In-situ growth of zeolite-A in the fiber surface for methane adsorption

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Abstract. Methane as an anthropogenic gas has an effect on the atmosphere and can be used as an alternative natural gas using adsorbent material. This research aims to determine the impact of activation conditions on the surface of fibers for zeolite-A crystal growth utilized for CH₄ adsorption. Glass fiber and pineapple fiber have been treated with an alkali used in this research. The concentration of NaOH and fiber immersion time determine the activation conditions. The activation process altered the crystallinity of the surface-deposited zeolite-A. Characterization by XRD and SEM revealed that zeolite-A covered the surface of those fibers when the NaOH concentration was 4M and the immersion time was 24 h. Thermal analysis revealed that the composite of zeolite-A/fibers undergoes two weight loss processes prior to achieving stability. The methane adsorption gravimetric measurements for zeolite-A supported glass fiber (glass wool) and pineapple fiber with high crystallinities are 4.644% wt and 3.461% wt, respectively.

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1 Introduction

Although methane is one of the greenhouse gases (GHGs) that cause air quality impacts and climate change, methane is the largest component of natural gas which has the potential as an alternative fuel to replace fossil fuels [1]. Natural gas has a weakness in storage techniques (0.12% of fossil fuels) although the value of the gravimetric energy density of natural gas is greater. Natural gas storage technology ANG (Adsorbed Natural Gas) is one solution to these problems. The obstacle faced in ANG technology is the ability of the adsorbent to absorb less natural gas when compared to other technologies such as CNG (Compressed Natural Gas) or LNG (Liquified Natural Gas) for the same tank size [2]. Therefore, the development of adsorbent materials continues to be carried out to comply with DoE (US Department of Energy) volumetric storage standards [3-4].

Several materials used for methane adsorption in previous studies were Mg-MOF-74 [5], activated carbon [6], ZIF-8 [7], MIL-101 [8], MOF-199-alumina composite [9], silica [10], and zeolite [11]. Activated carbon in its application as an adsorbent for methane gas requires a large pressure of up to 10 bar. Meanwhile, molecular sieve such as MOF, ZIF, and MIL materials use a chemical adsorption process requiring high energy to release bonds and relatively higher pressure. Therefore, zeolite has the potential to be developed as an adsorbent for methane gas with an easier physical desorption adsorption process at lower pressures [12].

Zeolite is a crystalline aluminosilicate material with a three-dimensional framework [13]. One example of a zeolite used to absorb methane gas is zeolite-A or commonly known as Linde zeolite. Type A (LTA). Zeolite-A is a zeolite with a low Si/Al ratio so the low silica content causes zeolite-A to have a high concentration of cations and is selective for CH$_4$ gas, which is weakly acidic, about 3-5 times greater than activated carbon material for gas absorption of CH$_4$/CO$_2$ [14].

Zeolite-A as a material for the adsorption of methane gas in the form of powder in its application must be formed into pellets, tablets, or granules with the addition of an adhesive substance. The addition of this adhesive material reduces the product efficiency, porosity and catalytic activity of the zeolite. Therefore, zeolites are deposited onto supporting materials such as fiber [15-16] and carbon [17] through an in-situ crystallization process. Fiber material has advantages over other materials because it has high flexibility to be easily formed, is more durable, and has good tensile strength. The fiber used in this research is pineapple leaf fiber as natural fiber and glass fiber as synthetic fiber. Pineapple leaf fiber was chosen because it has about 80% cellulose content and glass fiber was chosen because it has 90% amorphous silica content [18].

An important factor that affects the growth of zeolite-A crystals on the fiber is the modification of the fiber surface so that a covalent interface bond with the zeolite occurs [19]. Pineapple leaf fiber has lignocellulose, which is very hydrophilic, so it is not compatible with most hydrophobic matrices. Meanwhile, glass wool fiber as a synthetic glass fiber with amorphous silica content requires covalent linkage to bind to the matrix. The weakness of pineapple leaf fiber and glass wool fiber can be overcome by activation of the fiber surface using alkaline treatment. Alkali (NaOH) treatment can clean the fiber surface and improve the fiber-matrix adhesion properties [20]. The amount of NaOH concentration, temperature, pH and immersion time are some of the important factors of alkaline treatment [21]. Therefore, in this paper, we investigated the effect of fiber activation conditions on the growth of zeolite-A crystals on the fiber surface which is used as an adsorbent of methane gas.
2 Experimental

