

PAPER 142 – SYNTHESIS AND CHARACTERIZATION OF ZEOLITE A FROM ALOJI KAOLIN VIA HYDROTHERMAL METHOD

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ABSTRACT

This study focused on the synthesis and characterization of Zeolite A from Aloji kaolin via the hydrothermal method. The effect of short crystallization times (0.5h, 1h, 1.5h, 2h, and 3h) and high crystallization temperature of 115°C on the formation of Zeolite A as the final product was investigated. The characterization of the synthesized Zeolite A was conducted using Scanning electron microscope (SEM), X-ray diffraction (XRD), and Brunauer- Emmett- Teller (BET) analysis. The results showed a well-developed Zeolite A with cubic morphology and a crystallinity of 78.12%, as well as a surface area and pore size of 18.8832 m²/g and 178.461 Å respectively was successfully synthesized using high alkali concentration (5 mol/L) and a crystallization time of 3h. The findings provide a valuable insight into the synthesis of Zeolite A from kaolin and its potential application in various fields.

KEYWORDS: Kaolin, Zeolite, Crystallization, Temperature, Hydrothermal.

1. INTRODUCTION

Increase in global population as well as rapid industrialization has resulted in depletion of non-renewable resources, increasing pollution and thus various ecological and environmental problems. These problems have greatly transcended to degradation of the environment and human health which has greatly started people to become inquisitive about current model of industrialization procedure and production. Due to improvement in regulations and emergence of new policies there is a shift in the regular mode of pollution first then treatment later to a cleaner method of production. In the clean production methods harmful and very toxic substances that cause pollution are either avoided or reduced to the barest minimum. (He *et al.*, 2021).

Zeolites are porous materials that consist of a three-dimensional framework structure of crystalline aluminosilicate materials. Zeolites have uniform sized pores and usually known as molecular sieves (Johnson & Arshad, 2014). Zeolites have a very wide range of applications and have been applied in fields such as catalysis, adsorption processes, bacterial adhesion water treatment, air pollution remediation, detergent making, fuel cell and ion exchange. (Hartarti *et al.*, 2020). Zeolites exist in two categories, both as natural and synthetic. The natural occurring ones are mined from the earth while the synthetic zeolites are produced in the laboratory. Natural zeolites are found in sedimentary rocks that are near the earth's crust. Commonly found natural zeolite includes Clinoptilolite, Analcime, chabazite, heulandite, erionite, laumontite, and mordenite (Derbe *et al.*, 2020; Nasief *et al.*, 2021). Natural zeolites are known to contain contaminants like Fe²⁺, SO₄²⁻, SiO₂, and sometimes other zeolites, these impurities tend to reduce their pores and channels thereby making them unsuitable for commercial use where purity and uniformity are highly essential.

In order to eliminate the limitations associated with natural, it has prompted researchers to investigate the synthesis of synthetic zeolite. (Yoldi *et al.*, 2019). Synthetic zeolites are generally preferred due to the homogeneity in their composition (particle size and shape) as well as high crystallinity in comparison to the natural zeolite. This is majorly due to the ease with which desired structural properties and chemical compositions can be manipulated by varying the parameters during the synthesis operation. (Lim *et al.* 2021)

Synthetic zeolite preparation and synthesis are very challenging and the common synthesis methods involves using alumina and silica obtained from analytical/ synthetic chemicals to form aluminosilicate hydrogel which is then crystallized to obtain zeolite. This source of alumina and silica is very expensive and leads to high cost of zeolite in addition to causing several environmental burdens due to pollution. (Otieno *et al.*, 2019; Kumar and Jena 2022). In an attempt to reduce the cost of zeolite and pollution associated with using analytical grade chemicals, several other alternative sources of alumina and silica have been explored and are still currently being investigated. Kaolin has been found to be an alternative source for alumina and silica because of its low-cost benefit and it has a Si/Al ratio of 1 which suitable for the synthesis of low silica zeolites. (Lim *et al.* 2021; Binay, *et al.* 2019). Low silica zeolites like zeolite A also known as zeolite LTA are of very special interest due their high adsorption and ion exchange properties. (Arasi *et al.*, 2021; Kirdeciler & Akata 2020; Kamyab & Williams 2021).

