DISCUSSION

Composition Analysis

The chemical composition of the kaolin and the synthesized zeolite-4A is shown in Table 1. The major constituents in the kaolin are SiO₂ and Al₂O₃ representing 51.38 wt.% and 42.05 wt.% respectively with a SiO₂/Al₂O₃ ratio of approximately 1. The amount of Fe₂O₃ in the kaolin is less than 1 wt.% making it suitable for use in zeolite synthesis. Since the XRF of the zeolite-4A synthesized from kaolin calcined at 700 and 900°C is similar, the XRF of the zeolite-4A synthesized from kaolin calcined at 900°C was presented in Table 1. The amounts of Na₂O in the zeolite increased from 0.75 to 3.42 wt.%. This increase in the amount of Na₂O is due to the introduction of NaOH during the zeolite-4A synthesis. While all components present in the kaolin can be seen in the synthesized zeolite-4A indicating that the kaolin is stable at temperatures below 900°C.

Table 1
The chemical composition of Ajebo kaolin and Zeolite-4A

	Compound Amounts (weight %)									
	SiO ₂	Al ₂ O ₃	Fe ₂ O ₃	CaO	MgO	TiO ₂	Na ₂ O	K ₂ O	MnO	L.O.I
Kaolin	46.48	39.81	0.79	0.16	0.034	1.99	0.75	0.3	0.001	9.68
Zeolite-4A	58.9	22.76	0.15	0.05	0.05	0.019	3.42	0.89	0.005	13.756

Fourier Transform Infrared Spectroscopy (FTIR)

The FTIR spectra of the zeolite-4A synthesized from kaolin calcined at 700 and 900°C are shown in Figure 1. The FTIR spectra of the kaolin and metakaolin have been discussed elsewhere (Mgbemere et al., 2018). Both spectra show similar wavenumbers with a well-defined peak at 1000 cm⁻¹ and 1655 cm⁻¹. There are differences in wavenumbers between the zeolite-4A calcined at 700°C and 900°C. This includes the absence of peaks

at wavenumbers, 2200 cm^{-1} and 1500 cm^{-1} for the 900°C sample and differences in the peaks below wavenumbers 800 cm^{-1} . It has been enlarged to the right to highlight the differences which are associated with the degree of conversion from the metakaolin to zeolite-4A. The samples calcined at 900°C converted better than those at 700°C . The most significant vibration at 1000 cm^{-1} region is assigned to a T-O (where T can be an Al or a Si ion) stretching which involve motions that are primarily either associated with oxygen atoms or described as an asymmetric stretching mode $O-T \leftrightarrow O$ (Mozgawa et al., 2005).

The weak peaks below 1000 cm^{-1} wavenumber are possibly due to the vibration involving the $\equiv\text{Al-OH}$ nests created by the cation vacancies. The peaks at $700\text{-}750\text{ cm}^{-1}$ corresponds to the symmetric stretching vibration of SiO_4 groups while the bands around $450\text{-}650\text{ cm}^{-1}$ are related to either bending vibration of SiO_4 groups or in the vibration modes of the 4-membered rings of the silicate chains. The splitting of the peak at this region which is possibly due to higher O-Si-O angles in the structure (Kovo, 2011). The weak broad band at $3700\text{-}4000\text{ cm}^{-1}$ is attributed to the stretching vibration of both hydrogen group of H_2O molecules and amines present in the pores of the zeolites. After calcination, H_2O is reintroduced during the process of zeolite formation. The peaks between 1500 and 1700 cm^{-1} are from the bending vibration of H_2O while those at 3300 cm^{-1} and 3500 cm^{-1} are as a result of the OH stretching modes (Mozgawa et al., 2005).

