Characterization of Zeolite A from Coal Fly Ash Via Fusion-Hydrothermal Synthesis Method

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Abstract. Zeolite A has been successfully synthesized from coal fly ash by using fusion followed by hydrothermal method. This paper describes the characterization of zeolite A. The effects of hydrothermal time, Si/Al molar ratio, and alkalinity in the converting coal fly ash to zeolite A were also investigated. The coal fly ash was obtained from a local power plant at East Java, Indonesia and contained major oxides such as SiO$_2$ (18.60 wt%), Al$_2$O$_3$ (7.18 wt%), Fe$_2$O$_3$ (40.20 wt%), CaO (25.20 wt%). The fusion hydrothermal method consists of the following steps: pre-treatment, fusion of coal fly ash with sodium hydroxide, aging, and hydrothermal process. The synthesized material was characterized by using X-Ray Diffraction (XRD), Scanning Electron Microscope (SEM), Fourier Transform Infrared (FTIR), and specific surface area analytical method. The results show that the products contain zeolite A as the major phase, while the highest specific surface area of zeolite A is 37.121 m$^2$/g. It implies that zeolite A as a higher value added product can be obtained from a solid waste/by-product of power plant, which has wide range applications, including for ion exchange and heavy metal adsorbent from waste water.

1. Introduction
The majority of power generation is currently supplied from fossil fuel, especially coal. Based on World Energy Council 2016, coal-based thermal power plants supply forty percent of world’s electricity and is forecast to increase over the next three decades [1]. The combustion of coal not only generates energy, but also generates a large amount of by-products such as coal fly ash contributing environmental problem [2]. In refer to coal fly ash, utilization of coal fly ash is the key to reduce the significant amount of coal fly ash. Numerous studies have reported the utilization of this material as the raw material for zeolite synthesis due to their silica and alumina contents [3].

Zeolite is a crystalline material composed of aluminosilicates with a three-dimensional network of silicon and aluminium tetrahedral linked by oxygen atoms [4]. Various types of synthetic zeolites are zeolite A, zeolite X, ZSM-5, and others. Among the different types of synthetic zeolites, zeolite A has attracted attention to researchers due to its properties. Some of the noteworthy properties of zeolite A include high cation exchange capacity (CEC), high porosity and specific surface area, as well as high affinity towards polar molecules [5]. As a result, zeolite A can be applied as a low-cost adsorbent for pollutant removal from wastewater.

Two common methods for converting coal fly ash to zeolite are hydrothermal method (direct method) and alkaline fusion followed by hydrothermal method. For hydrothermal method, it has small fraction of reacted coal fly ash and low zeolite yields [6]. Compared to hydrothermal method, alkaline fusion
plays an important role in converting coal fly ash into large amounts of silicate and aluminosilicate which are soluble in alkaline solutions, thus the purity of the final product is relatively high [7].

In this paper, coal fly ash was used to synthesize zeolite A by the alkaline fusion followed by hydrothermal method. Several synthesizing factors that affect the type of zeolite product were investigated including hydrothermal time, Si/Al molar ratio, and the alkalinity of solution.

2. Experimental section
Coal fly ash was obtained from PT YTL Paiton East Java, Indonesia. It was pre-treated using hydrochloric acid technical grade. Sodium hydroxide and sodium aluminate were used in zeolite synthesis. Analytical grade of sodium acetate, ammonium hydroxide, acetic acid, and 99% isopropyl alcohol were used in the determination of the CEC.

The experiments were conducted in two steps including pre-treatment of coal fly ash and zeolite synthesis. In the pre-treatment step, coal fly ash was roasted at 850°C for 2 h. Then, it mixed with 10% of hydrochloric acid solution (ratio of 1 g : 25 ml) in a 500 ml three-neck flask. The mixture was heated at 80°C for 1 h and stirred constantly at 300 rpm. After that, pre-treated coal fly ash recovered by filtration, repeatedly washed with distilled water, and dried at 100°C for 24 h. For the main process, the zeolite synthesis step consists of fusion, aging, and hydrothermal. In fusion process, 10 g of pre-treated coal fly ash were mixed with 12 g of sodium hydroxide. The mixture was put into crucible nickel and left to fuse at 550°C for 1 h. The sintered granules of fused coal fly ash were cooled down, grinded, while sodium aluminate was added. To adjust the alkalinity and Si/Al molar ratio, water and sodium aluminate were added at different amounts. Furthermore, the mixture was shaken at 30°C for 16 h in incubator shaker for aging process and subsequently heated to temperature of 100°C during 1 h for hydrothermal process. After hydrothermal step was complete, the suspension formed was filtered and zeolite was washed repeatedly until pH of solution reached 9-10. Then, zeolite was dried at 105°C for 16 h.

