NIGERIAN JOURNAL OF MATERIALS SCIENCE AND ENGINEERING
NJMSE
ISSN 214-453-2

ZEOLITE NAY FROM KANKARA KAOLIN USING COMMERCIAL GRADE CHEMICAL: EFFECT OF CRYSTALLIZATION TIME AND TEMPERATURE

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ABSTRACT
Zeolite Y was synthesized using commercial sodium hydroxide and Kankara kaolin as starting material in the presence of sodium silicate formed from kaolinite clay. Synthesis was done at 90°C, 95°C and 100°C for crystallization time of 12, 18, 24 and 36 hours. Results showed that commercial sodium hydroxide could be used to successfully produce zeolite Y from Kankara kaolin when gelling ratios of $\frac{H_2O}{Na_2O} = 30, \frac{Na}{Na+K} = 0.8$ *and* $\frac{Na_2O}{SiO_2} = 0.7$ *are used. Zeolite Y with the best crystallinity was produced at 90°C for 18 hours. Crystallisation of zeolite materials from kaolin and low grade NaOH is quite different from commercial zeolite because the sources of Si and Al are relatively less reactive due to the presence of competitive cation ions, like* K^+, Mg^{2+}, *present in the monomer. Additionally, the sodium silicate, selectivity induces the formation of zeolite NaY and eliminate the processes of induction and nucleation. Cost analysis per unit catalyst, showed an overwhelming $185.524 difference between imported high grade chemicals and local chemicals in favour of locally obtained chemicals. The as-synthesized zeolite was characterized using XRF, XRD and SEM analyses. The resulting NaY zeolite can find application in refining process, as shown by the XRD results.*

Keywords: *NaY, Crystallization, dealumination, Kankara kaolin, sodium silicate*

INTRODUCTION

Zeolites are crystalline solids with micropores having engineered dimension capable of handling variety of chemicals and are highly selective to targeted products. They are aluminosilicate minerals containing regular arrays of pores and cavities that can accommodate a wide variety of cations (positively charged ions), such as Na^+, K^+, Ca^{2+}, as well as small molecules, such as water. Due to their immense importance as catalysts, adsorbents, and ion exchange material, there is great interest in the process by which different zeolites and relative molecular sieves are formed. This is so important, in order to control their phase distribution, composition, structures and macroscopic properties. Over 150 synthetic and 40 naturally occurring zeolites are known (Marcus and Cormier, 1999). Initially only natural zeolites are used but more recently, synthetic forms have been made on an industrial scale giving rise to tailor made zeolites that are highly replicable. Structurally, zeolites are framework alumino-silicates, which are based on infinitely extending three dimensional Al_2O_3 and SiO_2 tetrahedral linked to each other by sharing all the oxygen (Breck, 1974; Richardson, 1989). They can be represented by the empirical formula:

