Effect of Crystallization Time on the Hydrothermal Synthesis of Zeolites from Kaolin and Bauxite

B. Kwakye-Awuah, E. Von-Kiti, R. Buamah, I. Nkrumah, C. Williams

Abstract— Kaolin and bauxite were used as alumina and silica sources to synthesize zeolites hydrothermally. The source materials as well as the synthesized zeolites were characterized by X-ray diffraction (XRD) scanning electron microscopy (SEM), energy dispersive x-ray analysis (EDX) and Fourier transformed infrared spectroscopy (FTIR). XRD spectra of the bauxite showed Gibbsite phase whereas that of kaolin gave 32.4 % quartz and 67.6 %. The main phases of zeolites obtained after hydrothermal crystallizations were zeolite types LTA, analcime and zeolite X. Longer crystallization time resulted in phase change of the zeolites into sodalite. Hence, natural raw materials such as bauxite and kaolin have the attractive features of providing the staring reagents for the synthesis of ultrapure synthetic zeolites.

Index Terms— Synthesis, hydrothermal, zeolites, characterization, kaolin, bauxite, time.

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1   INTRODUCTION

Zeolites are microporous aluminosilicate with crystalline structure and unique ion exchange and sorption properties. They consist of either a silicon or aluminum atom as the center linked with four oxygen atoms at the corners in a tetrahedral manner. The tetrahedra are connected in such a way that cavities form [4 – 10]. The negative charge of the tetrahedra is balanced by cations such as ions of hydrogen, sodium, potassium, magnesium, calcium and ammonium. They are known as molecular sieves since the dimension of the pore tend to adsorb molecules of certain dimensions while rejecting those of larger dimensions [14]. Zeolites are of considerable commercial importance in their applications ranging from water softening to catalysis in the petrochemical industry [18] Zeolites occur naturally and synthetically (laboratory tailored ones). Extensive use of zeolites in terms of their applications has resulted in rapid increase in the large scale consumption which requires developments to synthesize zeolites from inexpensive sources. Synthetic zeolites are used more often than natural zeolites due to the purity of crystalline products and the uniformity of particle sizes [11]. Since the principal raw materials used to manufacture zeolites are silica and alumina, which are amongst the most abundant mineral components on earth, the potential to supply raw materials for zeolites synthesis is virtually unlimited [7].

Different clay minerals have been used as a starting material for zeolites synthesis: kaolinite [17, 20]., montmorillonite [20], bentonite [15], halloysite [2], interstratified illite–smectite [1], among others. Natural zeolites have been also used to synthesize zeolites possessing properties better than those of the starting material [19]. Kaolin is one of the most versatile industrial minerals and used extensively for many applications [21]. The synthesis of NaA zeolite from kaolin source has been worked on since 1970 [11] by the hydrothermal reaction of dehydroxylated kaolin with NaOH solution. Kovo and Holmes [2] and Reyes et al [12] have also synthesized zeolite from kaolin. Kang et al [19] synthesized 4A zeolite by mixing 5–15 wt.% bauxite with kaolin and calcination at high temperature, followed by reaction with sodium hydroxide, filtration, and drying. Successful synthesis of zeolite 4A from bauxite and kaolin has been reported by Xu et al [16] using different molar ratios of starting materials. The fusion temperature and time of 600 °C and 2 hours were maintained for optimum results. Furthermore, Kang et al [19] synthesized zeolite X using bauxite with chemical composition (wt. %) SiO_2: 58.1 and Al_2O_3 : 33.7 as starting material and sodium silicate solution. In this work, synthetic zeolites were synthesized from kaolin and bauxite both abundant in Ghana.

2.1 Materials and preparation

Kaolin was purchased from Anfoega in the Volta Region of Ghana. Bauxite was obtained from the Awaso Mines in the Western Region of Ghana. Sodium hydroxide was purchased from Sigma Aldrich, UK. Distilled water was obtained in the Water Research laboratory, Department of Civil Engineering, KNUST. The kaolin was ground and sieved with a 0.25 μm

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- *B. Kwakye-Awuah is currently a lecturer in the Department of Physics, Kwame Nkrumah University of Science and Technology, Kumasi, Ghana. E-mail: bkwakye-awuah.cos@knust.edu.gh*
- *E. Von-Kiti is currently pursuing PhD program Materials Science in Kwame Nkrumah University of Science and Technology, Kumasi, Ghana. E-mail: vonliz_05@yahoo.com*
- *R. Buamah is a Senior Lecturer in the Department of Civil Engineering, Kwame Nkrumah University of Science and Technology, Kumasi, Ghana. E-mail: rabuamah.coe@knust.edu.gh*
- *I. Nkrumah is a Lecturer in the Department of Physics, Kwame Nkrumah University of Science and Technology, Kumasi, Ghana. E-mail: inkrumah.sci@knust.edu.gh*
- C. Williams is a Professor of Mesoporous and Microporous materials in the University of Wolverhampton, UK. Email: c.williams@wlv.ac.uk

mesh. Bauxite from Awaso was obtained from the field and sieved to remove impurities.

