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Synthesis of zeolite ZSM-11 using bamboo leaf as silica source

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Abstract. Zeolite ZSM-11 is a synthesized zeolite that has catalytic properties and the ability to adsorb easily. In zeolite synthesis, various precursors are used and one of them is silica. The silica used in this study is silica isolated from agricultural waste, namely bamboo leaf. Bamboo leaves have a high silica content, thus have potential to be used as silica source for zeolite synthesis. The silica was obtained by isolation from bamboo leaves using NaOH solution. The silica isolated from bamboo leaf isolation has a purity percentage of 57.1%. The synthesis of zeolite ZSM-11 using silica derived from bamboo leaves was performed with a molar ratio of 1 SiO_2: 0.56 TBAOH: 40 H_2O using hydrothermal method at 170 ° C for 2 days. Synthesized zeolites were characterized using XRD, FTIR and SEM. XRD analysis results show Zeolite ZSM-11 with crystalline phase. The FTIR analysis results show the characteristic zeolite ZSM-11 absorption peaks. And the result of SEM analysis got coffin-shaped form with hexagonal-shaped crystal lattice.

1. Introduction

Zeolites are crystalline aluminosilicate group materials that have pores and frames in molecular dimensions (less than 2 nm), composed of tetrahedral units SiO_4^{4-} and AlO_4^{4-} interconnected with each other [1]. Zeolites are divided into two, namely natural zeolite and synthetic zeolite. Today many people are doing synthesis of zeolites. Some examples of synthetic zeolites include zeolite A [2], Na-X and Na-A [3], X [4], T [1], ZSM-5 [5], ZSM-11 [6], etc.

Zeolite ZSM-11 is a MEL type zeolite that has high silica content which was first reported by Kokotailo, et al in 1978. This zeolite has similarities with zeolite type MFI (ZSM-5) [7]. ZSM-11 zeolites are widely used as catalysts [8], adsorbents [9], and ion exchangers [8]. Zeolite synthesis in general, especially ZSM-11 zeolite synthesis is usually done by hydrothermal method using precursor solution containing silica, alumina, alkali metal cation and organic template. Organic template serves as a steering zeolite frame structure. Tetrabutyl ammonium hydroxide (TBAOH) is an organic template commonly used for the synthesis of ZSM-11 [9], where as the commonly used silica source for synthesis

of zeolites is generally TEOS or LUDOX. However, both silica source has drawbacks, i.e. the price is relatively expensive, difficult to obtain and the material is not environmentally friendly [10].

As an alternative solution, silica sources for zeolite synthesis can be obtained by isolation from plants. Silica from rice husk has been isolated by several researchers and then the silica was used for ZSM-11 zeolite synthesis [7]. In addition to rice husk there are many other plants that have a silica content that can be utilized as well. One of them is bamboo leaf.

In Indonesia, bamboo plants grow well in the lowlands to the mountains. So far, people only use the stem part of bamboo, while the utilization of leaves is still not common. Vaibhav et al (2014) have successfully extracted silica from bamboo leaves. The silica contained in bamboo leaves reached 82.78% [11].

In this research, zeolite ZSM-11 was synthesized using silica precursor derived from bamboo leaves. The use of silica from bamboo leaves for zeolite ZSM-11 synthesis is expected to increase the economic value and reduce bamboo leaf waste in Indonesia.

2. Methodology

2.1. Isolation of silica from bamboo leaves

Bamboo leaves used are the leaves of bamboo temen (awi temen) obtained from local source. Bamboo leaves were washed thoroughly and then dried in the sun for 2 days. The dried leaves were calcined at 650 °C for 5 hours to ash. The obtained bamboo ash was then dissolved with 1M NaOH while stirring and heated to 85 °C for 1 hour. The mixture was then filtered. 3 M H_2SO_4 solution was added dropwise to the filtrate until gel formed (pH = 7). The formed gel was then allowed to stand for 24 hours for aging process. The gel was filtered and washed with hot distilled water. The washed gel was then dried at 110°C for 24 hours. The dried solid was then crushed until smooth and characterized using XRF to know the percentage of SiO_2 contained. Furthermore, the solid was used as a source of silica in zeolite ZSM-11 synthesis.