The chemical composition of coal fly ash and pre-treated coal fly ash were determined by X-ray fluorescence equipment (Rigaku Supermini 200). To analyze the specific surface area, synthesized zeolites were analyzed by BET equipment (Quanochrome Instruments Nova 3200c) by applying the BET equation to the nitrogen adsorption data. Fourier Transform Infrared (Bruker Platinum-ATR) was used to identify functional groups contained in the synthesized zeolites. The morphology of synthesized zeolite was observed by scanning electron microscopy (Hitachi SU3500). The cation exchange capacity was determined using Method 9081.

3. Results

3.1. Pre-treatment of coal fly ash
As observed in Figure 1, the coal fly ash used in this study consists of amorphous phase and some amounts of crystalline phases such as quartz, mullite, calcium oxide, hematite, and magnetite, which is also confirmed from its chemical composition (Table 1). According to Molina and Poole (2004), Fe-bearing of coal fly ash may be decomposed during fusion process and these element are incorporated into the structure of zeolite [8]. Meanwhile, high CaO content may promote the formation calcium silicate hydrate phases [9]. In this work, pre-treatment process by hydrochloric acid successfully reduce the iron oxides and some of the alkali oxide, as shown in Table 1.
Figure 1. XRD pattern of coal fly ash. Q: quartz, Mu: mullite, Ca: calcium oxide, H: hematite, and M: magnetite.

Table 1. Chemical composition of coal fly ash and pre-treated coal fly ash.

| Component | Coal fly ash (% mass) | Pre-treated coal fly ash (% mass) | Component | Coal fly ash (% mass) | Pre-treated coal fly ash (% mass) |
|-----------|-----------------------|-----------------------------------|-----------|-----------------------|-----------------------------------|
| SiO₂      | 18.60                 | 65.60                             | SO₃       | 2.23                  | 0.42                              |
| Al₂O₃     | 7.18                  | 5.25                              | SrO       | 0.45                  | 0.12                              |
| Fe₂O₃     | 40.20                 | 17.30                             | BaO       | 1.04                  | 0.91                              |
| MnO       | 0.45                  | 0.14                              | Na₂O      | 0                     | 0.11                              |
| MgO       | 1.17                  | 1.37                              | ZrO₂      | 0                     | 0.11                              |
| CaO       | 25.20                 | 4.48                              | NiO       | 0                     | 0.03                              |
| K₂O       | 1.54                  | 2.29                              | ZnO       | 0                     | 0.06                              |
| TiO₂      | 1.46                  | 1.12                              | Rb₂O      | 0                     | 0.02                              |
| P₂O₅      | 0.48                  | 0.63                              |           |                       |                                   |

The morphological characteristics of coal fly ash and pre-treated coal fly ash is shown in Figure 2 and 3. After the pre-treatment process, the surface of pre-treated coal fly ash shows noticeable changes. It is observed that the hydrochloric acid rapidly disintegrates the outer layer of coal fly ash, where the leaching of some elements may take place.

Figure 2. SEM micrograph of coal fly ash.  
Figure 3. SEM micrograph of pre-treated coal fly ash.
3.2. Effect of hydrothermal time

Figure 4. XRD patterns of synthesized zeolites obtained by variation of hydrothermal time (a) 1 h, (b) 3 h, (c) 5 h, and (d) 7 h. A: zeolite A, S: hydroxysodalite.

