Investigation of n-Dodecane hydroisomerization catalyzed by SAPO-11 supported non-noble metal catalysts

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Abstract:
Hydrocarbon transportation fuels mostly found in linear forms have poor cold-flow properties. To upgrade its fuel properties, hydroisomerization of those linear forms into isomer forms is required. In this work, the selective hydroisomerization of n-dodecane (n-C₁₂) into iso-dodecane (i-C₁₂) was investigated by using the series of SAPO-11 supported non-noble metal Ni, Co, Cu, and Ni-Co, Ni-Cu alloy catalysts. The chemical properties of the catalyst which affected on catalyst performance were also investigated by using temperature-programmed desorption of ammonia (NH₃-TPD). The reaction testing was conducted in flow continuous reactor at a temperature of 300°C, H₂ pressure of 5 MPa, liquid hourly space velocity of 1 h⁻¹. The results showed that Ni showed highest selectivity of isomer products for monometallic catalyst. After the addition of second metal into Ni, the selectivity of isomer product increased over Ni-Co alloy catalyst. The addition of Co in Ni catalyst could create new acid surface area which benefit for hydroisomerization led to exhibit the highest isomers of C₁₂. This result may enhance the selectivity of isomer hydrocarbon products for jet fuel-like hydrocarbon production.

Keywords: Hydroisomerization; SAPO-11; Alloy; Metal catalyst; Branched alkane

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1. Introduction
Hydroisomerization of normal alkanes to the corresponding mono-branched or multi-branched alkanes is an important process for upgrading liquid fuel for transportation. The noble metal catalysts such as Pt on varieties of acidic support materials; SAPO-11 (Lv et al., 2018) or ZSM-22 (Liu et al., 2016) have been reported in hydroisomerization reaction. The fact that rarity of noble metals limiting the large-scale production and very expensive. Several publications have detailed the utilization of nickel catalysts for hydroisomerization applications. Therefore, the development of supported non-noble metal catalysts is of interest to achieve both technical and economic views; low cost catalysts with high catalytic performances of hydroisomerization. However, nickel prefers C–C cracking (De et al., 2016). This research focused on the investigation of the selective performance for the conversion of n-C₁₂ to iso-C₁₂ via hydroisomerization using SAPO-11 supported non-noble metal catalysts (Ni, Co, and Cu).

2. Material and methods
The catalysts were prepared by impregnation techniques. The certain amount of starting nitrate salt precursors was dissolved in DI water with metal loading of each 10wt% for monometallic metal and each 5wt% for bimetallic metal. The SAPO-11 support material was added to the solution afterward. Then, stirred and heated at 85°C for 12 h. After impregnation, the resultant sample was dried in vacuum oven at 80°C for another 12 h and then calcined at 500°C for 5 h to obtain the oxide form materials. Before catalytic testing, the catalyst powder was compressed to tablets, followed by crushing and sieving to the particle size of 0.5-1.0 mm.

The reaction testing was conducted in a tubular-flow continuous reactor. 4 mL of each catalyst was packed into the reactor and then were reduced with 50 cm³ min⁻¹ of H₂ at 700°C for 2 h. Then, the n-C₁₂ hydroisomerization was performed at a temperature of 300°C, H₂ pressure of 5 MPa, liquid hourly space velocity (LHSV) of 1 h⁻¹, and a H₂/feed ratio of 1,000 N (cm³ cm⁻³).
3. Results and discussion

The hydroisomerization of n-C\textsubscript{12} was tested on Ni, Co, Cu and NiCo, NiCu alloys supported on SAPO-11. Before catalytic performance, the reaction was tested by using bare SAPO-11 support. The n-C\textsubscript{12} conversion was only 10%. It can be clarified that the absence of metal sites loss the hydrogenation/dehydrogenation which is necessary for creating i-C\textsubscript{12}. After loading metal, the maximum catalytic conversion was occurred from monometallic Co catalyst which is only 20% conversion (see Fig. 1). Metal Co is reported to possess excellent hydrogenation function (Cao et al., 2018). However, the i-C\textsubscript{12} selectivity (6.1%) was lower Ni catalyst (23.3%). Once, Ni was modified by adding Co, the isomers selectivity was improved, up to 77.1%. Table 1 showed the composition of the isomer products. For the ratio of mono-/multi-branched, monometallic Ni catalyst can reach 22% while bimetallic Ni-Co can provide up to 69%. It may be resulted from the stronger acid sites (see Fig. 2). Not only the large amount of mono-branched was produced, but also more of the multi-branched was formed.

