Preparation of Na-P1 Zeolite with High Cation Exchange Capacity from Coal Fly Ash

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Abstract: Na-P1 zeolite having a high cation exchange capacity (CEC) was synthesized from coal fly ash using a modified conversion method into the zeolite by alkali fusion prior to conventional alkali hydrothermal reaction. For comparison, alkali hydrothermal and alkali fusion methods were studied at different conditions using NaOH as an alkali source; the CEC for NH₄⁺ ions was measured with the products under each reaction condition. The results are discussed in terms of the crystal structure of the products. The coal fly ash was converted into the zeolite by an alkali hydrothermal reaction, through the course of Na-P1 → hydroxy-sodalite with increasing NaOH concentration. The coal fly ash was mainly converted into sodium aluminum silicate by the alkali fusion method, without formation of any zeolite crystals. The products of the alkali hydrothermal reaction showed higher CEC values than did those obtained by fusion reactions because of crystal formation of Na-P1 zeolite. The coal fly ash was effectively converted into Na-P1 zeolite with high crystal purity and high conversion efficiency when using the modified method; it had a high CEC value of 221 meq/100 g.

Keywords: alkali fusion, alkali hydrothermal, coal fly ash, cation exchange capacity

Introduction

An enormous amount of coal fly ash is generated annually as solid waste from thermoelectric power plants, there is continued interest in recycling it. Many researchers have attempted to synthesize zeolitic materials that are applicable in wastewater purification by ion exchange, especially for heavy metals and ammonium ions. Among these approaches, the alkali hydrothermal reaction is a well-known synthetic method [1-3]. Because the conversion efficiencies are dependent on the contents of the non-reactive and resistant aluminum-silicate phases, such as mullite and quartz, the conventional hydrothermal method have the limitation to obtain the high conversion efficiency into zeolite from coal fly ash [4]. The types of zeolite synthesized from coal fly ash depend on the conversion method and chemical composition of the coal fly ash. In the case of using the alkali hydrothermal method, Na-P1, X, A, and hydroxy-sodalite-type zeolites are obtained predominantly under various reaction conditions, such as different reaction times and temperatures and alkali solution concentrations [5]. The Na-P1, X, and A-type zeolites have high CEC values in comparison with those of other zeolites [4]. Several technologies have been reported to increase the conversion efficiency and obtain zeolites in high purity [5-9]. Park and coworkers reported zeolite formation from a molten-salt system in which KOH and NaOH were employed as bases and KNO₃ and NaNO₃ as salts [7]. Shingemoto and coworkers investigated a modified conversion method for preparing zeolites by alkali fusion at 823 K prior to conventional hydrothermal treatment to obtain Na-X and Na-A-type zeolites [9]. Although many such techniques have been reported, a detailed and systematic study of the preparation of zeolites with high CEC from coal fly ash is still required to apply them as ion exchangers in the field of water purification.

In this study, the conventional hydrothermal and alkali fusion methods were studied in detail under different conditions.
conditions, and the CECs for NH$_4^+$ ions were measured for the products obtained under each reaction condition. The results are discussed in terms of the crystal structures of the products. We have also investigated the formation of Na-P1 zeolite with a high CEC from coal fly ash using a modified method in which an alkali fusion stage was introduced as a pre-treatment process prior to performing the conventional alkali hydrothermal reaction.

**Experimental**

**Materials and Methods**

The coal fly ash used in this study was obtained from the Seo-Chon thermoelectric power plant. The chemical composition of this coal fly ash was estimated by ICP (Inductively Coupled Plasma, EA1110); the results are summarized in Table 1. The coal fly ash was composed mainly of alumina and silica. The coal fly ash powder was used after drying at 110 °C and sieving below 180 mesh.

The alkali hydrothermal reaction was performed using a typical method with NaOH solution as an alkali source. The coal fly ash and NaOH solution were placed into a Teflon-lined glass vessel equipped with a stirrer and heated to 100 °C. After hydrothermal reaction during the desired time, the product was cooled to room temperature. The precipitates were then filtered and washed repeatedly with excess distilled water to eliminate the remnant sodium hydroxide. The resultant powders were dried in an oven overnight at 100 °C. The modified method in which an alkali fusion stage was introduced as a pre-treatment process prior to hydrothermal reaction was performed using a modified method prior to hydrothermal reaction was executed as follows. The mixture containing coal fly ash and NaOH powder was ground into a fine powder. The mixture was heated to a desired temperature in a nickel crucible for various reaction times. After cooling to room temperature, the product was roughly crushed, washed with distilled water, and dried at 100 °C. The modified method introducing method prior to hydrothermal reaction was executed as follows. The product of the alkali fusion reaction above was ground, dissolved in distilled water, and maintained at 100 °C for a given time with vigorous agitation. The resultant precipitates were filtered, washed repeatedly with distilled water, and dried overnight at 100 °C.