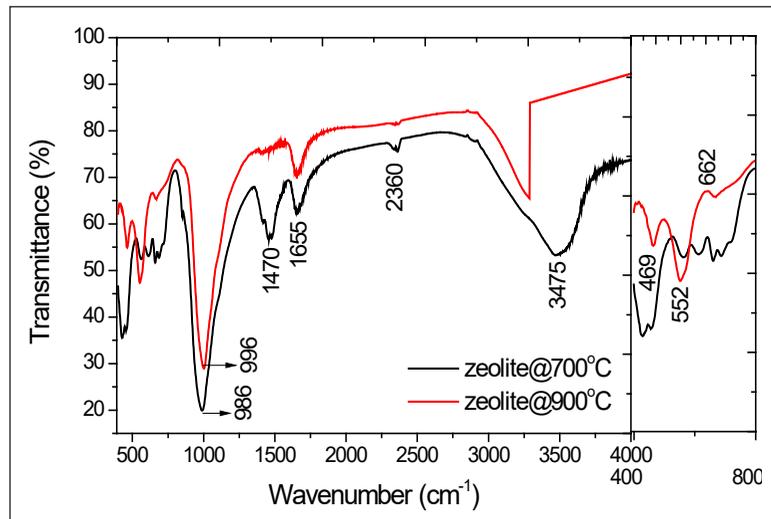


Figure 1. A graph of Transmission as a function of wavenumber for zeolites-4A samples from kaolin calcined at 700°C and 900°C . The inset on the right is the enlargement of the wavenumbers from 400 to 800 cm^{-1}

X-ray Diffraction

The XRD patterns for the synthesized zeolite-4A from kaolin calcined at 700 and 900°C measured under normal conditions are shown in Figure 2. Both heat treated samples show Bragg angles correlated to the formation of zeolite-4A as seen in 74-1183-ICDD, 2001

(Baerlocher et al., 2007; Ugal et al., 2010) and confirmed by the Structural Commission of the International Zeolite Association (Treacy & Higgins, 2001). The difference between the zeolites produced from calcining at both temperatures is in the intensity of their peaks as the zeolite calcined at 900°C has slightly more intense peaks indicating that the zeolite-4A synthesized from kaolin calcined at 900°C is more crystalline than that synthesized from kaolin calcined at 700°C. Zeolite-4A is the major constituent phase while the impurity phases are from quartz, hydroxysodalite and possibly unconverted metakaolin. The extra peaks observed in the patterns are due to the presence of other oxides associated with the precursor kaolin material.

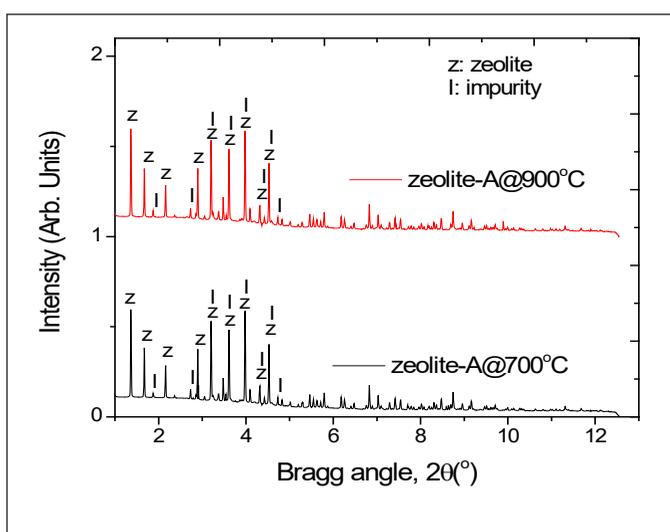


Figure 2. High resolution x-ray diffraction ($\lambda = 0.20716\text{\AA}$) patterns for zeolite-4A samples obtained from kaolin calcined at 700°C and 900°C respectively

Thermal Analysis of Zeolite-4A

The TG/DTA graphs of the zeolite-4A synthesized from kaolin calcined at 700 and 900°C are presented in Figure 3. Both zeolite samples exhibit very comparable trends in the TG/DTA measurements. The mass loss during the TG measurements is approximately 13.67% for both zeolite-4A samples. This value is similar to that of the loss on ignition (LOI) from the chemical analysis in Table 1. The DTA graph is used to show the reactions (exothermic and endothermic) that took place as samples were heated from room temperature. Strong exothermic reactions are observed at 243.09°C and 247.56°C for the zeolite synthesized from kaolin calcined at 700°C and 900°C respectively. The absence of a loss at temperatures below 100°C may be due to the absence of physically adsorbed moisture as the zeolites were effectively dried after synthesis. The DTA curves for the zeolite-4A indicate that the zeolites are stable at temperatures up to 700°C.

