A Study on the Application of Fly Ash-Derived Zeolite Materials for Pyrolysis of Polypropylene

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Received January 13, 2003; Accepted March 6, 2003

Abstract: Zeolites were synthesized from fly ash by the NaOH fusion method employing three different NaOH/fly ash weight ratios and the potential of these fly ash-derived zeolites as pyrolysis catalysts was assessed in terms of the yield and simulated boiling point distribution of the liquid pyrolysis products. The physical properties of the fly ash-derived zeolites were characterized and related to their catalytic performance for pyrolysis of polypropylene. It was found that H⁺-exchanged fly ash-derived zeolites were as effective as commercial HY zeolite. The catalytic performance of H⁺-exchanged fly ash-derived zeolites was the most satisfactory with the NaOH/fly ash weight ratio of 1.2. For the mass percentage of 80% on the simulated boiling point distribution curve, the boiling temperature obtained using this zeolite was significantly lower than that obtained without zeolite by as much as 108°C. This phenomenon was related to the formation of zeolite materials such as faujasite.

Keywords: pyrolysis, polypropylene, fly ash-derived zeolite, NaOH fusion, simulated boiling point distribution

Introduction

The amount of fly ash generated from coal-fired power plants in Korea was about 3.6 million tons in 1998 [1]. The annual generation of fly ash has been rapidly increasing and is expected to reach as much as about 5.7 million tons in 2005. However, currently only 30–40% of the fly ash is recycled for cement or concrete manufacture and the remaining amount is disposed of into fly ash ponds, causing serious environmental pollution. Therefore, it is necessary to develop diverse new and alternative utilization technologies for the promotion of recycling fly ash.

One of the potentially viable approaches for recycling fly ash as more valuable materials is to synthesize zeolites from it [2-10]. Due to the similarity in chemical composition of fly ash to some volcanic material, precursor of natural zeolites, many researchers have synthesized zeolites from fly ash and applied these fly ash-derived zeolites as cation exchangers for the removal of heavy metals from waste water [4-8,10] and also as molecular sieves for the separation and recovery of gases such as CO₂, SO₂ and NH₃ [10]. The application of fly ash-derived zeolites as cracking or pyrolysis catalysts has not been reported yet although natural zeolites have been applied for that purpose [11-13].

Fly ash-derived zeolites are synthesized mainly by conventional hydrothermal treatment in alkali solution [3,4,6,8-10] or by alkali fusion followed by aging and crystallization [2,5,7,10]. It has been reported that the alkali fusion can dissolve more silicates and alumino-silicates regardless of the composition of fly ash, and precipitate zeolites much more easily than the hydrothermal treatment [2,5]. With NaOH as the alkali source, different types of zeolites are obtained depending on the fusion conditions such as NaOH/fly ash weight ratio and temperature and the hydrothermal treatment conditions such as NaOH concentration and reaction temperature. Analcime (Na₃Al₂Si₅O₁₄·H₂O), hydroxysodalite (Na₆Al₂Si₅O₁₄·1.8H₂O), hydroxycancriite (Na₄Al₂Si₅O₁₄·6H₂O), herschelite (Na₆Al₂Si₅O₁₄·1.8H₂O), NaP1 (Na₆Al₂Si₅O₁₂·12H₂O), faujasite (Na₆Al₂Si₅O₁₄·6.7H₂O) and zeolite A (Na₆Al₂Si₅O₁₂·9H₂O) are the typical

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Table 1. Chemical Composition of the Fly Ash Used in This Study

<table>
<thead>
<tr>
<th>Component</th>
<th>Weight (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>SiO₂</td>
<td>53.56</td>
</tr>
<tr>
<td>Al₂O₃</td>
<td>27.71</td>
</tr>
<tr>
<td>Fe₂O₃</td>
<td>5.53</td>
</tr>
<tr>
<td>MgO</td>
<td>0.91</td>
</tr>
<tr>
<td>CaO</td>
<td>4.50</td>
</tr>
<tr>
<td>K₂O</td>
<td>0.94</td>
</tr>
<tr>
<td>Na₂O</td>
<td>0.37</td>
</tr>
<tr>
<td>Ignition loss</td>
<td>5.88</td>
</tr>
</tbody>
</table>

examples [2-10].
In this study, zeolites were synthesized from fly ash by NaOH fusion method employing three different NaOH/fly ash weight ratios and the potential of these fly ash-derived zeolites as pyrolysis catalysts was assessed in terms of the yield and simulated boiling point distribution of the liquid pyrolysis products [14,15]. The physical properties of the fly ash-derived zeolites were also characterized and related to their catalytic performance for the pyrolysis of polypropylene.