Since the Cu has inactive hydrogenation/dehydrogenation activity, the balance between the acid sites and metal sites were not available. The primary products included n-C\textsubscript{12} isomers and β-scission products were hardly detected. The reaction predominantly processed via hydrocracking at a part of the acid sites. Therefore, the Cu-based catalyst is not suitable to be used for further study.

Table 1 Hydroisomerization evaluation of metal supported SAPO-11 [LHSV 1 h\textsuperscript{-1}, 300°C, 50bar H\textsubscript{2}, H\textsubscript{2}:n-C\textsubscript{12} = 1000times, catalyst 4ml]

<table>
<thead>
<tr>
<th>Catalyst</th>
<th>n-C\textsubscript{12} conversion (%)</th>
<th>i-C\textsubscript{12} selectivity (%)</th>
<th>i/n ratio</th>
<th>Selectivity to Cracked products\textsuperscript{a} (%)</th>
<th>Isomer product (%)</th>
<th>Mono-branched\textsuperscript{b}</th>
<th>Multi-branched\textsuperscript{c}</th>
</tr>
</thead>
<tbody>
<tr>
<td>10Ni/SAPO-11</td>
<td>18.9</td>
<td>23.3</td>
<td>0.31</td>
<td>76.3</td>
<td>22.0</td>
<td>1.5</td>
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</tr>
<tr>
<td>10Co/SAPO-11</td>
<td>20.1</td>
<td>6.1</td>
<td>0.06</td>
<td>93.3</td>
<td>5.5</td>
<td>0.6</td>
<td></td>
</tr>
<tr>
<td>10Cu/SAPO-11</td>
<td>15.7</td>
<td>2.9</td>
<td>0.03</td>
<td>98.0</td>
<td>1.9</td>
<td>1.1</td>
<td></td>
</tr>
<tr>
<td>5Ni5Co/SAPO-11</td>
<td>8.8</td>
<td>77.1</td>
<td>4.39</td>
<td>21.8</td>
<td>68.9</td>
<td>8.2</td>
<td></td>
</tr>
<tr>
<td>5Ni5Cu/SAPO-11</td>
<td>5.3</td>
<td>1.8</td>
<td>0.03</td>
<td>98.2</td>
<td>1.7</td>
<td>0.1</td>
<td></td>
</tr>
</tbody>
</table>

\textsuperscript{a} <C\textsubscript{12}, \textsuperscript{b} mono iC\textsubscript{7}-C\textsubscript{12}, \textsuperscript{c} multi iC\textsubscript{7}-C\textsubscript{12}

![Fig. 1 Effect of metal types on n-C\textsubscript{12} conversion and isomers selectivity](image-url)
Fig. 2 NH$_3$-TPD profiles of (a) SAPO-11, (b) 10Ni/SAPO-11, (c) 10Co/SAPO-11, (d) 10Cu/SAPO-11, (e) 5Ni5Cu/SAPO-11, and (f) 5Ni5Co/SAPO-11

4. Conclusion
The hydroisomerization of n-C$_{12}$ was investigated over five non-noble metals supported on SAPO-11 catalysts. The results showed that the Co addition in Ni catalyst for bimetallic catalysts could create new acid surface area which benefit for isomerization led to exhibit the highest iso-/n-C$_{12}$ ratio. However, Ni-Co catalyst did not show good conversion compared to monometallic system. The conversion was only 95% while monometallic Ni and Co showed 100%.

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