Modification of zeolite acidity and its effect on the upgrading of biomass-derived oil

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ABSTRACT
In this study, the high silica ZSM-5 type zeolite was treated in high temperature steam and the effect to the acidity properties and catalytic upgrading of biomass-derived oil was evaluated. The steam treatment induced the dislodging of Al into extraframework and gave the contribution to the catalytic activity. As steam treatment duration prolonged, the Al extraframework might collapsed and decreased the overall catalytic activity. The effect of steam treatment on the creation of mesopores and catalytic activity is discussed.

Keywords: Zeolite; structure; acidity modification; thermal treatment; catalytic pyrolysis; biomass derived-oil.

[1] Introduction
Zeolite has been used widely in many catalytic applications, including catalytic upgrading of biomass-derived oil, due to its high catalytic activity and inexpensive cost. Despite its advantages, most of zeolites contain considerably high micropores which sometimes result in low catalytic activity for certain reactions, even though there are many acid sites, due to the transport limitation issue and the susceptibility of coke formation. Some researchers conducted post-treatment of zeolite to increase the mesopores proportion by dealumination [1], desilication [2], and steaming [1] at certain temperature. However, there are not so many studies on the effect of post-treatment, particularly steam treatment, to catalytic performance of zeolite for the upgrading of the biomass-derived oil. In this study, ZSM-5 type zeolite was steam-treated and the performance was evaluated in catalytic upgrading of biomass-derived oil.

[2] Experimental
High silica ZSM-5 zeolite (HSZ-890, TOSOH Corp, Si/Al = 1500) was heated at 500 °C for 1, 3, and 6 h in the mixture of steam (Psteam = 101.22 Pa) and argon stream followed by drying in argon stream at the same temperature for 2 h. The as-treated zeolite was then stored in 110 °C drying oven overnight prior to use. The effect of steam treatment to the acidity and surface area was evaluated using NH3-Temperature Programmed Desorption (NH3-TPD) method (Belcat, Japan) and N2 adsorption-desorption technique (NOVA 4200e, Quantachrome, USA). The catalytic performance and reusability of steam-treated zeolite was examined for the catalytic upgrading of Fallopia Japonica-derived oil at 600 °C in a fixed-bed reactor under inert condition. The composition of bio-oil was obtained using Gas Chromatography (GC) – Mass Spectroscopy (MS) method.

[3] Results and discussion
Fig. 1 shows the NH3-TPD profile of the steam-treated zeolite. The total amount of acid site was 0.605; 0.582; 0.567; and 0.578 for steam treatment of 0 (untreated), 1, 3, and 6 h, respectively. The amount of acid sites at high temperature indicates the number of Al framework [3]. Thus, the decrease of acid site by steaming correlated with the dealumination process. However, it can be seen that the desorption peak slightly shifted to higher temperature which means the acidity strength was enhanced. This indicated that the dislodged Al still remained in the extraframework [4].

Table 1. summarizes the surface area of the steam-treated zeolite. When the zeolite was steam-treated for 1 h, both the micropore and mesopore surface area increased, giving the rise of the total surface area. As the steaming time prolonged to 3 h, only the micropore surface area increased due to the dislodged Al [4] which opened up new micropores. The dislodged Al might blocked some of the mesopores, giving the decrease of mesopore surface area. After 6 h steaming treatment, the entire pentasil unit, in which the dislodged Al remained, might collapsed and the mesopore was created [4, 5]. It should be noted that the increase of mesopore surface area was not as significant as the increase of acid site. This implies that most of the opened acid site might located inside the micropores.

Fig. 2 depicts the hydrocarbon yield of zeolite catalyzed – bio oil. The hydrocarbon yield increased
significantly after steam treatment and reached the maximum for 3 h treatment, even though the acid sites and mesopore surface area were decreased to some extent. For prolonged steaming treatment, the hydrocarbon yield slightly decreased. This result confirmed that the Al extraframework had some contributions to the catalytic activity for bio oil deoxygenation.

![Image: Fig. 1 NH₃-TPD profile of the steam-treated zeolite](image)

**Fig. 1** NH₃-TPD profile of the steam-treated zeolite

<table>
<thead>
<tr>
<th>Steaming time (h)</th>
<th>S_BET a</th>
<th>S_micro b</th>
<th>S_meso</th>
</tr>
</thead>
<tbody>
<tr>
<td>0</td>
<td>302.9</td>
<td>271.5</td>
<td>31.4</td>
</tr>
<tr>
<td>1</td>
<td>315.0</td>
<td>283.4</td>
<td>31.6</td>
</tr>
<tr>
<td>3</td>
<td>327.9</td>
<td>296.9</td>
<td>31.0</td>
</tr>
<tr>
<td>6</td>
<td>339.0</td>
<td>307.0</td>
<td>32.0</td>
</tr>
</tbody>
</table>

*aBET method

b t-Plot method

![Image: Fig. 2 Hydrocarbon yield of zeolite catalyzed-bio oil](image)

**Fig. 2** Hydrocarbon yield of zeolite catalyzed-bio oil

Fig. 3 shows the chemical distribution of zeolite catalyzed-bio oil. One can see that the selectivity to aromatics also increased as the steaming treatment prolonged to 3 h, then decreased for 6 h steam treatment. In addition, the selectivity of carboxyl compound can be kept at the low level. This result also confirmed the contribution of Al extraframework for selective conversion of bio oil.

![Image: Fig. 3 Chemical distribution of zeolite catalyzed - bio oil](image)

**Fig. 3** Chemical distribution of zeolite catalyzed - bio oil

**4. Conclusions**

In this study, high silica ZSM-5 zeolite was treated using steam and the effect on the acid nature, and catalytic activity for upgrading of biomass derived-oil was evaluated. It was found that the steam treatment induced the dislodging of Al into extraframework which gave contribution to the catalytic activity. The 3 h steam treatment was found to be the best treatment duration. As the treatment duration prolonged to 6 h, the Al extraframework might collapsed and the catalytic activity decreased. In conclusion, besides acid site and mesopore surface area, the existence of Al extraframework should also be considered for obtaining optimum catalytic activity.

【References】

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