

Effect of Crystallisation Time on the Synthesis of Zeolite Y from Elefun Kaolinite Clay

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Abstract

In this study, the effect of crystallization time on the synthesis of zeolite Y from Elefun kaolinite clay was investigated. During the synthesis of zeolite Y, the raw Elefun kaolinite clay was beneficiated thoroughly with water for 7 days before it was calcined at a 850°C for 6 hours to thermally convert it to metakaolin. Dealumination of the metakaolin was then carried out using the novel method to achieve a target SiO₂/Al₂O₃ ratio of 6.5. A hydrogel solution was prepared by mixing the dealuminated metakaolin with sodium hydroxide and water in calculated proportions. The mixture was heated to a temperature of 95°C between a time range of 12 to 60 hours. The crystallized product was then washed thoroughly with deionized water and then dried. Analysis was carried out on the dried product sample using two different characterization techniques; X-ray diffraction (XRD) and X-ray fluorescence (XRF). The results from the analysis indicated the formation of zeolite Y from Elefun Kaolinite clay and the maximum crystallization time obtained for the synthesis of zeolite Y from Elefun Kaolinite clay at 95°C was 48 hours.

INTRODUCTION

Nigeria is richly endowed with huge reserves of oil and gas [1], [2], [3]. Apart from its crude oil potentials, Nigeria also has comparative advantage in the solid minerals sector owing to the large deposits of clay minerals scattered in different parts of the country [1], [2]. Kaolin is one of the industrial minerals that can be found in commercial quantity. In fact, Nigeria has widely distributed reserves of kaolin to support the choice of kaolinite clay as a base material for zeolite Y production [3].

A zeolite is a natural or synthetic aluminosilicate crystal of which framework is composed by the assembling of SiO₄ and AlO₄ tetrahedral units [4], [5]. Zeolite materials are micro porous with crystalline structure within which there are large number of small cavities which are interconnected. These

cavities and channels are precisely uniform in size. The material is known as molecular sieve since the dimension of the pore is to accept for adsorption molecules of certain dimension while rejecting those of larger dimension [6], [7]. Zeolites have been widely used in many applications due to their unique properties (thermal stability, acidity, ion-exchange capacity, adsorption for gas and vapor and catalytic properties). Zeolites are becoming increasingly relevance in several industrial applications. Today zeolite Y plays a major role, as a catalyst, in the fluid catalytic cracking of petroleum products [1], [4], [8].

Zeolite Y belongs to the class of zeolites known as Faujasites, a class of aluminosilicate zeolites containing three-dimensional void spaces within their structure [8]. The synthesis of zeolite Y is performed by a hydrothermal crystallization process using commercial chemicals serving as sources of silica and alumina [8], [9]. These chemicals are generally expensive and their process of production is complicated. However, production of zeolites from a low cost and abundant material such as clay (kaolin), as a source of alumina and silica is feasible and profitable.

Zeolites are thermodynamically metastable crystalline aluminosilicates with framework type structures and as such in the crystallization of zeolites the Ostwald's law of successive transformations is obeyed [10], [11]. The transformation proceeds from amorphous to metastable to more stable phase. During this structural transformation the crystallinity of the zeolites changes with crystallization time [12].

This research work is to focus on the effect of crystallization time on the synthesis of zeolite Y using Elefun kaolinite clay as the silica-alumina source. The products obtained will be characterise using X-ray fluorescence (XRF) and X-ray diffraction (XRD).

MATERIALS AND METHODS

The crude kaolinite clay was obtained in Elefun, Ogun state (Nigeria). It is naturally found in large quantity as white soft lumps which need to be crushed into small size to increase the surface area of exposure of the clay to the beneficiation process.

Beneficiation

Raw kaolin collected from Elefun situated in Ogun state, Nigeria was beneficiated using the wet process in order to purify the sample. The process was carried out repeatedly for 7 days with predetermined intervals of masticating, stirring, decanting and sieving.