2.2. Synthesis and characterization of ZSM-11 zeolite

Zeolite ZSM-11 synthesis used the isolated silica from bamboo leaves, tetrabutyl ammonium hydroxide (TBAOH) and water. The molar ratio used in the synthesis was 1 SiO_2 : 0.56 TBAOH : 40 H_2O refers to the research of Lu, et al [9], but was modified due to the percentage difference in silica. 6.248 mL TBAOH was stirred using a magnetic stirer inside the polypropylene bottle, then 5 grams of SiO_2 was added. After that, 30.96 mL aqua DM was added. The mixture is stirred for 3 hours in room temperature. Allow the solution to age for a night, then put into the autoclave. The mixture was heated in the oven at 170 °C for 2 days. After filtration, the residue (zeolite) obtained was washed using demineralized water until the pH of the filtrate was neutral, then dried in the oven at 100°C for 12 hours. The zeolite was then calcined at 600°C for 4 hours. The crystallinity of the zeolite was investigated by X-Ray Diffraction analysis (XRD). The bonds in the zeolite structure were analyzed using infrared spectroscopy (FTIR). The morphology of the zeolite was analyzed by scanning electron microscope (SEM).

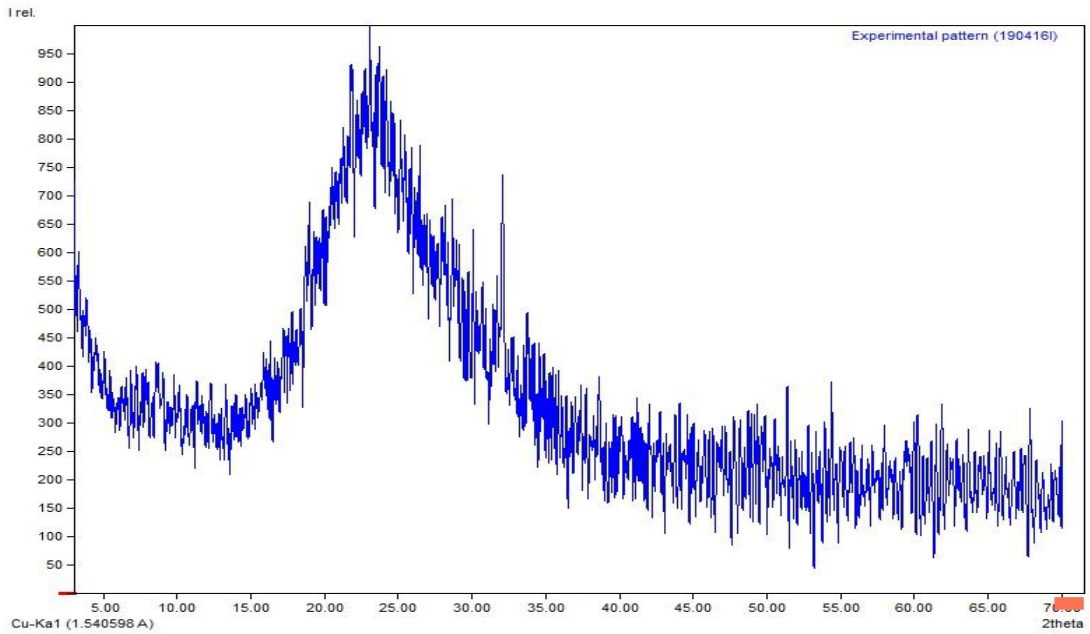
3. Results and discussion

3.1. Isolation of silica from bamboo leaf and its characterization

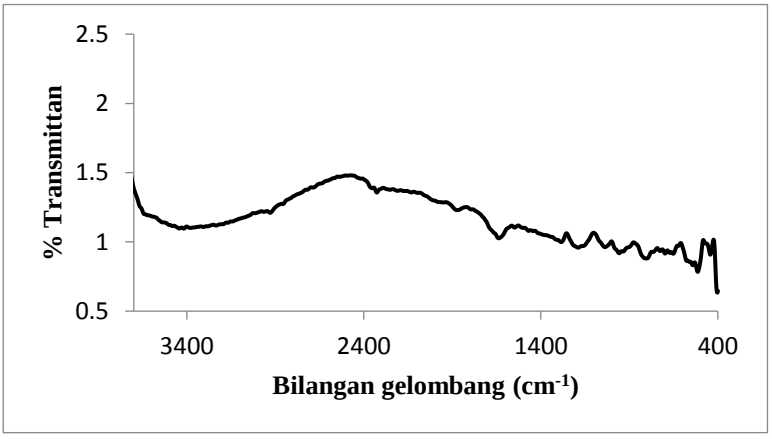
Isolated silica from bamboo leaf was analyzed using XRF and it was found that the percentage of silica purity was equal to 57,1%. Figure 1 (A), shows the X-ray diffraction characteristics of silica from bamboo leaves has the highest peak intensity at $2\theta = 23.22^{o}$. In the diffractogram also seen the widening of the peak, this shows that the silica of bamboo leaf isolation has an amorphous phase. To know the amorphous or crystalline phases, it can be seen from the peak width of the diffractogram, the amorphous phase will give a wider peak shape than the crystalline phase. The amorphous phase shows that the silica is more reactive than the crystalline phase, due to the presence of the siloxane (Si-O-Si) group which is

the active side of the surface. However at 2θ = 32.18° peak formed with high intensity. The peak may indicate a low cristobalite structure [12].

Figure 1 (B) shows the FTIR spectra results of isolated silica from bamboo leaf. In the wavenumber 513- 760 cm^{-1} shows the bending vibration of the Si-O-Si bond. Absorption at 800, 830 and 1188.93 cm^{-1} indicates the vibration of the Si-O-Si bond. While at 3443.268 cm^{-1} indicates the vibration of the H-O-H group [11].



(A)



(B)

Figure 1. X-ray Diffractogram (A) and FTIR spectrum (B) of isolated silica.

3.2. Synthesis of zsm-11 zeolite and its characterization

