Synthesis and Characterization of Zeolite Lynde Type A (LTA): Effect of Aging Time

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Abstract. Zeolite Lynde Type A (LTA) has been widely applied, such as adsorbent, catalyst, membrane, ion exchanger, and even molecular sieve. As molecular sieve, the zeolite LTA has high dehydration ability and has a prospect as separation agent such as water removal from the ethanol-water mixture to obtain high purity bioethanol. Furthermore, it can repeatedly be used, lower energy usage, and environmentally friendly. Due to the number of advantages possessed, this research conducted to synthesize the zeolite LTA. The sources of silica and alumina used are from Coal Bottom Ash (CBA), PLTU Tarahan, Indonesia. CBA is a waste of coal burning that has not fully utilized. This effect of aging time was examined to obtain the highest percentage of its crystallinity. The results showed that 36 hours aging gave a product of zeolite with the best characteristics. The XRD analysis reported that this zeolite had 89.43% of crystallinity. The FTIR identification showed the presence of double rings structure which is characteristic of zeolite LTA. Finally, the result of SEM expressed the morphology of zeolite A on 3.163 μm of crystal size.

INTRODUCTION

The world's fuel energy crisis is getting worse due to the depletion of fossil fuel supply. Besides, the problem of global warming makes bioethanol is potential in realizing environmentally friendly fuel. The mixture of bioethanol and gasoline can functionalize as an alternative fuel for gasoline motors. Production of bioethanol with fermentation process produces bioethanol with a low purity rate (4-10%), to obtain bioethanol with purity >99.5% need further treatment. The process of purifying bioethanol after the fermentation process is made in 2 stages, namely distillation and dehydration. In the distillation process purity of bioethanol that can achieved about 95% [1]. Dehydration purification process consumes the highest energy. In order to reduce the energy needed, dehydration of water by adsorption process via a molecular sieve could be used as an alternative method. This method is relatively in expensive and simple. Also, the advantage of using molecular sieve is that it can be used repeatedly, low energy use, high dehydration, and environmentally friendly[2].

The molecular sieve used is zeolite because it has good adsorption capacity and good intensity in separating water from a water-bioethanol mixture. In industry, the synthetic zeolite is often used because it has higher purity and crystallinity than natural zeolite. However, the synthetic zeolite LTA is more expensive than natural zeolite because it is synthesized from commercial chemicals, yet produced in Indonesia, and must be imported from abroad. Whereas the synthetic zeolite LTA can be synthesized from materials containing silica and alumina, such as natural

materials, minerals and industrial wastes, whose existence is abundant, low cost, and is a waste that pollute the environment, such as rice husk, CFA (Coal Fly Ash), CBA (Coal Bottom Ash), bagasse, kaolin, low quality nature zeolite, and others.

In this study, CBA is used as the basic material for making zeolite LTA. CBA has not been widely applied. Meanwhile, its counterparts, CFA, has been utilized by cement factories to mix cement production. Also, CBA is easy to obtain, and the source is abundant in Indonesia, especially in Lampung because it is a solid waste of coal combustion from Steam Power Plant Tarahan. From coal combustion yields 10-20% bottom ash and 80-90% fly ash composition. If the coal ash is left alone without being processed and used, it will mount and need a vast land, causing problems for the environment. From the XRF (X-Ray Fluorescence) analysis CBA has a high silica (SiO_2) content of 77.68% ; alumina (Al_2O_3) 16.538%; K_2O 0.348%; CaO 1.854%; MgO 1.308%; $C_{O3}O_4$ 1.004%; and the rest is impurities.

Several factors influence the synthesis of zeolite, which is the molar ratio of reactants, the temperature of synthesis, the time of synthesis, the source of raw materials, the time of aging, and so on. For the synthesis of zeolites LTA using CBA takes some synthesis procedures from previous researchers and modifies them. In the synthesis of the LTA zeolite, the silica-alumina gel composition was obtained from research by Mirfendereski and Mohammadi [3] and step change methods obtained from Hui and Chao[4]. Based on study done by Mirfendereski and Mohammadi [3], synthesized LTA zeolites using commercial chemicals, while Hui and Chao[4] using CFA as the raw material for the synthesis of LTA zeolite and without any aging process.

In the synthesis of the LTA, the zeolite is studied the effect of aging time. Zeolite aging gel will have an effect on the nucleation period, the crystallization process, and purity of the final product, as well as on the size of the formed zeolite. The zeolite gel aging process effectively will shorten the hydrothermal time. Increasing the aging time of the gel will shorten the nucleation period, accelerate the crystallization process, increase product purity, and decrease the final size of the product crystals. The longer aging time, the smaller zeolite crystals will be obtained [5].

