Light olefins synthesis from syngas over Sulfide-Zeolite bifunctional catalyst

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Abstract: Bifunctional catalysts consisting of metal oxide and zeolite have been reported to perform excellent light olefins selectivity from syngas and attract much attention. We demonstrate here that a new sulfide (MoS$_2$) – zeolite (SAPO-34) bifunctional catalyst which could catalyze the production of light olefins. The side reaction of methanation and hydrogenation of olefins to paraffins are suppressed by the introduction of potassium. Characterization results show that the introduction of potassium could enhance the formation of K–Mo–S structure, at which the alcohol precursor formed. The optimized bifunctional catalyst performs 61.2% C$_2$–C$_4$ olefins selectivity, beyond the limitation of Anderson-Shultz-Flory distribution.

Keywords: synthesis gas, light olefins, bifunctional catalyst.

1. Introduction
The development of the global economy leads to a rising demand for light olefins, which are the basic chemical raw materials. Recently, a series of bifunctional catalysts consisting of metal oxide and zeolite have been reported to perform excellent light olefins selectivity from syngas and attract much attention [1, 2]. Many studies have revealed that the challenge of selective conversion of syngas to light olefins lies in the suppression of the methane formation and hydrogenation of olefins [3].

In this article, a new sulfide (MoS$_2$) – zeolite (SAPO-34) bifunctional catalyst was studied for syngas conversion to light olefins. It was found that, the side reaction of methanation and hydrogenation of olefins to paraffins was suppressed by the introduction of potassium to MoS$_2$. Characterization results showed that the introduction of potassium could enhance the formation of K–Mo–S structure, at which the alcohol precursor formed. The optimized bifunctional catalyst MoS$_2$-0.6K+SAPO-34 performed 12.5% CO conversion and 61.2% C$_2$–C$_4$ olefins selectivity.

2. Experimental
The unsupported MoS$_2$-based catalysts were prepared by co-precipitation method [4]. Briefly, aqueous solutions of acetic acid (CH$_3$COOH) and ammonium tetrahydroxymolybdate ((NH$_4$)$_2$MoO$_4$) were simultaneously added to a container under continuous stirring. Hydrogen ion reacted immediately with the thiomolybdate and a black suspension was formed. The precipitate was aged at 70 °C for 2 h, and then filtered. The filtered cake (precipitate) was repeatedly rinsed with ethanol. The solid was dried at 100 °C for 12 h, followed by mixing with K$_2$CO$_3$ to thermal decomposition at 500 °C under N$_2$ for 2 hour to obtain unsupported MoS$_2$ catalysts. The MoS$_2$ catalysts promoted by potassium are denoted as MoS$_2$-xK (x= 0, 0.2, 0.4, 0.6, 0.8, 1.0), where x is the molar ratio of K/Mo.

3. Results and discussion
To expand the application bifunctional catalysts and search appropriate CO activation sites with strong CO conversion capacity and weak hydrogenation ability of olefins, the performance of several representative alcohol synthesis catalysts coupling with SAPO-34 are investigated and compared in Table 1. LiFeMnRh/SiO$_2$+SAPO-34 showed high CH$_4$ selectivity of 74.0%. While, the C$_2$–C$_4$ paraffins became the to the mainly products over CuZnAl+SAPO-34 and CoMoS-0.6K/AC+SAPO-34 bifunctional catalysts.

MoS$_2$-0.6K with weaker hydrogenation ability might prevent the olefin intermediate products from further hydrogenation, so high C$_2$–C$_4$ olefins selectivity could be achieved over the Sulfide-Zeolite system.
Table 1. Catalytic test results over LiFeMnRh/SiO₂, CoMoS-0.6K, CoMoS-0.6K/AC, CuZnAl with and without SAPO-34 a

<table>
<thead>
<tr>
<th>Catalysts</th>
<th>CO conversion / %</th>
<th>CH₄</th>
<th>C₂-C₄ olefins</th>
<th>C₂-C₄ paraffins</th>
<th>C₅+ hydrocarbons</th>
<th>Oxygenates</th>
<th>C₂-C₄ olefin/paraffin</th>
</tr>
</thead>
<tbody>
<tr>
<td>LiFeMnRh/SiO₂ + SAPO-34 b</td>
<td>21.7</td>
<td>74.0</td>
<td>1.4</td>
<td>22.7</td>
<td>0.3</td>
<td>1.6</td>
<td>0.06</td>
</tr>
<tr>
<td>CoMoS-0.6K/AC + SAPO-34 b</td>
<td>3.4</td>
<td>8.6</td>
<td>5.5</td>
<td>75.8</td>
<td>3.6</td>
<td>6.5</td>
<td>0.07</td>
</tr>
<tr>
<td>CuZnAl+ SAPO-34 b</td>
<td>37.9</td>
<td>3.6</td>
<td>1.6</td>
<td>90.8</td>
<td>4.0</td>
<td>0</td>
<td>0.02</td>
</tr>
<tr>
<td>MoS₂-0.6K + SAPO-34 b</td>
<td>19.7</td>
<td>14.6</td>
<td>58.9</td>
<td>22.5</td>
<td>3.7</td>
<td>0.3</td>
<td>2.62</td>
</tr>
</tbody>
</table>

a Reaction conditions: p = 4.0 MPa, GHSV = 4000 h⁻¹, T = 400 °C, n(H₂)/n(CO) = 1.

b Mass ratio of alcohol catalysts: SAPO-34 = 1:1.

Table 2 compared the catalytic performance of the K modified MoS₂+SAPO-34 bifunctional catalysts. MoS₂+SAPO-34 provided 70.4% CH₄ with a high CO conversion, but seldom C₂-C₄ olefin was formed. Modification of the MoS₂ with K₂CO₃ yielded more than 80% C₂-C₄ hydrocarbons and reduced the methane selectivity. It is notable the C₂-C₄ olefin/paraffin ratio increased with the mount of K increased.

Our results suggested that the CO hydrogenation sites significantly affected the product distribution in the subsequent conversion of C₁ intermediate. C₁ intermediate would easily be reduced to CH₄ over MoS₂ [5], which exhibited highest hydrogenation activity, rather than desorbed and migrated to the coupling active sites. K was found to be effective additive to weaken the hydrogenation ability of MoS₂ [5, 6]. With the introduction of K, CO conversion and CH₄ selectivity decreased, while more C₁ intermediate was able to migrate to the coupling active sites, resulting the increase of the C₂₆ product selectivity. The hydrogenation of olefins to paraffins could lead to the consumption of olefins. By weakening the hydrogenation ability, the introduction of K could suppress the side reaction, and enhance the C₂-C₄ olefin/paraffin ratio. So, a balance of hydrogenation and coupling functions associated with K and MoS₂ was required to produce an optimum yield of C₂-C₄ olefins and to minimize the paraffins formation. And, 60% K introduction could significantly enhance the production of light olefins from syngas.

4. Conclusions

Light olefins synthesis from syngas over the Sulfide-Zeolite bifunctional catalyst has been investigated in this work. By the introduction of potassium, the hydrogenation ability of MoS₂ catalyst was weakened, the side reaction of methanation and hydrogenation of olefins to paraffins was suppressed. The optimized bifunctional catalyst MoS₂-0.6K+SAPO-34, which performed 19.7% CO conversion and 58.9% C₂-C₄ olefins selectivity, could significantly enhance the production of light olefins from syngas. Due to the resistance to sulfur poisoning and high olefin/paraffin ratio, the Sulfide-Zeolite bifunctional catalyst showed potential application prospect in the light olefins synthesis.

References