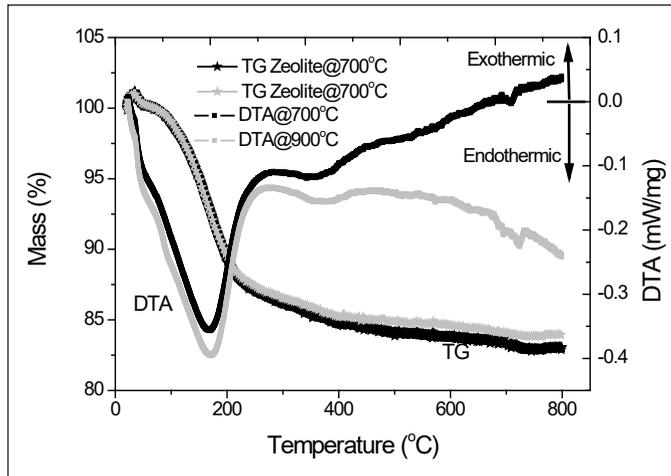


Figure 3. TG/DTA curves for Ajebo zeolite-4A calcined at 700°C and 900°C respectively. The data was acquired on heating the sample from room temperature

Scanning Electron Microscopy

The SEM image of the zeolite-4A synthesized from kaolin calcined at 700 and 900°C are presented in Figure 4. The morphology of the zeolite-4A samples shows cubic crystalline structures with well-defined edges with average sizes of 5 μm as well as aggregates especially for zeolite-4A calcined at 700°C. The EDS of the aggregates show that the major elements Al, Si, O and C are present. The starting materials for the synthesis of zeolites have an effect on the size of the zeolite-A crystals produced. Naturally occurring raw materials such as kaolin and fly ash tend to form larger zeolite crystals due to the presence of other oxides such as F_2O_3 , CaO, and MgO in the kaolin (Petkowicz et al., 2008). These

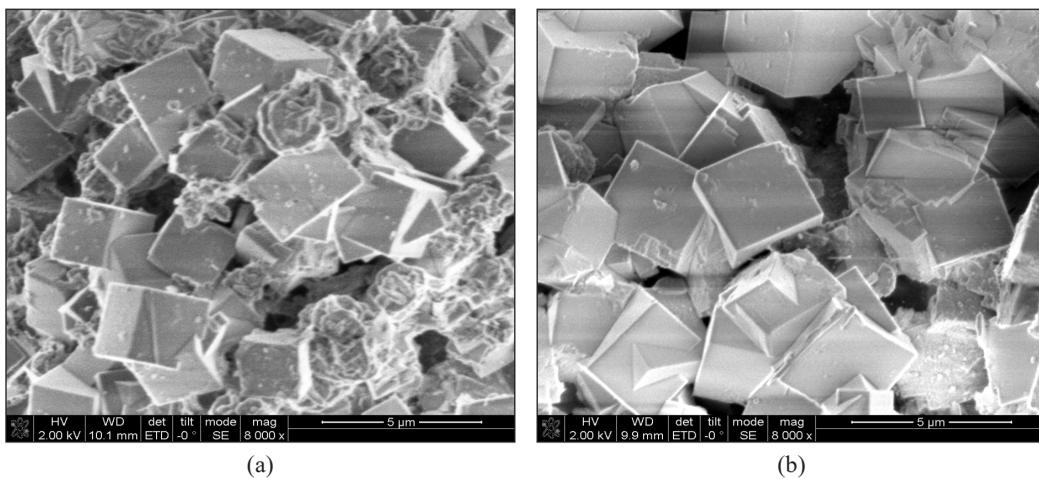


Figure 4. Scanning electron microscope images for Zeolite-4A synthesized from kaolin calcined at (a) 700°C and (b) 900°C

oxides serve as heterogeneous nucleation sites for the crystals and also help to quicken the crystallization kinetics. The nature of the metakaolin used to synthesize the zeolite can also determine the shape of the crystals. For instance for kaolin that has not completely undergone the meta-kaolinization process during the synthesis of zeolite-4A, Sodalite is produced instead of Zeolite-A (Reyes et al., 2010; Zhao et al., 2010). The Si/Al ratio also appears to have an effect on the shape of the crystals. For example, when the Si/Al ratio is 1.5, beveled edges as opposed to sharp well defined edges are obtained (Ismail et al., 2010).