$$M_{2/n}O \bullet Al_2O_3 \bullet xSiO_2 \bullet yH_2O$$

In this oxide formula, x is generally equal to or greater than 2 since tetrahedral AlO4 are joined only to tetrahedral SiO4 and n is the valency of the cation. They are traditionally formed from high grade chemicals such as sodium silicate, sodium aluminate and sodium hydroxide (Cundy and Cox, 2005). However, the preparation of synthetic zeolites from chemical sources of silica and alumina is expensive. Such costs may be reduced by the use of clay minerals, volcanic glasses (perlite and pumice), rice husks, diatomite, fly ash or paper sludge ash as starting materials (Adamczyk and Bialecka, 2005; Querol *et al*., 1997; Saija *et al*., 1983; Tanaka *et al*., 2004; Walek *et al*., 2008; Wang *et al*., 2008), though with rather less crystallinity and sometime associated allowable unwanted phases. Zeolite has also been developed by the transformation of one zeolite type into other zeotypes (Rios *et al*., 2007; Sandoval *et al*., 2009). Apparently, some mineral ores and waste materials could serve as good source for the necessary monomers for zeolite synthesis (Barrer, 1988; Chandrasekhar and Pramada, 1999; Murat *et al.*, 1992; Tavasoli, *et al.*, 2014 and Atta *et al.*, 2007). Amongst different zeolite groups, faujasites, particularly zeolite Y has attracted lots of interest due to its application in the fluidized catalytic cracking unit of refineries. Factors affecting synthesis of zeolite Y includes: nature of reactant, chemical composition and pre-treatment, overall homogeneity of the mixture, ageing, pH (alkalinity), seeding and conditions of crystallization (i.e. temperature and time). Numerous studies have been and are still undertaken to deepen understanding of the formation, kinetics and mechanisms of zeolite Y formation from alkaline precursor solutions (Liu *et al*, 1998) Wang *et al*., (2008), investigated the role of NaOH in zeolite synthesis and concluded that NaOH concentrations determine compositions, molar ratio of prepared initial gel, and then affect structural formation, morphology, particle size distribution and in some cases, type of zeolite formed. Ajayi (2012), identified inadequate depolymerisation of the aluminosilicate by sodium hydroxide used as one amongst several factors affecting the successful synthesis of zeolite Y from Kankara kaolin. Imported high grade chemicals are mostly used to help solve this problem. However, these high-grade chemicals are very expensive and it takes several weeks running to months to arrive the country, impeding the swiftness of the research. This work

attempts to address the trade-off between quality/purity of chemicals used and pace/cost of research. Throughout this research, locally obtained chemicals were used to reduce cost of production of zeolite Y, without affecting its end application as catalyst for refining process, while investigating the effects of crystallization time and temperature on the final product phase.

METHODOLOGY

Raw kaolin obtained from Kankara, Katsina State, Nigeria, was wet beneficiated for 3 days and the slurry sieved to get rid of coarse particles with a 53 µm sieve. The fine suspension thus obtained was allowed to settle and the supernatant water decanted. The sediment was dried at atmospheric condition and in an oven at 100°C for 6 hours, milled and calcined in a furnace at 750°C for 6 hours to obtain metakaolin, a more reactive phase of kaolin. The metakaolin was dealuminated to obtain Si/Al ratio adequate for zeolite Y synthesis. 80g of dealuminated metakaolin was measured and mixed with the required amount of water from the mole ratio $\frac{H_2O}{Na_2O} = 30$ and then thoroughly mixed with a high torque mixer for ten minutes. The required mass of sodium hydroxide from the mole ratio $\frac{Na}{Na+K} = 0.8$ *and* $\frac{Na_2O}{Sio_2} = 0.7$ were prepared and added to the mixture. Sodium silicate synthesis from Kankara clay by our group was added, while keeping the silica-alumina ratio of the mixture at level good enough for the targeted zeolite Y. The resulting gel was placed in a polypropylene bottle and aged for five days. The aged gel was placed in an oven at 90°C. After specified crystallization reaction time of 12 to 36 hours, the samples were removed washed and dried. The same procedure was thereafter repeated for same reaction times but at temperatures of 95 and 100°C. The products obtained were subjected to characterization.

Characterization techniques

Chemical composition was conducted using X-ray fluorescence (XRF) technique (PW 1400 spectrometer, Philips). The structural analysis was carried out using X-ray diffraction (XRD) patterns were recorded on a PW 1840 diffractometer (Philips), with Ni filtered Cu kα radiation at 40 kV and 40 mA. The measurements were carried out with a step width of 0.03_ 2h and scan rate of 1 s per step. The morphology was recorded by scanning electron microscopy (SEM) using a JEOL 6400.