Experimental

Materials
Fly Ash
The fly ash sample used in this study was obtained from Boryung Power Plant in Korea. Table 1 shows the chemical composition of the fly ash. As can be seen in this table, the major components of the fly ash are SiO₂ and Al₂O₃. Besides them, small amounts of Fe₂O₃ and CaO can be found.

Commercial Zeolites
For comparison purposes, commercial NaY and HY zeolites were supplied by Zeolyst International. The SiO₂/Al₂O₃ mole ratios were 5.1 and 5.2 for NaY and HY zeolites, respectively.

Polypropylene
Polypropylene (PP) was obtained from Honam Petrochemical Company.

Synthesis and Physical Characterization of Fly Ash-Derived Zeolites
A mixture of 100 g of fly ash with a known amount of NaOH powder (NaOH/fly ash weight ratio = 0.7, 1.2, 1.7) was ground in a ball mill rotating at 24 r.p.m. for 24 h in a 1000 cm³ ceramic jar with 5 mm ceramic balls as the grinding medium. The ground fly ash/NaOH mixture was fused at 600°C for 1 h and 30 min. This fused fly ash was ground again for 24 h. After grinding, 100 g of the fused fly ash was mixed with 500 g of water, aged at 25°C for 8 h, and crystallized at 100°C for 10 h. BaTiO₃ powder (BaTiO₃/fly ash weight ratio = 0.04) was added to the fused fly ash solution prior to the aging and used as a standard in the X-ray measurement of the relative amount of zeolite phases obtained. The crystallized fly ash was recovered by filtration, washed using distilled water repeatedly until the pH of filtrate decreased to between 10~11, and dried overnight at 60°C in a convection oven.
The crystallized fly ash, which is considered to be a mixture of various zeolite phases and unreacted fly ash, was designated as FAZ (fly ash-derived zeolite). FAZ (0.7), FAZ (1.2) and FAZ (1.7) corresponded to the NaOH/fly ash weight ratios of 0.7, 1.2 and 1.7, respectively. In order to improve the acidity, FAZ was treated in 1 M NH₄Cl solution for ion-exchange and this NH₄Cl treated FAZ was designated as HFAZ (H⁺-exchanged fly ash-derived zeolite). HFAZ (0.7), HFAZ (1.2) and HFAZ (1.7) corresponded to FAZ (0.7), FAZ (1.2) and FAZ (1.7), respectively. The NH₄Cl treatment was conducted three times at room temperature for 20 h each. The results of the analysis of chemical composition of fly ash-derived zeolites by ICP-OES (Perkin-Elmer Co.) showed that the SiO₂/Al₂O₃ mole ratio was not significantly changed after the NH₄Cl treatments. However, the Na₂O contents was greatly reduced from 18.5% of FAZ (1.2) to 2.3% of HFAZ (1.2) and from 17.7% of FAZ (1.7) to 3.8% of HFAZ (1.7), respectively.
The XRD patterns of the fused and crystallized fly ash samples were obtained using an X-ray diffractometer (Model X'Pert-MPD, Phillips Analytical). The morphologies of the samples were analyzed using a scanning electron microscope (Model XL 30, Phillips Electron Optics). The N₂ BET specific surface areas (Quantasorb, Quantachrome Corp.) and NH₃-temperature programmed desorption (TPD) spectra were also measured. The results of these characterizations were related to the catalytic performance of the zeolites.

