Synthesis zeolite y from kaolin bangka belitung: activation of metakaolin with various concentration of sulfuric acid

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Abstract. Zeolite Y has been synthesized from Kaolin Bangka Belitung as precursor through activation of metakaolin with acid. The synthesis of zeolite Y consist of metakaolinitation, activation metakaolin with sulfuric acid using various concentrations (3, 6, 9, 12, and 15 M), aging, hydrothermal process for 24 hours at 100 °C. The solid products were characterized with X-ray Diffraction (XRD), Infrared Spectroscopy (FTIR), and Scanning Electron Microscopy-Energy Dispersive X-ray (SEM-EDX). The result of XRD and FTIR indicated that zeolite Y formed at the variations 3, 6, 9, 12, and 15M. Based on XRD pattern of the results, phase of zeolite P formed at the variation 3M. The surface morphology and ratio of Si/Al of Zeolite Y was analyzed using SEM-EDX. The SEM micrograph of zeolite Y and P with variation of sulfuric acid 3, 6, 9, 12, and 15M like octahedral and sphere form and the ratio of Si/Al of the products based on EDX are 1.7; 1.6; 1.58; 1.64; and 1.59 respectively.

1. Introduction
Zeolites are micropore aluminosilicate crystals that have a tetrahedral structure TO₄ (T = Si or Al) [1]. The zeolite framework of tetrahedral [SiO₄]⁴⁻ and [AlO₄]⁵⁻ which is where this framework will form different open structures and contain cations which are located in a specific position on the zeolite framework [2]. Zeolite can be applied as an adsorbent of CO₂ to reduce the greenhouse effect [3]. In addition, zeolite can be applied as a catalyst, both for transesterification, esterification and cracking catalyst reactions [4-6], and it can be applied to other fields, such as control pollution, management of radioactive waste, gas purification, agriculture, molecular filters and dust absorbers [7].

One of the most commonly used raw materials for zeolite synthesis is kaolin. Until 2011 it was reported that the abundance of kaolin in Indonesia was 1,036,857,260 tons [8]. Kaolin is an alumina-silicate mineral with a crystal structure consisting of weakly bound layers. The high content of SiO₂ and Al₂O₃ in kaolin, ie 53.86% and 32.45%, caused kaolin to be used as a source of Si and Al for the synthesis of zeolite [2].

Kaolin has an inert nature and is less active, so it takes effort to change kaolin to be more reactive when used as a precursor for zeolite synthesis. One way to activate kaolin is to convert kaolin to metakaolin [9]. Metakaolin is obtained by calcination at certain temperatures, starting from 400 °C to more than 700 °C [10]. Previous studies have reported that zeolite Y has been successfully synthesized through the pre-treatment stage of kaolin to metakaolin [11].

Metakaolin is the metastable phase obtained from the calcination process of kaolin between a temperature of 550-950 °C. Precursors such as kaolin and metakaolin have been used as sources of Si
and Al for the synthesis of zeolite Linde Type A, X, Y, P, 4A, Sodalite, and several other types of zeolites. Recently the synthesis of Y zeolite from metakaolin has been reported which shows characteristics of structures comparable to commercial zeolites Y. In general, Y zeolite is synthesized using the hydrothermal method at low temperatures. The hydrothermal method is much easier and cheaper than other methods [12].

This is in accordance with the research conducted by Alaba et al. (2017) [11] regarding the synthesis of Y zeolite from kaolin through the activation phase of metakaolin with sulfuric acid at a concentration of 6 M. The variation in acid concentration also influences zeolite formation. The higher the acid concentration used, the higher the solubility of Al$^{3+}$ and the mole ratio of SiO$_2$/Al$_2$O$_3$ [13]. Based on the explanation above, further research is done on the synthesis of Y zeolite from kaolin Bangka Belitung through the stage of activation of metakaolin with sulfuric acid in variations of concentrations 3, 6, 9, 12, and 15 M.

2. Methods

2.1. Activation of Metakaolin

Kaolin is calcined at a temperature of 720 °C for 4 hours. The next step is characterization using FTIR (Fourier Transform Infrared), and XRD (X-ray Diffraction) to determine elemental composition, graphical structure, and functional groups.