2.2 Zeolite synthesis

50 g of kaolin was calcined at 600 °C for 2 hours to obtain metakaolin after which it was added to 2 M NaOH solution and heated at 110 °C for 2 hours. Meanwhile, 25 g of bauxite was heated in caustic soda (1 M NaOH) at 150 °C for 5 hours after which the slurry was filtered. The filtrates from the metakaolin and bauxite were added in varying ratios to obtain a molar ratio of SiO_2/AlO_3 = 1-1.5. For the reaction mixture, the sodium aluminate solution (from bauxite) was added to the sodium silicate solution (from kaolin) to obtain a gelatinous solution. The gel was stirred for 20 minutes until it was homogenized. The reaction was then aged at 24 hours at room temperature in Teflon bottles and later crystallized at 95 °C in an electric oven for 3 hours. The whole procedure was repeated for crystallization times of 5, 24 and 94 hours. Following filtration and washing with distilled water, the samples were dried overnight at 100 °C, crushed into powder and stored in plastic containers.

2.3 Characterization technique

To asertain the crystal structure and the composition of the synthesized zeolite, it was essential to characterize the zeolite. The X-ray diifraction XRD) pattern of the un-heated and heated bauxite which gives a measure of phase purity were recorded were recorded on Empyrean X-ray powder diffractometer over 2θ range of 3° to 70° (PANalytical, UK Ltd, Cambridge). The diffractometer was equipped with a graphite monochromated $Cu\ K_\alpha$ radiation source (8987 eV; $\lambda = 1.5418$ Å). Data processing was carried out using High Score Plus software with a search/match facility and an ICDD database on a DEC Microvax Minicomputer interfaced to the diffractometer. The surface morphology of the un-heated and heated bauxite as well as the elemental composition was examined by scanning electron microscopy (SEM) using a Zeiss EVO 50 equipped with energy dispersive X-ray spectrometer (EDX) (Zeiss, UK). Aluminium stubs were prepared prior to the analysis with an adhesive coating. The samples were sprinkled on the stubs. Where necessary, the samples were gold-coated using an Emscope SC500 Sputter coater to reduce static charging. Electron micrographs were obtained at various magnifications. Particle size distribution per unit volume was analyzed using a Mastersizer long bed analyzer (Malvern Instruments, UK). Samples of the un-heated and heated bauxite were taken for particle size analysis. Before measurements were made, the laser lenses were aligned in a straight line. Settings were set to obscuration value of 0.2. After steady conditions, 0.1 mg of each sample was loaded into an MSX 15 sample handling unit that uses the mechanical action of stirring to ensure that 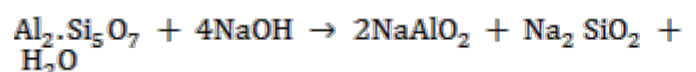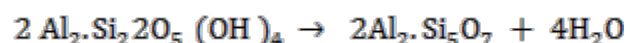the zeolite particles did not flocculate. Sodium Amalgam was then added to disperse adhering particles. Measurements were then recorded on a computer connected to the instrument. The vibrational properties were investigated by Fourier transformed infrared spectrometry (FTIR). Measurements were done using 100 scans at 4 cm^{-1} resolution, units of log (1/R) (absorbance), over the mid-infrared mid-IR region of 1200-400 cm^{-1}. An air background spectrum was collected at the start of the sample analysis. A small sample of each of the un-heated or heated bauxite was centred on the ZnSe plate to ensure that it covered the entire crystal surface, and a pressure clamp was used to apply pressure on the sample. The zeolite samples were analyzed three times for three different samples. A background spectrum was measured before samples were scanned to compensate for atmospheric conditions around the FT-IR instrument. Thermogravimetric analysis (TG –DTA) was performed using a Perkin Elmer TGA 7 (Perkin Elmer, UK) with differential thermal analysis. The study was carried out by heating at 10 °C /min heating rate starting from room temperature, with sensitivity of 0.2 mV in atmospheric conditions, and the changes in the sample due to heating were observed. The temperature range for the analysis was 50 °C to 800 °C.
images as separate files.