In this work Aloji kaolin was used as an alternative source for alumina and silica because of its low-cost benefit and it has a Si/Al ratio of 1 which is suitable for the synthesis of low silica zeolites. The work involves the synthesis of zeolite A from Aloji kaolin. This will be achieved by refining raw kaolin and then converting this to metakaolin by calcination. The metakaolin will then be used in synthesizing zeolite A.

2. MATERIALS AND METHODS

2.1 Materials

Raw Kaolin was obtained from Aloji in Kogi state, Nigeria. The only chemical reagent used was analytical grade sodium hydroxide (NaOH) pellet obtained from Sigma Aldrich. Also, the deionized and distilled water used were all obtained within Chemical Engineering Laboratory of the Federal University of Technology, Minna and were used as at when received.

2.2 Method

2.2.1 Refining and Metakaolinization of Kaolin clay

Raw Aloji kaolin was crushed mildly and sieved using an 850 μ m sieve mesh. This was then transferred into a 1000ml beaker where it was soaked using deionized water for 12h. The mixture was then stirred continuously for about 30 minutes after which the lighter fraction (supernatant) was collected. After sedimentation the Kaolin was decanted and dried in the oven. The refined Kaolin was then calcined in a muffle furnace at 850 °C for 2h to obtain metakaolin which is a more reactive form of Kaolin.

2.2.2 Synthesis of Zeolite A

Zeolite A was synthesized from Aloji kaolin using the conventional hydrothermal method. Refined Kaolin was converted to metakaolin at 850 °C. The metakaolin obtained were then mixed with 5M concentration of sodium hydroxide and the resulting mixture was stirred using a magnetic stirrer. The homogenous solution was aged and then heated in a Teflon lined stainless steel autoclave at 115 °C for 0.5h, 1h, 1.5h, 2h and 3h. The resultant product obtained was continuously washed with deionized water until a pH of 7 was obtained, after which the zeolite sample was dried in an oven at 100 °C for 8h and the zeolite crystals obtained stored in an air tight container.

2.3 Zeolite Characterization

2.3.1 X-Ray Diffraction (XRD).

X-ray diffraction (XRD) is an efficient and effective technique that is used to identify crystallographic structure of solids. XRD can be used to determine the crystal size of zeolites, study the crystal structure of zeolite, as well as determine the crystallinity of zeolites. The XRD analysis was performed using an **Ultima IV, Rigaku, UK and with Cu-K α radiation having a fixed power source (40 kV, 40 mA), and** a diffraction angle (2θ) in the range of 5-90 $^{\circ}$ and these were detected at a scan rate of 0.01. the percentage crystallinity was calculated using Equation 1

$$\text{Percentage crystallinity} = \frac{\text{Sum of relative intensities of synthesized zeolite}}{\text{Sum of relative intensities of standard zeolite}} \times 100 \dots\dots\dots 1$$

2.3.2 Scanning Electron Microscopy (SEM).

Scanning electron microscope (SEM) is a technique that is used to study the surface of solids (zeolite crystals) as it shows the crystal shape and size. It also provides various signals that describe the morphology and topology of the zeolite.

2.3.3. Brunauer- Emmett- Teller (BET).

Nitrogen adsorption_ desorption isotherms were observed using Quantachrome Corporation instrument. The specific surface area was calculated using Brunauer- Emmett- Teller equation. The pore volume was obtained based on the amount of nitrogen adsorbed at P/P $_0$ 0- 0.99.

3.0 RESULT AND DISCUSSION

3.1 XRD ANALYSIS

XRD analysis was carried out for the metakaolin and each of the zeolite samples synthesized at various crystallization times during zeolite synthesis. This is because the phase composition was obtained from the XRD analysis would determine the success of the synthesis of Zeolite A. The XRD pattern shown in Figure 1 gives the analysis of result for the metakaolin used in the Zeolite A synthesis. The diffraction pattern obtained shows that peaks associated with kaolinite mineral can be seen at 2θ values of 12.38 and 24.94. The metakaolin also contains impurities like quartz and mica as seen by the diffraction peaks at 26.67 and 20.84 respectively.