2.1 Material

The tools used are glassware, polypropylene (PP) bottles, dropper pipettes, a hot plate set, magnetic stirrer, oven, hydrothermal reactor (stainless steel autoclave), analytical balance, X-Ray Diffraction (XRD), Scanning Electron Microscopy (SEM), and a set of gas adsorption devices using the gravimetric method. The materials used are demineralized water, solid sodium aluminate (NaAlO₂), sodium silicate solution (NaSiO₃), NaOH pellets (99% p.a), glass fiber (glass wool) and pineapple leaf fiber as materials, fiber, and Ultra High Purity (UHP) methane (99.99% CH₄).

2.2 NaOH concentrations variation in fiber activation

Glass fiber (glass wool) and pineapple leaf fiber were weighed as much as 1 gram and soaked with NaOH solution in a polypropylene container. The concentration variations were 1, 4, and 8 M for 1 day at room temperature. Glass fiber was washed with demineralized water to pH 7 and dried at 100 °C.

2.3 Immersed time variation in fiber activation

Glass fiber (glass wool) and pineapple leaf fiber as supporting materials in this study were activated with 4 M NaOH solution. The activation process was carried out by varying the immersion time for 12, 24, and 36 h at room temperature. Then, the glass fiber was washed with demineralized water to pH 7 and dried at 100°C.

2.4 Zeolite-A synthesis supported by fiber surface

The synthesis of zeolite-A supported by glass fiber was made with a molar composition ratio of 3.165 Na₂O: 1 Al₂O₃: 1.926 SiO₂: 128 H₂O. The precursor is made by mixing NaOH, alumina and silica. The stirred solution was put in a hydrothermal reactor and then added glass fiber. Next, a hydrothermal process was carried out with a temperature variation of 100 °C for 15 h. The results of the hydrothermal process were filtered and washed with demineralized water to pH 8, then dried in an oven at 100 °C for 12 - 15 h.

2.5 Characterization of Zeolite-A material

Characterization techniques used in this study include XRD (X-Ray Diffractometer), TGA (Thermal Gravimetry Analysis), and SEM (Scanning Electron Microscope).

2.6 Methane adsorption

Prior to the Methane adsorption test, the sample was put in an oven and degassed under vacuum using a tubular furnace at 350 °C for 3 h. Adsorption was carried out using a temperature of 30 °C for 30 minutes with a gas flow rate of 20 ml/second. Data is taken every one minute.
3 Results and Discussion

3.1 Methane adsorption

Fiber activation by alkali treatment modified the fiber surface so that the fiber-zeolite interface adhesion increases. In glass fiber, the Si element in the Si-OH bond is released, so that Si will form a soluble silicate salt. While in pineapple leaf fiber, activation will help the delignification process and dissolve extractive media or impurities such as pectin and wax. H$^+$ ions from cellulose molecules in natural fibers will exchange with Na$^+$ ions, producing more hydrophobic fibers. The activated fiber will lose some of its constituent elements and make the zeolite grow well on its surface [22].

Zeolite-A crystals resulting from the hydrothermal process are deposited on the fiber surface as shown in Figure 1. In activated glass fiber, silica will form a zeolite framework along with silica and aluminum elements in the aluminosilicate gel. While in pineapple leaf fiber, the hydroxyl ions in the aluminosilicate gel will damage the hydrogen bonds between the cellulose chains. Not only that, the interaction between zeolite precursors with silica or cellulose will cause the amorphous aluminosilicate gel to undergo rearrangement and accelerate the nucleation of the zeolite crystal core growth. The process of zeolite crystallization begins with a condensation reaction and polymerization of a saturated solution to form new Si-O-Al bonds which then undergo agglomeration to form larger zeolite crystal particles [22].