**Instrumental Analysis**

XRD patterns were obtained using the powder method with Ni-filtered Cu Kα radiation at 40 kV and 30 mA at a scanning speed of 2°/min. Scanning electron micrographs were obtained using a JEOL model 35C scanning electron microscope after coating the samples with gold. The CEC of the products was measured using a 0.1 N NH$_4$OAc standard method (CEC$_{SM}$) at pH 7 and 25 °C; the sample was saturated with NH$_4^+$ using 0.1 N NH$_4$OAc (pH 7.0) solution. It was then mixed with solutions of methyl red, methylene blue, and bromo cresol green as indicators after leaching and distillation using 4 % boric acid solution and MgO powder. Finally, the sample was titrated with a 0.1 N H$_2$SO$_4$ standard solution. The CEC values of the products were calculated using the following equation:

$$CEC \ (\text{meq}/100 \ g) = \frac{V_i}{W_i} \times C_i \times 100$$

(1)

where $V_i$ is the volume of the H$_2$SO$_4$ solution (mL), $W_i$ is the weight of the product (g), and $C_i$ is the concentration of the H$_2$SO$_4$ solution (N). The CEC measurements were repeated three times and average values were obtained.

**Result and Discussion**

**Alkali Hydrothermal Method**

Figure 1 shows X-ray diffraction patterns of zeolitic materials synthesized through the alkali hydrothermal reaction using 2.5 M NaOH solution at 100 °C for various reaction times. Figure 1(a) confirms that the coal fly ash used in this study was composed mainly of mullite and quartz, which can act as resistant aluminum-silicate phases lowering the conversion efficiency. In Figures (b)−(e), we observed that the intensities of characteristic peaks on Na-P1 type zeolite increased upon increasing the reaction time. The coal fly ash was mainly converted into Na-P1-type zeolite after hydrothermal reaction for 8 h. Consequently, it seems that crystal growth increased up a reaction time of 8 h, but decreased thereafter. This result is in good agreement with the suggestion that a reaction time of at least 8 h is required for the crystallization of zeolitic materials when using the alkali hydrothermal reaction [10]. However, we observed that the characteristic peaks of mullite and quartz components of coal fly ash were not completely dissolved. Figure 2 shows the changes that occurred to the CEC values upon increasing the reaction time of the

<table>
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<tr>
<th>Component</th>
<th>Al$_2$O$_3$</th>
<th>SiO$_2$</th>
<th>Fe$_2$O$_3$</th>
<th>K$_2$O</th>
<th>MgO</th>
<th>Na$_2$O</th>
<th>CaO</th>
<th>TiO$_2$</th>
<th>Others</th>
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<td>Content (wt%)</td>
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<td>1.70</td>
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alkali hydrothermal reaction using 2.5 M NaOH solution at 100 °C. The CEC values of the products increased initially upon increasing the reaction time, but decreased somewhat after 8 h. It seems that the increase of CEC value is due to crystal formation of the Na-P1-type zeolite, known as a high-CEC material, from coal fly ash. The changes of the crystal structures upon increasing the NaOH concentration are represented in Figure 3. Na-P1-type zeolite was formed mainly at NaOH concentrations of 2 and 2.5 M, while the diffraction intensity of Na-P1-type zeolite decreased at NaOH concentrations above 4 M, due to the formation of hydroxyl-sodalite-type zeolite. This phenomenon is due to the change of the crystal structure from Na-P1 zeolite to hydroxy-sodalite, via co-crystallization between Na-P1 and hydroxy-sodalite, upon increasing the NaOH concentration [11,13,16]. We also observed that the mullite and quartz components of coal fly ash still remained despite the increasing NaOH concentration. Therefore, we conclude that the alkali hydrothermal reaction has the limitation to obtain zeolite with high conversion efficiency and high purity from coal fly ash. SEM images of the coal fly ash samples treated with different NaOH concentrations are shown in Figure 4. Figure 4(a) confirms that the coal fly ash particles typically had spherical shapes and smooth surfaces. As shown in Figures 4(b) – 4(l), the formation of zeolite crystal like egg white on the surfaces of the fly ash particles occurred upon increasing the NaOH concentration without changing the original spherical shape [5,13]. However, in the case of the products treated with high NaOH concentrations (6 and 12 M; Figures (e) and (f)), we observed that the spherical fly ash particles collapsed and became covered with large spherical and cubic crystals that are characteristic of hydroxyl-sodalite-type zeolite, in accordance with X-ray diffraction results shown in Figure 3 [12-15]. These results are due to dissolution of mullite and quartz by the high NaOH concentration and the change of the crystal structure from Na-P1 to hydroxy-sodalite. Figure 5 shows the CEC values of the products synthesized from alkali hydrothermal reactions performed with increasing NaOH concentrations at 100 °C for 8 h. The CEC of the sample treated with 2.5 M NaOH had the highest value; the CEC values decreased upon increasing the NaOH concentration. Na-P1-type zeolites generally have higher CEC
Figure 4. Scanning electron micrographs of zeolitic materials synthesized by hydrothermal reactions at 100 °C for 8 h with various concentrations of NaOH solution ((a) fly ash; (b) 2 M; (c) 2.5 M; (d) 4 M; (e) 6 M; (f) 12 M).

