

## Effects of Sodium Hydroxide Concentration on Zeolite Y Synthesized from Elefun Kaolinite Clay in Nigeria

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### Abstract

Zeolite Y was synthesized hydrothermally from Elefun kaolinite clay. The raw kaolinite was calcined at 850°C to obtain more reactive clay (metakaolin). The metakaolin was dealuminated using non-heating methods to obtain the optimum dealumination route desired silica to alumina ratio between 3 and 7. The non-heating method proved successful in producing a desired ratio of 4 which was used in producing the aluminosilicate gel. The aluminosilicate gel was aged for 7 days at 95°C for 36 hours with varying Na<sub>2</sub>O/SiO<sub>2</sub> ratios of 0.60, 0.65, 0.70, 0.75 and 0.80 to produce zeolite Y. The synthesized zeolites were characterized by X-ray diffraction (XRD) analysis. The effect of NaOH concentration was studied using the XRD patterns of synthesized zeolite Y samples with reference to a standard zeolite Y. The results indicated zeolite Y of low crystallinity accompanied with other impure phases. Furthermore, the concentration of NaOH improved the intensity of the zeolite Y crystal peaks. The Na<sub>2</sub>O/SiO<sub>2</sub> ratio that gave the highest crystallinity optimal ratio was found to be 0.75 with NaOH concentration of 3.88M.

### INTRODUCTION

The increasing world demand for energy has intensified the processing of heavy petroleum feedstock. Fluid Catalytic Cracking is an important refining process used in upgrading these heavy hydrocarbons to high valued products. Since this process came into existence, it has continuously undergone changes and major improvements related to the technology as well as the catalyst [1], [2], [3]. Approximately 1,100 tons of catalyst is manufactured every day to be used worldwide in over 200 Fluid Catalytic Cracking Units [4], [5], [6], [7].

Zeolites as a type of porous material are important for catalytic processing, either in the cracking of crude oil distillate for fuel manufacture or in the conversion of crude oil fractions to gasoline in the presence of hydrogen in hydro cracking processes. Zeolites are crystalline solid structures made of silicon, aluminium and oxygen that form a framework with cavities and channels where cations, water and/or small particles may reside. Many of them occur as minerals in nature and are extensively mined in various parts of the world for industrial applications and in medicine [1], [8]. Alternatively, zeolites have been synthesized by the hydrothermal method. It involves silica, alumina, and/or phosphorus species, metal cations, organic molecules, and

water, which are converted via an alkaline supersaturated solution into microporous crystalline zeolites [4], [9], [10].

Some of the processes involved in zeolite synthesis are thermally activated and occur at elevated temperatures in order to achieve a high yield of crystals in an acceptable period of time. The variables in the synthesis of zeolites are crystallization time, temperature, alkalinity (pH), and chemical composition, of the reactant mixtures [4].

According to [2], the most common industrially important zeolites were discovered between 1950 and 1970 and they are classified based on their Silica to Alumina ratio in their frameworks: low silica or aluminium rich zeolites A and X (ratio Si/Al  $\approx$  1), intermediate silica zeolites Y and L (ratio Si/Al of 2 to 5) and high silica zeolites ZSM-5 (ratio Si/Al  $\geq$  10).

Type Y zeolite, especially, among the Faujasite type zeolites with their large pores is of great importance in the petroleum industry, due to its application in the area of fluidized catalytic cracking (FCC), as about 40% of the gasoline production is obtained through FCC process [11], [12]. Nigeria is richly endowed with huge reserve of oil and gas and kaolin (mineral containing the silica and alumina) for zeolites synthesis. The three Nigerian refineries use imported zeolitic catalysts and other related catalysts, at the cost of US\$2000 per ton with the Refineries' annual import showing import of 500,000 tonnes, at 60% capacity utilization [13], [12]. Hence, there is a great need for more research efforts in production of zeolite Y from kaolinite clay owing to the huge deposits of the raw material in Nigeria.

Owing to the increasing import of zeolite Y catalyst by the Nigerian petroleum refineries, there is need to improve on production on zeolite Y catalyst locally. Research efforts have shown successful synthesis of zeolites from diverse clay sources. The attempt to synthesize zeolite from various Nigerian kaolinite clays have proved successful. Previous attempts have been made in synthesizing zeolite Y from Nigerian kaolin clay and interesting results have been obtained from Kankara kaolin in Kastina state [13], [14] and Ahoko kaolin [15]. However, there is little reference to synthesis of zeolite Y from Elefun kaolinite clay obtained in Ogun state, Nigeria.

