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

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Abstract: Fly ash-derived zeolite materials could be used as catalysts for the pyrolysis of polypropylene. This study focused on the conversion of coal fly ash into zeolites by the fusion method. It follows our previous study that concentrated on the change of activity of synthetic zeolites with respect to the NaOH fusion ratio. In the previous study, the activity change of a synthetic zeolite was investigated for the pyrolysis of polypropylene. This study concentrates upon the change in the synthetic zeolites upon changes to the crystallization temperature and time, rather than the fusion ratio. The characterization of the fly ash-derived zeolite materials was carried out in terms of analyses of the crystalline structure (XRD), BET specific surface area, and catalytic performance for the pyrolysis of polypropylene. In this study, the zeolites synthesized from coal fly ash were zeolite types X, NaP1, and hydroxyaludalite. For the pyrolysis of polypropylene, these synthetic zeolites showed much higher reactivity than observed when no catalyst was used. Among the three types of fly ash-derived zeolite materials, zeolite X showed the highest catalytic performance. Zeolite X resulted in a lower degradation temperature than did either NaP1 or hydroxyaludalite. It also gave a lower boiling point distribution of liquid products than did the other synthetic zeolites. It seems that these results occurred because of the larger pore size of zeolite X than that of the others. In the fusion method, the effective conditions for the synthesis of zeolite X were a crystallization temperature of 100°C at each crystallization time.

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

Introduction

A large amount of fly ash, exceeding 40% of raw coal material, is generated annually from coal combustion in power plants [1]. Fly ash can be converted into zeolite because it has a similar composition to a precursor of natural zeolite [2]. There are many reports on the synthesis of zeolite from fly ash by hydrothermal methods. In those studies, the synthesized zeolites were used considerably for the removal of water and air pollutants [3-9]. Table 1 shows the reported zeolitic phases synthesized from fly ashes by hydrothermal reactions [10]. These zeolites can be used as catalysts for pyrolysis because of their thermal stability and molecular sieve effects [11-13].

Pyrolysis is an alternative technology for the recycling of plastic wastes into useful fuel. There are two pyrolytic methods: catalytic and non-catalytic pyrolysis. Catalytic pyrolysis has the advantages of a reduction in the degradation temperature, a higher decomposition speed, and yielding a relatively constant quality fuel oil [14-16]. Therefore, this study was carried out to synthesize fly ash-derived zeolites (FAZs) by the fusion method. The fusion method employs grinding, heating, and mixing steps before the traditional NaOH hydrothermal reaction [3,4,6,9]. This method causes the dissolution of Si and Al in the fly ash to be more readily performed than it is in the traditional NaOH hydrothermal reaction, and so it is a more-effective method for the synthesis of zeolites than is the traditional method. In this study, FAZs were ion-exchanged from Na to H (HFAZs) to improve the catalyst activity. The HFAZs were then used as catalysts
Table 1. Zeolitic Phases Synthesized from Fly Ashes using Hydrothermal Reactions, and their XRD JCPDS Codes, Divided into High and Low Industrial Application Groups based on the CEC [6]

<table>
<thead>
<tr>
<th>Zeolitic product</th>
<th>JCPDS</th>
</tr>
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<tbody>
<tr>
<td>NaP1 zeolite</td>
<td>39-0219</td>
</tr>
<tr>
<td>Phillipsite/ KM-zeolite</td>
<td>30-0902</td>
</tr>
<tr>
<td>K-Chabazite</td>
<td>12-0194</td>
</tr>
<tr>
<td>F linde zeolite</td>
<td>25-0619</td>
</tr>
<tr>
<td>Herschelite</td>
<td>31-1271</td>
</tr>
<tr>
<td>Faujasite</td>
<td>12-0228</td>
</tr>
<tr>
<td>Zeolite A</td>
<td>43-0142</td>
</tr>
<tr>
<td></td>
<td></td>
</tr>
<tr>
<td>Low industrial application</td>
<td></td>
</tr>
<tr>
<td>Perlitite</td>
<td>38-0395</td>
</tr>
<tr>
<td>Analcime</td>
<td>19-1180</td>
</tr>
<tr>
<td>Hydroxy-sodalite</td>
<td>31-1271</td>
</tr>
<tr>
<td>Hydroxy-cancrinite</td>
<td>28-1036</td>
</tr>
<tr>
<td>Kalsilite</td>
<td>33-0988</td>
</tr>
<tr>
<td>Tobermorite</td>
<td>19-1364</td>
</tr>
</tbody>
</table>

**Figure 1.** SEM micrographs of the coal fly ash.

for the pyrolysis of polypropylene (PP) to investigate the most effective conditions for the synthesis of zeolites suitable for use in the pyrolysis of PP.