Figure 4 illustrates the XRD patterns of synthesized zeolites from coal fly ash at Si/Al molar ratio of 0.50 during the hydrothermal time of 1, 3, 5, and 7 h. According to the XRD patterns, all synthesized zeolites contain zeolite A as the major constituent phase, whereas hydroxysodalite is found as the minor phase. Hydroxysodalite is a denser phase and has small pore size of 2.8 Å [10]. In addition, XRD patterns indicate that intensities of the hydroxysodalite gradually increase with the increasing hydrothermal time. These results are likely to reflect the fact that zeolite A as metastable phase is decomposed gradually with an increase the hydrothermal time results in the supersaturation of liquid phase with aluminosilicate anions. Furthermore, it promotes the formation of hydroxysodalite nuclei [11]. Thus, the formation of zeolite A requires shorter hydrothermal time and it is considered that the stages of transformation are coal fly ash – zeolite A – hydroxysodalite.

Table 2. Properties of synthesized zeolite obtained at varied hydrothermal time.

| Hydrothermal time (h) | Degree of crystallinity (%) | CEC (meq/g) | Specific surface area (m²/g) |
|-----------------------|----------------------------|-------------|-----------------------------|
| 1                     | 92.85                      | 4.64        | 26.583                      |
| 3                     | 90.61                      | 4.23        | 24.920                      |
| 5                     | 89.80                      | 4.01        | 24.259                      |
| 7                     | 87.09                      | 3.62        | 24.101                      |

Based on Table 2, the degree of crystallinity reduce with an increase of hydrothermal time. This behaviour occurs due to short induction and nucleation periods as well as the rapid formation of zeolite A, especially in the system with high alkalinity. Subsequently, zeolite A dissolve in alkaline solution and result in a decreasing degree of crystallinity. In addition, the CEC and specific surface area reduce from 4.64 meq/g to 3.62 meq/g and 26.583 m²/g to 24.101 m²/g when the hydrothermal time is increased from 1 h to 7 h.
3.3. Effect of Si/Al molar ratio

Si/Al molar ratio is one of important aspects in determining a pure zeolite A. After conducting the fusion process, sodium aluminate is added to increase its concentration in liquid phase and to adjust the Si/Al molar ratio at 0.50, 0.625, and 0.75. Figure 5 illustrates the XRD patterns of synthesized zeolites which are obtained by variation of Si/Al molar ratio at hydrothermal time of 1 h. In all cases, the peaks of hydroxysodalite are detected. The intensities of hydroxysodalite are varied and are showed in Table 3.

![XRD patterns of synthesized zeolites](image)

**Figure 5.** XRD patterns of synthesized zeolites obtained by variation of Si/Al molar ratio (a) 0.50, (b) 0.625, and (c) 0.75. A: zeolite A, S: hydroxysodalite.

| 2 theta | Si/Al molar ratio | Intensities of hydroxysodalite |
|---------|-------------------|--------------------------------|
| 13.96   | 0.50              | 290                            |
| 24.42   | 0.625             | 253                            |
|         | 0.75              | 189                            |

According to Murayama et al. (2002), amount of Na$^+$ ions in the alkali solution controlled the crystallization rate [12]. At Si/Al molar ratio of 0.50, the Na$^+$ ions is at most because sodium aluminate introduced in alkali solution is at most too. It can be inferred that crystallization rate of synthesized zeolite with Si/Al molar ratio of 0.50 is the fastest and result in the highest intensities of hydroxysodalite.

| Si/Al molar ratio | Degree of crystallinity (%) | CEC (meq/g) | Specific surface area (m$^2$/g) |
|-------------------|-----------------------------|-------------|---------------------------------|
| 0.50              | 92.85                       | 4.64        | 26.583                          |
| 0.625             | 93.95                       | 4.63        | 31.797                          |
| 0.75              | 92.87                       | 5.05        | 37.530                          |

The degree of crystallinity, CEC, and specific surface area of the synthesized zeolites are shown in Table 4. The degree of crystallinity slightly increase with an increase in the Si/Al molar ratio ranging from 0.50 to 0.625. Furthermore, the degree of crystallinity decrease at Si/Al molar ratio of 0.75. From these results, it is considered that the degree of crystallinity increase with increasing the amount of Na$^+$ ions up to a certain amount and then it indicates a decreasing tendency. However, the highest CEC value
and specific surface area are obtained at Si/Al molar ratio of 0.75. This phenomenon describes that the main factor affected the CEC value and specific surface area is the purity of the synthesized zeolite A [13].