The focus of this research is to study the effects of alkali concentration on the synthesis of zeolite Y obtained from Elefun kaolinite Clay and to characterise the zeolite Y produced by using X-ray Fluorescence (XRF) and X-ray

Diffraction (XRD) analyses. The kaolinite clay to be used is a local raw material sourced from Elefun area of Ogun state in the western region of Nigeria.

## MATERIALS AND METHODS

### Clay beneficiation

This was carried out to remove the impurities such as sand and soluble salts present with the raw kaolinite clay. In carrying out the beneficiation, 7.5 kg of the raw kaolinite clay obtained from Elefun was soiled in 10L bucket of water for 24 hours. During the soaking period, the clay was masticated at intervals to break into small lumps. Floating dirt was also removed by discarding the water on top and adding fresh water afterwards. After 24 hours, the mixture was decanted several times to get rid of the sand, stony particles, heavy impurities and soluble salts present. This was repeated for five days.

### Drying

After 5 days, the decantation was carried out finally and the resulting slurry was dewatered. The resulting clay was spread on a polythene sheet to dry under atmospheric conditions for 3 days. The clay material was then put in an oven to be dried further at 150°C for 3hrs. The mass of the resulting sample was recorded and part was packaged for XRF analysis.

### Calcination

The dried clay was calcined in a programmable electric furnace at 850°C. The temperature was increased from room temperature to the calcination temperature for six hours. The resulting metakaolin was then transferred to air tight plastic containers and sample was subjected to XRF analysis.

### Dealumination

The dealumination process involves the reduction of the alumina content in the metakaolin to a desired Si/Al ratio of 4. The novel method used in the dealumination of the meta kaolin involved the reaction of the meta kaolin with sulphuric acid (H<sub>2</sub>SO<sub>4</sub>) and deionised water, without heat application. 50mL of distilled water was added to 20g of the meta kaolin. 44mL of 0.1M sulphuric acid (based on the dealumination calculation) was then added for reaction to take place for a specified reaction time.

As soon as the reaction time elapsed, the reaction was terminated by adding 450mL of distilled water. The resulting mixture was stirred and left to completely settle before the supernatant formed was poured off leaving the dealuminated meta kaolin. Dealuminated meta kaolin obtained was then washed with 400mL of distilled water to remove unreacted sulphuric acid that may be present. The dealumination procedure was carried out at varied reaction time.

### Gel formation

The ratio of Sodium oxide to silica was varied between 0.60 and 0.80. The silica to alumina ratio was obtained from the compositional analysis of the dealuminated sample. The mass of sodium hydroxide and volume of water required for gellating 10g of dealuminated metakaolin were calculated. The dealuminated sample was put in a conical flask and mixed with half of the required quantity of deionized water until the dealuminated sample was dissolved completely. The required quantity of NaOH was then added to the solution and stirred vigorously before the remaining quantity of deionized water was added. The content was continuously stirred for 30 mins. The resulting gel was then put in a Teflon bottle, sealed and left to age for 7 days at room conditions.

### Crystallisation

The enclosed gel obtained was then placed in the electric oven at 95°C for 36 hours for crystallization to take place. The sample was washed free of excess NaOH using deionized water. The pH was monitored (using litmus paper) while washing to obtain neutral pH. The sample was then dried before packaging for XRD analysis.

## RESULTS AND DISCUSSION

Table 1 show an increase in Al<sub>2</sub>O<sub>3</sub> and reduction in SiO<sub>2</sub> through beneficiation and calcination. Also, that there was slight reduction in the quantity of impurities (unwanted components) present through beneficiation and calcination. For example, SO<sub>3</sub>, K<sub>2</sub>O, CaO, TiO<sub>2</sub>, Cr<sub>2</sub>O<sub>3</sub>, MnO, Fe<sub>2</sub>O<sub>3</sub>, were reduced during beneficiation and calcination.