Pyrolysis Experiments
Pyrolysis experiments were carried out in a laboratory scale reaction system shown in Figure 1. The inside volume of the reaction vessel was 1000 cm³. In each run, a mixture of 100 g of PP with 10 g of zeolite was placed in the reaction vessel. The inside reaction temperature of the reaction vessel was controlled using an electric heater and a PID controller. The temperature was initially raised at 5°C/min from room temperature for 50 min, kept constant at 250°C for 20 min, raised at 5°C/min for 16 min., kept constant at 330°C for 30 min, again raised at 2°C/min for 95 min, and finally kept constant at 520°C for 30 min.
Pyrolysis products were mostly liquid vapor and gas. The amount of solid residue was negligible. During the
Figure 1. A schematic of the laboratory pyrolysis system.

pyrolysis experiments, 60 cm³/min of N₂ gas was supplied to the inside of the reaction vessel in order to promote the moving of liquid and gaseous products to a condenser and cold trap. The gaseous product was vented to the atmosphere and the liquid vapor product was recovered as a condensed pyrolysis oil. The boiling point distribution of the recovered pyrolysis oil was analyzed by SIMDIS (Simulated Distillation) method (ASTM D2887) [14,15] using an HP 6890 Gas Chromatograph as a measure of the catalytic performance of zeolites.

Results and Discussions

Characterization of Fly Ash-Derived Zeolite Samples

XRD

Figure 2 shows the XRD pattern of the as-received fly ash used in this study. As shown in this figure, quartz (SiO₂), mullite (3Al₂O₃ · 2SiO₂) and hematite (Fe₂O₃) are the major crystalline substances in the fly ash.

Figures 3(a), (b) and (c) show the XRD patterns of the fused fly ash samples with the NaOH/fly ash weight ratio at 0.7, 1.2 and 1.7, respectively. From these figures, it can be found that significant amounts of sodium silicates and sodium aluminum silicates were formed by the

Figure 2. XRD pattern of the fly ash.

Figure 3. XRD patterns of the fused fly ash samples obtained with different NaOH/fly ash weight ratios: (a) 0.7, (b) 1.2, (c) 1.7.
NaOH fusion. This finding indicates that the NaOH fusion was very effective in dissolving silicates and aluminosilicates from the fly ash [5]. Some quartz (SiO₂) still remains unreacted in these figures. It is clear that the intensity of this unreacted quartz is significantly lower at higher NaOH/fly ash weight ratios (1.2 and 1.7) than at a lower NaOH/fly ash weight ratio (0.7).

Figures 4(a), (b) and (c) show the XRD patterns of the crystallized fly ash samples: FAZ (0.7), FAZ (1.2) and FAZ (1.7). As shown in Figure 4(a), NaP1 is the only zeolite phase in FAZ (0.7). In addition, aluminum sodium silicate and unreacted quartz phases coexist. As can be seen in Figure 4(b) for FAZ (1.2), the intensity of NaP1 is significantly lower and faujasite can be found. This finding suggests the possibility that some NaP1 was transformed into faujasite as the NaOH/weight ratio was increased. Based on the report by Querol and coworkers [10], faujasite has larger pore size (7.3 Å) than NaP1 (4.6 Å). Figure 4(c) for FAZ (1.7), NaP1 does not exist and faujasite is the only zeolite phase. Faujasite coexists with other unnamed sodium aluminum silicate hydrates at this condition. It seems that the intensity of faujasite does not increase with increasing NaOH/fly ash weight ratio from 1.2 to 1.7. The XRD intensity of faujasite relative to that of BaTiO₃ at the NaOH/fly ash weight ratios of 1.2 and 1.7 were 3.17 and 1.92, respectively. Shigemoto and coworkers [2] and Rayalu and coworkers [7] reported that the optimum NaOH/fly ash weight ratio was 1.2 and faujasite was transformed into other zeolite phases at excessively high NaOH/fly ash weight ratios over 1.2.

**SEM**

Figure 5 shows the SEM micrographs of the as-received fly ash. The as-received fly ash has a spherical shape and the average diameter is about 28 μm.

Figures 6(a), (b) and (c) show the SEM micrographs of the crystallized fly ash, which is a mixture of zeolite phases, silicates and unreacted fly ash: FAZ (0.7), FAZ (1.2) and FAZ (1.7). These figures correspond to Figures 4(a), (b) and (c), respectively. At low NaOH/fly ash ratio (0.7) as shown in Figure 6(a), FAZ (0.7) has an agglomerate shape of fine flakes. At medium NaOH/fly ash weight ratio (1.2) as shown in Figure 6(b), FAZ (1.2) has a relatively distinct crystalline structure. At high NaOH/fly ash weight ratio (1.7) as shown in Figure 6(c), FAZ (1.7) also has a crystalline structure, but it appears that the crystallite size is slightly smaller, possibly due to the transformation of zeolite phases.