3 RESULTS AND DISCUSSIONS

Kaolin and bauxite samples were both analyzed for their chemical and mineralogical properties. The main crystalline phases in bauxite were gibbsite and rutile. Kaolin from Anfoega had its main crystalline phase being kaolinite (67.6%) and quartz (32.4%). XRF analysis was used to ascertain the chemical compositions of both bauxite and kaolin (Table 1). XRD pattern as shown by Figure 1 for bauxite exhibited gibbsite as its major mineral composition of 99.6 %. Gibbsite is known to have high solubility in H_2SO_4, HCl and NaOH (ref). Bauxite reacts with NaOH (caustic soda) to form sodium aluminate ($Na_2Al_2O_4$) while the silica reacts to form a complex compound of $Na_2O \cdot Al_2O_3 \cdot SiO_2$. Since the silica content of the bauxite used in the study was relatively low, the formation of this compound is negligible. The impurities like Fe_2O_3 and TiO_2 remain insoluble in the mud.

$$Al_2O_3 \cdot 3H_2O + 2NaOH \rightarrow Na_2Al_2O_4 + 3H_2O$$
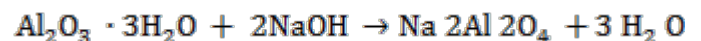
Kaolinite activity can be increased by altering its properties with thermal, mechanical or chemical treatment. Calcining above 550 °C, converts kaolin into metakaolin by removal of structural OH ion making it reactive.

$$2\ Al_2.Si_2O_5\ (OH)_4 \rightarrow 2Al_2.Si_5O_7 + 4H_2O$$

$$Al_2.Si_5O_7 + 4NaOH \rightarrow 2NaAlO_2 + Na_2SiO_2 + H_2O$$

Kaolinite reacted with NaOH to form sodium aluminosilicate solution with a high saturation towards its silicate content.

TABLE 1
Chemical composition of bauxite and kaolin as determined by EDX

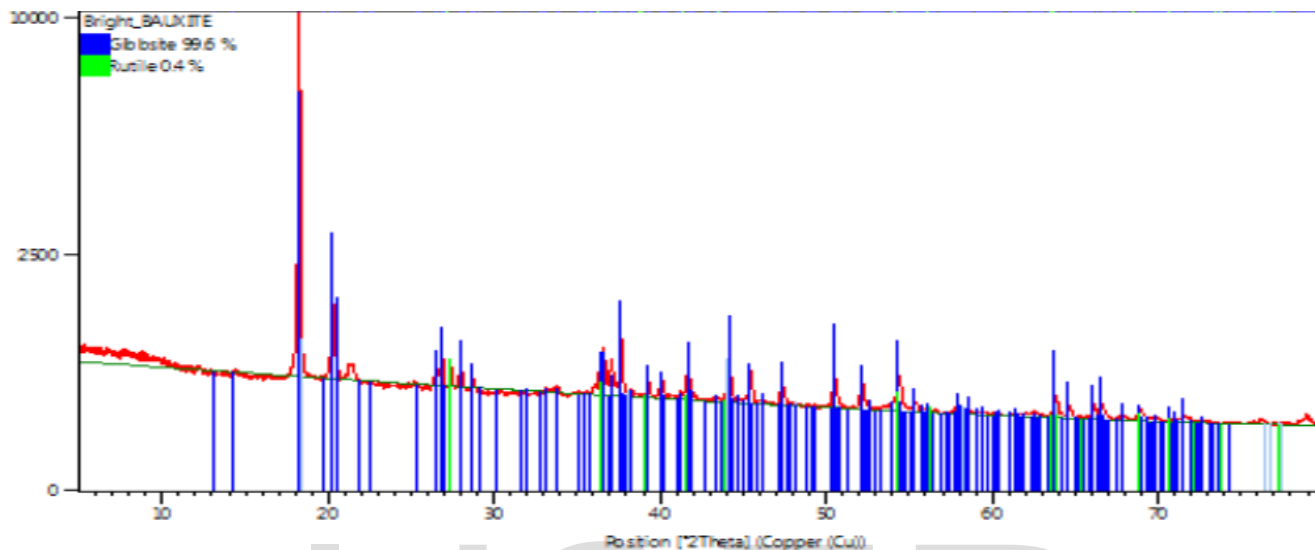|	SiO_2	Al_2O_3	K_2O	TiO_2	Fe_2O_3	Na_2O	MgO
Bauxite wt.%	1.12	98.6	trace	1.2	0.4	-	-
Kaolin wt.%	69.58	20.54	5.59	0.95	1.08	0.28	1.98