Pore Size Analysis

The BET surface area, Langmuir surface area, pore volume and pore size of both samples have been summarized in Table 2. Both zeolites have lower surface areas due to the larger crystal size described in the previous section. Moreover, the surface area of each sample decreased with an increase in calcination temperature used during the process of zeolite synthesis. Higher calcination temperature results in a decrease in surface area and this can be attributed to the further crumbling and shrinkage of the metakaolin structure at high temperatures. The pore volume and pore size increases with an increase in calcination temperature hence, the sample calcined at a higher temperature (900°C) appears to have a looser amorphous structure than that calcined at lower temperature (700°C). The pore size of the zeolite-4A synthesized from Ajebo kaolin is higher than that reported for type A zeolite which is approximately 4Å (Mgbemere et al, 2017; Ugal et al., 2010) when pure Al₂O₃ and SiO₂ are used. The difference in pore size between the zeolite-4A synthesized from pure chemicals and that synthesized from kaolin may be due to the presence of oxides other than SiO₂ and Al₂O₃ in the kaolin. As stated earlier, these impurities serve as nucleation sites for the formation of zeolite crystals hence increasing the pore size of the zeolite (Farang & Zhang, 2012).

Table 2
Brunauer-Emmet-Teller (BET) analysis of zeolites calcined at 700°C and 900°C respectively

	Compound Amounts (weight %)	
	Ajebo 700°C	Ajebo 900°C
BET Surface area (m ² /g)	5.6629	5.5472
Langmuir Surface Area (m ² /g)	5.4165	5.0353
Pore volume (cm ³ /g)	0.009897	0.002000
Pore size (nm)	6.999103	7.58527

Figure 5 shows the BET surface area plot for both zeolite-4A synthesized from kaolin. The changes in surface area and crystallinity have been measured using the BET N₂ adsorption. According to Yates (Yates, 1967), for fresh zeolites, all points falls on a 45° line with no loss in surface area or crystallinity but when majority of the points falls above

the line, it indicates less loss in crystallinity than in surface area while when majority of the points falls below the line it indicate more loss in surface area than in crystallinity.

From figure 5a below, there are 4 points below the 45° line and 4 above it which is an indication that there is an equal amount of losses in the surface area as well as in crystallinity of both zeolites. While from figure 5b all point falls below the 45° line an indication that there are greater lose in surface area than in crystallinity.

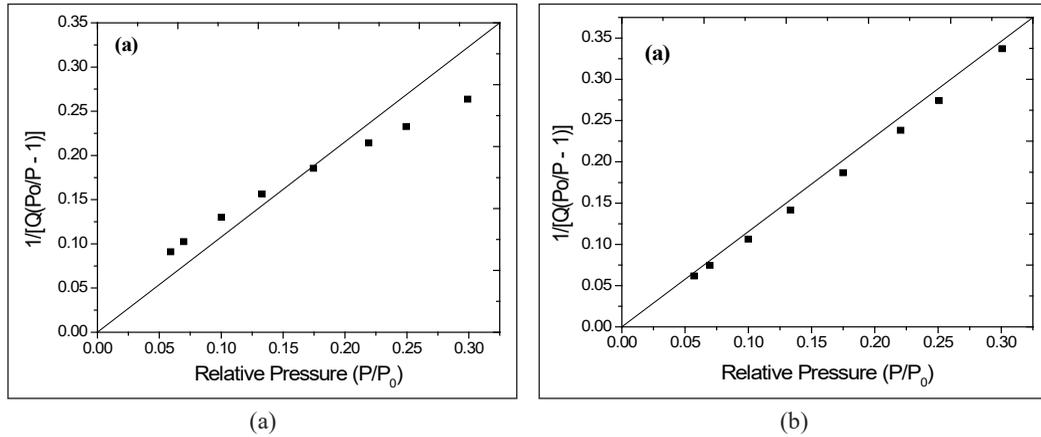


Figure 5. BET surface area plot of zeolite-4a samples from kaolin calcined at (a) 700°C and (b) 900°C