3.4. Effect of alkalinity of solution

Alkalinity is defined in terms of the H₂O/Na₂O molar ratio. Figure 6 shows the XRD patterns of synthesized zeolites at different H₂O/Na₂O molar ratio of 26.26 and 39.04. All samples were synthesized at hydrothermal time of 1 hour. XRD patterns clearly reveal that relatively pure zeolite A without hydroxysodalite phase is detected at H₂O/Na₂O molar ratio of 39.04. Thus, it is considered that hydroxysodalite is not form in lower alkalinity and shorter time.

![Figure 6. XRD patterns of synthesized zeolites obtained by variation of alkalinity of solution (a) 39.04 and (b) 26.26. A: zeolite A, S: hydroxysodalite.](image)

Table 5 shows the degree of crystallinity, CEC, and specific surface area. In this study, the degree of crystallinity and specific surface area are not vary greatly with an increase of H₂O/Na₂O molar ratio. Meanwhile, CEC value at H₂O/Na₂O molar ratio of 39.04 is higher than 26.26. The results of CEC indicate that relatively pure zeolite A without hydroxysodalite has good capability to absorb metals than zeolite A with impurities hydroxysodalite.

| H₂O/Na₂O molar ratio | Degree of crystallinity (%) | CEC (meq/g) | Specific surface area (m²/g) |
|-----------------------|----------------------------|-------------|----------------------------|
| 26.26                 | 92.87                      | 5.05        | 37.530                     |
| 39.04                 | 92.52                      | 5.14        | 37.121                     |

The XRD pattern of synthesized zeolite at H₂O/Na₂O molar ratio of 39.04 is in good agreements with the SEM and FTIR as shown in Figure 7 and Figure 8. Based on Figure 7, it can be seen that relatively pure zeolite A without hydroxysodalite phase is cubic-shaped which corresponds to the typical shape of zeolite A [14]. In addition, there are no spherical particles in relatively pure zeolite A without hydroxysodalite phase, indicating the conversion of coal fly ash to zeolite A is high.
Figure 7. SEM micrograph of relatively pure zeolite A without hydroxysodalite phase.

Based on Figure 8, IR spectra clearly shows zeolite A characteristic bands, indicating the band at wavelength 462.92 cm\(^{-1}\); 549.71 cm\(^{-1}\); 667.37 cm\(^{-1}\); 1,006.84 cm\(^{-1}\); 1,656.85 cm\(^{-1}\); and 3,412.08 cm\(^{-1}\). The band at 549.71 cm\(^{-1}\) is assigned to external vibration of double four-rings, which is characteristic of zeolite A. The internal symmetric stretching vibration is indicated at 667.37 cm\(^{-1}\), the internal asymmetric stretching is shown at 1,006.84 cm\(^{-1}\), and the internal linkage vibration of the TO\(_4\) (T = Si or Al) is observed at 462.92 cm\(^{-1}\). In addition, there are two well-defined band at 1,656.85 cm\(^{-1}\) and 3,412.08 cm\(^{-1}\) associated with the presence of water content and hydroxyl groups in the zeolite framework [15].

Figure 8. FTIR of relatively pure zeolite A without hydroxysodalite phase

4. Conclusion
A relatively pure zeolite A without hydroxysodalite is successfully synthesized from coal fly ash by alkaline fusion followed by hydrothermal method. The optimum hydrothermal time are 1 h with Si/Al molar ratio of 0.75 and H\(_2\)O/Na\(_2\)O molar ratio of 39.04. The important aspects are the prolongation of hydrothermal time and higher alkalinity can result in unwanted product: hydroxysodalite phase. A relatively pure zeolite A without hydroxysodalite has degree of crystallinity of 92.52 %, CEC of 5.14 meq/g, and specific surface area of 37.121 m\(^2\)/g.

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