Fig 1: XRD spectrum bauxite. The predominant phase was Gibbsite (99.6 %) with a minor rutile phase of 0.4 %
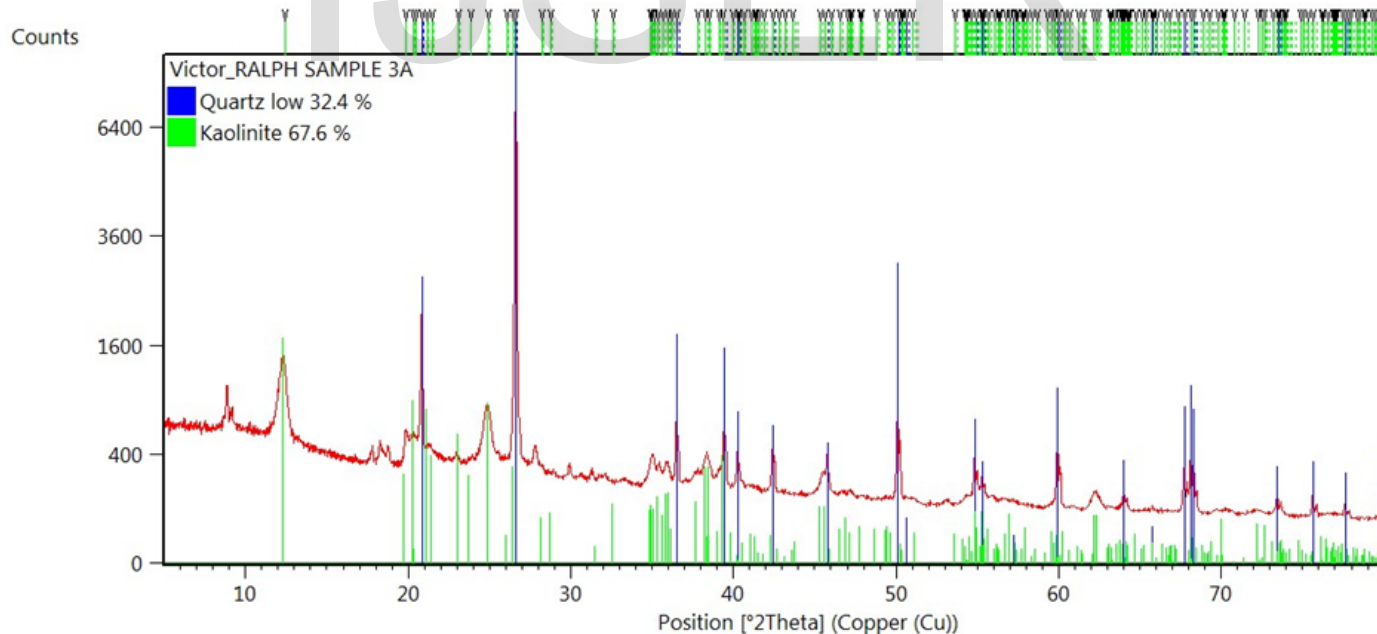