![Fig. 1. Schematic illustration of fiber surface activation for zeolite growth](image)

The resulting zeolite-A without fiber (ZA) and fiber-supported zeolite-A samples in the variation of NaOH concentration are depicted in Figure 2. The results generally showed the same peak characteristics as the standard zeolite-A at $2\theta = 7.18$, 10.07, 12.46, 16.11, 21.67, 23.99, 27.11, 29.94, and 34.18°. The peak intensity of zeolite-A supported by pineapple leaf fiber and glass wool increased until the activation concentration of NaOH reached 4 M and decreased peak intensity at 8 M NaOH activation concentration. The peak intensity of zeolite-A crystals on the surface of glass fiber (glass wool) decreased as indicated by the ZA-G8M1H sample. This happens because NaOH at high concentrations can dissolve silica in glass fibers (glass wool). The surface of the glass wool fiber becomes amorphous and damaged, so the nucleation process of zeolite-A crystals does not occur. The decreased intensity also indicates a decrease in the crystallinity of zeolite-A because it is possible for the appearance of sodalite crystals due to the metastable nature of zeolite-A if the concentration of base used in the synthesis is high enough (>4 M). The formation of sodalite crystals is supported by the XRD diffractogram, which shows the typical peak of sodalite crystals at $2\theta = 24.65°$ [23]. The ZA-N8M1H sample did not experience a significant decrease in the intensity of the crystal peaks because the cellulose fibers were not damaged.
at high alkaline concentrations. Pineapple leaf fiber fibrils undergo rearrangement and become more compact at high alkaline concentrations. This causes the zeolite crystals to agglomerate and grow on the surface of the pineapple leaf fiber [24].

Fig. 2. Zeolite-A diffractogram supported by synthetic fibers with various activation concentrations of NaOH

Figure 3 supports the previous XRD pattern, namely the decrease in the intensity of the zeolite peak which is not too significant indicating that the relative crystallinity of zeolite-A sample ZA-N8M1H is still high.

Fig. 3. Graph of the effect of NaOH concentration on the crystallinity of zeolite-A on the fiber surface (a) pineapple leaf fiber (b) glass wool fiber

The condition of decreasing crystallinity in fiber-supported zeolite samples from a concentration of 4 M to a concentration of 8 M was confirmed by characterizing the surface.
morphology of the zeolite solid and shown in Figure 4. The zeolite-A crystal lattice form obtained has a cubic geometric pattern. The SEM micrograph in Figure 4 (A-D) shows a tendency to decrease the growth of zeolite-A crystals on the fiber surface as the NaOH concentration increases. The ZA-N8M1H sample has high crystallinity because the crystal lattice size on the surface of the pineapple leaf fiber is still uniform as shown in Figure 4 (F). Meanwhile, ZA-G4M1H experienced a significant decrease in crystallinity due to distortion on the crystal side, resulting in overgrowth of agglomeration of sodalite crystals with non-uniform crystal size and in accordance with previous studies [25-26].

The XRD results of the immersion time effect on leaf fiber and glass wool fiber for zeolite A growth are depicted in Figure 5. The results did not show a typical peak of sodalite crystals. The peak intensity increased up to 24 h immersion variation and decreased at 36 h fiber immersion time. The immersion time determines the interaction of NaOH and fiber on the growth of zeolite crystals on the fiber surface. The results of this study are in accordance with research conducted by Hastuti et al (2012) which explains that the optimum conditions of immersion of fiber in alkaline solution occur in the temperature range of 20-180°C for 15 min - 48 h. A study conducted by Siregar et al (26) it was also explained that the maceration of fiber in alkaline solution for more than 24 h will reduce the interface and adhesion between the fiber and the matrix composite.

The decrease in crystal intensity for ZA-N4M36J and ZA-G4M36J was due to the more damaged fiber morphology with the longer NaOH-fiber interaction time. Glass wool fiber soaked for 36 h turned into an amorphous phase because most of the main content of silica was soluble. In the 24-hour immersion of pineapple leaf fiber, elements other than cellulose such as hemicellulose, pectin, lignin, and wax will dissolve. Meanwhile, immersion for more than 24 h will result in delignification and damage to the cellulose in the pineapple leaf fiber because the cellulose begins to dissolve [26].
Figure 6 shows the relative crystallinity of zeolite-A with glass wool fiber and pineapple leaf fiber as supporting material, which shows the same trend, which is highest at 24 h variation. The crystallinity decreases with increasing fiber immersion time. NaOH hydroxyl groups initially disrupt the hydrogen bonds in the fiber and cause the fiber to have an active site so that it can bind to aluminosilicate oligomers in zeolite [19]. However, increasing the immersion time damaged the morphology and dissolved the active substance on the fiber surface. The damage to the fiber surface is the main factor in reducing the crystallinity of the zeolite sample at the 36-hour immersion time variation.

