EXAFS Analysis of Zeolite Supported Rhenium Oxide Catalyst for Direct Phenol Synthesis

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Introduction
Rhenium catalysts have been reported to be highly active for direct methylal synthesis from methanol[1] and propene ammoxidation[2] by our group.

Recently, we found that a zeolite-supported rhenium catalyst was active for direct phenol synthesis from benzene and molecular oxygen. It was found that the pretreatment of catalysts with ammonia was essential to the activity. In this study, EXAFS analysis was performed to elucidate the structure of rhenium oxide species over zeolite and the effect of zeolite supports.

Experimental
Catalyst Preparation
The zeolite-supported rhenium catalysts were prepared by chemical vapor deposition (CVD) method[2]. The precursor of rhenium was methyltrioxorhenium (MTO, STREM Chem.). Zeolites were provided by TOSOH.

Phenol Synthesis
The catalytic activities were measured using a fixed-bed flow reactor. The reactions were performed at 573 K under the condition of W/F = 6.7 gcat h mol⁻¹ and He(carrier):O₂:NH₃:benzene = 22.4:3.2:3.2:2.1.

Products were analyzed by TCD-GC and FID-GC.

EXAFS Measurement
Rhenium L₃-edge EXAFS spectra were measured by transmission mode at room temperature. After background subtraction, k³ weighted EXAFS functions were Fourier transformed into R space and the first shell was analyzed by curve fitting.

Results and Discussion
Table 1 shows the effect of zeolite support in direct phenol synthesis. 0.40 wt% Re/H-ZSM-5 (SiO₂/Al₂O₃ = 39.4) showed the highest catalytic activity and selectivity. The second best support was H-Mordenite (SiO₂/Al₂O₃ = 220). H-ZSM-5 and H-Mordenite are known as strong acid supports. It was suggested that phenol synthesis reaction needed the strong acidity or the active rhenium species formed only on the strong acid sites.

Rhenium L₃-edge EXAFS spectra of Re/H-ZSM-5 (39.4) and Re/H-Mordenite (220) before reaction were shown in figure 1 and 2, respectively. Over H-ZSM-5, Re-O single bond was major and it seemed that rhenium existed as 7⁺ cation. The CN and R remained almost unchanged after reaction. On the other hand, Re-Re metal bond was observed over H-Mordenite. After reaction, the Re-Re bond disappeared. It is indicated that the Re oxide structure affected catalysts in its selectivity.

<table>
<thead>
<tr>
<th>Zeolite</th>
<th>Re Loading / wt%</th>
<th>TOF / 10⁻⁵ s⁻¹</th>
<th>Phenol Sel. / %</th>
</tr>
</thead>
<tbody>
<tr>
<td>H-ZSM-5(39.4)</td>
<td>0.40</td>
<td>7.75</td>
<td>25</td>
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<tr>
<td>H-ZSM-5(193)</td>
<td>0.50</td>
<td>3.10</td>
<td>7</td>
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<tr>
<td>H-Beta(37.1)</td>
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<td>2.93</td>
<td>5</td>
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<tr>
<td>H-USY(29.0)</td>
<td>0.60</td>
<td>Trace</td>
<td>-</td>
</tr>
<tr>
<td>H-Mordenite(220)</td>
<td>0.55</td>
<td>7.52</td>
<td>8</td>
</tr>
</tbody>
</table>

1) A value in parentheses refers to SiO₂/Al₂O₃ molar ratio.

References

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