Figure 5. CEC values of the products synthesized by alkali hydrothermal reaction at 100 °C for 8 h plotted with respect to the NaOH concentration.

values for NH$_4^+$ cations than do hydroxy-sodalite zeolites, which have a smaller pore size (2.3 Å) than do the Na-P1-type zeolites [4,12]. Consequently, our results seem to be due to the crystal structure changing from Na-P1 to hydroxy-sodalite at high NaOH concentrations [12]. Murayama and coworkers recently investigated the mechanism of zeolite synthesis from coal fly ash through the alkali hydrothermal reaction. They suggested that three steps, namely, dissolution, condensation and crystallization, occur during alkali hydrothermal reactions for zeolite synthesis from coal fly ash. They also reported that the OH$^-$ ions in the alkali solution contribute remarkably to the dissolution of Si$^{4+}$ and Al$^{3+}$ in coal fly ash, while Na$^+$ ions in the alkali solution contribute to the crystallization into the zeolite P [13]. Therefore, we suggest that an increased reaction time for the alkali hydrothermal reaction results in an increase in the degree of crystallization into Na-P1 zeolite rather than dissolution of mullite and quartz, while an increased NaOH concentration results in an increase in the degree of both dissolution and crystallization.

Alkali Fusion Method

Figures 6 and 7 show X-ray diffraction patterns of zeolitic materials prepared using the alkali fusion method for different reaction times at 300 and 500 °C, respectively at a NaOH(s)/coal fly ash ratio of 0.75. Characteristic peaks of hydroxy-cancrinite zeolite at 2θ=18.4, 21.3, 24.2, and 27.3 (JCPDS File No. 28-1036) [4] and of sodium aluminosilicate at 2θ=30.4 and 31.5 (JCPDS File No. 02-0723) and 2θ=35.4, 35.8, and 46.6 (JCPDS File No. 37-0072) were observed. Berkgaut and coworkers reported that Na aluminosilicate with the approximate composition Na$_{15}$Si$_4$Al$_3$O$_{20}$ was formed through the fusion of fly ash with NaOH at 170–80 °C [16]. Park and coworkers also reported that sodalite was obtained by fusion of fly ash with NaOH at 350 °C [7]. Although its diffraction intensity was small, hydroxy-cancrinite-type zeolite was observed in this study, but we found that the
Preparation of Na-P1 Zeolite with High Cation Exchange Capacity from Coal Fly Ash

Figure 6. X-ray diffraction patterns of the products synthesized by the alkali fusion method at 300 °C at a NaOH(s)/coal fly ash weight ratio of 0.75 presented with respect to the reaction time; AS: sodium aluminum silicate; HC: hydroxy-cancrinite; M: mullite; Q: quartz; (a) fly ash; (b) 1 h; (c) 2 h; (d) 3 h; (e) 4 h.

Figure 7. X-ray diffraction patterns of the products synthesized by the alkali fusion method at 500 °C at a NaOH(s)/coal fly ash weight ratio of 0.75 presented with respect to the reaction time; AS: sodium aluminum silicate; HC: hydroxy-cancrinite; M: mullite; Q: quartz; (a) fly ash; (b) 1 h; (c) 2 h; (d) 3 h; (e) 4 h.

Product was mainly a mixture of sodium aluminum silicate, which was not clearly identified for its composition. The disagreement with the previous study seems to be due to differences in the chemical composition of coal fly ash and in the NaOH/coal fly ash weight ratio. Meanwhile, the XRD results showed that the mullite and quartz components of coal fly ash had almost dissolved. These results indicate that mullite and quartz of coal fly ash were completely dissolved by intimate contact with NaOH during the fusion reaction and that the coal fly ash was eventually converted into sodium aluminum silicate [16].