EXPERIMENTAL

CBA in an amount of 11.727 g was pulverized using a mortar and selected its size on a mesh sieve. Sodium hydroxie with amount of 10 g was dissolved 182.48 g of H_2O to obtain NaOH solution. This solution was then divided into two parts with volume equal, namely, A and B.

Dissolve 11.727 grams of CBA into solution A which has been made in the previous step and homogenized at 60^{o}C for an hour by stirring. In the same procedure, about 6.139 g of Al_2O_3 dissolved into solution B. The sodium silicate and sodium aluminate solutions were mixed to form a homogeneous alumina-silica gel and kept it for 1 hour.

The aging time processing varied, i.e., 0, 12, 24 and 36 hours respectively. The alumina-silica gel after this treatment in serted into polypropylene (PP) bottle and reacted hydrothermally to the water bath. The crystallization process took place in a two-step change method : 90℃ for 1.5 hours and 95℃ for 2.5 hours. After the hydrothermal process was complete, the sample was removed from the water bath and then filtered using filter paper to separate the solids from its mother liquor (filtrate). The mother liquor was stored in a bottle. The solid product was washed several times using distilled water to neutralized its pH and dried in an oven for 2 hours at 100℃. The solid was then cooled in a desiccator and stored for further analysis (XRD, FTIR, and SEM).

RESULTS AND DISCUSSION

FTIR Analysis Results

FTIR spectra showed in Fig. 1. consist of several major absorption bands which represent the characteristics of zeolite A, that is at wavelength 370-400 cm^{-1} is an open pore, 400-500 cm^{-1} is a bending vibration of SiO or AlO, 550-600 cm^{-1} is a double ring, 1000-1500 cm^{-1} is vibration strains asymmetry of O-Si-O or O-Al-O.

The peaks of zeolite A without aging gradually weaken, not sharp, and the intensity was decreased. Meanwhile, the peaks of the zeolite A with aging tended to be more intense and stronger while increasing aging time. When it was compared to not aging zeolite, it was found that zeolites A with 36 hours aging time, 385, 490, 580, 1100 cm^{-1} absorption bands were more intense. This result showed an increase in the degree of polymerization of the tetrahedral SiO_4 and the appearance of zeolite A seeds due to the presence of sodium alumina-silica [6].

In contrast, for non-aging zeolite A, there was no the increase in the degree of SiO_4 tetrahedral polymerization and no seeds from zeolite A.

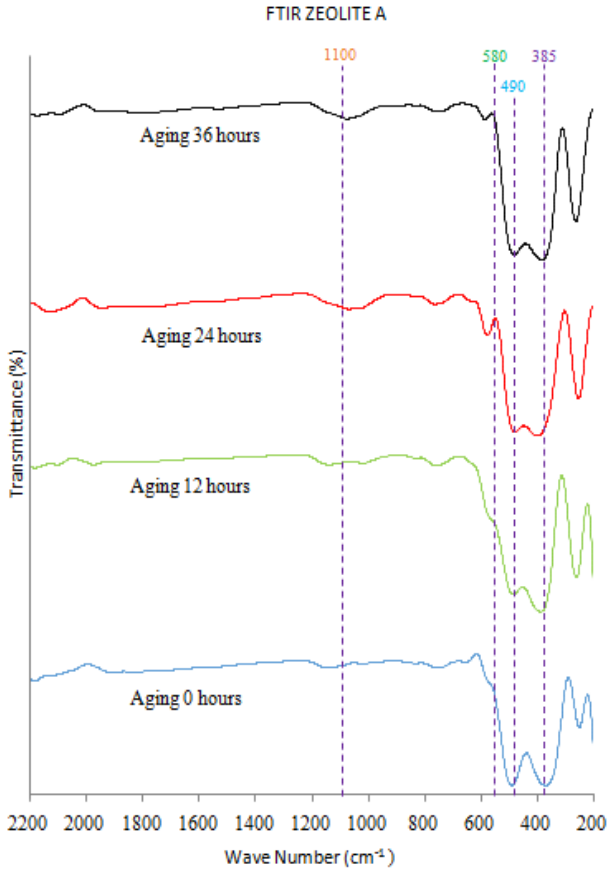


FIGURE 1.FTIR Spectrum of Zeolite A aging for 0, 12, 24, and 36 hours.

Zeolite A without aging showed no clear band in the wavelength region of 550-600 cm^{-1} characterizing double rings. On the other hand, zeolite A aging for 24 and 36 hours indicated a clear absorption band in the wavelength range 500-600 cm^{-1}. Double rings were characteristic of the zeolite A structure. Double rings were an external link between zeolite layers with one another [7]. When zeolite A with aging compared to that without aging, it was found that 24 hours and 36 hours of aging gave double rings as indicated by the adsorption band at 580 cm^{-1} wavelengths. These phenomena showed that the nuclei of crystal zeolite had been formed in the aging process at room temperature [5],[6].