**Table 1:** XRF compositional Analysis of the raw, beneficiated and calcined Elefun kaolinite Clay

Elements	Elefun Clay (weight %)		
	Raw	Beneficiated	Calcined
Na <sub>2</sub> O	0.000	0.211	0.000
MgO	0.658	1.037	0.537
Al <sub>2</sub> O <sub>3</sub>	52.079	53.785	54.275
SiO <sub>2</sub>	41.271	39.930	39.519
SO <sub>3</sub>	0.387	0.538	0.200
K <sub>2</sub> O	0.299	0.096	0.334
CaO	0.044	0.039	0.041
TiO <sub>2</sub>	2.824	1.999	2.740
Cr <sub>2</sub> O <sub>3</sub>	0.027	0.020	0.026
MnO	0.002	0.004	0.002
Fe <sub>2</sub> O <sub>3</sub>	2.390	2.332	2.306
ZnO	0.004	0.000	0.004
SrO	0.014	0.010	0.014

From Table 2, there was a significant reduction in the level of  $Al_2O_3$  and an increase in  $SiO_2$  level when compared to the values obtained in Table 1. This implies that the dealumination process adopted (a deviation from the convectional approach that requires direct heating before reaction could occur) is an encouraging one.

**Table 2:** XRF compositional analysis of dealuminated metakaolin obtained at different dealumination process time

Elements	Dealuminated Metakaolin (weight %)	
	@ 3 minutes	@ 5 minutes
$Na_2O$	1.170	1.040
$MgO$	0.830	0.710
$Al_2O_3$	27.400	27.000
$SiO_2$	62.200	61.900
$K_2O$	0.000	0.026
$CaO$	0.295	0.314
$TiO_2$	6.690	7.090
$Cr_2O_3$	0.045	0.048
$MnO$	0.000	0.020
$Fe_2O_3$	1.100	2.430
$V_2O_5$	0.190	0.210

By calculation, the reduction of the alumina content in the metakaolin gave a desired result of silica to alumina ratio (approximately 4) required for zeolite synthesis (Table 3). Also, reaction time of 5 minutes gave a more reliable value of

silica to alumina ratio.

**Table 3:** Calculated Si/Al ratio of Dealuminated Metakaolin obtained at different dealumination time

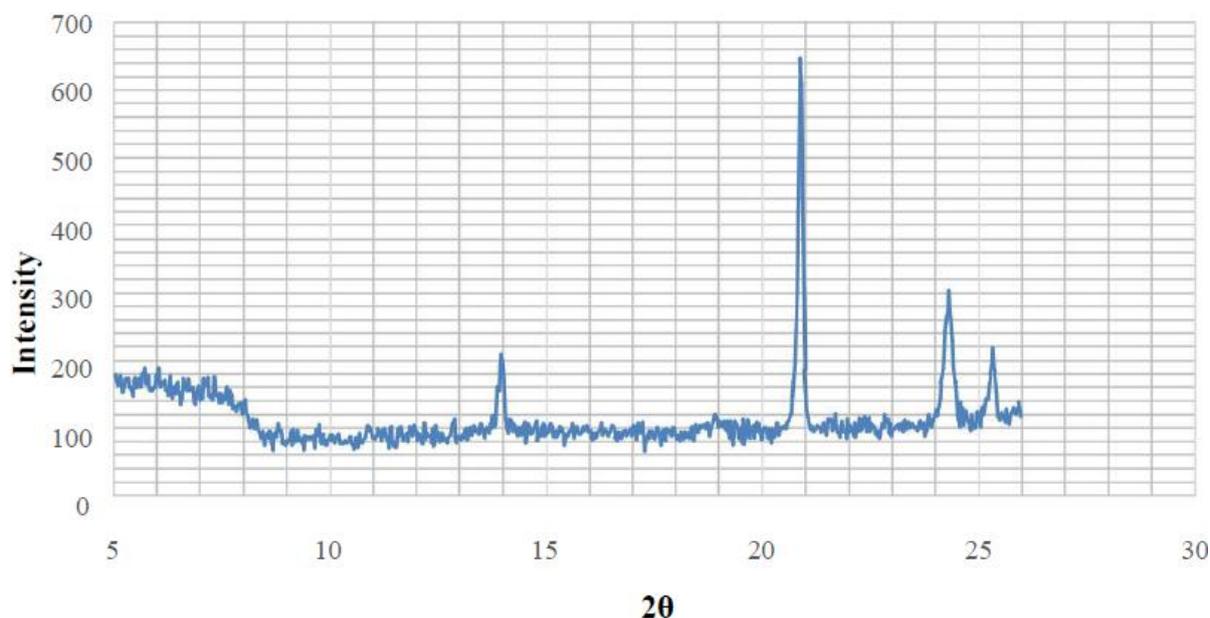
Reaction Time	3 minutes	5 minutes
Si/Al ratio	3.859	3.897