The kaolin was first soaked in water before it was masticated. The mastication was done to properly grind the clay and also to remove the stony particles by handpicking. The mixture was then agitated thoroughly and allowed to settle. After each stage of sedimentation, water was decanted and replaced with fresh one. A sieving mesh was also used to sieve the mixture in order to obtain fine particles of kaolin clay. After sieving, the mixture was allowed to settle (the silica being denser than the alumina settled at the bottom of the container).

This process of agitation, sedimentation, sieving and decanting was done repeatedly until the solid sediments at the bottom of the container reduced significantly. The final sieved material was then dewatered using cloth sacks and air dried on polythene bags for 3 days and further dried at 150°C in an electric oven for 3 hours. After drying, the lumped kaolin clay was further reduced to very fine particle sizes using a mortar and pestle.

Calcination

The calcination process was done to thermally activate the kaolin by convert it to meta kaolin. The beneficiated clay was evenly spread in fabricated crucibles at a predetermined depth of 1.5cm in order to achieve a relatively good heat distribution during heating. The thermal treatment took place in an electric furnace at a temperature of 850°C for 6 hours. The meta kaolin obtained was allowed to cool before being subjected to XRF analysis

Dealumination

The aim of the dealumination process was to reduce the alumina content in the meta kaolin. The novel method used in the dealumination of the meta kaolin involved the reaction of the meta kaolin with sulphuric acid (H₂SO₄) 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 also repeated but heat was applied.

Gel Formation

Gel was obtained from a silica/alumina ratio of 6.5 (SiO₂/Al₂O₃ = 6.5), a sodium dioxide/silica ratio of 7.0 (Na₂O/SiO₂ = 7.0) and a water/sodium dioxide ratio of 30 (H₂O/Na₂O = 30) by mixing calculated amounts of meta kaolin, sodium hydroxide solution and deionized water.

Deionized water was first added to the meta kaolin and mixed thoroughly before adding NaOH pellets into the mixture. The pellets were allowed to dissolve completely and the mixture was thoroughly stirred as well for 30 minutes. Then the slurry was transferred into polyethylene containers and allowed to age under atmospheric conditions for seven days.

Crystallization

To obtain crystallized form, the gel samples were heated at 95°C in an electric oven. The crystallization time of each of the gel samples was varied (12hours, 24hours, 36hours, 48hours and 60hours). When removed, each gel sample was immediately washed with deionized water, filtered using a suction pump and then allowed to dry under atmospheric conditions.

Characterization

The crystalline of the final zeolitic product was studied using two different characterization techniques; XRF (for the elemental composition) and XRD (for the crystallographic structural status and phases of the entire component in a material) analysis. X-ray diffraction operated with Cu radiation (45 kV and 40 mA) and data collection was carried out in the 2θ range 5-30 degrees, with a step size of 0.026 and scan step time 3.57Sec. The Analysis was carried out on the product samples at different stages of the synthesis.

RESULTS AND DISCUSSION

Effects of Beneficiation and Calcination

XRF analysis was carried out on the raw, beneficiated and calcined kaolin samples to identify their elemental compositions (Table 1). The analysis showed the importance of beneficiation and calcination by reducing the amount of SiO₂ from 41.3wt% (raw sample) to 39.9wt% (beneficiated)

then to 39.5wt% (calcinated); and also increased the amount of Al₂O₃ from 52.1wt% (raw sample) to 53.8wt% (beneficiated) and to 54.3wt% (calcinated). These changes converted the sample obtained to one that was close (in property) to pure kaolinite.

Table 1: XRF analysis of the raw, beneficiated and calcined samples

Element	Raw Sample (wt%)	Beneficiated Sample (wt%)	Calcinated Sample (wt%)
Na ₂ O	0.000	0.211	0.000
MgO	0.658	1.037	0.537
Al ₂ O ₃	52.079	53.785	54.275
SiO ₂	41.271	39.930	39.519
SO ₃	0.387	0.538	0.200
K ₂ O	0.299	0.096	0.334
CaO	0.044	0.039	0.041
TiO ₂	2.824	1.999	2.740
Cr ₂ O ₃	0.027	0.020	0.026
Mn ₂ O ₃	0.002	0.004	0.002
Fe ₂ O ₃	2.390	2.332	2.306
ZnO	0.004	0.000	0.004
SrO	0.014	0.010	0.014

Effect of Dealumination

Table 2 shows the XRF analysis of the elemental composition (wt%) of the dealumination of the meta kaolin that involved both the heating method and the novel method.

