3–5–4  Methanol Synthesis from Carbon Dioxide over Modified Cu-Zn based Catalyst

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SYNOPSIS
Cu/ZnO-based catalysts prepared by successive precipitation method were investigated for the reaction of carbon dioxide hydrogenation. The catalyst Cu/ZnO/ZrO₂/Al₂O₃ showed higher activity than ternary catalysts (Cu/ZnO/Al₂O₃, Cu/ZnO/ZrO₂), especially for methanol synthesis. It showed much higher activity and high stability toward methanol synthesis from carbon dioxide hydrogenation even under low temperature and low pressure. Excellent performances of Cu/ZnO/ZrO₂/Al₂O₃ were assumed to be partly attributed to the high dispersion of Cu, and the added Zr component promoted the reduction of Cu. The methanol formation from CO₂ hydrogenation was assumed to pass through two routes: one is the direct hydrogenation of CO₂ to methanol, another is the route which pass through CO formation.

1. Introduction
Utilization of carbon dioxide has become an important global issue due to the significant and continuous rise in CO₂ concentrations, accelerated growth in the consumption of petrified carbon-based energy in the worldwide, depletion of carbon-based energy resources. Catalytic hydrogenation of carbon dioxide to produce various kinds of chemicals and fuels such as methanol has been recently considered as one of the most promising processes for the utilization of CO₂ because of its wide variety of usage. Recent studies have shown that Cu/ZnO-based catalysts are among the most useful systems for the catalytic hydrogenation of CO₂ to methanol.

Recently, many works concerned with methanol synthesis from CO₂/H₂ mixture have been presented. Generally, methanol is produced from CO₂ hydrogenation over Cu/ZnO-based oxide catalysts under high temperature (above 250 °C) and high pressure (more than 5 MPa). Therefore, developing an active and stable catalyst under low temperature and low pressure process will attract important attention from the point of the CO₂ utilizing technology. In the case of CO₂ utilization for methanol synthesis, the formation of water vapor is inevitable (CO₂+3H₂O→ CH₃OH+H₂O). Therefore, the catalyst must be water tolerant toward water under reaction conditions. Generally, the high temperature water (steam) oxidizes metal to metal oxide.

In the present study, we have prepared a series of Cu/ZnO-based multicomponent catalysts and investigated their catalytic performance for methanol synthesis from CO₂ under low pressure. The ZrO₂-Al₂O₃ supported catalyst on the methanol synthesis reaction was examined in detail.

2. Experimental
The investigated catalysts were prepared by the co-precipitation method. For convenience, these catalysts will be designated by an abbreviation, CZA (Cu/ZnO/Al₂O₃), CZZA (Cu/ZnO/ZrO₂/Al₂O₃), CZZ (Cu/ZnO/ZrO₂) throughout this paper as shown in Table 1.

Table 1 Characters of Cu/ZnO-based catalysts for methanol synthesis

<table>
<thead>
<tr>
<th>Cat</th>
<th>BET (m²/g)</th>
<th>Pore Volume (cm³/g)</th>
<th>Pore diameter (nm)</th>
</tr>
</thead>
<tbody>
<tr>
<td>CuO</td>
<td>9.8</td>
<td>0.11</td>
<td></td>
</tr>
<tr>
<td>CuO/ZnO</td>
<td>29.8</td>
<td>0.40</td>
<td>55.8</td>
</tr>
<tr>
<td>CZA</td>
<td>78.5</td>
<td>0.35</td>
<td>29.5</td>
</tr>
<tr>
<td>CZZA</td>
<td>106.3</td>
<td>0.54</td>
<td>16.6</td>
</tr>
<tr>
<td>CZZ</td>
<td>90.9</td>
<td>0.44</td>
<td>16.6</td>
</tr>
</tbody>
</table>

A pressurized flow type reaction apparatus with a fixed-bed reactor was used for this study. The apparatus was equipped with an electronic temperature controller for a furnace, a tubular reactor with an inner diameter of 8 mm, thermal mass flow controllers for gas flows and a back-pressure regulator. A thermocouple was set at the axial center of the tubular reactor. 1 g of catalyst was placed in the reactor with inert quartz sands above and under the catalyst. All catalysts were reduced in a flow of 5% H₂ in nitrogen at 250 °C for 4 h before CO₂ exposure. All the products from the reactor were introduced in gaseous state and analyzed by on line gas chromatography (GC).

3. Results and Discussion
XRD characteristics. The XRD curves of catalysts were presented in Figure 1.

In the XRD patterns of CZA and CZZA, there were several rather weak peaks which can be assigned to CuO, which was the main component of these two catalysts. These peaks appeared at 2θ=35.5°, 38.5°, and 48.8°. It indicates that ZnO, Al₂O₃ and ZrO₂ existed in an amorphous or microcrystalline state. In addition to the above three peaks, in the XRD patters of CZZ, there also appeared peaks that were assigned to ZnO at 31.8°, 48°, 56.6°, 62.8°, 68°.
An important aspect of the catalyst is the improved catalyst stabilities in the reaction condition. For the catalyst CZZA, no significant decrease in the activity was observed in the 50 h on stream test, as shown in Figure 2, and the methanol yield is not found to decrease from its initially stabilized value, which is close to the equilibrium value. On the other hand, the CO$_2$ conversion over CZA decreased from 21.4 to 19.5%, and the corresponding methanol yield decreased from 11.1 to 9.3%, respectively.

![Figure 1 XRD patterns of calcined catalysts. (●, CuO; ▲, ZnO). a, CZA; b, CZZA; c, CZZ.](image)

![Figure 2. Stability of CZZA and CZA catalysts.](image)

CZZA: ■ The conversion of CO$_2$, ▲ the yield of CH$_3$OH, ● the yield of CO; CZA: ○ The conversion of CO$_2$, △ the yield of CH$_3$OH, ◆ the yield of CO; Dotted line corresponds to equilibrium values of methanol yield.

Test conditions: 3.0 MPa, 230 °C, the ratio of H$_2$ to CO$_2$ is 3, at W/F of 10 g·cat·h/mol.

4. Conclusion

A better CO$_2$ hydrogenation to methanol catalyst CZZA was obtained by addition of Zr and Al. The activity of the CZZA was the highest in the methanol synthesis reaction compared with either Al$_2$O$_3$ or ZrO$_2$ supported Cu/ZnO-based catalysts, and exhibited the relative high activity even under low temperature and pressure. The stability of CZZA catalyst was the satisfactory with time on stream over 50 h, while slightly deactivated. The methanol formation from CO$_2$ was assumed to pass through two routes: one is the direct hydrogenation of CO$_2$ to methanol, another is the route which pass through CO formation.

Acknowledgment

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References