RESULTS AND DISCUSSION

Beneficiation, as expected reduces the silica content from 58.3 to 55.768, which was achieved through floatation and dissolution of free silica, the molar Si/Al reduced from 2.55 to 2.3 as a result, which is still rather higher than theoretical value. Dealumination increased the Si/Al ratio to about 4.5 which is within the range stipulated for the synthesis of Zeolite Y from kaolin, which was later altered to 4.7 with introduction of freshly prepared kaolinite derived sodium silicate. The structural and morphological analyses of the kaolinite clay and sodium silicate were already discussed in an earlier paper (Ajayi, 2016).

Zeolite synthesis -Crystallization Conditions

Figures 1-3 show formation of faujasite zeolite comprising mainly of Y and traces of X and undepolymerized quartz. From the composition of the phases it could be safely deduced that the NaOH used depolymerised a high percentage of the silica in the precursor, despite the presence of quartz noticed. The peaks at 2 theta position of about 6.3 agrees with the principal peak of Na-Y (Treacy and Higgins, 2007). From Figure 1, it can be deduced that crystallization at 90°C for 18hrs had a relatively higher intensity for the zeolite Y characteristic peak.

Figure 3 shows that at 100°C Na-Y was synthesized along with Na-X and spikes of ZSM-5, ZSM-11 and TNU-7 and quartz. It was noted remarkably, that there was a progressive increase in the number of phases attributed to zeolite Y from Figure 1 to 3 which implies that a slight increase in the temperature between 90°C to 100°C affects the phases of zeolites Y formed (Li *et al.*, 2010). Additionally, the intensity of quartz was noticed to improve with increase in temperature, justifying the speculation of metastability of zeolite Y and formation of thermodynamically favoured product. (Bouchiba *et al.*, 2011).

Effect of crystallization time and temperature on crystallinity of zeolite

The crystallinity of zeolite Y phase increased as depicted in Figure 4 between 12-18 hours of crystallization time for all temperatures. This trend agrees with literature that crystallinity increases with time (Sang *et al.*, 2006).

The disordered form of the aluminosilicate in the gel favours the formation of zeolitic material than its already ordered counterpart, quartz, in Figure 5, hence the sharp increase in crystallinity for Na-Y. Above 18 hours the trend slopes downward, indicating decrease in crystallinity with time. This inconsistency could be attributed to the effect of impurities and/or metastability of formed zeolitic materials for prolonged crystallization time.

The sample with the highest crystallinity was gotten at 18hours at 90°C. The SEM image for this sample is shown in Figure 6, depicting its high crystallinity after other associated zeolitic phases.

Table 1. Composition of Kaolin

Oxide	SiO_2	Al_2O_3	Na_2O	SO_3	Fe_2O_3	CaO	K_2O	ZnO	PbO	MnO	Si/Al (mol)
RKK[1]	58.300	32.200	0.120	0.189	3.160	0.150	1.260	0.176	0.043	0.090	2.55
BK[2]	55.768	40.750	0.074	0.185	1.320	0.113	0.981	0.175	0.042	0.019	2.3
DK[3]	71.895	24.470	0.106	0.258	0.908	0.103	1.516	0.065	0.039	0.009	4.499

