The Effect of an Ultrasound Radiation on the Synthesis of 4A Zeolite from Fly Ash

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Abstract. The use of coal as a fuel source generates a lot of solid waste fly ash. Thus, efforts to reduce or utilize the amount of fly ash are urgently needed. This paper presents zeolite synthesis from fly ash. The fly ash was activated by using NaOH solution prior to fusing process with a weight ratio of 1:2 and mixing with distilled water at a weight ratio of 1:5. Thereafter, the addition of alumina with a concentration of 0.71%, 1.42%, 2.12%, and 2.8% w/v was performed. The effects of heating and ultrasound radiation on the characteristic of zeolite products were investigated. The results showed that the addition of alumina 2.8% w/v resulted in the Si/Al ratio of zeolite 4A is ~1. SEM images demonstrated that the presence of ultrasound wave resulted in crystals structure morphology as also supported by XRD characterization. The average crystal size for the ultrasonic treatment was 42.46 nm.

Keywords. Fly ash, zeolite, and ultrasonic.

1. Introduction

In the last decades, coal has become the second largest energy source in the world. However, coal has also contributed around 45% of all energy-related carbon emissions and air quality degradation [1]. The large quantities of coal consumption generate a high amount of coal fly ash, which becomes the major solid waste of coal combustion. The utilization of coal fly ash has widely developed in various applications such as construction industry, ceramic industry, catalysis, and environmental uses [2].

On the other hand, many researchers have developed several techniques to synthesize zeolite from coal fly ash. Coal fly ash may be a suitable substrate for the zeolite synthesis because of its composition, where a major amount of Al and Si is found [1]. The conventional hydrothermal process was the oldest technique to synthesize zeolite from coal fly ash [3]. Although this method could provide the highest conversion, the resulted supernatant as a waste of this method was very harmful to the environment.

Park et al. [4] used the molten salt technique to reduce the by-product and water consumption. However, the molten salt method produced irregular product morphology with lower yield and conversion. Several studies have performed to increase the yield and the properties of zeolite from molten stages [5–7]. Nevertheless, the modified molten stages or multi-step treatment methods require...
a higher cost with longer preparation time and also complex procedures. Shigemoto and co-workers [8] introduced alkali fusion method, which could produce better property with higher yield and lower process time. However, the loss of weight during fusion process could affect the final product properties.

Querol et al. [9] revealed that microwave-assisted hydrothermal process could reduce activation time in alkali fusion method. Recent studies also reported that microwave heating could reduce the process cost and produce smaller zeolite crystals [10,11]. However, this method still provides lower yield and needs a significant study to apply the process in industrial scale. Musyoka et al. [12] reported that an ultrasonic-assisted hydrothermal technique could improve zeolite crystallization and decrease the time process. Other studies documented the use of sonication could produce more stable zeolite and reduce the required energy compared to conventional hydrothermal process [13,14]. However, the ultrasonic-assisted hydrothermal process also needed a high cost and further study to upscale this method.

Previous studies suggested that the ultrasonic-assisted hydrothermal process showed a proper product despite its high cost. Therefore, this research tries to reduce the cost by using a simple ultrasonic apparatus with a low-frequency wave to synthesize 4A zeolite. The effects of alumina addition, heating and ultrasound wave on the characteristic of 4A zeolite product were investigated.

2. Materials and methods

2.1. Materials

F class fly ash (47.26 % Si and 8.13 % Al) was obtained from Paiton coal-fired power plant located in Probolinggo, Indonesia. NaOH and Al₂O₃ were purchased from Merck (Germany). Aquadest was provided by Membrane Research Center (Mer-C), Diponegoro University (Indonesia).

2.2. Zeolite synthesis

Two different methods of synthesis were used, i.e. (i) a conventional hydrothermal process, and (ii) an ultrasonic assisted hydrothermal process. The conventional process was started with fusing fly ash and NaOH (1:2 weight ratio) then the mixture was heated at 550 °C for 1.5 h. The resulting solid was crushed, and the fine powder was mixed with aquadest (1:5 weight ratio) and stirred for 2 h. The liquid phase from the resulting slurry was separated using decantation and filtration. The separated liquid phase was mixed with alumina solution (0.64 g solid alumina and 4.67 g NaOH in 34.5 mL aquadest) to get precursors solution. Finally, the precursor solution was heated and stirred at 80 °C for 3 h. The ultrasonic assisted hydrothermal process was performed after precursor solution was obtained. The ultrasonic wave (40 kHz, using local production ultrasonic transducer) was applied in the precursor solution with and without heating (80 °C) for 3 h. Detail composition and operating condition of each sample are presented in Table 1. The resulting solid from synthesis process was separated using decantation and filtration then dried at 60 °C for 48 h.

| Sample | Ultrasonic (kHz) | Time (h) | Temperature (°C) | Alumina Addition (%w/v) |
|--------|------------------|----------|------------------|------------------------|
| 1      | 40               | 3        | 80               | 0.71                   |
| 2      | 40               | 3        | 80               | 1.42                   |
| 3      | 40               | 3        | 80               | 2.12                   |
| 4      | 40               | 3        | 80               | 2.8                    |
| 5      | -                | 3        | 80               | 0.71                   |
| 6      | 40               | 3        | 25               | 0.71                   |

Table 1. Detail composition and operating condition of synthesis.
2.3. Characterization
Si/Al ratio of produced 4A zeolite was characterized using atomic absorption spectrophotometry (AAS; Shimadzu AA-7000) with 640 nm (Si) and 475 nm (Al) wavelength. Morphological investigation of the zeolite was performed by scanning electron microscopy (SEM; JEOL JSM-6510LA). Crystalline structure analysis was carried out by using X-ray diffraction (XRD; Shimadzu XRD-7000).