Figure 6 shows the nitrogen adsorption/desorption isotherm for the synthetic zeolite-4A. The location of the hysteresis loop in the N₂ isotherm is a type IV hysteresis loop which is an indication of the presence of mesoporosity. This is used to determine the type of pores present in the zeolite for example, a regular framework pore or inter-particle voids such as

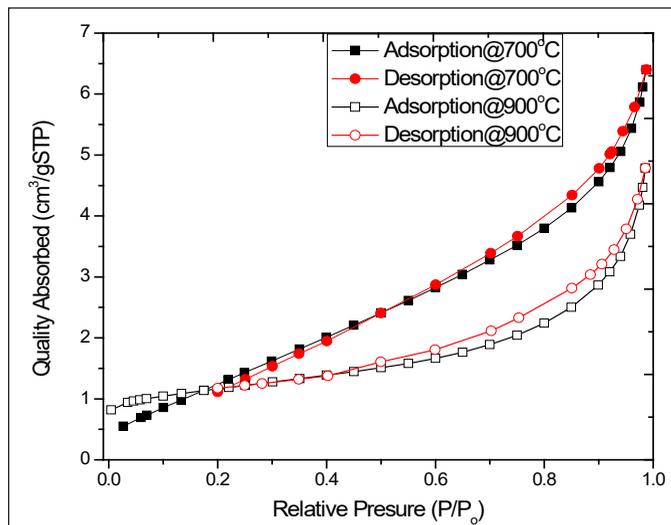


Figure 6. N₂ adsorption/desorption isotherms for the synthesized zeolite-4A samples

a textured pore. The porosity between 0.4 and 0.75 P/P_0 in the N_2 isotherm of the zeolite-4A gives an indication that the porosity is related to a framework porosity and a value between 0.8 and 1 P/P_0 is a textural porosity arising from aggregate voids and spaces formed by intra-particle contacts. The zeolite-4A synthesized from kaolin calcined at 700°C shows a higher rate of adsorption and desorption compared to the zeolite-4A synthesized from kaolin calcined at 900°C, this is as a result of the presence of more amorphous gel in the zeolite-4A synthesized from kaolin calcined at 700°C.

Water Adsorption Capacity Test

Table 3 shows the water adsorption capacity data for zeolite-4A synthesized from kaolin calcined at 700 and 900°C. The synthesized zeolite-4A shows highly promising prospects for water adsorption as the water adsorption capacity was found to be 28.89 and 28.96 % for the zeolite-4A synthesized from kaolin calcined at 700 and 900°C respectively. These are higher than the 25.9 % for commercial zeolite-A reported in the literature (Miao et al., 2009).

Table 3

Water adsorption capacity results for Zeolite-4A synthesized from Ajebo kaolin

Water Adsorption Capacity Test		
	zeolite@700°C	zeolite@900°C
Wt. of Beakers (g)	104.48	48.64
Wt. of Beaker + Wt. of Dry Zeolite-4A (g)	108.12	52.21
Wt. of Beaker + Wt. of wet Zeolite-4A (g)	109.17	53.24
% Water Adsorption	28.89	28.96

CONCLUSION

Crystalline, microporous zeolite-4A was successfully synthesized using Ajebo kaolin as the precursor material. Temperatures of 700 and 900°C were used successfully to convert kaolin to metakaolin for the purpose of synthesizing the zeolite-4A. The DTA/TGA plots showed that both zeolites were stable at temperatures below 700°C with a weight loss of about 13.67 wt.% due to loss of water of crystallization. The FTIR spectra and XRD patterns confirmed the presence of characteristic zeolite peaks with the zeolite-4A synthesized from kaolin calcined at 900°C having higher peaks and intensity indicating better crystallinity than that synthesized from kaolin calcined at 700°C. While the SEM clearly showed the formation of cubic crystal structured zeolite-4A at both calcination temperatures with that synthesized from kaolin calcined at 900°C resulting in more crystals and less amorphous gel. The synthesized zeolite-4A showed promising signs for use in water adsorption, as both had water adsorption capacity of 28.89 and 28.96 % for the zeolite-4A synthesized from kaolin calcined at 700 and 900°C with that from 900°C being slightly higher. The

zeolite-4A synthesized from Kaolin calcined at 900°C showed better properties than that synthesized from kaolin calcined at 700°C.

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