[1]Raw Kankara Kaolin [2]Beneficiated Kaolin [3]Dealuminated Metakaolin

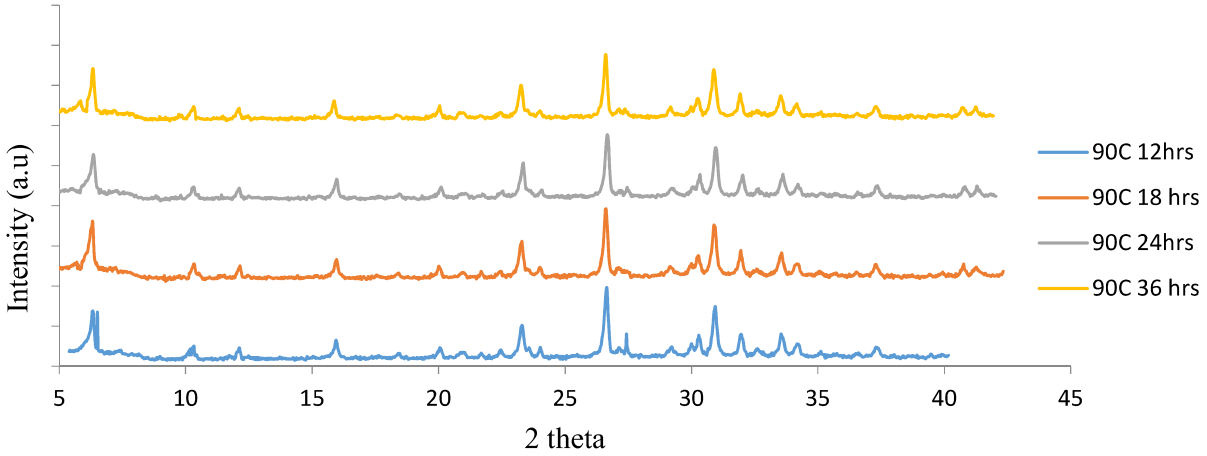

Fig.1. XRD patterns of zeolites synthesized at 90º C

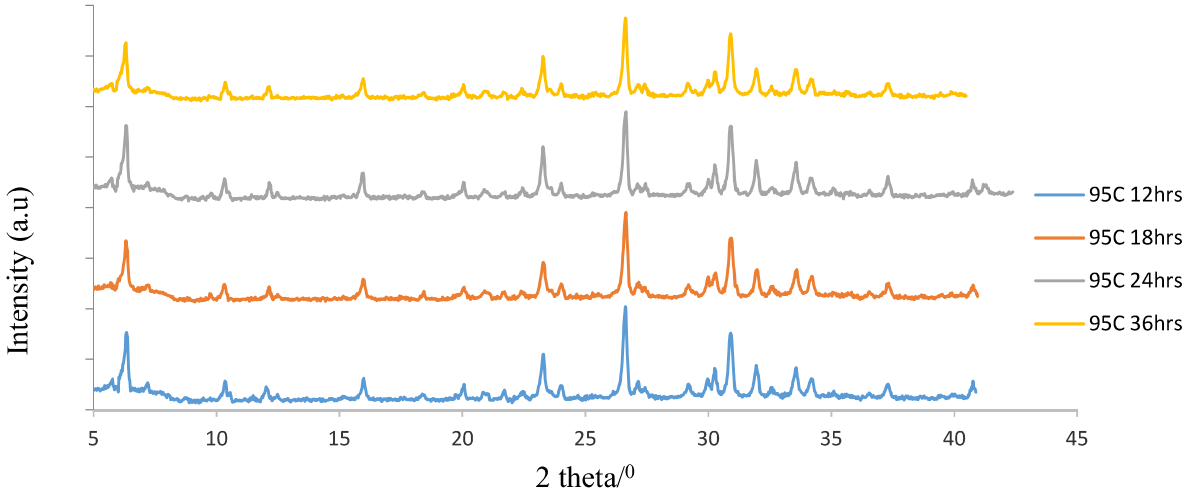

Fig.2. XRD patterns of zeolites synthesized at 95º C

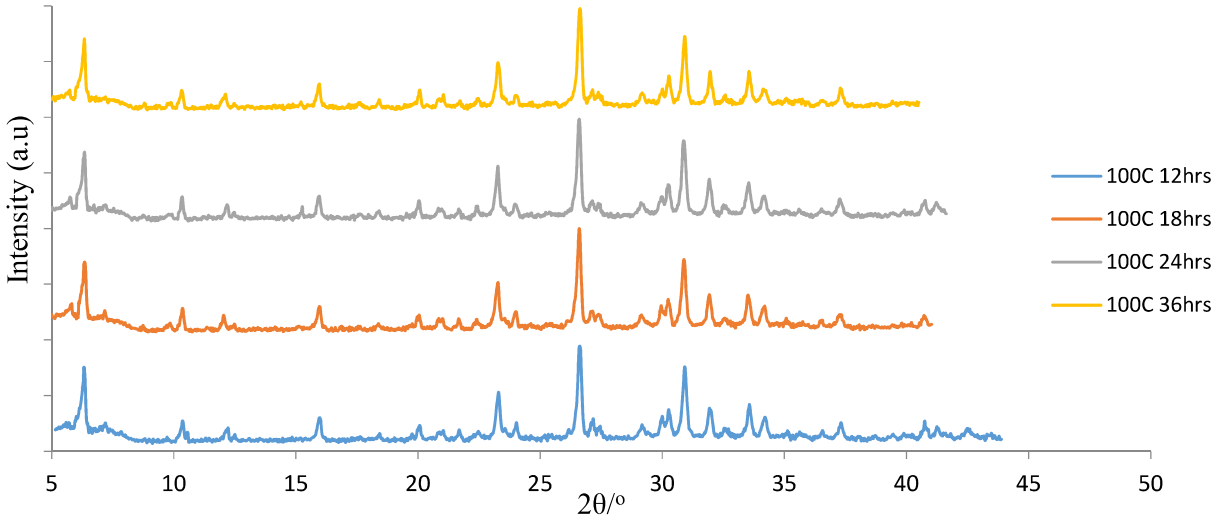

Fig. 3.XRD patterns of zeolites synthesized at 100º C

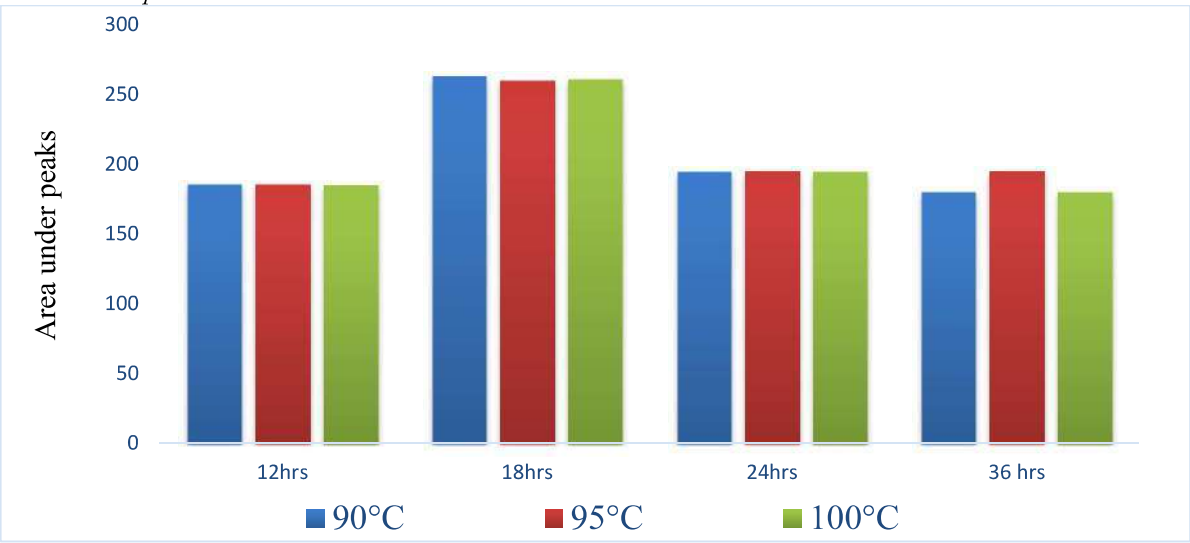

Fig.4. Na-Y phase at 90° – 100° C for various time

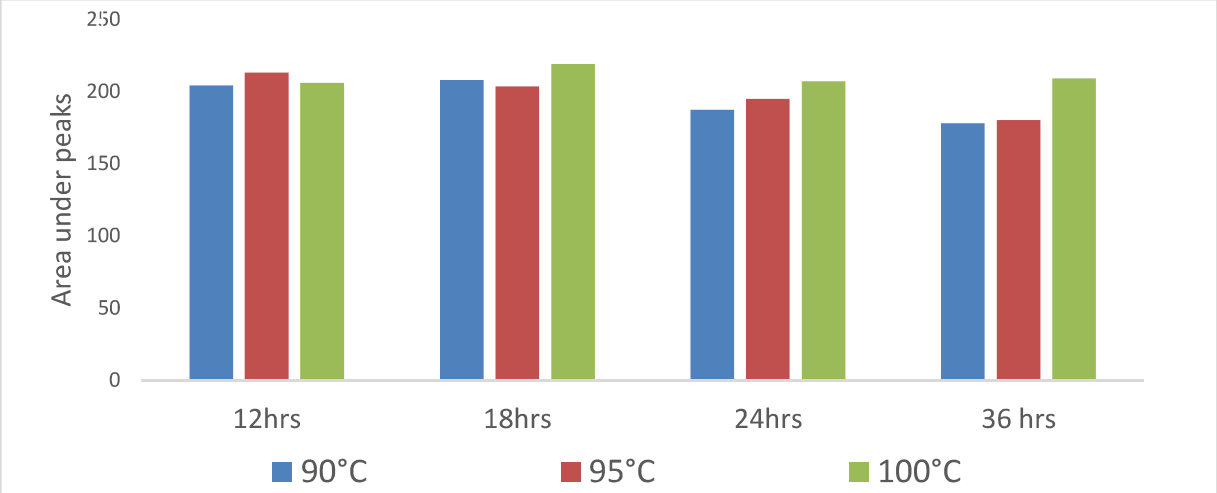

Fig.5. Unconverted (quartz phase) at 90° – 100° C for various times.

