Pyrolysis of polypropylene over mesoporous MCM-48 material

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Abstract

The catalytic performance of mesoporous MCM-48 materials in the degradation of polypropylene (PP) was evaluated using a thermogravimetric analyzer and batch reactor. The activation energy of PP degradation was significantly lowered by the addition of Al-MCM-48. The catalytic conversion was also higher over Al-MCM-48 than over Si-MCM-48. Al-MCM-48 mainly generated C\textsubscript{7}–C\textsubscript{10} hydrocarbons, while Si-MCM-48 exhibited a relatively broader distribution of oil products (C\textsubscript{7}–C\textsubscript{14}). Al-MCM-48 showed high catalytic stability for the PP degradation.

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1. Introduction

At present, most waste plastics in Korea are landfilled or incinerated, despite the high potential for recovering these valuable compounds. Effective methods have been sought for the recycling of waste plastics. Particularly, the recent sharp rising in oil prices may possibly make the pyrolysis of waste plastics economically competitive. The pyrolysis of waste plastics, however, has suffered from the disadvantages of a broad product spectrum and high energy input [1].

Catalytic pyrolysis can improve the product selectivity and reduce the energy input. Most previous studies on the catalytic pyrolysis of waste plastics have used microporous materials, such as zeolites [2–5]. Owing to their large pore openings, mesoporous materials have the advantage of higher accessibility of bulky substances, such as HDPE, to their inner active sites. Recently, MCM-41 [6], which is one of the most common mesoporous catalysts, was reported to allow higher conversion and excellent selectivity for gasoline [7]. However, few studies have been performed on the application of MCM-48, which contains three-dimensional pore openings, to the pyrolysis of polypropylene (PP). As MCM-48 is expected to be resistant to pore blocking, it also would be expected to exhibit much higher activity than MCM-41, which has only one-dimensional openings [8,9]. This paper addresses the catalytic performance of MCM-48 on the pyrolysis of PP with regard to the pyrolysis kinetics and product characteristics.

2. Experimental

The silica form of MCM-48 was synthesized using hydrothermal synthesis methods [10], with cetyltrimethyl ammonium bromide as the templating agent. The aluminium-incorporated forms (Al-MCM-48, Si/Al = 30 and 60) of MCM-48 were synthesized via a post-grafting route [11].

The catalysts synthesized in this study were characterized using inductively coupled plasma-atomic emission spectrometer (ICP-AES), X-ray diffraction (XRD), N\textsubscript{2} sorption...
and ammonia-temperature-programmed desorption (TPD) methods. The catalytic performance of MCM-48 was assessed via thermogravimetric analysis (TGA), with batch reactor experiments performed following the procedure described in our previous literature [12].

3. Results and discussion

3.1. Catalyst characterization

Fig. 1 shows the XRD patterns of Si-MCM-48, Al-MCM-48 (Si/Al = 30) and Al-MCM-48 (Si/Al = 60). The XRD pattern of Si-MCM-48, synthesized using a surfactant blend of CTAB and Brij-30, clearly showed eight peaks, consistent with 211, 220, 321, 400, 420, 332, 422 and 431 planes. The unit cell parameter (a0) calculated from the d-spacing value of the 211 plane was 9.40 nm. The XRD patterns of Al-MCM-48 materials exhibited similar to that of Si-MCM-48, with the exception of a slightly contracted unit cell parameter, which might have been due to the heat treatment at 550 °C following the incorporation of Al. The nitrogen adsorption–desorption isotherm and corresponding pore size distribution obtained for MCM-48 exhibited sharp inflections characteristic of the sorption of capillary condensation for pores with a diameter of about 2.6 nm. As shown in Table 1, the Si-MCM-48, Al-MCM-48 (Si/Al = 60) and Al-MCM-48 (Si/Al = 30) showed high BET surface areas of 1035, 996 and 994 m² g⁻¹, and total pore volumes of 1.01, 0.86 and 0.85 cm³ g⁻¹, respectively. From Fig. 2, it could be seen that the incorporation of aluminum into the mesoporous silica material generated higher acid sites which are required for acid-catalyzed reactions, whereas, the pure silica materials did not possess sufficient intrinsic acidity or reactivity for use as a catalyst. In addition, there are more acid sites in the Al-MCM-48
than in the Al-MCM-48 (Si/Al = 60). This indicates that the number of acid sites increases with the rise of the aluminum content.