### Experimental

#### Synthesis of Zeolite from Coal Fly Ash Materials

Coal fly ash was obtained from Boryung Power Plant located at Chungnam Province in Korea. Its major chemical composition was SiO₂, 53.56%; Al₂O₃, 27.71%; Fe₂O₃, 5.53%; MgO, 0.91%; CaO, 4.50%; K₂O, 0.94%; and Na₂O, 0.37%; its ignition loss was 5.88%. The morphology is shown in Figure 1. Coal fly ash consists of spherical particles having average diameters in the range from 20 to 30 μm. The X-ray diffraction pattern of coal fly ash, presented in Figure 2, shows that the major mineral species are quartz, mullite, and hematite.

#### Synthesis/Analysis

Fly ash was fused with NaOH in the ratio of 1.2:1 because this ratio was the optimum one that we found for the pyrolysis of PP in our previous report [11]. The mixture was ground in a ceramic vessel at 24 rpm for 24 h and then fused at 600°C for 1.5 h. The fused mixture was cooled at room temperature and milled at 24 rpm for 24 h. The fused powder was mixed with distilled water in a solid/liquid ratio of 0.2 (w/w). The fused slurry was added into the autoclave for aging and crystallization. The aging was conducted at 25°C for 8 h, and then the crystallization, by hydrothermal reaction, was carried out at various temperatures and times. The crystallization temperatures were 40°C [FAZ(40)], 100°C [FAZ(100)], and 130°C [FAZ(130)] at a fixed crystallization time of 10 h; the crystallization times were 5 h [FAZ(5)], 10 h [FAZ(10)], 15 h [FAZ(15)], and 20 h [FAZ(20)] at a fixed crystallization temperature of 100°C. The crystallized FAZs were filtered and washed repeatedly with distilled water until the pH of the filtrate decreased into the range 10-11. The FAZs were dried at 60°C in a convection oven and
then ion-exchanged to improve the catalytic activity.

The ion-exchange of the FAZs was carried out by treatment with 1 M NH₄Cl [17]. The NH₄Cl treatment was repeated three times at room temperature for 24 h each time. After NH₄Cl treatment, the NH₄FAZs were converted to HFAZs by a calcination conducted at 500°C for 4 h.

For the analysis of the HFAZs, we measured the crystalline structure, using an X-ray diffractometer (Model X’Pert-MPD, Phillips Analytical), and the BET specific surface area (Quantsorb, Quantachrome Corp.).

**Pyrolysis of Polypropylene**

Materials
The PP used in this study was obtained from SK Corp. For the investigation of the catalytic performances, the HFAZs were compared with commercial zeolite HY at an acidity of 5.2. The catalytic performance was analyzed in terms of the degradation temperature and the boiling point distribution of the liquid products obtained from the pyrolysis of PP. The commercial zeolite was supplied by Zeolyst International.

Pyrolysis
Pyrolysis experiments were carried out in a laboratory-scale autoclave. The ratio of catalyst/plastic was 0.1 (w/w).

**Results and Discussion**

**Effects of Crystallization Temperature on the Pyrolysis of PP**

Characterization of HFAZs
The main crystalline structures of the HFAZs synthesized at the various crystallization temperatures are shown in Figure 3. We find that HFAZ(40) and HFAZ(100) are NaP1-types with small amounts of hydroxysodalite and zeolite X, respectively. However, HFAZ(130) exhibits little of the crystalline structure of a zeolite. The BET specific areas of the HFAZs changed with respect to the temperature, as shown in Figure 4. Among the three types of HFAZs, HFAZ(100) has the largest surface area, which causes it to have the highest catalytic activity, and HFAZ(130) has the smallest surface area, resulting in its
low catalytic activity [20].

Degradation Temperature

The changes in the degradation temperatures as a function of the catalyst used are depicted in Figure 5. The HFAZs show higher degradation temperatures than does the commercial zeolite HY, but they are lower than when no catalyst was used. These results indicate that the catalytic effects of the HFAZs are smaller than that of the commercial zeolite HY, but the reactivity is higher than it is when no catalyst is used for the pyrolysis of PP. Among the HFAZs, the catalytic effects follow the order HFAZ(100) > HFAZ(40) > HFAZ(130). The order agrees with that of the BET specific surface areas in Figure 4. Zeolite X of HFAZ(100) is most effective for the pyrolysis of PP, while amorphous HFAZ(130) shows the smallest effect in this study. NaP1 of HFAZ(40) results in a higher degradation temperature than does zeolite X because zeolite X has a larger pore size (7.3 Å) than does NaP1(4.6 Å) and, thus, is comparatively more suitable to cracking the carbon backbone in PP [9].