The synthesis of zeolite ZSM-11 in this study used the hydrothermal method, which is a method of zeolite synthesis which refers to the reaction that occurs by using high temperature (> 100°C) and pressure 1-100 Mpa in water medium or organic solvent. For such conditions it is usually used a special vessel or an autoclave that is resistant to temperature and high pressure [13]. In this study, ZSM-11 zeolite synthesis was carried out at 170°C in an oven using an autoclave for 2 days.

From the molar ratio of 1 SiO_2: 0.56 TBAOH: 40 H_2O will then form a tetrahedral skeleton of zeolite. Tetrahedral is formed by oxygen with a metal cation (TO_4), it is this bond that finally makes it possible to form a zeolite framework. Any tetrahedral angle that has been bonded into a secondary building unit will allow the forming of the n-ring and the zeolite building unit to become more complex (polyhedral).

In ZSM-11 zeolite, the tetrahedral skeleton formed is SiO_4 because ZSM-11 zeolite is a zeolite with high silica content and also in this synthesis there is no use of aluminate precursors. The SiO_4 tetrahedral skeleton then binds back to the other tetrahedrals to form a secondary building unit. The secondary building unit formed for ZSM-11 zeolite is pentasil (5-2). Furthermore, several pentacyl secondary building units will be joined and arranged regularly to form a complex zeolite frame and produce a cavity or ring. A ring formed for zeolite ZSM-11 is a 10-ring or double-five ring (D5R).

The use of TBAOH as an organic template aims to form a zeolite pore structure that has high silica content. The template will form a mold and is surrounded by zeolite frame-forming ions. Once the zeolite crystals are formed, the template must be removed by calcination, because if the organic template is not removed it will disrupt the stability of the zeolite.

The mixture of TBAOH, SiO_2 and water is stirred in a polypropylene bottle and subsequently aged to form a gel. At the time of aging the polymerization process occurs, i.e the growth of the silica chain formed becomes longer. The gel formation indicates the interaction between silica on the formation of zeolite crystal nuclei [14].

Figure 2 shows the XRD results of zeolite ZSM-11. The resulting peaks are at 2θ = 7.852°, 8.786°, 14.785°, 22.964°, 23.853°, 29.808°, 44.990°, and the highest peak and the sharpest at 7.852°. These peaks are similar with the ZSM-11 zeolite standard peaks, 2θ = 7.94°, 8.82°, 14.82°, 23.16°, 23.99°, 29.82°, and 45.23° [15]. The formed zeolite has crystalline phase or it has been perfectly crystallized, this is indicated by a significant sharpness of the formed peaks.