XRD Analysis

Figure 2 illustrates XRD results of the zeolite A produced. The XRD analysis of Zeolite A without aging reported that the largest of the mineral constituent was corundum and mullite indicated by the sharp intensity at 2Θ = 26,2; 35.1; 43.3; 54.7; 57.5; 66.4; and 68.1. Meanwhile, XRD analysis of Zeolite A aging 12, 24, and 36 hours showed that the largest of the mineral constituent was sodium alumina silicate which showed sharp intensity at 2Θ = 7,2; 10.2; 12.5; 16.1; 21,7; 24.05; 27.2; 30.02; and 34.3.

This result meant, for zeolite A without aging that zeolite crystals were not formed (or formed but in few amounts). For zeolite A aging for 12, 24, and 36 hours, that crystal formed as the primary product, indicating that raw bottom ash material can decay into zeolite A.

The intensity of the XRD diffraction peak of zeolite A without aging was weaker than others since this produced amorphous matter (Tong et al., 2014). In zeolite A without aging,the composite product was mostly corundum (62.29%) and mullite (27.03%), while silica sodium alumina (zeolite A) has a small amount of 9.63%.

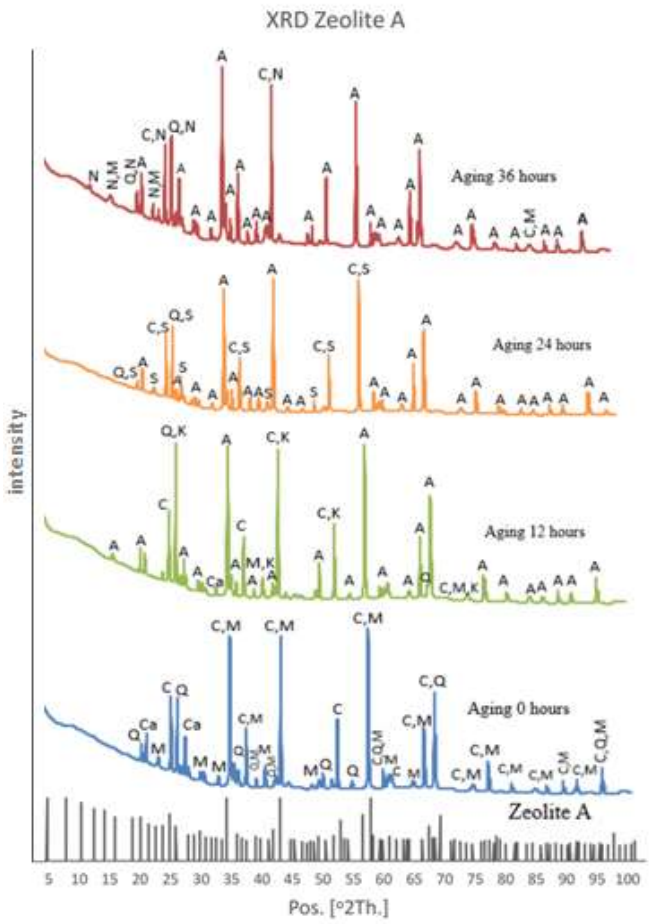


FIGURE 2. Analysis of XRD on the zeolite aging 0, 12, 24, and 36 hours. A = Zeolite Lynde Type A; Q = Quartz; M = Mullite; C = Corrondum; Ca = Calcium Aluminum Silicate; K = Kyanite; S = Muscovite; and N = Anorthite.