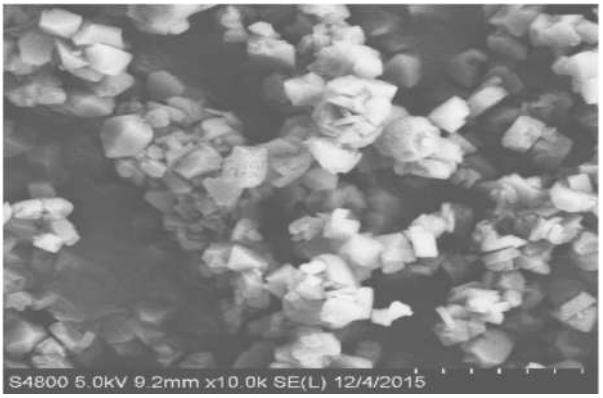

Figure 6: SEM image for as-synthesized zeolite at 900C for 18hrs

The product (whose SEM is shown in Figure 6) compositional ratios were determined and shown in Table 2. The silica to alumina ratio of zeolite Y was within the range of 3-5 from literature (Magee, and Mitchell). Comparing compounded ratios and product ratios, there was an increase in Na/(Na+K) from 0.8 to 0.947, Previous works of Breck, 1974 and Ajayi *et. al.*, (2013), concluded that the closer this ratio is to one, the lesser the eclipsing effect of potassium. They also opined that a reduced Na_2O/SiO_2 and Si/Al favours the formation of zeolite Y.

Reduction in ratios Na_2O/SiO_2 and Si/Al were seen from 0.7 to 0.162 and 4.99 to 3.01, respectively. The reduction in Na_2O/SiO_2 suggests that the sodium hydroxide used was active enough to depolymerize about 77% of the inherent SiO_2. This was responsible also for the reduction noticed in molar ratio of Si/Al. The aforesaid give credence to the successive synthesis of zeolite Y using low-cost locally obtained chemicals.