Table 2: Elemental composition (wt%) of dealuminated meta kaolin samples

Components	Dealuminated Sample (wt%) (Heating method)	Dealuminated Sample (wt%) (Novel method)
SiO ₂	80.480	61.900
Al ₂ O ₃	3.200	27.000
K ₂ O	0.110	0.026
CaO	0.276	0.314
TiO ₂	10.800	7.090
V ₂ O ₅	0.290	0.210
CrO ₂	0.021	0.048
MnO	0.010	0.020
Fe ₂ O ₃	1.210	2.430
Na ₂ O	2.430	1.040
MgO	0.980	0.710
SO ₃	0.190	-

Table 3: Silica/Alumina ratio of the dealuminated samples

Sample	Silica/alumina ratio
Heating method (wt%)	42.70
Novel method (wt%)	3.89

The silica/alumina ratios of the two samples involving heating and novel method were calculated. From the results, a SiO₂/Al₂O₃ ratio of 3.89 was obtained for the novel method while a SiO₂/Al₂O₃ ratio of 42.70 was obtained for heating method. The calculated value of 3.39 for novel method was closer to the target SiO₂/Al₂O₃ ratio of 6.5. Hence, the novel method was seen to be a better and more accurate method for dealumination. The difference in the calculated value (for novel method) and the target SiO₂/Al₂O₃ ratio could be as a result of the presence of impurities.

Effect of Crystallization Time

Figures 1 – 5 showed the results obtained when the crystallization time during the synthesis of zeolite Y was varied.

