Propene oligomerization over ZSM-5 zeolites with varying crystal size

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Introduction
ZSM-5 zeolite plays an important role as catalysts for high-pressure conversion of light olefins to liquid fuels. The effect of the Si/Al ratio of ZSM-5 zeolites on catalytic activity has been extensively investigated[1,2]. In these investigations, the activity increasing as Si/Al ratio decreased was observed. It was also reported that the activity of ZSM-5 zeolites decreased with increasing crystal size in several probe reactions[3]. However, it was not clear to what extent the increasing crystal size affected the activity of the catalyst. In this work, the effect of crystal size on the catalytic properties of ZSM-5 was investigated to understand the effect of the crystal size on the catalytic properties of ZSM-5 zeolites.

Results and Discussion
Table 1 shows some characteristics of ZSM-5 zeolites. It was found that the characteristics of catalysts under study differed remarkably. The relative crystallinity of HZ-38, HZ-41 and HZ-40 zeolites determined by XRD increased from 93 to 100 in the order with the size of crystallites. From SEM pictures, it could be observed that HZ-38 consisted of polycrystalline spherical particles with an average size of 0.4µm. In contrast, HZ-41 and HZ-40 were twinned polyhedral crystallites of different sizes with the habit of “intergrown discs”.

A typical acid site distribution was obtained over each catalyst by TPD[3]. Topsøe et al.[4] assigned the low- and high-temperature peaks to silanol groups or impurities and strong Brønsted sites, respectively. It was observed that the total acidity increased with decreasing Si/Al ratios and the number of the acid sites of different strengths didn’t follow this trend.

The catalytic activity and selectivity of all catalysts were studied in the conversion of propene under a total pressure of 4.0 MPa, 503K and a WHSV of 1.5h⁻¹. Fig.1 shows the catalytic activities versus time-on-stream for propene conversion over the above catalysts. As the Si/Al ratio increased, the total acidity decreased and the initial activity

<table>
<thead>
<tr>
<th>Catalyst</th>
<th>Si/Al</th>
<th>Average crystal size(µm)</th>
<th>Strong acid sites mmol/g</th>
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</thead>
<tbody>
<tr>
<td>HZ-38</td>
<td>38</td>
<td>0.4</td>
<td>0.33</td>
</tr>
<tr>
<td>HZ-41</td>
<td>41</td>
<td>1.2</td>
<td>0.26</td>
</tr>
<tr>
<td>HZ-40</td>
<td>40</td>
<td>2.8</td>
<td>0.28</td>
</tr>
</tbody>
</table>
followed the same trend. The results indicated that HZ-38 consisting of small crystallites yielded the best lifetime and activity for the catalysts. The higher catalytic activity and longer lifetime over HZ-38 might be due to the presence of a large number of strong acid sites and small crystallites. To show the effect of crystal size more clearly, HZ-41 with the morphology and Si/Al ratio very similar to that of HZ-40 were investigated. Fig.1 illustrates that the different oligomerization activities and catalytic lifetime were obviously correlated with differences between the sizes of the crystals. The ratio of deactivation increased as the crystal size of catalyst increased. The rapid deactivation of HZ-40 consisting of large crystal size could be due to the differences in external surface and pore properties which caused relatively rapid coke deposition.

![Fig.1. Catalytic activities versus time-on-stream for C3H6 conversion](image1)

![Fig.2. Selectivity for C3H6 conversion over catalysts with varying crystal size](image2)

The selectivity of each oligomer fraction were obtained at initial activity in Fig.2. The catalysts generally exhibited a preference for trimer and tetramer fractions. However, the distribution of oligomer compounds change remarkably with varying crystal size. The diesel fraction taken to be C12+ fraction increased form 43.0 to 59.2 wt% with increasing crystal size of the crystallites. These results indicated that the crystal size had a significant effect on the activity and selectivity of the ZSM-5 zeolites.

References