Table 2. Mineral composition of zeolitic product

Oxides	Na_2O	MgO	Al_2O_3	SiO_2	SO_3	K_2O	CaO	TiO_2	Mn_2O_3	Fe_2O_3
(w/w%)	12.28	0.37	30.87	53.20	0.231	1.011	0.110	0.358	0.015	1.492

Gel composition: Na/(Na+K)=0.8 ***Product Composition***: Na/(Na+K)=0.947
Na_2O/SiO_2=0.7 Na_2O/SiO_2=0.162; Si/Al=4.99 Si/Al=3.01

Table 3. Zeolitization Process Economy

Unit process	Chemical	Cost and Sources of Chemicals ($)	
		Commercial chemicals	Sigma-Aldrich chemicals
Dealumination	H_2SO_4 (1L)	21.21	152.958
Gelation	NaOH (500g)	9.696	63.472
Total Cost ($)		30.906	216.43

From Table 3, the cost on unit weight basis is $0.85/gram of zeolite Y produced. Though reagent grade chemicals are purer and may give better results, the high cost of reagent grade chemicals and it not being readily available was a source of concern. A difference in cost of $185 is significant enough to cause concern to Nigerian researchers and tilt them towards the use of commercial chemicals which hitherto were considered not good enough for zeolite Y production. The results from XRD and SEM confirms the applicability of the synthesized zeolite in cracking process, since the commercial FCC zeolite are often blended with amorphous material, which is not necessary for the one presented here. The differential cost difference of $185 is much when we take into consideration the quantity of this zeolite used in FCC unit and also their life span during the process.

CONCLUSION

Zeolite NaY was successfully synthesized from kaolin using industrial grade NaOH in the presence of sodium silicate sourced from kaolin. The use of commercial grade sodium hydroxide in the synthesis of zeolite was successful as it was able to depolymerize silica in Kankara Kaolin, besides saving cost, it ensured that the research went without delay for arrival of chemicals from overseas. The ratios employed for chemicals used ensured adequate depolymerisation and help to conceal the effect of impurities such potassium which constitute a nuisance in the synthesis of zeolite Y from Kankara kaolin. The process economy tends to favour investment in local production of zeolite NaY using this route, for about $185 can be saved per unit cost of production.

REFERENCES

Adamczyk, Z., Bialecka, B., 2005. Hydrothermal synthesis of zeolites from polish coal fly ash. Pol. J. Environ. Stud. 14 (6), 713–719.

Ajayi, O.A (2012). Development of large pore zeolites from kaolinite clay. Ph.D Thesis, ABU, Zaria.

Ajayi, O. A. Mamman, J and Adefila, S.S (2016). Comparative Synthesis of Sodium Silicate from Rice Husk and Kaolin. Paper submitted to Nigerian Journal of Materials Science and Engineering (NJMSE).

Atta, A.Y., Ajayi, O.A., Adefila, S.S., (2007). Synthesis of Faujasite zeolites from Kankara kaolin clay. J. Appl. Sci. Res. 3 (10), 1017–1021.

Barrer, R.M (1988). Zeolite Synthesis: An Overview. Chapter in a book titled: Surface Organometallic Chemistry: Molecular Approaches to Surface Catalysis, Volume 231 of the series NATO ASI Series, pp 221-244, Published by Springer, Netherland. DOI: 10.1016/j.matlet.2005.10.110

Bouchiba, N., M.L.A. Guzman Castillo, A. Bengueddach, F. Fajula and F. Di Renzo (2011). Zeolite metastability as a function of the composition of the surrounding solution: The case of faujasite and zeolite omega. Microporous and Mesoporous Materials 144 (2011) 195–199. DOI: 10.1016/j.micromeso.2011.04.015

Breck D.W. (1984). *Zeolite molecular sieves*. New York: John Wiley & Sons.

Chandrasekhar, S., Pramada, P.N., 1999. Investigation on the synthesis of zeolites NaX from Kerala kaolin. J. Porous. Mater.6 (4), 283–297.