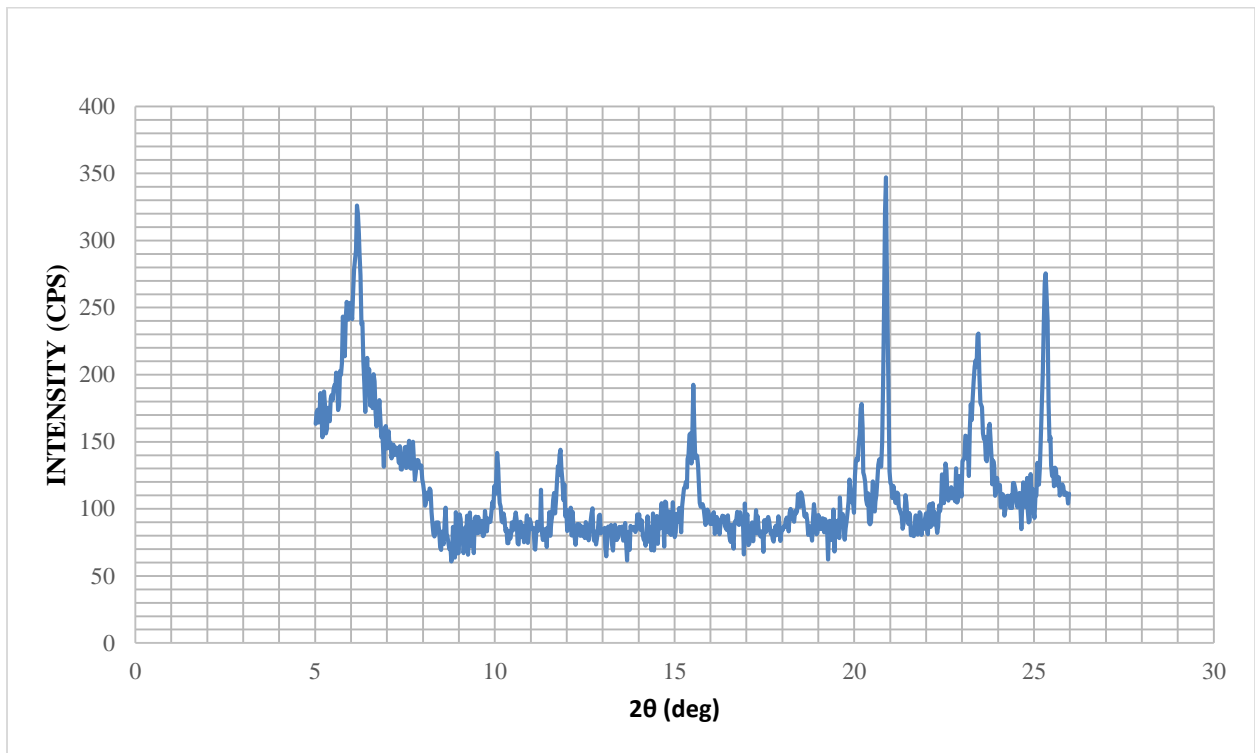


Figure 1: X-ray diffraction patterns of the final product (Zeolite Y) after 12 hours

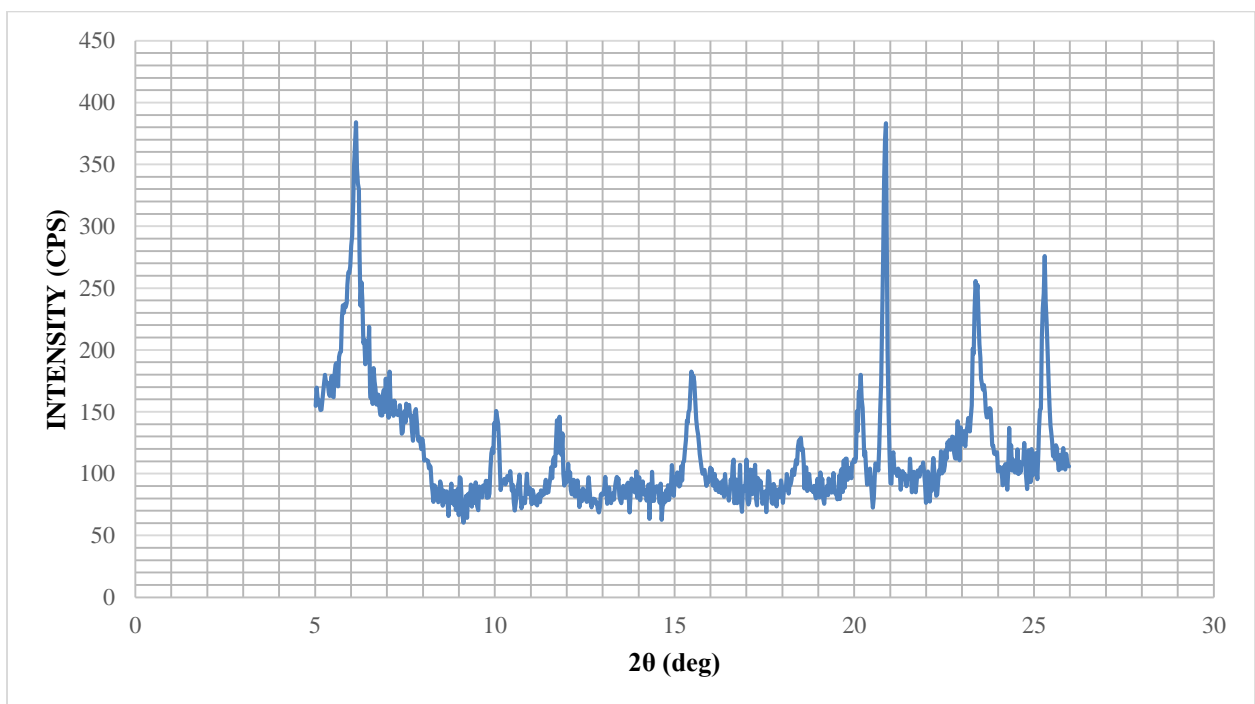


Figure 2: X-ray diffraction pattern of the final product (Zeolite Y) after 24 hours