The dealumination process is based on the principle that involves the use of indirect heat of sulphonation resulting from mixing acid and water to carry out the reaction. The heat resulted into an increase in the boiling water volume and buoyancy. And the buoyancy assisted in the agitation, increased level of collision and subsequently the overall ability of acid-water mixture to do the work required for the chemical reaction [13], [16]. This approach allows dealumination process to take place at lower temperature, compared to the convectional method.

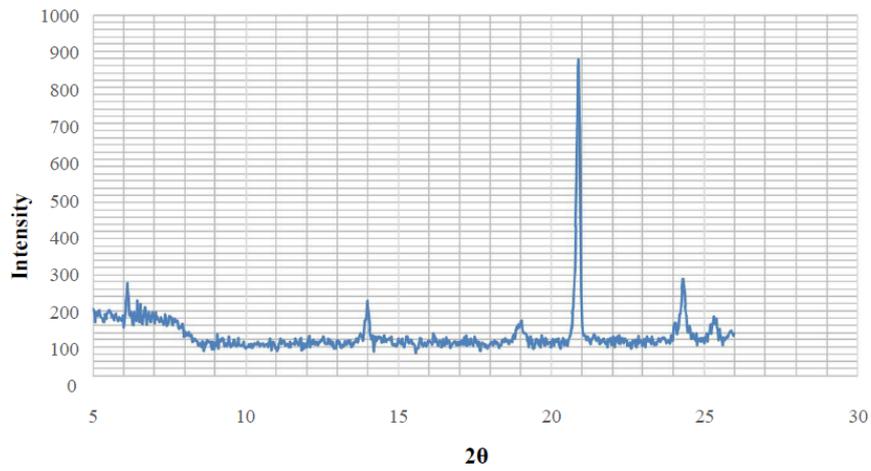
It can also be inferred that leaching occurred in sequential manner due to attack at the octahedral layer as the composition of alumina reduced from 27.4 to 27.0 in 3 to 5 minutes.

#### XRD analysis on synthesized Zeolite Y samples

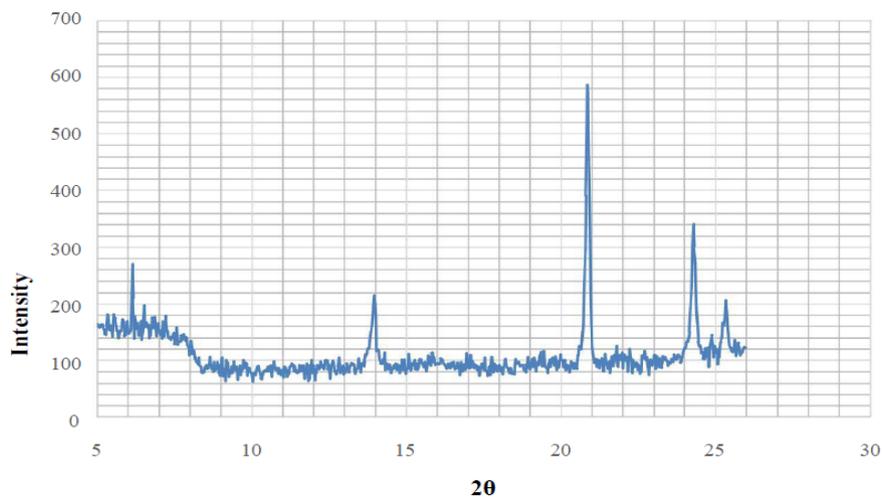
The solids obtained from the synthesis experiment were identified using Powder X-ray (EMPYREAN) diffractometer. Figures 1 – 6 show the X-ray Diffraction obtained from the synthesized Zeolite Y samples (at different  $Na_2O/SiO_2$  ratios between 0.6 and 0.8) and the standard Zeolite Y sample.