Figure 6. Crystallinity graph of zeolite-A synthesis results with fiber support with variations in immersion time (a) pineapple leaf fiber (b) glass wool fiber
The influence of fiber surface morphology on the crystallinity of zeolite is supported by SEM data in Figure 7. Zeolite-A crystals grew more and more when the fiber activation immersion time was getting longer until the fiber surface was damaged at a variation of 36 h. The damaged surface will cause the zeolite crystals to grow less and less as shown in Figure 7 (C2).

![SEM micrograph of zeolite-A on fiber surface with variation of immersion time](image)

**Fig. 7.** SEM micrograph of zeolite-A on fiber surface with variation of immersion time 1500 times magnification (A1) ZA-G4M12J (B1) ZA-G4M24J (C1) ZA-G4M36J and 8000 times magnification (A2) ZA-G4M12J (B2) ZA-G4M24J (C2) ZA-G4M36J

The thermal stability of fiber-supported zeolite-A is determined by thermogravimetric analysis (TGA) and differential thermogravimetric (DTG) curves which are measured from changes in the sample mass and its mass derivative as a function of temperature. The samples used were sample ZA-N4M1H (zeolite-A supported by pineapple leaf fiber with 4M NaOH activation conditions in 1 day immersion) and ZA-G4M1H samples (zeolite-A supported by glass wool fiber with 4M NaOH activation conditions in 1 day immersion time). Thermal decomposition of the sample was carried out at a temperature of 0 °C – 1200 °C with a heating rate of 10 °C/min and the results of the analysis are presented in Figure 8.
Fig. 8. TGA/DTG analysis of fiber-supported zeolite-A sample (a) ZA-G4M1H (zeolite-A composite/glass wool fiber) (b) ZA-N4M1H (zeolite-A composite/pineapple leaf fiber)

Based on Figure 8a) the TGA/DTG curve, the thermal decomposition of the ZA-G4M1H sample occurs in two stages of mass reduction, namely at a temperature of 52.36 - 230.55 °C due to dehydration of water physically bound to zeolite-A crystals and at a temperature of 351.36 – 365.71°C due to the dehydroxylation process on the glass wool surface as reported in previous studies [27]. Thermal decomposition of the ZA-N4M1H sample also occurs in two stages of mass reduction. The first decrease in mass at a temperature of 59.92 - 213.88°C was due to the dehydration process of water and the second decrease in mass at a temperature of 284.78 - 361.39°C was due to the degradation of lignin, hemicellulose, and the oxidation of polysaccharides such as cellulose into volatile products.

Differential Scanning Calorimetry (DSC) analysis to determine the phase transition as a function of temperature of the fiber-supported zeolite-A sample is shown in Figure 9. Samples ZA-G4M1H and ZA-N4M1 Characteristics of both samples showed the same DSC peak at a temperature of 100-200 °C. The endothermic peak indicates the energy required for the water-physisorption evaporation process on the surface of zeolite-A and supports the TGA/DTG data [28].

Fig. 9. DSC analysis of fiber-supported zeolite-A sample (a) ZA-G4M1H (zeolite-A composite/glass wool fiber) (b) ZA-N4M1H (zeolite-A composite/pineapple leaf fiber)
3.2 Methane Adsorption Capacity Test

The results of the synthesis of zeolite-A supported by fiber material in this study were carried out by applying methane gas adsorption materials. The samples analyzed were sample ZA-N4M1H (zeolite-A composite/pineapple leaf fiber) and sample ZA-G4M1H (zeolite-A composite/glass wool fiber) because they had the highest crystallinity in the variety of fibers used. Figure 10 shows the trend of the adsorption pattern which increases the adsorption capacity every minute until it is constant at a certain minute. The increase in the curve indicates the presence of pore filling in zeolite-A, while the constant curve shows that the pores of zeolite-A in the three materials have been saturated and have been filled with methane gas, as a result, they are no longer able to absorb methane gas.