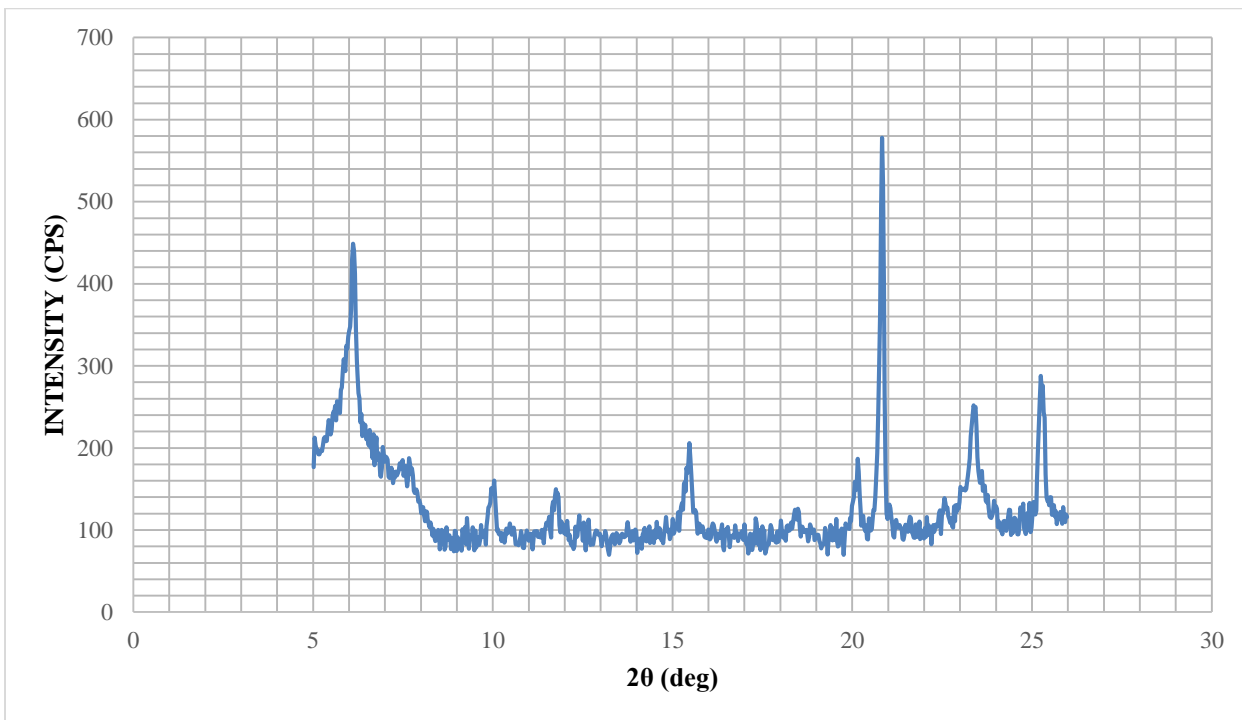


Figure 3: X-ray diffraction pattern of the final product (Zeolite Y) after 36 hours