The process of activation of metakaolin with acid in this study refers to the research procedure of Alaba et al. (2017) [11] using sulfuric acid (6M H$_2$SO$_4$). Metakaolin in krusibel ceramic is added with sulfuric acid (H$_2$SO$_4$) with a ratio of 1.7:1, dripped slowly and thoroughly then stirred evenly. The mixture of metakaolin and sulfuric acid (H$_2$SO$_4$) was activated at 90 °C for 2 hours, dried at 110 °C for 12 hours, and calcined at 550 °C for 2 hours using a muffle furnace. Amorphous aluminosilicate formed from the mixture was crushed until smooth then characterization with FTIR (Fourier Transform Infrared) and XRD (X-ray Diffraction) to determine the functional groups and crystal structures. In this study variations in the concentration of sulfuric acid were 3, 6, 9, 12, and 15 M. The sample named as A-3, A-6, A-9, A-12, and A-15 respectively.

2.2. Synthesis of Zeolite Y

The procedure of synthesis zeolite Y with molar composition of 6Na$_2$O: 10SiO$_2$: Al$_2$O$_3$: 180H$_2$O. NaOH solution mixed with acid-activated metakaolin. Then ludox as silica source added to the mixture and stirred for 30 minutes. The mixture was aged for 24 hours at room temperature and then carried out the hydrothermal process for 24 hours at 100 °C. After hydrothermal process, it filtered to separate the residue from the filtrate. The residue washed with aqua DM to neutral pH (pH = 7) then dried at 105 °C for 6 hours. Dry solids were characterized using FTIR (Fourier Transform Infrared), XRD (X-ray Diffraction) SEM-EDX (Scanning Electron Micsroscope-Energy Dispersive X-ray). The sample given name as AZ-3, AZ-6, AZ-9, AZ-12, and AZ-15.

3. Result and Discussion

3.1. Activation of metakaolin

The results of the characterization of Bangka Belitung kaolin with XRD showed the same typical peak at an angle of 2θ = 12.24; 20.43; 24.94; and 38.46 ° as shown in Figure 1 (i). The metakaolin diffractogram pattern showed that the loss of some typical peaks of kaolin was replaced by the emergence of a specific peak of quartz at an angle of 2θ = 19.69 ° and 26.59 °.
The appearance of quartz minerals is caused by the dehydroxylation process (hydroxyl group release). Mineral quartz has not changed because it tends to be stable and will change its structure at higher temperatures around 1100 °C [2].

Characterization of kaolin and metakaolin using FTIR can be seen in Figure 1 (ii). Diko et al. (2016) [14] shows that kaolin peaks appear in several wave numbers, 3692 and 3619 cm\(^{-1}\), indicating stretching vibrations for hydroxy (OH) groups on Al-O-H bonds in the octahedral layer of kaolin. Stretching vibrations and bending vibrations of H-O-H bonds for water molecules (H\(_2\)O) are shown at wave numbers around 3404 and 1653 cm\(^{-1}\).

Based on Figure 1 (ii) there is difference between kaolin and metakaolin that indicated the transformation.

The diffractogram of X-rays and IR spectra of metakaolin that was activated by acid compared to metakaolin which can be seen in Figure 2. The diffractogram shows the presence of quartz peaks on the activation of metakaolin with acid. This indicates that quartz has a stable nature of the acid so that it still gives rise to the characteristic peak of quartz at an angle of 2\(\theta\) around 26.6° [15]. In addition, there is an aluminum sulfate peak based on JCPDS No.30-0043 which appears at an angle of 2\(\theta\) = 15.22; 21.05; 25.43; 30.67; 33.77; and 34.25.

Figure 1 (i) XRD pattern and (ii) IR spectra of (a) kaolin (b) metakaolin

Figure 2 (i) XRD pattern and (ii) IR spectra of (a) metakaolin (b) A-3 (c) A-6 (d) A-9 (e) A-12 (f) A-15
FTIR spectra show that at wave numbers around 3446 and 1651 there are stretching vibrations and bending OH groups of \( \text{H}_2\text{O} \) molecules [16]. Based on research from Zhou et al. (2013) [17] reported that the emergence of new peaks after treatment with sulfuric acid around wave number 1170 cm\(^{-1}\) indicates an asymmetrical stretching and symmetrical vibrations in anions (SO\(_4\))\(^2-\). At wave number 673 and 610 cm\(^{-1}\) indicates the existence of asymmetrical bending vibrations in anions (SO\(_4\))\(^2-\) [18].