Fig 2: XRD spectrum kaolin. The predominant phase was kaolinite (67.6 %) with a minor low quartz phase of 0.4 %
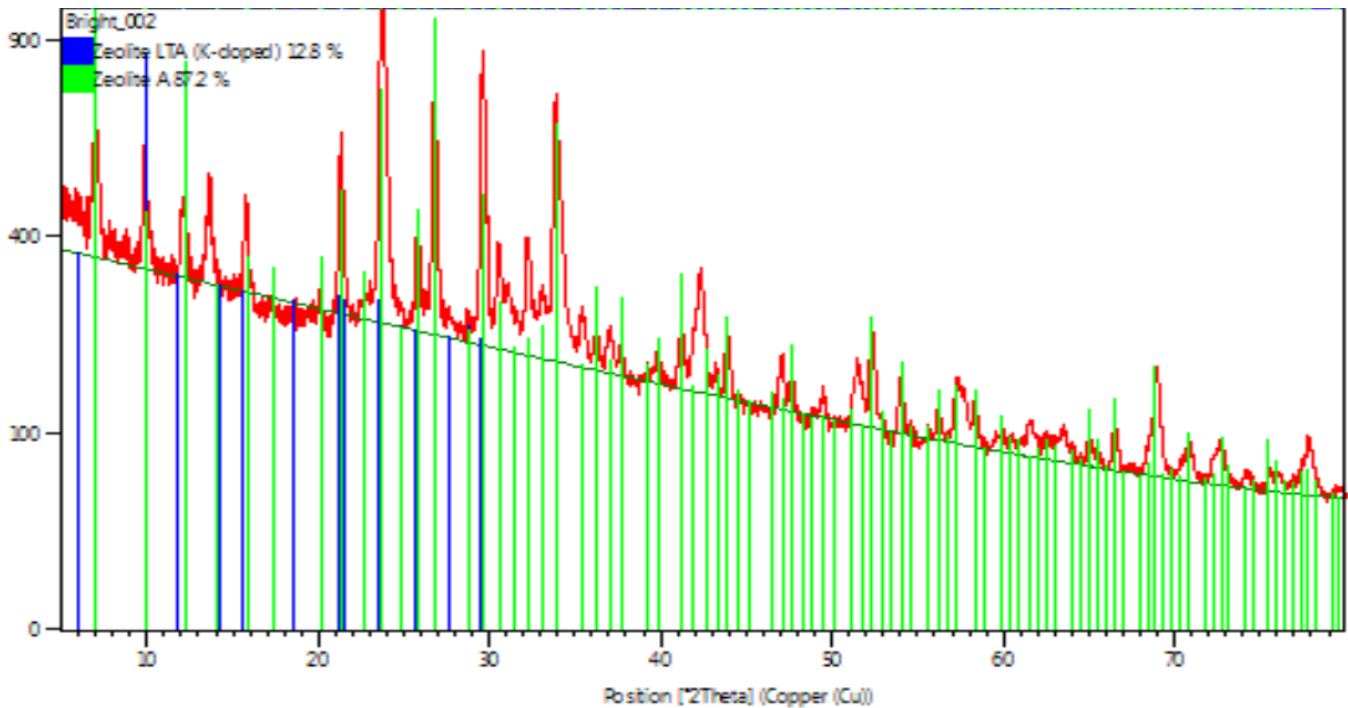
Fig 3: XRD spectrum of synthesized zeolite from bauxite and kaolin for a crystallization time of 3 hours. Zeolite A (=LTA) was obtained as the major phase.
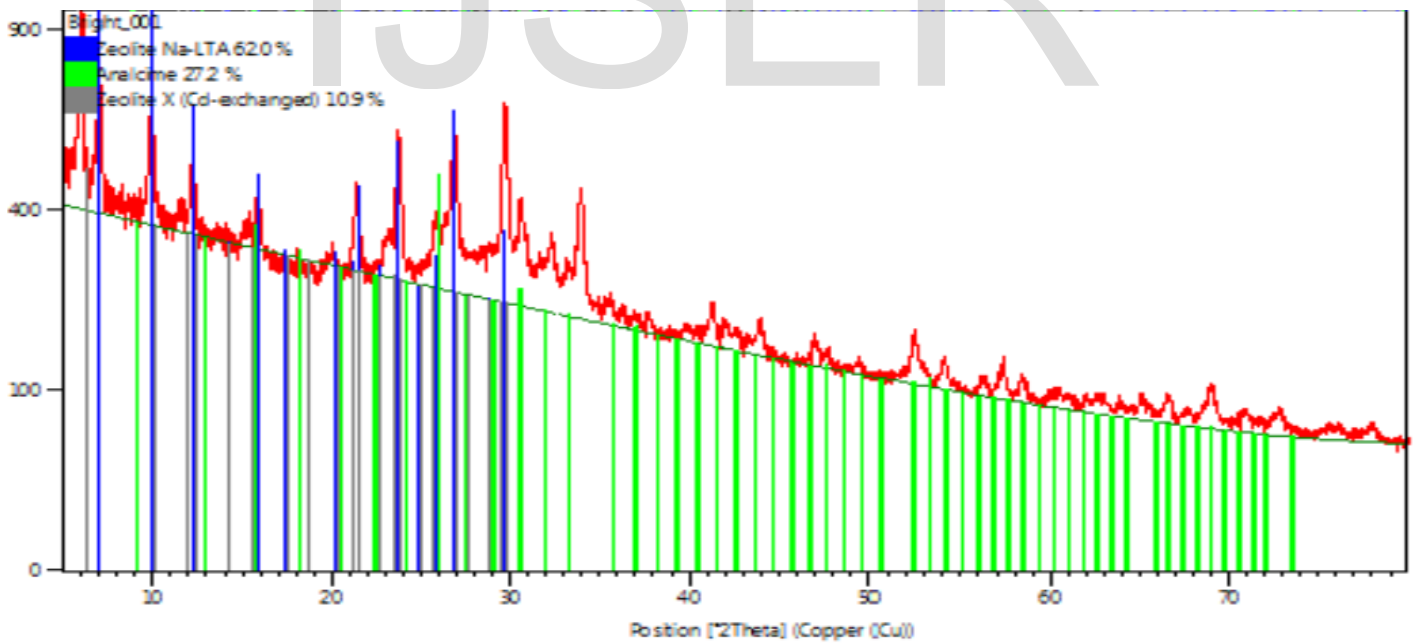

