2-30. 活性炭担持 Co 触媒による
1-へキセンのヒドロホルミル化反応

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Hydroformylation of 1-Hexene over Cobalt Catalyst Supported on Active Carbon
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1 Introduction
The emissions (smoke, particulate matter, CO, etc.) from diesel engine can be decreased by the addition of oxygen-containing compounds into fuel. Great efforts have been concentrated on the synthesis of oxygenates. Cobalt and/or rhodium carbonyl, have been employed in the hydroformylation commercial process. In order to prevent the decomposition of the carbonyl intermediate, the high operation pressure of synthesis gas (about 100–200 atm) is necessary to apply to the system, but this will result in the extra economic investment for the high-pressure reactor and other operation systems at the completion stage (about 20–30 atm) of Fischer-Tropsch synthesis. Therefore, it is of great importance to develop a solid-catalyzed to produce oxygenates from synthesis gas under mild reaction conditions.

2 Experimental
The supported active carbon (20-40 mesh) was obtained from Kanto Chemical Co. The support was impregnated with aqueous solution of cobalt nitrate. The weight percent of cobalt metal in catalyst was 10 wt%. The catalyst precursor was heated in nitrogen flow at 673 K for 4 h and reduced under hydrogen flow at 673 K for 6 h. The reduced catalyst was passivated by 1% O₂/N₂ flow before use.

Catalytic reactions were carried out in a semi-batch slurry-phase reactor. The amount of catalyst was 0.2 g, 120 mmol of 1-hexene was used as a model olefin. Solvent/1-hexene = 2/1 (molar ratio). The flow rate of syngas (CO/H₂/Ar = 47.8/48.2/4.0) in the reaction was set to 80 ml/min.

The gaseous products were analyzed by an on-line GC equipped with an active charcoal column. The liquid products were analyzed by gas chromatography equipped with a capillary column.

3 Results and Discussion
3.1 Effect of noble metal promoter

Figure 1 CO conversion versus time on stream in methanol over 10 wt% Co/active carbon.
(403 K; 3.0 MPa)

The CO conversion over 10 wt% Co/active carbon dependence on reaction time is shown in Figure 1. For the passivated 10 wt% Co/A.C., an induction period exists at the beginning of the reaction, lasting for about two hours. In order to find out what the function of this induction period is, catalytic reactions over 0.5% Ru-added catalysts and 10 wt% Co/A.C. without passivation were performed under the same reaction condition. Results are also compared in Figure 1. No induction period was observed for these two catalysts. We can assumed that the induction period partly involves a reduction process in the presence of methanol solvent and synthesis gas, which provide more active metallic sites available for the hydroformylation.

For passivated and non-passivated cobalt catalyst, isomerization of 1-hexene both gave about 15% yield (See Figure 2). But for the non-passivated cobalt catalyst, the yield of oxygenates, including aldehyde (C7-al) and ether, was about 56%, which was higher than that for passivated catalyst (31% oxygenates yield). The passivated catalyst with addition of only 0.5 wt% of Ru promoter improved
As shown in Table 1, the 0.5 wt% Ru/A.C. catalyst showed little hydroformylation activity, giving a large amount of isomer in the product. The short induction period for the Ru-added catalyst should be attributed to the spillover effect which promotes the reduction of passivated cobalt. The hydroformylation activity of the Ru-added catalyst was also promoted by methanol solvent as demonstrated in Table 1. Its hydroformylation activity is very low either in non-solvent or in octane solvent system.

3.2 Reaction network

In order to find out the product distributions during the reaction proceeding, the liquid analysis was conducted as a function of time. It is clearly shown in Figure 3, that for the CO conversion, the beginning two hours is the induction period and there was no product formed at that time. As the reaction proceeded, at every moment, ether appeared to be the main product. The yield of C7-al, ether and isomer all increased with the reaction time until 6 h and keep almost constantly in another two hours, even though at that time CO conversion and the yield of isomer decreased a little bit.

4. Conclusions

The addition of small amount of Ru to the cobalt supported on active carbon catalyst remarkably enhanced catalyst activity and shortened the induction period. A conclusion that at every moment, ether is the main product was drawn on the base of the reaction network.

<table>
<thead>
<tr>
<th>Catalyst</th>
<th>Solvents</th>
<th>1-hexene</th>
<th>Yield /%</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td>conv. /%</td>
<td>Oxy.</td>
</tr>
<tr>
<td>0.5 wt% Ru/AC(K)</td>
<td>no</td>
<td>28.22</td>
<td>0.27</td>
</tr>
<tr>
<td>0.5 wt% Ru/AC(K)</td>
<td>Methanol</td>
<td>56.75</td>
<td>1.39</td>
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<tr>
<td>10 wt% Co+0.5 wt% Ru/AC(K)</td>
<td>no</td>
<td>11.59</td>
<td>3.28</td>
</tr>
<tr>
<td>10 wt% Co+0.5 wt% Ru/AC(K)</td>
<td>Methanol</td>
<td>79.08</td>
<td>51.44</td>
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<tr>
<td>10 wt% Co+0.5 wt% Ru/AC(K)</td>
<td>n-Octane</td>
<td>15.78</td>
<td>6.27</td>
</tr>
</tbody>
</table>