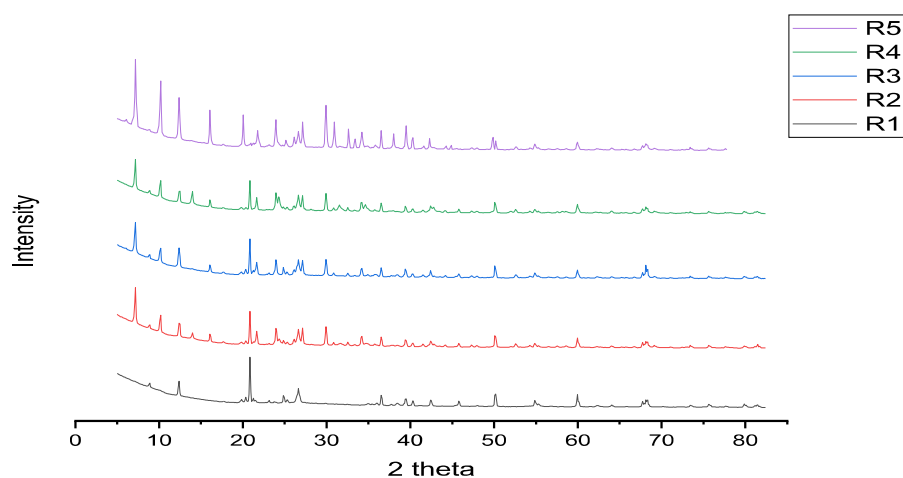
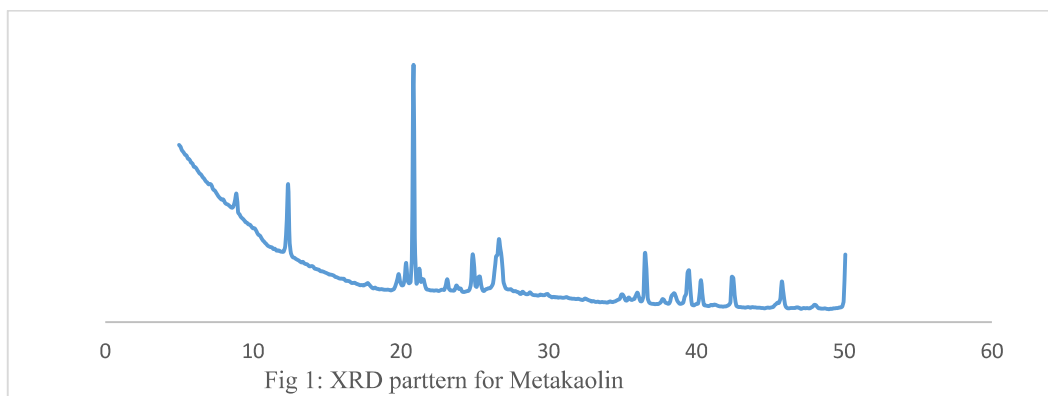


Fig 2: XRD pattern for synthesized zeolite at various crystallization times

In the study of zeolite synthesis, XRD analysis was carried out. Figure 2 shows the XRD pattern for the zeolite synthesized at various crystallization time. It can be seen from the result that the XRD obtained after 0.5h of crystallization (R1) showed peaks only similar to those found in the metakaolin. These are kaolinite peaks at 2 theta values of 12.51, 24.64 and quartz peaks at 26.67. However, at a crystallization time of 1h as indicated by plot R2, other diffraction peaks became visible. Here peaks characteristic of zeolite A began to emerge. The diffraction peaks at 2θ values of 7.18, 10.24, 12.49, 16.04, 20.46, 30.89, and 34.21 were obtained. Similarly, a peak characteristic of faujesite was obtained at 2θ value of 14.21; this readily disappeared as crystallization time increased to 1.5h. The diffraction peaks obtained at 1.5h (R3) has similar peaks as those at 1h. it was observed that more peaks characteristic to zeolite A were added and the faujesite peak disappeared. New peaks that emerged at 1.5h were obtained at 2θ values of 19.98, 24.13, 36.67, 39.65, 42.31 and 42.74. The diffraction peaks obtained after 2h (R4) crystallization time were seen at 2 theta values of 7.18, 10.24, 12.49, 16.04, 20.46, 24.13, 30.89, 34.21, 36.67, 39.65, 42.31, 42.74, 44.25 and 47.34. These peaks are characteristic peaks obtained for zeolite A according to Tracey and Haggins (2001). This confirms that zeolite A formation begins even after 1h crystallization time and continues to new peaks emerges with increasing time. The peaks obtained for zeolite synthesized at 3 h in this study gave the highest crystallinity of 78.12 % and the diffraction peaks were observed at 2θ values of 7.18, 10.24, 12.49, 16.04, 20.46, 21.71, 24.04, 25.15, 30.01, 30.89, 32.68, 34.21, 36.64, 38.04, 39.62, 40.27, 42.38, 44.20, 44.85, and 49.83. These peaks obtained from this work were in close agreement with to that obtained from the works of Yusriadi *et al.*, (2020); Maia *et al.*, (2019) and Vegree *et al.* (2020). Furthermore, it can be seen from Figure 2 that diffraction peaks obtained from the zeolite crystallized at 3h had peaks of higher intensities than the other zeolites synthesized, this may explain the reason for a higher percentage crystallinity obtained by this zeolite.

