DIMETHYL ETHER DIRECT SYNTHESIS WITH A SLURRY BED REACTOR

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SYNOPSIS: DME synthesis catalysts were prepared by a conventional precipitation method. Nitrates of Cu, Zn and Al (molar ratio was 6:6:1) were precipitated by 0.5M and 1M of Na2CO3 solution using with an automatic micro pump and a chemical glass pipette, respectively. The first catalyst (CZA-γAl2O3 (L)) prepared from the diluted precipitation agent gave a larger surface area, pore volume and smaller particle size of active Cu species compared to those of the last catalyst (CZA-γAl2O3 (P)). Two catalysts were evaluated under the same reaction conditions (H2:CO–1:1, GHSV–1000 ml/g·h, T–260°C, P–4 MPa) with a slurry bed reactor. The CZA-γAl2O3 (L) provided the highest catalytic activity of 76% CO conversion and 55% DME selectivity (in C-mol%) after 9h reaction. It is supposed that the diluted concentration of Na2CO3 precipitation agent caused a formation of the fine and uniform distribution of active metal species of DME direct synthesis catalyst.

1. INTRODUCTION

Synthesis of clean liquid fuel from low rank coal is the most promising and efficient technology for Mongolia which has a plenty of brown coal resource, and imports almost all of petroleum products from foreign countries. Consequently, our team in the National University of Mongolia aim to develop the catalytic gasification processes of Mongolian brown coals for the production of syngas (H2 + CO) and the synthesis of clean liquid fuel – dimethyl ether (DME) from syngas. We have prepared a bifunctional catalyst for the fixed bed and slurry bed reactors of DME direct synthesis.

2. EXPERIMENTAL

DME synthesis catalysts were prepared by a conventional precipitation method. Nitrates of Cu, Zn and Al (molar ratio was 6:6:1) were dissolved in distilled water at 50°C. 0.5M and 1M solutions of Na2CO3 were used as precipitation agents, which were dropped using by an automatic micro pump (Longer) and a chemical glass pipette, respectively. The dropping speed was almost the same (4 ml/min). The corresponding catalysts were named as CZA-γAl2O3 (L) and CZA-γAl2O3 (P), respectively. The precipitate was aged under the same temperature for 2h, and then washed with hot water to remove the remained Na ion. The precipitate was filtrated and dried at 110°C for 12h, and then calcined at 300°C for 6h. The precipitated methanol metal catalyst and the commercial dehydration γ-Al2O3 catalyst, which was pretreated by calcination at 450°C for 4h, were mechanically mixed by the weight ratio of 2:1. The catalyst particles less than 250 mesh sizes were used for further reaction. The slurry phase reaction was carried out with a 250 ml well agitated autoclave reactor. About 5 g of catalyst was slurried with 130 ml of paraffin solvent. Catalyst was reduced in-situ by 10% H2 for 12 h. The analysis of the effluent gas stream was performed by two online GC with TCD and FID. The fresh and used catalysts were characterized using by BET and XRD analysis methods.

3. RESULTS AND DISCUSSION

When about 400 ml aqueous solution of Cu, Zn and Al nitrates (molar ratio was 6:6:1) were precipitated for catalysts, the Na2CO3 aqueous solution with different concentrations (1M and 0.5M) were dropped using by a chemical glass pipette and an automatic micro pump, respectively. An automatic micro pump was used for dropping of the diluted 0.5M solution of the precipitating agent. Table 1 shows that when metal catalysts were precipitated by more diluted solution of Na2CO3, the catalyst surface area and pore volume were larger and crystalline size of active Cu species was smaller compared to those of the catalyst prepared by the concentrated 1M solution of Na2CO3.
Table 1. Surface characteristics and particle sizes of DME catalysts prepared using by a chemical glass pipette and an automatic micro pump

<table>
<thead>
<tr>
<th>Catalyst</th>
<th>$S_{\text{BET}}$, m$^2$/g</th>
<th>$V_p$, cm$^3$/g</th>
<th>$D_{\text{CuO}}$, nm</th>
</tr>
</thead>
<tbody>
<tr>
<td>CZA-γAl$_2$O$_3$ (P)</td>
<td>83.21</td>
<td>0.41</td>
<td>18</td>
</tr>
<tr>
<td>CZA-γAl$_2$O$_3$ (L)</td>
<td>100.8</td>
<td>0.61</td>
<td>3</td>
</tr>
</tbody>
</table>

The CZA-Al2O3 (P) and CZA-Al2O3 (L) catalysts were evaluated under the same reaction conditions, as shown in Table 2. The reaction results show that catalytic activity and DME selectivity of the catalyst prepared using by the diluted precipitation solution and an automatic micro pump were higher than those of the catalyst prepared by the concentrated precipitation solution. It is supposed that the high activities of the CZA-Al2O3 (L) catalyst was caused by the large surface area, pore volume and fine particles of Cu species generated during the precipitation reaction of metal nitrates and Na$_2$CO$_3$ with the diluted concentration of 0.5M.

Table 2. Activity results of the catalysts prepared using by a chemical glass pipette and an automatic micro pump (H$_2$:CO – 1:1, GHSV – 1000 ml/g·h, T -260°C, P – 4 MPa, reaction time – 9h)

<table>
<thead>
<tr>
<th>Catalyst</th>
<th>CO conversion %</th>
<th>DME selectivity %</th>
</tr>
</thead>
<tbody>
<tr>
<td>CZA-γAl2O3 (P)</td>
<td>39</td>
<td>9.8</td>
</tr>
<tr>
<td>CZA-γAl2O3 (L)</td>
<td>76</td>
<td>55</td>
</tr>
</tbody>
</table>

The activity changes of CZA-Al2O3 (L) catalyst in 9h are illustrated in Figure 1. It is observed that at the beginning of reaction, DME selectivity in products was very low, however as reaction proceeded further, both a CO conversion and DME selectivity were increased, and the catalyst activities were kept constantly until 9h reaction. These results confirmed that with a slurry phase reaction, a duration time was necessary to reach the chemical reaction equilibrium in the phases of feed syngas and internal pore surface of catalyst. Within 9h reaction at 260°C under 4MPa, it was found from the XRD analysis data of the used CZA-Al2O3 (L) catalyst that a sintering of Cu active species in a slurry phase was not almost occurred due to the fine and uniform distribution of the catalyst particles.

DME synthesis with the CZA-Al2O3 (L) catalyst has been carried out by varying the temperature from 260°C to 280°C and maintaining the remaining operation parameters constant. The increased temperature lowered the CO conversion slightly from 74% to 65%. In particular, DME selectivity decreased significantly from 55% to 36% at a higher reaction temperature of 280°C. However a product distribution showed the increases in the selectivity to CH4 and C2-5 products.

4. SUMMARY

Catalyst preparation condition in particular, a diluted concentration of precipitation agent effected on forming the fine and uniform distribution of active Cu species, which caused the improved CO conversion and DME selectivity during a slurry phase reaction.

REFERENCE