**BET Specific Surface Area**

Table 2 lists the BET specific surface areas of FAZ and HFAZ samples. From this table, it can be found that FAZ (1.7) has the largest BET specific surface area, followed by FAZ (1.2) and FAZ (0.7) among FAZs. This finding
Figure 6. SEM images of the crystallized fly ash samples: (a) FAZ (0.7), (b) FAZ (1.2), (c) FAZ (1.7).

Table 2. \( \text{N}_2 \) BET Specific Surface Areas of FAZ and HFAZ Samples

<table>
<thead>
<tr>
<th>Sample</th>
<th>BET Specific Surface Area (m(^2)/g)</th>
</tr>
</thead>
<tbody>
<tr>
<td>FAZ (0.7)</td>
<td>23.2</td>
</tr>
<tr>
<td>FAZ (1.2)</td>
<td>74.4</td>
</tr>
<tr>
<td>FAZ (1.7)</td>
<td>169.0</td>
</tr>
<tr>
<td>HFAZ (0.7)</td>
<td>89.8</td>
</tr>
<tr>
<td>HFAZ (1.2)</td>
<td>187.4</td>
</tr>
<tr>
<td>HFAZ (1.7)</td>
<td>249.7</td>
</tr>
</tbody>
</table>

may be attributed the increase of the amount of porous or crystalline substances including zeolites as the NaOH/fly ash weight ratio is increased. It is interesting that FAZ (1.7) having largest BET specific surface area looked slightly finer than FAZ (1.2) in Figure 6. The BET specific surface area of FAZ (1.7), 169 m\(^2\)/g in Table 2, is much smaller than that of commercial NaY zeolites, which is generally as large as 400 ~ 500 m\(^2\)/g [7]. This is because FAZ (1.7) synthesized in this study is actually a mixture of zeolites and unreacted fly ash rather than a high purity zeolite. In Table 2, the BET specific surface areas of HFAZs are significantly higher than those of FAZs. Probably this phenomenon may be attributed to

Figure 7. \( \text{NH}_3 \)-TPD spectra of zeolite samples.

dissolution of Na and other mineral ions during the \( \text{NH}_4\text{Cl} \) treatment of FAZs.

**\( \text{NH}_3\)-TPD**

Figure 7 shows the \( \text{NH}_3\)-TPD spectra of two \( \text{H}^+ \)-exchanged HFAZ samples and a commercial HY.
The areas under the TPD curves for the three H⁺-exchanged samples in the temperature range between 300 and 500°C are significantly large, indicating that these H⁺-exchanged samples have strong acidity. In Figure 7, it is noteworthy that HFAZ (1.2) and HFAZ (1.7) synthesized in this study have acidity as strong as commercial HY zeolite.

Pyrolysis Experiments

Pyrolysis can be conducted with or without catalyst. The advantages of catalytic pyrolysis against noncatalytic pyrolysis are lower reaction temperatures and narrower molecular size distributions of product [11,16]. The most widely employed catalysts for pyrolysis of plastics are zeolites because of their high acidity and product selectivity attributed to steric effects [17,18]. However, zeolites are generally expensive and have relatively short catalyst life in the pyrolysis process. Therefore, a series of pyrolysis experiments were conducted to evaluate the potential of the fly ash-derived zeolites synthesized in this study as an alternative nonregenerative pyrolysis catalyst.

Figures 8(a) and (b) show the cumulative yields and simulated boiling point distributions of liquid pyrolysis products using polypropylene obtained over fly ash-derived zeolites which are in Na or H form, together with that obtained over a commercial HY zeolite for comparison purpose.