Fig. 10. Graph of CH₄ gas adsorption at 30°C against fiber-supported zeolite-A (a) glass wool fiber (ZA-G4M1H) (b) pineapple leaf fiber (ZA-N4M1H) (c) zeolite-A without fiber (ZA)

Zeolite-A, without the support of the synthesized fiber material in this study has a much smaller methane adsorption capacity than the porous material in previous studies [29-31]. Temperature is the main parameter in the physisorption process. At high temperatures during the degassing process, the zeolite pore cavity opens, then at room temperature the molecules will release excess pressure and trap gas in the pores. The event of decreasing adsorption capacity with increasing temperature is also related to thermodynamic studies of gas adsorption where the thermodynamic quantities used are isosteric adsorption enthalpy (ΔH_ads), adsorption entropy (ΔS_ads), absorption capacity (n_a), and free energy of adsorption (ΔG_ads). The adsorption temperature is inversely proportional to the adsorption enthalpy value so that the higher the temperature, the value of the adsorption capacity will decrease [30].

Zeolite-A supported by fiber has a higher methane absorption capacity when compared to zeolite-A in this study. The fiber matrix deposited into the zeolite through the in-situ crystallization process will help the zeolite crystal nucleation process and distribute the zeolite crystal more homogeneously for the gas diffusion process and is in accordance with previous studies [32].

The adsorption capacity of zeolite-A supported by synthetic fiberglass wool is 4.6% greater than that of zeolite-A supported by natural fibers (pineapple leaves) which is 3.4% as shown in Figure 10. A composite/fiber must have hydrophobicity. Where the material can adhere to the gas-solid interface to form an adsorptive layer and the morphology of the fiber has active groups to bind to the adsorbate molecule through hydrogen bonds and Van der Walls forces. Although both fibers have been activated using alkaline treatment, the nature
of the two fibers still has a major contribution to the adsorption process. Morphologically, pineapple leaf fiber with a fibril diameter of 20-80 µm has a high content of cellulose which is a carbohydrate polymer and polyvalent alcohol where the hydroxyl group shows hydrophilic properties. In contrast to pineapple leaf fiber, glass wool fiber with fibril diameter <17µm has a high silica content on its surface with highly hydrophobic silanol (SiOH) groups [33]. This hydrophobic character makes zeolite-A grow more on the surface of glass wool fibers and the crystallinity value of ZA-G4M1H becomes larger. The greater crystallinity value will be proportional to the adsorption capacity of methane gas which is nonpolar. This is in accordance with previous studies which explained that the regularity of the structure with high crystallinity will increase the orientation of the adsorbate molecules in the diffusion and adsorption processes [34].

4 Conclusion

Zeolite-A with fiber support material in this study was successfully synthesized using glass wool fiber and pineapple leaf fiber which was first activated by alkaline treatment. Through the activation conditions of the two fibers, namely variations in NaOH concentration of 1M-8M and variations in fiber soaking time for 12 h-36 h, it was found that fiber activation conditions affected the nucleation process of zeolite-A crystals that grew on the fiber surface. The activation process with a long soaking time and high concentration will cause less growth of zeolite-A due to the damage to the surface morphology of the fiber. The optimum conditions for activation of glass wool and pineapple leaf fibers were 1 day with a NaOH concentration of 4M. The crystallinity and thermal stability of zeolite-A supported by glass wool fiber is greater than that of zeolite-A supported by pineapple leaf fiber. SEM analysis showed that the zeolite-A crystals on the fiber surface were in the form of a cube. The adsorption capacity of methane gas in zeolite-A supported by glass wool fiber (ZA-G4M1H) and zeolite-A supported by pineapple leaf fiber (ZA-N4M1H) was 4.6% by weight and 3.4% by weight, respectively.

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References

5. G. Zhang, Y. Liang, G. Cui, B. Dou, W. Lu, Q. Yang, X. Yan, Energy Reports, 9, 2852-2860 (2023)
6. J. R. Rugarabamu, D. Zhao, S. Li, R. Diao, K. Song, Petroleum Research, 8, 103-117 (2023)
15. N. Widiastuti, P. R. Shara, Akta Kimia Indonesia, 4, 50-62 (2019)