From these results, we conclude that the dissolution and resultant condensation steps were predominant, and that crystallization into the highly crystalline zeolite was difficult to achieve during the alkali fusion reaction. CEC values of products synthesized by the alkali fusion method for various reaction times at a NaOH(s)/coal fly ash ratio of 0.75 are exhibited in Figure 8. The results show that the products synthesized at 300 °C had higher CEC values than those of the products synthesized at 500 °C, but no remarkable changes of the CEC values occurred with an increase of the reaction time. Figure 9 shows X-ray diffraction patterns of the products prepared by the alkali fusion method with various NaOH(s)/coal fly ash weight ratios at 300 °C for 2 h. The crystal structures of the products exhibited mainly sodium aluminum silicate and the peak intensities decreased upon increasing the NaOH(s)/coal fly ash weight ratio. We also observed diffraction peaks at 2θ=33, 37.9, and 39.4, which are characteristic peaks of sodium aluminum oxide. This finding seems to be due to formation of sodium aluminum oxide mediated by the presence of excess NaOH. These results indicate that an increase in the amount of NaOH added in the fusion stage contributes to the dissolution step, but has little effect on the crystallization into the zeolite. CEC values of the prepared products are displayed in Figure 10; they increased slightly upon increasing the NaOH(s)/coal fly ash weight ratio up to 1.2, and then decreased considerably thereafter.

Modified Method

From these results, we determined the optimal conditions for the preparation of a zeolite having a high CEC
through both alkali fusion and alkali hydrothermal reactions. Consequently, the modified conversion method into zeolite by alkali fusion at a NaOH(s)/coal fly ash ratio of 0.75 at 300 °C for 2 h prior to alkali hydrothermal reaction at 100 °C for 8 h was undertaken. X-ray diffraction patterns of the prepared products are exhibited in Figure 11. As shown in Figure 11(c), the mullite and quartz components of coal fly ash were completely dissolved, and the crystal structure showed mainly Na-P1 type zeolite. Figure 12(b) shows SEM images of the products prepared using our modified method. The changes of the crystal structure before and after hydrothermal reaction are in accordance with the XRD observations. As a result, we suggest that the modified method in this

Figure 9. X-ray diffraction patterns of the products synthesized by the alkali fusion method at 300 °C for 2 h with various NaOH(s)/coal fly ash weight ratios; AS: sodium aluminum silicate; HC: hydroxy-cancrinite; M: mullite; Q: quartz; (a) fly ash; (b) 0.6 ; (c) 1.2; (d) 1.8; (e) 2.4).

Figure 10. CEC values of the products synthesized by the alkali fusion method at 300 °C for 2 h plotted with respect to the weight ratio of NaOH(s)/coal fly ash.

Figure 11. X-ray diffraction patterns of zeolitic materials synthesized by the modified method (alkali fusion method was introduced as a pre-treatment stage) at a NaOH(s)/coal fly ash weight ratio of 0.75 at 300 °C for 2 h prior to hydrothermal reaction at 100 °C for 8 h; P: Na-P1 type zeolite; AS: sodium aluminum silicate; HC: hydroxy-cancrinite; M: mullite; Q: quartz; (a) fly ash; (b) only by alkali fusion at 300 °C for 2 h; (c) by the modified method).

Figure 12. Scanning electron micrographs of the products prepared by the alkali fusion reaction at a NaOH(s)/coal fly ash ratio of 0.75 at 300 °C for 2 h prior to hydrothermal reaction at 100 °C for 8 h (a) before hydrothermal reaction; (b) after hydrothermal reaction.)
study is very effective for obtaining Na-P1-type zeolite with a high conversion efficiency and a high crystal purity from coal fly ash. A comparison of the CEC values obtained using the different synthetic methods in this study, at each optimal condition, is displayed in Figure 13. The CEC value obtained after using the modified method (221 meq/100 g) was highest among these methods. It seems that this result is due to crystal structural uniformity and the high conversion efficiency to the Na-P1-type zeolite of this modified method.

### Conclusion

1) The coal fly ash was converted into the zeolite by the alkali hydrothermal reaction through the course of Na-P1 → i-droxy-sodalite upon increasing the NaOH concentration. CEC values of the products of the alkali hydrothermal reaction were higher in comparison with those from the fusion method, at each optimal condition, because of crystal formation of Na-P1 type zeolite.  

2) The coal fly ash was converted mainly into sodium aluminum silicate by the alkali fusion method, without formation of any zeolite crystals. An increase in the amount of NaOH added in the fusion stage contributes to the dissolution of mullite and quartz, but has little effect on the crystallization into the zeolite. 

3) The products prepared by alkali fusion prior to performing the alkali hydrothermal reaction exhibited a high CEC value (221 meq/100 g) as a result of crystal structural uniformity and a high conversion efficiency into the Na-P1 zeolite. It seems that the modified conversion method used in this study is a very effective method for the preparation of zeolites with high CEC from coal fly ash.

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### References