Fig 4: XRD spectrum of synthesized zeolite from bauxite and kaolin for a crystallization time of 5 hours. The main phases were zeolite LTA, analcime and zeolite X.
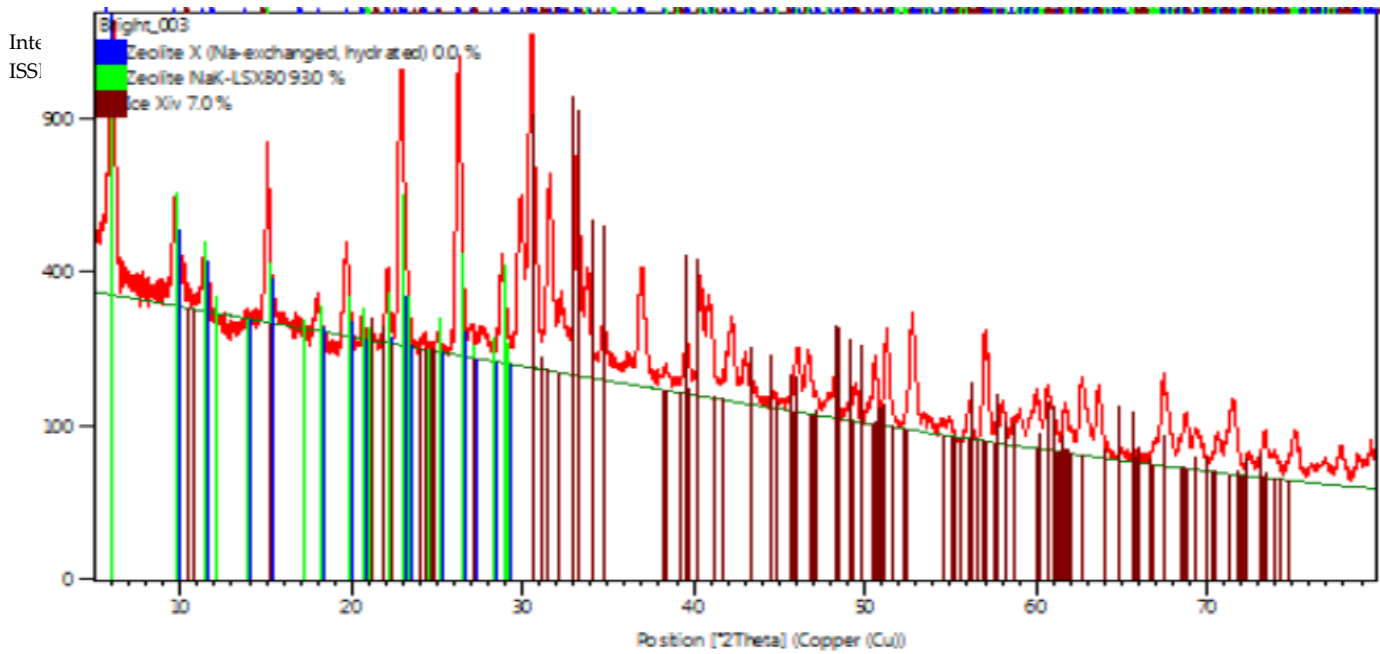
Fig 5: XRD spectrum of synthesized zeolite from bauxite and kaolin for a crystallization time of 24 hours. The main phase was zeolite zeolite X with the appearance of ice crystals.
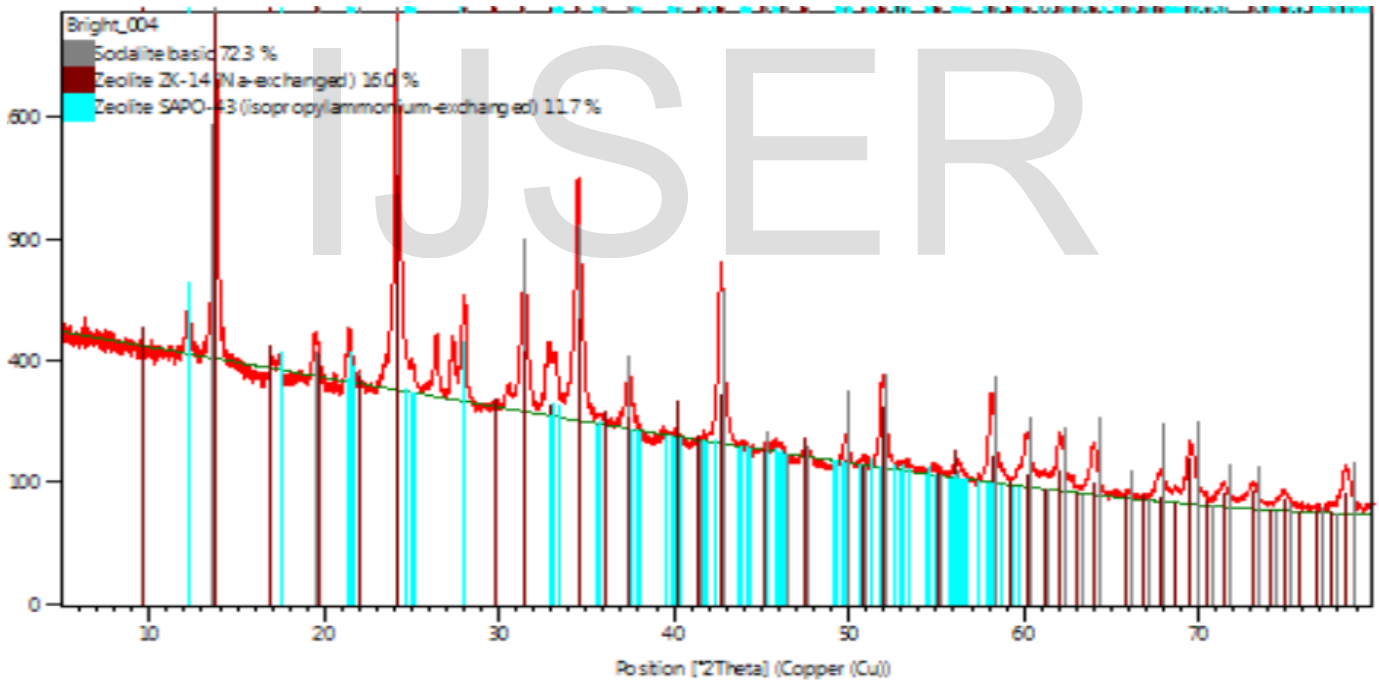