3.2. SEM ANALYSIS

The zeolite samples synthesized were viewed under the microscope to study the changes occurring as the synthesis time was increasing. Figure 3a-f gives the micrographs for the changes in the morphology of the zeolite during synthesis. It was observed from the micrographs that the metakaolin used as shown in Figure 3a were flat plated and had hexagonal shaped particles scattered within the plates. With a crystallization time of 0.5h, the micrograph in Figure 3b still depicted dominantly flat plated hexagonal shaped morphology. This goes to confirm the XRD pattern that at this crystallization time the XRD pattern was similar to that obtained for metakaolin having peaks only characteristic of kaolinite at 2 theta values of 12.51, 24.64 and quartz peak 26.67.

The micrograph in Figure 3c gives the zeolite sample formed at 1h crystallization time. The figure shows a mixture of both cubic and hexagonal shaped morphology for samples. However, the micrograph also showed an improvement from the originally flat plated metakaolin to transforming cubic shape (Gougazeh & Buhl, 2014). In a similar manner it agrees with the XRD result that peaks characteristic of zeolite was formed, since cubic shaped crystals were observed. Furthermore, in Figure 3d for 1.5h crystallization time and a similar pattern was identified as samples were seen to contain crystals of both cubic and hexagonal crystals.

In Figure 3e, the micrographs showed crystals that have predominantly cubic morphology, with very few flat plated and hexagonal shaped crystals present. The XRD result obtained confirms that zeolite samples crystallized for 2h produced more peaks that are characteristic of zeolite A than those crystallized at lesser time. The micrograph was almost similar to that of zeolite sample crystallized at 3h. Although the sample crystallized at 3h showed better formed cubes. This is clearly shown in figure 3f image cubic morphology for zeolite LTA using kaolin as starting raw material.