Cundy, C. and Cox, P. (2005*)* The hydrothermal synthesis of zeolites: precursors, intermediates and reaction mechanism. Microporous and Mesoporous Materials, 82 (1-2). pp. 1-78. ISSN 1387-1811 DOI: 10.1016/j.micromeso.2005.02.016

Li, Q., Zhang, Y., Cao, Z., Gao, W., and Cui, L (2010). Influence of synthesis parameters on the crystallinity and Si/Al ratio of NaY zeolite synthesized from kaolin. Petroleum Science Volume 7, Issue 3, pp 403–409. DOI: 10.1007/s12182-010-0085-x

Liu, C., Gao, X., Ma, Y., Pan, Z. and Tang, R. (1998). Study on the mechanism of zeolite Y formation in the process of liquor recycling. Microporous and Mesoporous Materials Volume 25, Issues 1–3, pp 1–6.

Magee, J.S. and M.M. Mitchell (1993). Fluid Catalytic Cracking: Science and Technology, Technology & Engineering, pp 109-110, Published by Elsevier, Netherland

Marcus, B.K., Cormier, W.E., 1999. Going green with zeolites. Chem.Eng. Prog. 95 (6), 47–53.

Murat, M., A. Amokrane, J. P.bastide and l. Montanaro (1992). Synthesis of zeolites from thermally activated Kaolinite: Some observations on nucleation and growth. Clay Minerals 27, 119-130

Querol, X., Plana, F., Alastuey, A., Lopez-Soler, A., 1997. Synthesis of Na-zeolites from fly ash. Fuel 76, 793–799.

Richardson, J.T., 1989. Principles of Catalysts Developments. Plenum Press, New York and London.

Rios, C.A., Williams, C.D., Maple, M.J., 2007. Synthesis of zeolites and zeotypes by hydrothermal transportation of kaolinite and metakaolinite. BISTUA 5 (1), 15–26.

Saija, L.M., Ottana, R., Zipelli, C., 1983. Zeolitization of pumice in ash-sodium salt solutions. Mater. Chem. Phys. 8, 207–216.

Sandoval, M.V., Henao, J.A., Rios, C.A., Williams, C.D., Apperley, D.C., 2009. Synthesis and characterization of zeotype ANA framework by hydrothermal reaction of natural clinker. Fuel 88, 272–281.

Sang, S., Liu, Z., Tian, P., Liu, Z., Qu, L and Zhang, Y (2006). Synthesis of small crystals zeolite NaY. Materials Letters 60, 1131.

Tanaka, H., Miyagawa, A., Eguchi, H., Hino, R., 2004. Synthesis of a pure-form Zeolite A from coal fly ash by dialysis. Ind. Eng. Chem.Res. 43, 6090–6094.

Tavasoli, M., Kazemian, H., Sadjadi,S. and Tamizifar, M (2015). Synthesis and Characterization of Zeolite NaY using Kaolin with Different Synthesis Methods. Clays and Clay Minerals. DOI: 10.1346/CCMN.2014.0620605

Treacy, M. M., and Higgins, J. B. (2007). *Collection of Simulated XRD Powder Patterns for Zeolites Fifth (5th) Revised Edition*. Elsevier.

Walek, T.T., Saito, F., Zhang, Q., 2008. The effect of low solid/liquid ratio on hydrothermal synthesis of zeolites from fly ash. Fuel 87, 3194–3199.

Wang, C. F., Li, J. S., Wang, L. J., & Sun, X. Y. (2008). Influence of NaOH concentrations on synthesis of pure-form zeolite A from fly ash using two-stage method. *Journal of Hazardous Materials*, *155*(1), 58-64.

Wang, C.F., Li, J.S., Wang, L.J., Sun, X.Y., 2008. Influence of NaOH concentrations on synthesis of pure-form zeolite A from fly ash using two-stage method. J. Hazard. Mater. 155, 58–64.