Fig 6: XRD spectrum of synthesized zeolite from bauxite and kaolin for a crystallization time of 94 hours. The main phases were sodalite, with some formation of zeolite ZK and SAPO-43.

It was found that the 94 hour crystallization yielded 72.3% of basic sodalite, 16% of zeolite ZK-14 and 11.7% of SAPO- 43. Prolonged crystallization time in zeolite A (LTA) and zeolite X has been observed to dissolve to form zeolites sodalite (SOD) and P (GHS) respectively when synthesized in alkaline alumi-

nosilicate gel (ref). As reported by Chandrasekhar and Pramada (1999), formation of multiphase (zeolites) crystalline products is achieved from the use of heterogeneous aluminosilicates as against the use of soluble silicates and aluminates that often result in the formation of pure zeolite types. The FTIR spectra of the kaolin and metakaolin showed different peaks in their structure. The intense bands occurred at 900–1200 cm^{-1} and 430–520 cm^{-1} for kaolin and 900 – 1050 cm^{-1} and 430 – 500 cm^{-1} for metakaolin. The first is assigned to an asymmetric stretching mode and the second one to a bending mode of the T–O bond. All these bands are more or less dependent on the crystal structure. The transformation of kaolinite to metakaolinite can be observed by the loss of peaks at 3618 -3370 cm^{-1} being the stretching vibrations of hydroxyl groups present in kaolin but absent in metakaolinite. the loss of Al-OH bands (925 and 910 cm^{-1}), changes in the Si-O stretching bands (1002 cm^{-1}, 1019 cm^{-1}) and the reduction in intensity of Al-O-Si bands at 796 and 778 cm^{-1} confirm the transformation.

at 913 cm^{-1} is due to Al – O - H group deformation vibration. Bands appearing at around 448, 540, 662, 1100 cm^{-1} are assigned to the Si–O vibration. Assignments of vibrational framework of the synthesized zeolites at different synthesis products are given in Table 2. The SEM photographs of the synthesized zeolites are showed in fig. 8. The shape of the crystals for 3 and 5 hour crystallization were cubic. The cubic crystalline shape is associated with zeolite A. The average crystal sizes were 4.4 µm and 5 µm respectively. However, increased synthesis time resorted to the zeolite A modifying to X with hexagonal crystal shapes after 24 hours typical of zeolite X from reagents. The crystal size was approximately 3 µm. The 94 hour synthesis time had orthorhombic shaped crystals with a size of 1.65 µm.