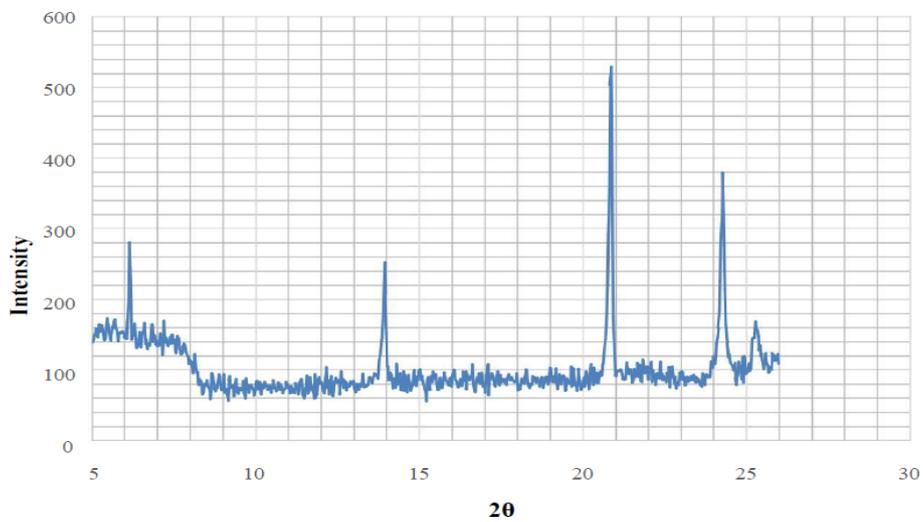
**Figure 1:** XRD Analysis obtained from the synthesized Zeolite Y at  $Na_2O/SiO_2$  of 0.60



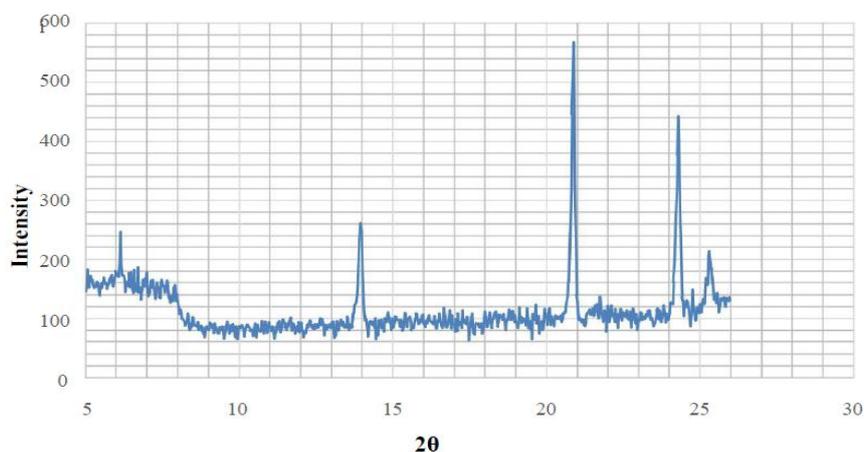
**Figure 2:** XRD Analysis obtained from the synthesized Zeolite Y at  $\text{Na}_2\text{O}/\text{SiO}_2$  of 0.65