Boiling Point Distribution of Liquid Products

Figure 6 illustrates the changes in the boiling point distribution of the liquid products produced through the pyrolysis of PP using the HFAZs. The boiling point distributions over these HFAZs are higher than that of commercial zeolite HY and lower than that when no catalyst was used. This finding indicates that the effects of the HFAZs are smaller than that of the commercial zeolite HY, but that the reactivity is better than it is when no catalyst was used; these results are consistent with the degradation temperatures obtained by MSB. Among the three types of HFAZs, zeolite X of HFAZ(100) shows the lowest boiling point distribution. Despite of crystalline structure of NaP1 in HFAZ(40), it does not show any significant differences from those of amorphous HFAZ (130) in the boiling point distribution. This situation is due to the small pore size of NaP1. Because the pore size is too small to crack the bonds in PP, the pyrolysis effects caused by the pores of this catalyst are also small. Although the degradation temperature of HFAZ(40) is lower than that of HFAZ(130), its boiling point distribution is similar to that of HFAZ(130). It seems that the degradation temperature is affected by the acidity of the catalysts and the boiling point distribution depends on not only the acidity but also the pore size of catalyst. Therefore, the results of the degradation temperature and boiling point distribution measurements can be different from one another.

Effects of Crystallization Time on the Pyrolysis of PP Characterization of HFAZs

Figure 7 presents the main crystalline structures of the HFAZs synthesized upon varying the crystallization time. It shows that few differences exist among the HFAZs. The dominant zeolite structure is zeolite X and its amount also did not change significantly. Moreover, the changes in the BET specific surface areas shown in Figure 8 are not remarkable.

Degradation Temperature

The catalytic performances of these HFAZs did not differ significantly in terms of the degradation temperatures shown in Figure 9. These results agree with the results of the characterization of the HFAZs. Therefore, we believe that the reason why the performances are similar, is because the characteristics of the HFAZs are similar in Figures 7 and 8.

Boiling Point Distribution of Liquid Products

Figure 10 shows the boiling point distributions of the
liquid products. As for the results of the degradation temperatures, there is no significant change among the boiling point distributions of these HFAZs. We found, however, that the yield of the liquid products changed with respect to the crystallization time. There is the difference in yield of about 7% between HFAZ(10) and HFAZ(15). This finding can be explained by considering Figure 11, which depicts the yields of liquid products relative to the pyrolysis temperature over the HFAZs synthesized at various crystallization times. The peak of the yield obtained over HFAZ(15) appears at a lower pyrolysis temperature than does that of HFAZ(10). This observation indicates that the pyrolysis temperature that produces
liquid products at the highest rate, is lower for HFAZ(15) than it is for HFAZ(10). High pyrolysis temperatures cause a high possibility of re-cracking of the cracked substance. A high possibility of re-cracking can cause an increase in the amount of non-condensable gas and concurrently, a decrease in the amount of liquid product. Therefore, it is understandable that the amount of liquid products formed over HFAZ(10) is smaller than that over HFAZ(15).

Conclusions

This study concentrated on the conversion by the fusion method of coal fly ash into zeolites that are suitable for the pyrolysis of PP. The synthesis was conducted using various crystallization temperatures and times. The characterization of the fly ash-derived zeolite materials was carried out through analyses of the crystalline structure (XRD), the BET specific surface area, and the catalytic performance for their pyrolyses of PP. Based on the experimental results obtained, the following conclusions can be drawn:

1) In this study, the zeolites synthesized (HFAZs) from coal fly ash were zeolite X, NaP1, and hydroxysodalite.

2) The catalytic performances of the HFAZs were generally much higher than that obtained when no catalyst was used for the pyrolysis of PP. Among the three types of HFAZs, zeolite X showed the highest catalytic activity.

3) Zeolite X was formed at a crystallization temperature of 100°C. At 40 and 130°C, NaP1 and amorphous-type zeolites were formed, respectively. It was interesting that although HFAZ(40) had the crystalline structure of NaP1, it did not show any significant differences from that of the reactivity of amorphous HFAZ(130) in its boiling point distribution because of the small pore size of NaP1. Especially, while the boiling point distribution of HFAZ(40) was similar to that of HFAZ(130), its degradation temperature was lower than that of HFAZ(130).

4) Zeolite X was formed dominantly at all crystallization times. Moreover, there were no remarkable differences in the BET specific surface areas. Therefore, the changes in the catalytic effects were not significant when analyzed by either the degradation temperature or the boiling point distribution, but the yields of liquid products were different. The highest yield was observed at a crystallization time of 15 h.

Acknowledgment

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References