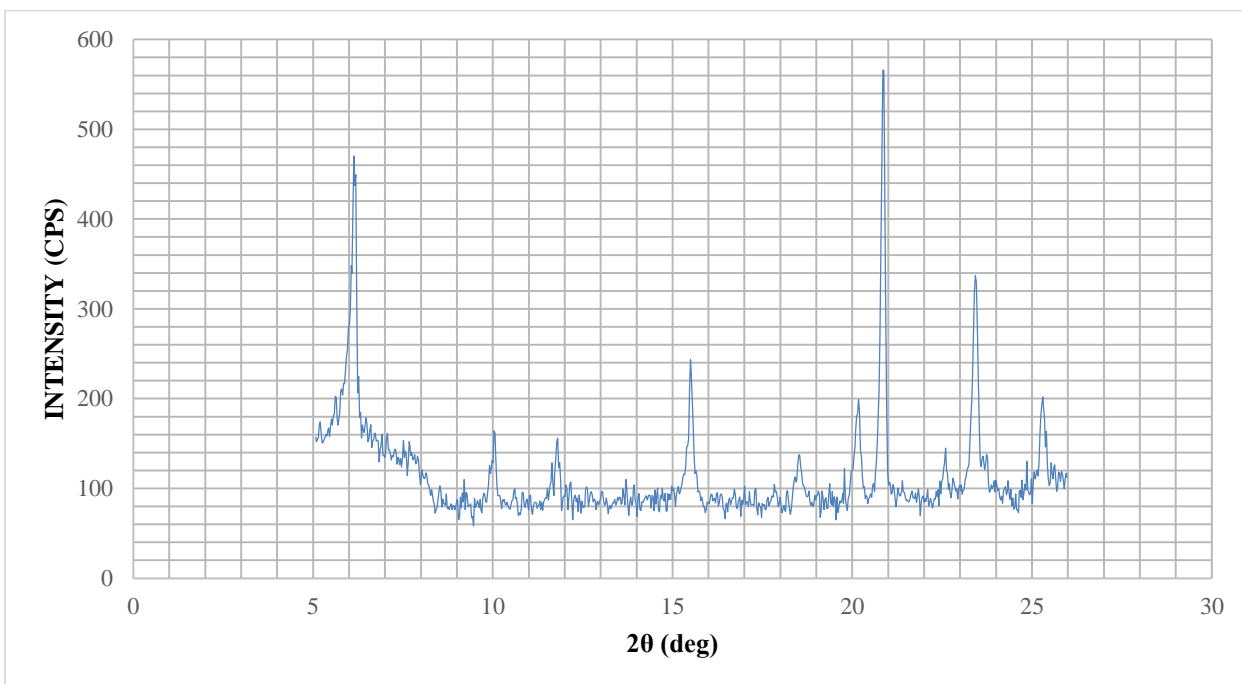


Figure 4: X-ray diffraction patterns of the final product (Zeolite Y) after 48 hours