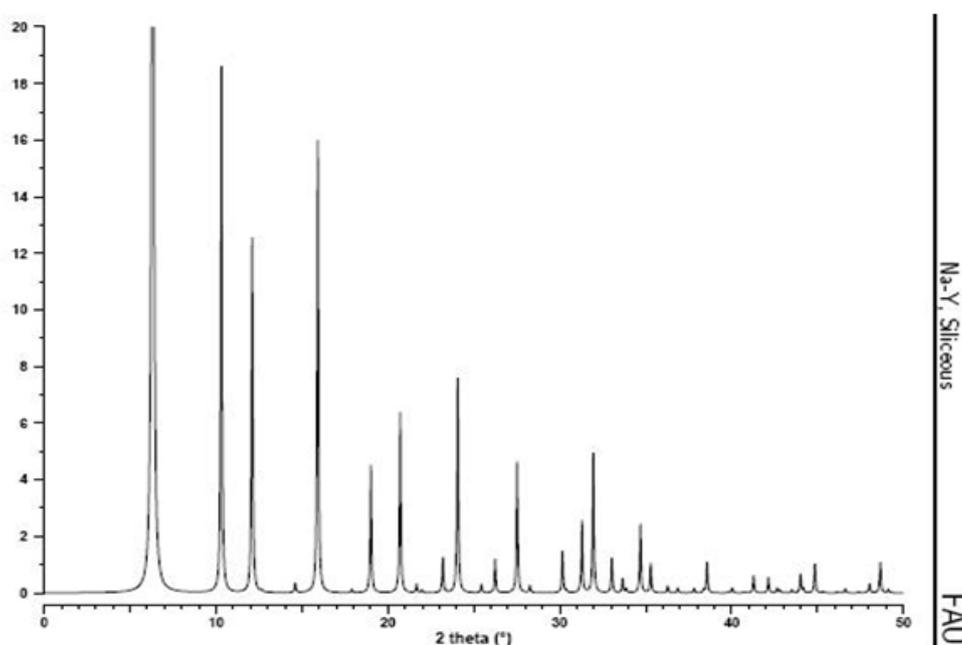
**Figure 3:** XRD analysis obtained from the synthesized Zeolite Y at  $\text{Na}_2\text{O}/\text{SiO}_2$  of 0.70



**Figure 4:** XRD analysis obtained from the synthesized Zeolite Y at  $\text{Na}_2\text{O}/\text{SiO}_2$  of 0.75



**Figure 5:** XRD analysis obtained from the synthesized Zeolite Y at  $\text{Na}_2\text{O}/\text{SiO}_2$  of 0.80



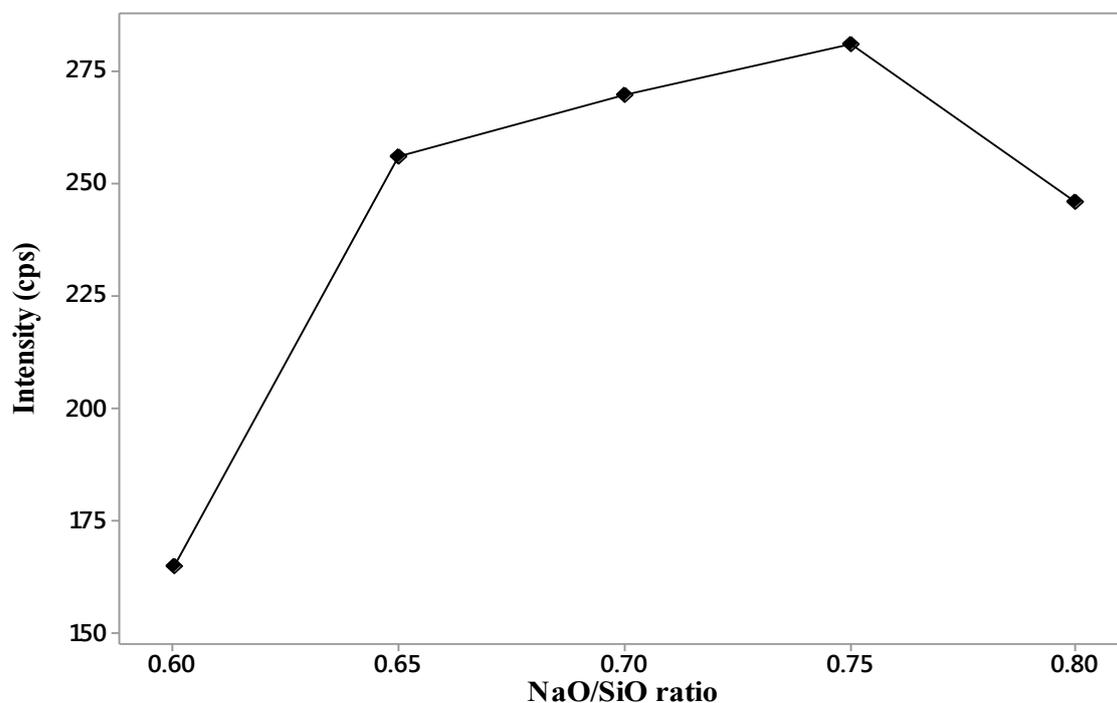
**Figure 6:** XRD pattern for standard Zeolite Na – Y (Source: collection of powder XRD patterns for zeolites by Treacy and Higgins, 2001)