As can be seen in Figure 8(a), the cumulative yield begins to rise at around 420°C and reaches a final steady state value of 90.2% without zeolite. The cumulative yields obtained over HY, HFAZ (1.2) and HFAZ (1.7) begin to rise at much lower temperatures by as much as 90°C. Comparison of Figure 8(a) with Figure 7 suggests that the high acidity of these H⁺-exchanged zeolites accelerated the reaction [19,20]. On the other hand, FAZ (1.2) does not significantly affect the cumulative yield in Figure 8(a). One of the possible reasons for this fact may be the weak acidity of this sample in Na-form.

It is shown in Figure 8(b) that the simulated boiling point distribution of liquid pyrolysis products over FAZ (1.2) is not significantly different from no zeolite case due to its weak acidity. On the other hand, the simulated boiling point distributions obtained over HFAZ (1.2) and HFAZ (1.7) are significantly improved over no zeolite case. Especially, the boiling point distribution obtained over HFAZ (1.2) is as low as that obtained over the commercial HY zeolite. For the mass percentage of 80% on the simulated boiling point distribution curve, the boiling temperature obtained using this zeolite was significantly lower than that obtained without zeolite by as much as 108°C. These facts are in agreement with the NH₃-TPD results in Figure 7, where the acidities of HFAZ (1.2) and HFAZ (1.7) were as strong as HY zeolite. Although HFAZ (0.7) is also a H⁺-exchanged fly ash-derived zeolite, the simulated boiling point distribution obtained over this zeolite is not so much improved as HFAZ (1.2) and HFAZ (1.7), indicating that the acidity of HFAZ (0.7) may not be so much strong as HFAZ (1.2) and HFAZ (1.7). One of the other possible reasons for this finding is that the zeolite phase in HFAZ (0.7) is mainly NaP1 as shown in Figure 4-(a), whereas HFAZ (1.2) and HFAZ (1.7) include faujasite as can be seen in Figures 4-(b) and (c). Since the pore size of faujasite (7.3 Å) is much larger than that of NaP1 (4.6 Å) as reported by Querol and coworkers [10], faujasite may be more effective for cracking hydrocarbon molecules than NaP1.

Conclusions

Zeolites were synthesized from fly ash by NaOH fusion method employing three different NaOH/fly ash weight
ratios and a series of pyrolysis experiments were conducted to evaluate the potential of this fly ash-derived zeolites as an alternative nonregenerative catalyst for pyrolysis of polypropylene. The catalytic performance of fly ash-derived zeolites were expressed in terms of the yield and simulated boiling point distribution of the liquid pyrolysis products. The physical properties of the fly ash-derived zeolites were also characterized and related to their catalytic performance. The major findings of this study can be summarized as follows:

1. Within the experimental conditions of this study, the fly ash-derived zeolite was a mixture of zeolite phases, silicates and unreacted fly ash. At low NaOH/fly ash weight ratio (0.7), NaP1 was the major zeolite phase. At medium NaOH/fly ash weight ratio (1.2), NaP1 coexisted with faujasite. At high NaOH/fly ash weight ratio (1.7), only faujasite existed. In terms of the amount of faujasite, the optimum NaOH/fly ash weight ratio seems to be 1.2.

2. The catalytic performance of fly ash-derived zeolite in Na form was poor, but that of H+-exchanged fly ash-derived zeolites was significantly improved.

3. The catalytic performances of H+-exchanged fly ash-derived zeolites obtained with fusion at medium and high NaOH/fly ash weight ratios (1.2 and 1.7) were as great as that of commercial HY zeolite. Especially, the boiling temperature obtained using the H+-exchanged fly ash-derived zeolite with medium NaOH/fly ash weight ratio (1.2) was significantly lower than that obtained without zeolite by as much as 10°C for the mass percentage of 80% on the simulated boiling point distribution curve. One the other hand, the catalytic performance of H+-exchanged fly ash-derived zeolite obtained with low NaOH/fly ash weight ratio (0.7) was less satisfactory. One of the possible reasons for these phenomena seems to be that the zeolite phase formed with low NaOH/fly ash weight ratio (0.7) was mainly NaP1 having small pores, whereas the zeolite phases formed with medium or high NaOH/fly ash weight ratio (1.2 or 1.7) include faujasite having larger pores.

Acknowledgement

This work was financially supported by the National Research Lab. Program of Korean Ministry of Science and Technology.

References