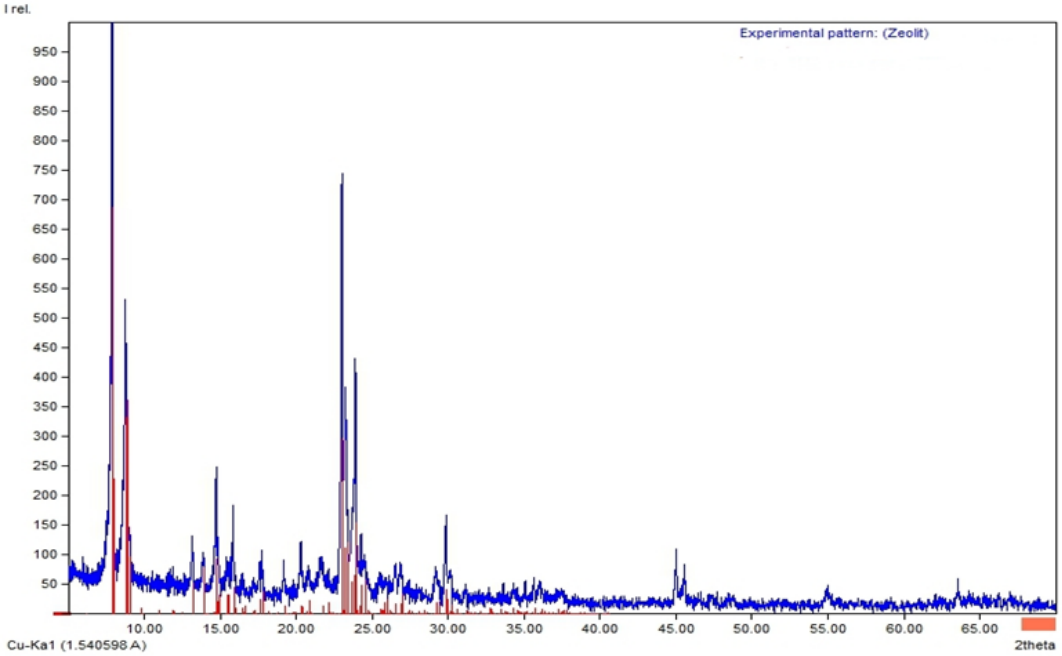


Figure 2. Diffractogram of synthesized ZSM-11 zeolite.

Figure 3 shows the results of ZSM-11 zeolite analysis using FTIR. The FTIR analysis is performed on the wavenumber 1700-400 cm^{-1}, the wavelength is where fingerprints belong to the zeolite to indicate which functional group is present. Absorption at 495.687 cm^{-1} was due to the the bending vibration TO_4 (T = Si). Absorption at 526.743 and 1220.926 cm^{-1} was the bending vibration of the double 5-ring (D5R) in the zentol structure of ZSM-11 zeolite. Double 5-ring is an external link between the layers of zeolites with one another. Absorption at 811.090 and 1021.146 cm^{-1} was due to the vibrations of the Si-O-Si [7] [16].

Figure 4 shows the SEM result of ZSM-11. The formed zeolite has been crystallized quite perfectly and evenly. The crystalline morphology of ZSM-11 has a hexagonal lattice and has a shape almost similar to that of ZSM-5 which is coffin-shaped [17]. The resulting morphology is different from SEM results in a study conducted by JunPing Dong et al., which was spherical and nano-shaped zeolite crystals. This difference could be occurred due to temperature difference and incubation time. In this research, the incubation time for ZSM-11 zeolite synthesis was done for 2 days at 170 °C, while in the research JunPing Dong et al incubation time for synthesis was done for 7 days at temperature 114 °C [18]. This indicates that the higher the temperature used will then form a larger crystal size.