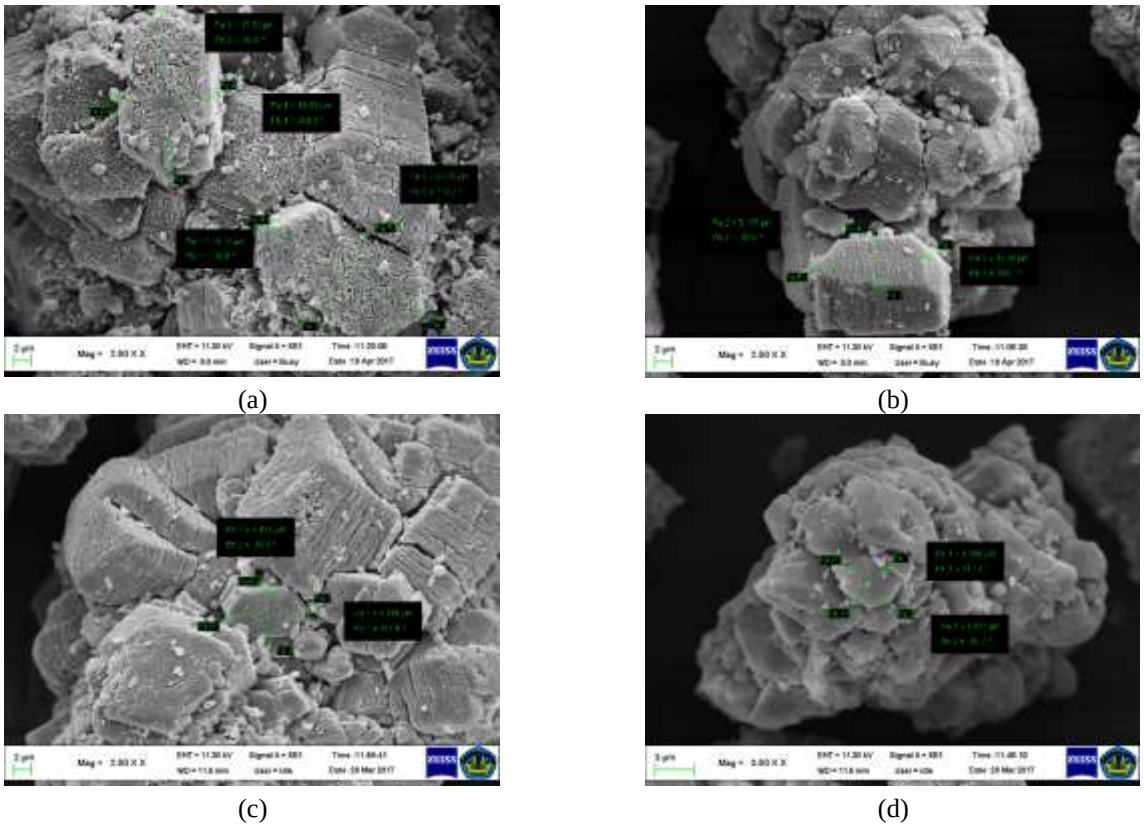
Calculation of percent relative crystallinity to the three products based on the previous study [8]. It was clearly shown that there was a percent increase in the relative crystallinity of zeolite A with the rise of aging time. An increase in aging time will encourage the acceleration of zeolite crystallization, increase in crystallization rate and the number of crystal nuclei formed.

Aging at ambient temperatures increased interaction between species, which in turn led to an increase in precursor species concentrations in the nucleation process, further accelerating nucleation. The seeds of the zeolite crystals were formed in the gel during the aging process. The crystal nucleus was predominantly formed during the hydrogel deposition process, and during the hydrogel aging, this is due to the reaction of the reactive species on the surface area and the area below the surface of the gel particles. The nucleus may grow in contact with the solution, so it must remove from the gel matrix at the beginning of the crystallization process. With an increase in aging time it will allow the formation of more nuclei close to the surface. Therefore, the overall reaction becomes faster, the size of the crystalline product formed becomes smaller, and the specific number increases[5], [9], [10]. Therefore, that silica sodium alumina gel can produce more crystals at a longer aging time.

SEM Analysis

SEM analysis was taken on zeolite A aging for 0, 12, 24, and 36 hours. SEM analysis was used to determine the morphology and particle size. The result of SEM analysis can be seen in Figure 3. In zeolite A aging 24 and 36 hours, the product formed was dominantly crystal with a small portion of amorphous. The percentage of crystallinity

of zeolite A without aging was relatively lower and contrast from zeolite A aging for 12, 24, and 36 hours. These results indicated that during the zeolite gel aging process at room temperature, nuclei of zeolite crystal had formed.



(a) (b)

(c) (d)

FIGURE 3. Morphology of the zeolite produced through SEM Analysis without aging (a), aging for 12 hours (b), aging for 24 hours (c), and aging for 36 hours (d)

From the results of SEM analysis can be seen that the size of the product decreases as the aging time increases. Obtained from the SEM analysis, the size of zeolite A without aging product was 19.14 μm wile zeolite A aging for 12, 24 and 36 hours, the size were 13.26; 9,166; and 3,163 μm respectively. This result was in line with Kovo and Holmes explaining the rise of aging time can cause the insertion of additional silica into aluminosilicate solids, and this will increase the number of smaller nuclei that give better and higher zeolite results[11]. Thus, longer aging time will lead to the formation of zeolite A crystals in a smaller size.

CONCLUSION

The aging time during the zeolite preparation affected the characteristic of zeolite produced. The best aging time of this research was 36 hours. The crystallinity of the product was 89.45% according to XRD analysis. The presence of a double ring structure obtained from FTIR analysis characterized the zeolite A. The morphology structure of the zeolite as a result of SEM analysis showed that the size of crystal produced was 3.163 μm.

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