TABLE 2
Bands obtained from the FTIR spectra (not shown) for bauxite and kaolin and for hydrothermal synthsis at 3, 5, 24 and 94 hours respectively

Band Assignments	Range	3 hours	5 hours	24 hours	94 hours
Internal tetrahedral:		1156 1090 1070 1026	1093 985 963		
Asymmetric stretch	1250 – 950	963	660	950	
Symmetric stretch	720 – 650	672	452 423	664	701 659
T–O bend	420 – 500	421		447	
External linkage:			549		
Double ring	650 – 500	551 642		558	615 561
Pore opening	300 – 420		795		415
Symmetric stretch	750 – 820	819 793	1093	742	
Asymmetric stretch	1050 - 1150	1070 1090 1026			
Band Assignments	Range	3 hours	5 hours	24 hours	94 hours
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T–O bend	420 – 500	421		447	
External linkage:			549		
Double ring	650 – 500	551 642		558	615 561
Pore opening	300 – 420		795		415
Symmetric stretch	750 – 820	819 793	1093	742	
Asymmetric stretch	1050 – 1150	1070, 1090, 1026			

These changes are similar to those reported in other studies [4 – 9, 12, 23 – 25]. The characteristic bands observed in the bauxite were 1017, 790, 738, 662, 555, 448 and 407 cm^{-1}. Bauxite showed in the region of Al - O - H vibration stretching bands around 3618 – 3370 cm^{-1}. The bands around 3524, 3452 and 3392 cm^{-1} are assigned to O-H stretching of gibbsite. The band
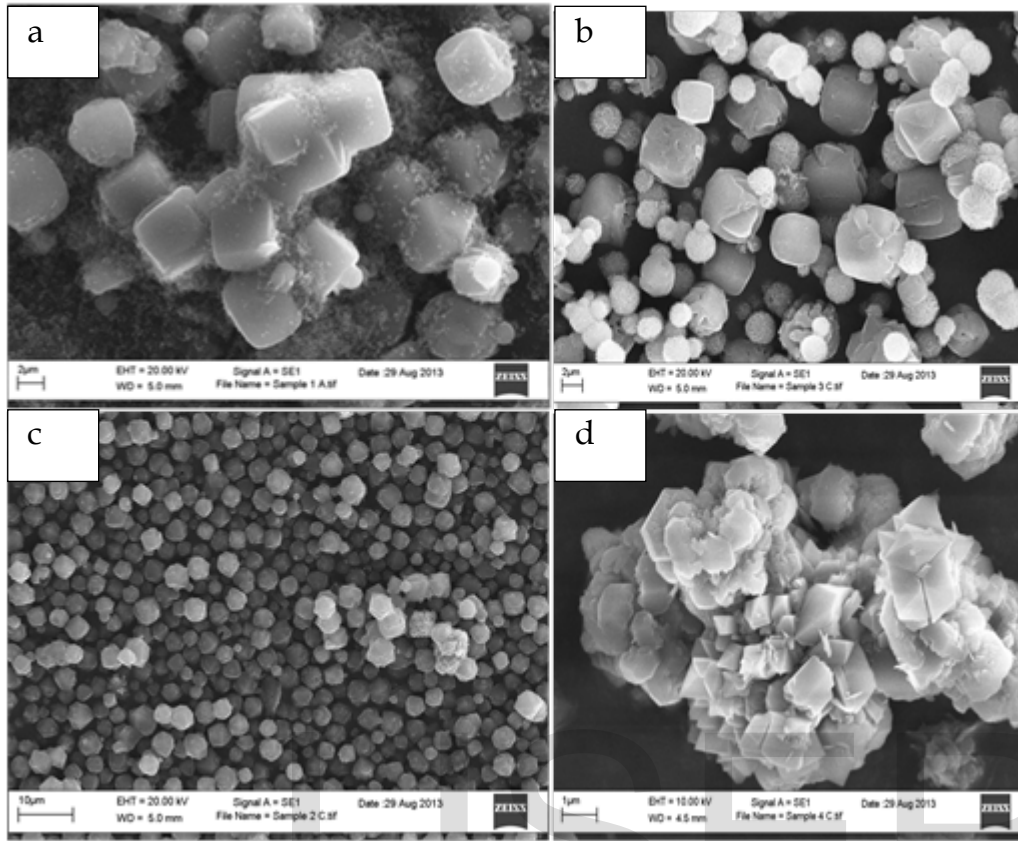
Fig 7: Scanning electron micrographs of the zeolite crystals obtained for crystallization time of (a): 3 hours, (b): 5 hours, (c): 24 hours and (d): 94 hours.

4 CONCLUSION

Zeolite synthesis was successful from bauxite and kaolin. The main crystalline phases in kaolin were quartz and kaolinite whilst that of bauxite was gibbsite. These phases were converted to zeolite types at varying crystallization times. The effect of crystallization time on the type of zeolite was investigated. 87.2% zeolite A was obtained at 5 hours crystallization time and zeolite Na LSX with a yield of 93% was obtained after 24 hours. Comparing the results showed that zeolite synthesis is greatly affected by the crystallization time. Zeolite synthesis has been confirmed to be successful at low temperatures (ref). The cost of synthesized zeolite was lower than that of commercial zeolite as well as that prepared from reagents.

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