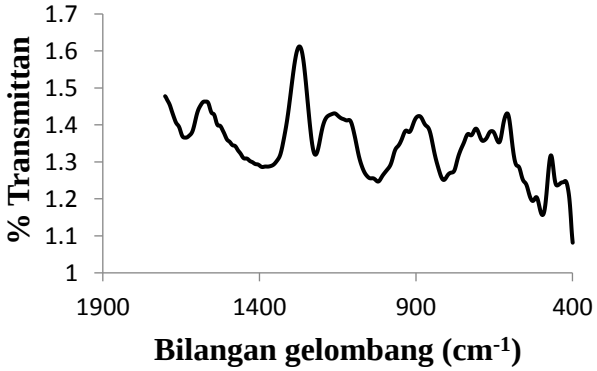


Figure 3. FT-IR Spectrum of ZSM-11 zeolite.

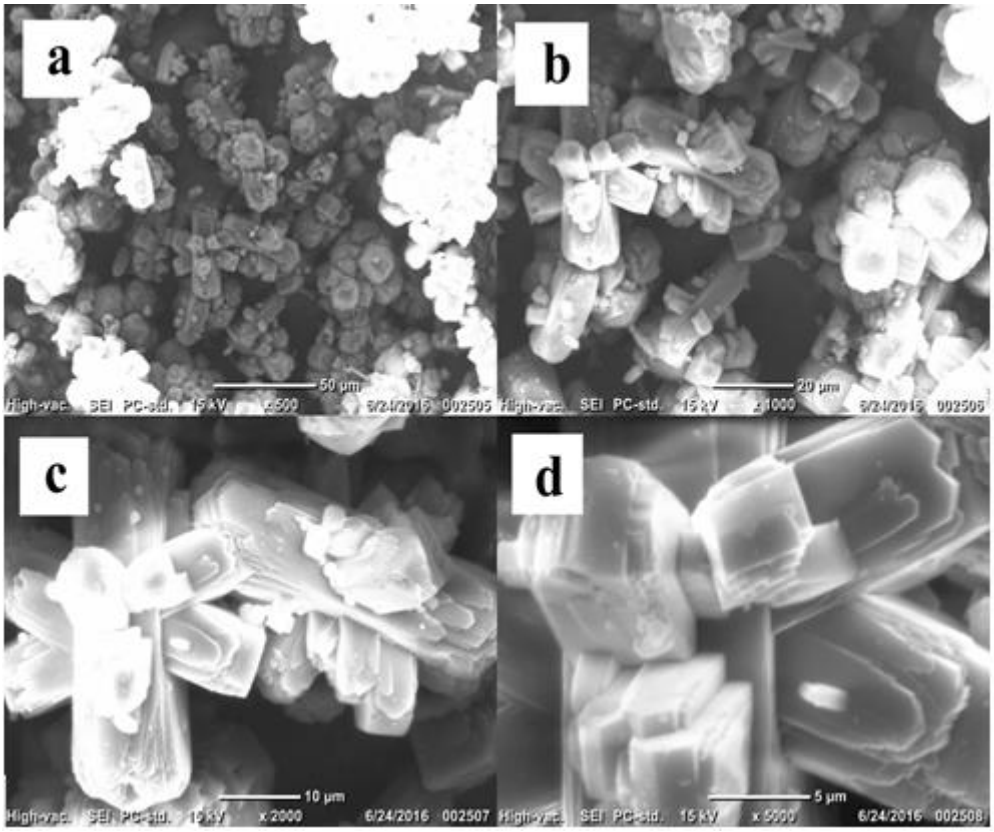


Figure 4. Morphology of ZSM-11 Zeolite (a) magnification of 500x; (b) magnification of 1000x; (c) magnification of 2000x; (d) magnification of 5000x.

4. Conclusion

ZSM-11 zeolite can be synthesized by using isolated silica from bamboo leaves using hydrothermal method. Characterization with XRD shows the formation of ZSM-11 zeolite with high crystallinity. Characterization with FTIR indicates that zeolite framework has been characterized by the absorbing band at 400-1200 cm^{-1} which is a typical zeolite absorption area and absorption in the region of 1100-800 cm^{-1} which is the fingerprint of Si-O-Si. Characterization with SEM obtains its morphology which is hexagonal lattice with a coffin-shaped crystalline form.

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