3. Results and discussion

3.1. Effect of alumina addition on the 4A zeolite Si/Al ratio
Firstly, the effect of different alumina addition on the 4A zeolite characteristic was investigated. Figure 1 demonstrates the Si/Al ratio of the synthesized 4A zeolite as the function of alumina concentration.

Figure 1. The Si/Al ratio of synthesized 4A zeolite in various alumina concentrations

The Si/Al ratio decreased with the increase in alumina concentration. The results also showed that the addition of alumina at 2.8 % w/v resulted in the Si/Al ratio of zeolite ~1. This phenomenon indicates that the sufficient amount of alumina added would lead to initiate better zeolite crystallization. The addition of alumina was required to initiate the precursor solution which in super saturation state to drive the crystallization process [13]. Another study also revealed that addition of alumina in hydroxide or sodium state could increase the amount of alumina in precursor solution and regulate the required Si/Al ratio [15]. Furthermore, this result suggests that the optimum alumina addition for 4A zeolite synthesis using ultrasonic-assisted hydrothermal process was 2.8 % w/v.

3.2. Effect of heating and ultrasonic wave on the 4A zeolite Si/Al ratio
The investigation was performed to compare the ultrasonic-assisted process, conventional heating process, and the combination of both process in zeolite crystallization process. The 40 kHz of ultrasonic wave was applied in the ultrasonic-assisted process while the 80 °C of temperature was applied in the conventional process. Figure 2 shows the Si/Al ratio of produced 4A zeolite with different synthesis processes.
As seen in Figure 2, the ultrasonic-assisted without heating process showed the highest Si/Al ratio while the conventional process (heating only) displayed similar Si/Al ratio with the ultrasonic-assisted with heating. These results indicated that the heating process has a vital role in zeolite crystallization. Belviso et al. [16] reported that the function of ultrasonic to bind the Si and Al on solid particle would not work optimally at room temperature. Another study also revealed that the minimum temperature for zeolite crystallization process was 50 °C [17], while the electro-mechanic wave from ultrasonic could not provide sufficient heat to fulfill the required temperature. Figure 2 also shows that the combination of both processes obtained similar Si/Al ratio with heating process only. Musyoka and co-workers [15] documented that ultrasound wave could initiate the cavitation phenomenon which leads a nucleus seed forming then the seed would grow to be a crystal core. Other research also elaborated that the ultrasonic treatment could accelerate Al and Si dissolution from amorphous alumina silicate state, improve the polycondensation process, and enhance the transition of semi-crystalline to crystalline phases [13]. Hence, the combination of ultrasonic-assisted and conventional hydrothermal process gave a better characteristic in 4A zeolite synthesis due to its synergistic effect on zeolite crystallization process.

3.3. SEM Results
The morphology of synthesized 4A zeolite was visualized using SEM. As seen in Figure 3a, the morphology of coal fly ash was glassy microsphere with hundred micrometers in size. This result was similar to a previous study [14]. Then, when coal fly ash was transformed to precursor solution, the morphology changed to be irregular crystal shape (Figure 3b). The shape of a solid phase of precursor solution suggests that the crystal growth has started at this stage.

Figure 3c displays the square crystal structure of the synthesized 4A zeolite, which was prepared using ultrasonic-assisted hydrothermal process. The 4A zeolite shape was completely formed and had the same tendency with previous studies [13,15]. These results demonstrate that the impact of the ultrasound wave on crystal structure growth was observed. The formed square crystals had a bit longer shape compared with other studies because of shorter process duration in this study. A longer duration of synthesis process would produce a shorter crystal due to a more Si-Al dissolution. Figure 4d is the image of the 4A zeolite with the addition of 2.8 % w/v alumina, and Si/Al ratio was ~1. The shape of the resulting 4A zeolite showed bolder form than the produced 0.71 % w/v alumina addition 4A zeolite (Figure 3c). Overall, these images confirmed that the optimum alumina addition in ultrasonic-assisted hydrothermal process was 2.8 % w/v.
3.4. **XRD Results**

XRD analysis was employed to characterize the mineralogical and crystalline structure of synthesized 4A zeolite. Figure 4 presents the XRD analysis of 4A zeolite with the addition of 2.8 % w/v alumina, and Si/Al ratio was ~1 (sample 4) prepared using ultrasonic-assisted hydrothermal process. XRD data demonstrated that crystals of sodium alumina silicate (NaAlSiO₄) were obtained. The peaks were identified at 2θ value: 26.3, 27.8, 30.3, 33.1, 34.4, 34.7, 35.5, 38.2, 40.1, 41.7, 41.9, 44.3, 46.5, and 48.4. The presence of identified crystals indicates that the 4A zeolite has really been synthesized [5, 14]. The calculation using Debye Scherrer equation [18] showed that the size of synthesized 4A zeolite which produced using ultrasonic-assisted hydrothermal process was 42.46 nm.

**Figure 4.** XRD result of synthesized 4A zeolite using ultrasonic-assisted hydrothermal process.
4. Conclusions
This study suggests that the optimum alumina addition on 4A zeolite synthesis using ultrasonic-assisted hydrothermal process was 2.8 % w/v. The alumina had an important role to initiate the zeolite crystallization process. The combination of ultrasonic-assisted and conventional hydrothermal process resulted in a better characteristic in 4A zeolite synthesis. SEM images demonstrated that the presence of ultrasound wave resulted in crystals structure morphology. Types of crystals obtained were indicated by XRD characterization, which were crystals of sodium alumina silicate at level 4. The average crystal size for the ultrasound treatment was 42.46 nm.

Acknowledgements
The authors thank Universitas Diponegoro for the financial support. The authors also thank smart city project by USAid Shera for the opportunity given to increase the quality of this paper.

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