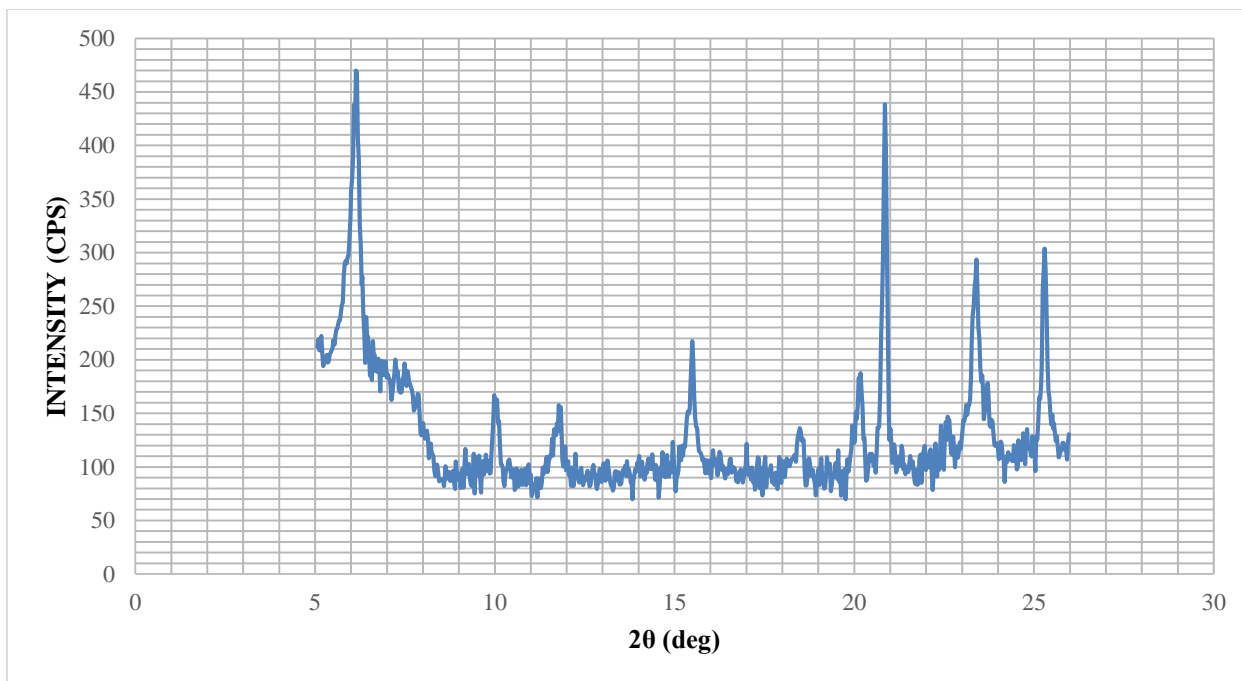


Figure 5:

X-ray diffraction patterns of the final product (Zeolite Y) after 60 hours

The peak positions of XRDs are usually measured in 2θ . From the results obtained the most distinct peaks occurred between 6° to 30° and this confirms the presence of a zeolite phase (Ruren et. al., 2007).

The X-ray diffraction patterns revealed both amorphous and crystalline forms in the samples. Small zigzag peaks indicated the presence of amorphous material while the Strong peaks represented full crystalline phases. According to [13], the first peak for zeolite Y appears within $6-10^\circ$ and the first peak (Zeolite Y) was observed at $2\theta = 6.13^\circ$. The other distinct peaks indicate the formation of other forms of zeolite and this shows the meta-stability of zeolites (ability of zeolites to transform from one phase to a more stable phase).

Zeolite Y peaks become more intense with increasing crystallization time. The reason for the increase in intensity is due to increase in density of the samples. The density increase confirms crystal growth in the sample. This confirms the relationship between the intensity of the peaks and the degree of crystallinity of zeolitic materials [1], [2].

The relative intensities of the peaks was then used to determine the relative crystallinity of each sample. Considering American Society for Testing and Materials (ASTM) standard, the crystallinity percent (%) was determined using:

$$\text{Crystallinity (\%)} = \frac{\text{Intensity of peak (sample)}}{\text{Intensity of peak (reference)}} \times 100\% \quad ..1$$

Table 4 shows the variations of the intensity peaks and crystallinity with respect to crystallization time.

Table 4: Variations of the intensity peaks and crystallinity with respect to crystallization time

Crystallization Time (hour)	INTENSITY PEAKS					Max height	% Relative crystallinity
	6.13	15.49	20.88	23.43	25.27		
12	292.8	156.7	347.0	229.1	236.8	1262.4	69.7
24	384.0	172.7	383.2	252.7	245.5	1438.1	79.4
36	440.7	187.4	394.0	249.9	269.4	1541.4	85.1
48	470.2	243.4	565.9	337.1	194.5	1811.1	100
60	470.0	217.3	396.6	267.1	283.6	1634.6	90.3

In Table 4, the sample with the most intense peaks was taken as reference (100% crystallinity) and the percentage crystallinity of the other samples was calculated relative to the reference. The transformation of the amorphous aluminosilicates gel to the crystalline phases is presented in Figure 6, showing a plot between the crystallization times versus the intensity of each phase.