3.2. Synthesis of Zeolite Y

Solids from zeolite synthesis with variations in sulfuric acid concentrations 3, 6, 9, 12, and 15 M were compared with simulated zeolite Y from Treacy et al., 2001 and zeolite P from IZA Zeolite. The XRD pattern of zeolite samples with variations in sulfuric acid concentrations 3, 6, 9, 12 and 15 M can be seen in Figure 3 which shows the formation of one phase when the acid-activated metakaolin used is 6, 9, 12, and 15 M and two phases when the acid-activated metakaolin used is 3M. All of sample was indicated faujasite (Y zeolite) were formed and gismondin (P zeolite) was the impurity of this sample. The results of zeolite in this research indicate as zeolite Y. It can be seen from figure 3 (i) that its have similar XRD pattern with simulated zeolite Y.

XRD analysis results on zeolite samples with variations in the concentrations of sulfuric acid 3, 6, 9, 12, and 15 M were dominated by the peak characteristic of zeolite Y (faujasite phase). However, in the sample variations in concentration of 3M sulfuric acid there is another impurity phase formed, namely gismondin (P zeolite) but in small amounts. Other peaks that appear indicate the formation of other zeolite phases. This shows a metastability in zeolites where zeolites Y are able change from one phase to a more stable phase.

![Figure 3](image)

Figure. 3 (i) XRD pattern and (ii) IR spectra of (a) AZ-3 (b) AZ-6 (c) AZ-9 (d) AZ-12 (e) AZ-15 (f) Zeolite Y (g) Zeolite P

The results of synthesised zeolite Y are consistent with the research conducted by Wang et al. (2016) where the zeolite Y peak in the wave number area is 980, 756, 670, 565, 465 cm\(^{-1}\). The absorption peak at wave
number 980 cm\(^{-1}\) shows the asymmetrical stretching vibration of Si-O-Al. In addition, the wave numbers 756 and 670 cm\(^{-1}\) show symmetrical external and internal stretching vibrations O-T-O (T = Si, Al). The absorption peak at wave number 565 cm\(^{-1}\) shows the external ring double vibration. At wave number 465 cm\(^{-1}\) shows the bending vibration TO4 (T = Si, Al).

FTIR analysis results on Y zeolite synthesized by Wang et al (2016) [9] and zeolites with variations in sulfuric acid concentrations 3, 6, 9, 12, and 15 M are shown in Figure 6. From the picture it can be seen that the zeolite Y synthesis results in almost the same spectra.

SEM characterization is used to determine the morphology of samples. The micrographs of the synthesized zeolite crystals show uniform particle shape.

FTIR analysis to determine the elemental composition of the synthesized zeolite samples. The results of EDX characterization in each variation of the synthesized zeolite are shown in Table 1. The EDX results indicate that the three synthesized samples contain elements such as those used in precursors, namely Si, Al, Na, and O. Si / Al ratios obtained from calculations using % atom data on EDX results. The Si / Al ratio in the synthesis sample of each variation is 1.70; 1.48; 1.58; 1.65; and 1.40 are shown in Table 1.

**Table 1. EDX analysis**

| Sample | % Atom | Ratio | Si/Al |
|--------|--------|-------|-------|
|        | Si     | Al    | Na    | O     |       |
| AZ-3   | 18.46  | 10.84 | 12.47 | 58.24 | 1.70  |
| AZ-6   | 19.29  | 12.95 | 12.95 | 55.71 | 1.48  |
| AZ-9   | 18.13  | 11.47 | 12.5  | 57.90 | 1.58  |
| AZ-12  | 20.29  | 12.30 | 12.33 | 55.07 | 1.65  |
| AZ-15  | 19.50  | 12.20 | 12.26 | 56.04 | 1.60  |

**4. Conclusion**

Based on the research that has been done, it can be concluded that the variation in the concentration of sulfuric acid at the stage of activation of metakaolin with acid affects the results of the synthesis of zeolite Y from kaolin Bangka Belitung. The results of the characterization using X-ray Diffraction (XRD) and Fourier Transform Infrared (FTIR) showed the formation of zeolite Y in all sample variations. However, in the variation of the concentration of 3M sulfuric acid, another impurity phase is formed although in small amounts.
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