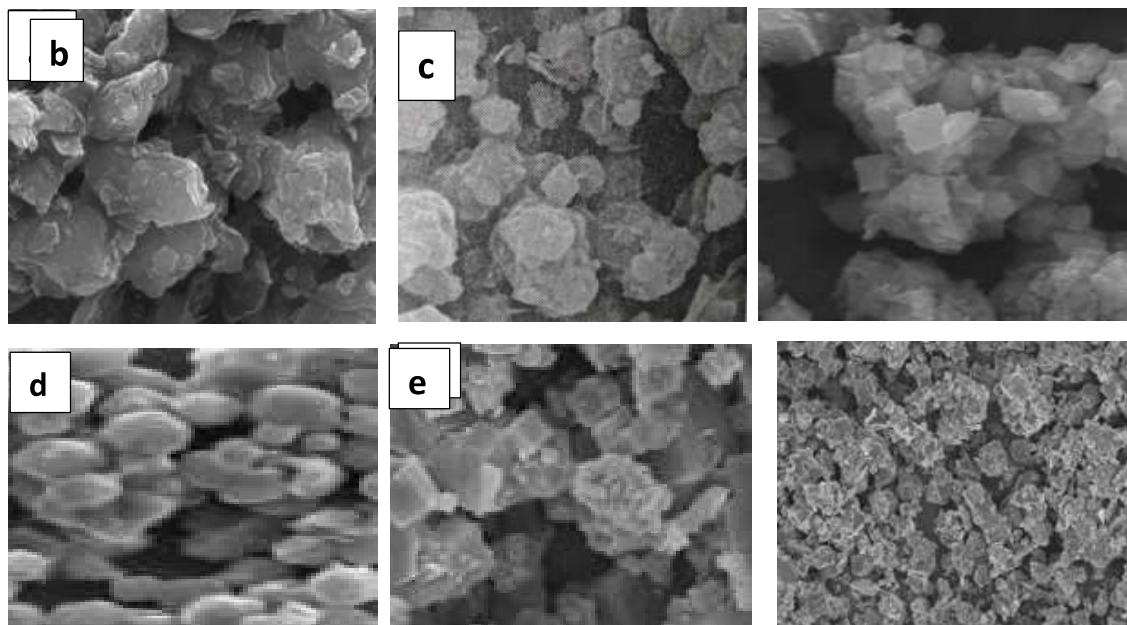


Fig 3: SEM images for zeolite A obtained at various crystallization times

The morphology of the synthesized zeolite A after 3h crystallization time with higher magnification is shown in Figure 4. The micrograph depicts some well-developed cubic crystals that is typical of zeolite A. This shape is in conformity with Kirdeciler *et al.*, (2020) and Salimkhani *et al.* (2021) that reported obtaining image cubic morphology for zeolite LTA using kaolin as starting raw material.

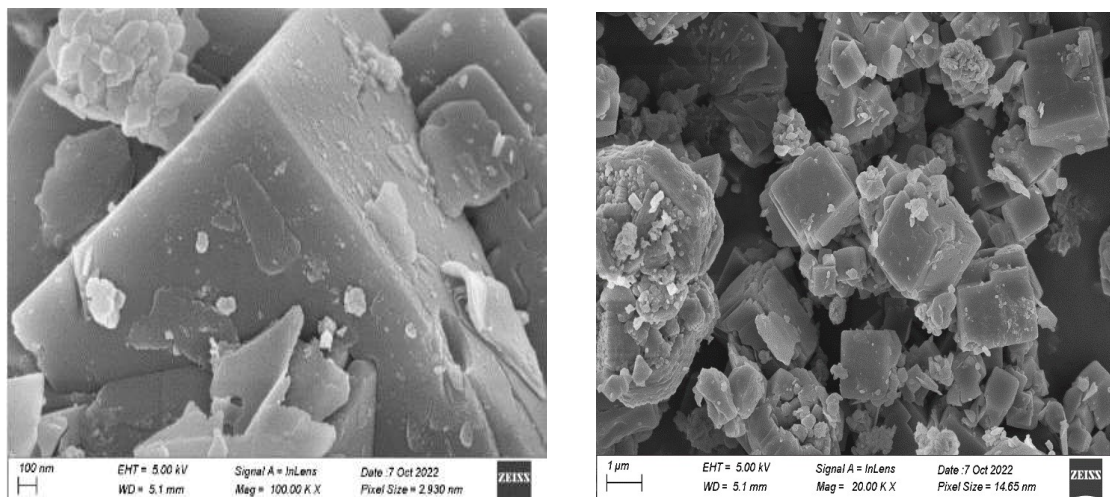


Fig 4: SEM images for zeolite A obtained at 3h crystallization time.

3.3 BET RESULTS

The pore size, pore volume as well as the surface area of the zeolite with the best crystallinity (R5) was determined using BET. The BET results show that the surface area pore size and pore volume of the synthesized zeolite was obtained as 18.8832 m²/g, and 178.461 Å, and 0.070864 cm³/g respectively, thus, the synthesized zeolite has pore size in the mesoporous range. The values were a much better and different than the values obtained as surface area, pore size and pore volume for the refined kaolin. These values were obtained as 14.15 m²/g, 166.593 Å, and 0.001326 cm³/g respectively. This also shows that the synthesis process resulted in an increase in surface area, pore size and the pore volume of the final product zeolite A.

4. CONCLUSION

In conclusion, the present study has demonstrated the successful synthesis of zeolite A from Aloji kaolin via hydrothermal method. The effect of varying crystallization times and temperature on the synthesis of zeolite A was investigated, and it was found that a crystallization time of 3 h on an alkali concentration of 5 mol/L resulted in a well-developed zeolite A crystal with high crystallinity and desirable morphological and textural properties. The characterization results obtained through XRD, SEM, and BET analysis confirmed the formation of Zeolite A with a cubic morphology, high surface area and pore size. These findings suggest that Aloji kaolin can serve as a potential source of raw material for the synthesis of zeolite A which could have potential application in various fields such as catalysis, separation and adsorption.

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