The powder X-ray diffractometer made use of  $\text{Cu } K\alpha$  radiation to determine sample crystallinity. In identifying an unknown zeolitic material, the three most pronounced peaks as well as the low angle peaks before  $2\theta$  equals  $10^\circ$  should be compared with the corresponding reflections [17], [18]. The formation of zeolite Y phase was confirmed when compared the diffractograms of all synthesized samples to the diffractogram of the reference zeolite Y which indicates an FAU structure. From literature, the first peak of zeolite Y in a range of  $2\theta$  having  $2 - 50^\circ$  appears within  $6 - 10^\circ$ . And the first peak was observed at  $2\theta = 6.14^\circ$  and three other distinct peaks occur at  $13.99^\circ$ ,  $20.90^\circ$  and  $24.31^\circ$ . The small zigzag peaks refer to the presence of amorphous material while the peaks confirm the presence of crystalline phases though not necessarily the desired phase. There were not as many peaks in the synthesized samples as there is in the case of the

reference zeolite Y.

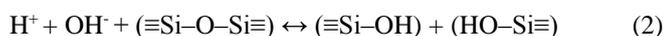
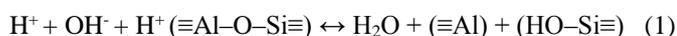
From Figures 1 – 6, it is observed that the intensities of the first peak at  $6.14^\circ$  are not as pronounced as that of the standard zeolite Y. This is as a result of the low crystalline phase of the zeolite Y in the synthesized samples which can be attributed to factor like as the presence of impurities in the alumina and silica used (clay).

Figure 7 shows that the crystallinity of zeolite Y (based on the intensity of the observed peak at  $6.14^\circ$ ) increases with increase in NaOH concentration. However, the intensity of the peak drops after  $\text{Na}_2\text{O}/\text{SiO}_2$  ratio of 0.75. According to [19], the zeolite generation reaction from kaolin is considered to consist of a dissolution process for soluble Si species and soluble Al species. This indicates that zeolite production is promoted with a higher NaOH concentration.



**Figure 7:** Variation of the intensities (at  $2\theta = 6.14$ ) against NaOH concentration

These findings also indicate increasing the alkalinity of the synthesis solution will reduce the dissolution time of the silica and alumina in the metakaolin hence, increasing the overall reactivity as well as the depolymerization of silica species. This is because when NaOH comes in contact with the metakaolin, it produces OH<sup>-</sup> ions. When these OH<sup>-</sup> ions are released into the system, it favours the breakdown of Si-O-Si, Si-O-Al and Al-O-Al bonds in the metakaolin. As a result, silicon and aluminium ions are released into the system to form Si-OH and Al-OH bonds necessary for the zeolite Y formation according to Equations (1) and (2).



Hence, with increasing alkalinity, more OH<sup>-</sup> ions are released into the system, favouring the depolymerization of the silica and alumina bonds necessary for zeolite Y formation. However, when the alkalinity is excessively high as in the case of Na<sub>2</sub>O/SiO<sub>2</sub> ratio of 0.8, the crystalline structure of zeolite Y, in the metastable state, is liable to dissolve and the crystallinity will decrease.

The presence of other prominent peaks (i.e. at  $2\theta$  values of 13.99<sup>o</sup>, 20.90<sup>o</sup> and 24.31<sup>o</sup>) indicates the presence of highly siliceous materials in the products obtained because the alumina bonds (Al-O) are more readily broken down than the silica (Si-O) bonds in the aluminosilicate gel.

## CONCLUSION

Zeolite Y was synthesized from Elefun kaolinite clay with low crystallinity with optimal ratio of Na<sub>2</sub>O/SiO<sub>2</sub> of 0.75, aging period of 7 days, crystallization time of 36 hours and temperature of 95<sup>o</sup>C. The concentration of NaOH used in gel synthesis influences the level of crystallinity of the zeolite obtained, higher concentration of NaOH up to Na<sub>2</sub>O/SiO<sub>2</sub> of 0.75 increases the crystallinity of zeolite Y.

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