### 3.2. Catalytic performance

Si-MCM-48, Al-MCM-48 (Si/Al = 60) and Al-MCM-48 (Si/Al = 30) materials reduced the temperatures required for the degradation of PP to 440, 335 and 320 °C, respectively, compared to the 475 °C required for thermal degradation alone. Table 2 shows the results of the apparent activation energies for the degradation of PP over these catalysts. The activation energies over Al-MCM-48 materials were much lower than over Si-MCM-48. This result suggests that Al-MCM-48 material may be a promising catalyst for the degradation of PP. Table 3 shows the product distribution obtained for the degradation of PP. The conversion via catalytic degradation was much higher than via thermal degradation. Particularly, Al-MCM-48 (Si/Al = 30) exhibited better activity than Al-MCM-48 (Si/Al = 60) due to the higher amount of acid sites, indicating that the catalytic activity is closely related to the amount of acid sites.

Table 2

<table>
<thead>
<tr>
<th>Catalyst</th>
<th>Without catalyst</th>
<th>Si-MCM-48</th>
<th>Al-MCM-48 (Si/Al = 60)</th>
<th>Al-MCM-48 (Si/Al = 30)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Activation energy (kJ mol(^{-1}))</td>
<td>216.7 ± 28.7</td>
<td>131.1 ± 7.3</td>
<td>102.2 ± 5.1</td>
<td>96.1 ± 6.1</td>
</tr>
</tbody>
</table>

Table 3

<table>
<thead>
<tr>
<th>Catalyst</th>
<th>Without catalyst</th>
<th>Si-MCM-48</th>
<th>Al-MCM-48 (Si/Al = 60)</th>
<th>Al-MCM-48 (Si/Al = 30)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Conversion (%)</td>
<td>3.3</td>
<td>75.3</td>
<td>90.2</td>
<td>95.7</td>
</tr>
<tr>
<td>Yield (wt%)</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Oil</td>
<td>2.1</td>
<td>58.3</td>
<td>72.2</td>
<td>76.5</td>
</tr>
<tr>
<td>Gas</td>
<td>1.2</td>
<td>17.0</td>
<td>18.0</td>
<td>19.2</td>
</tr>
</tbody>
</table>

PP: catalyst = 5:1 (w/w); reaction temperature, 380 °C; reaction time, 1 h.

Table 4

<table>
<thead>
<tr>
<th>Catalyst</th>
<th>Product distribution (wt%)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>CH(_4)</td>
</tr>
<tr>
<td>Without catalyst</td>
<td>0.9</td>
</tr>
<tr>
<td>Si-MCM-48</td>
<td>0.1</td>
</tr>
<tr>
<td>Al-MCM-48 (Si/Al = 60)</td>
<td>0.1</td>
</tr>
<tr>
<td>Al-MCM-48 (Si/Al = 30)</td>
<td>0.1</td>
</tr>
</tbody>
</table>

PP: catalyst = 5:1 (w/w); reaction temperature, 380 °C; reaction time, 1 h.

Fig. 3. Product distribution of oil.

Fig. 4. TG curves of five repetitive catalytic degradation of PP over Al-MCM-48 (Si/Al = 30).
maintained during the repetitive experiments, while that of one-dimensional Al-MCM-41 was gradually decreased. This suggests that for PP degradation, Al-MCM-48 is the superior catalyst to Al-MCM-41.

4. Conclusion

Mesoporous MCM-48 materials were employed as catalysts for the degradation of PP. The catalytic activity of Al-MCM-48 was much higher than that of Si-MCM-48. Al-MCM-48 mainly generated C_{7–10} hydrocarbons, while Si-MCM-48 exhibited a relatively broader distribution of oil products (C_{7–14}). Al-MCM-48 showed high catalytic stability for the degradation of PP. In view of these facts, Al-MCM-48 can be considered a promising catalyst for the degradation of other waste plastics.

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References