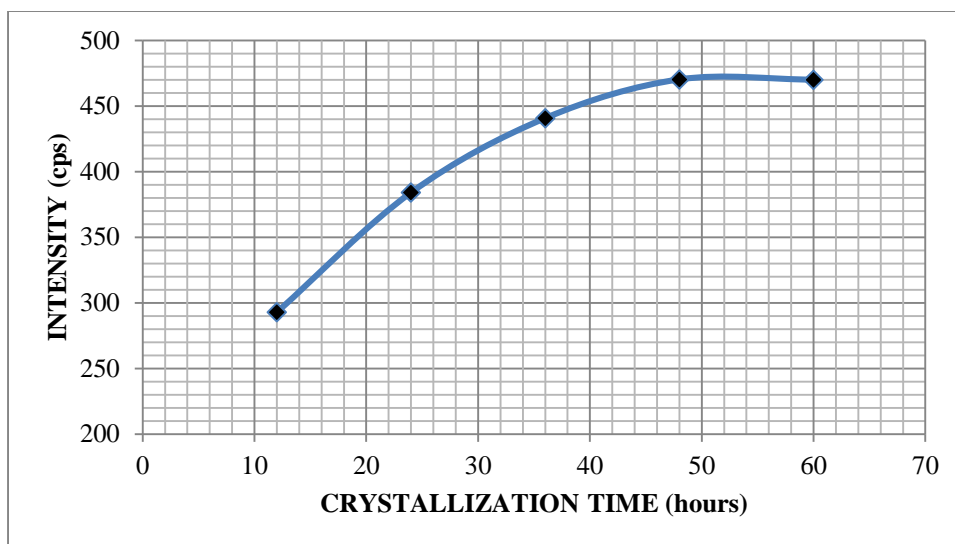


Figure 6: Variation of intensity with crystallization time

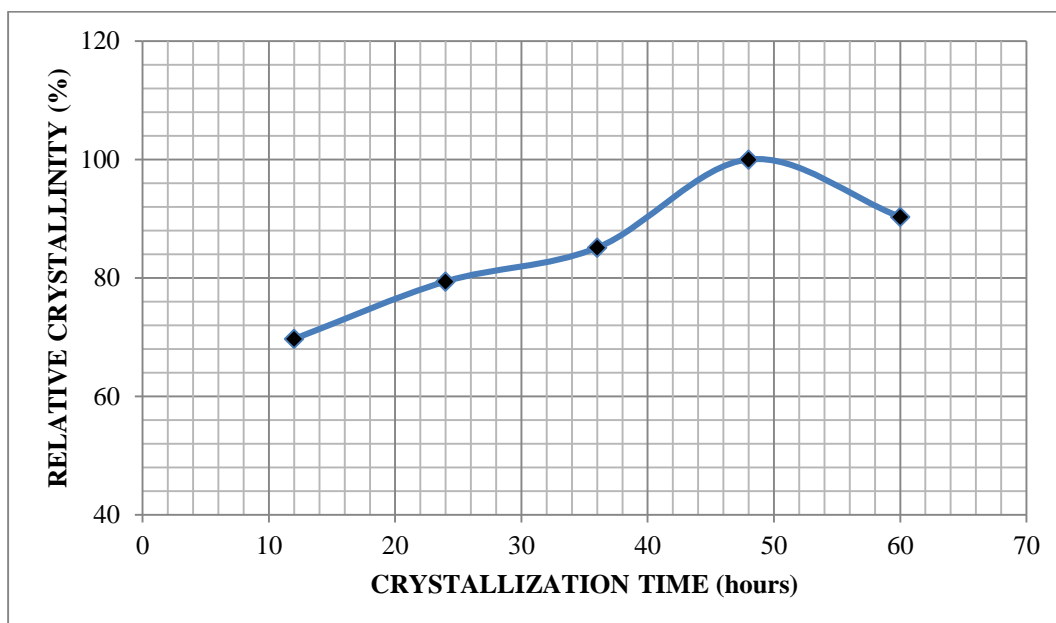


Figure 7: Variation of relative crystallinity with crystallization time.

Figure 7 shows the relationship between crystallinity and crystallization time. The relative crystallinity increases progressively with time until 48 hours afterward the crystallinity is kept at high level with less change.

It could be inferred that the intensity in peak heights grows during the crystallization time reached its maximum at 48 hours of reaction after which the characteristic peaks of faujasite zeolite Y started to decrease in intensity. The reduction in peak intensities after 48 h may be as a result of the transformation of zeolite Y to other forms of zeolite.

CONCLUSION

This research showed that Elefun kaolinite clay is a good silica-alumina source for the production of zeolite Y and crystallization time is also a major parameter that influences the synthesis of zeolite Y. Also, the maximum degree of crystallinity for zeolite Y can be attained at a crystallization time of 48 hours at 95°C.

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