Highly Ordered Mesoporous Fe₂O₃-ZrO₂ Bimetal Oxides for an Enhanced CO Hydrogenation Activity to Hydrocarbons

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Abstract: Highly ordered mesoporous Fe₂O₃-ZrO₂ mixed bimetal oxides (FeZr) were applied to convert syngas to value-added hydrocarbons through Fischer-Tropsch synthesis reaction. To promote the catalytic activity and structural stability, the irreducible metal oxide of ZrO₂ was incorporated as a structural promoter. At an optimized amount of zirconia (Zr/Fe = 0.25), the activity and structural stability were significantly improved. These enhanced surface properties were mainly due to the formation of the active iron carbide species (χ-Fe₅C₂) with insignificant structural collapses by strong interactions between iron nanoparticles and the ZrO₂ structural promoter, which also suppressed the inactive coke depositions.

Keywords: ordered mesoporous Fe₂O₃-ZrO₂ oxides, structural promoter of ZrO₂, stable χ-Fe₅C₂

1. Introduction

Ordered mesoporous metal oxides have been widely utilized in the field of heterogeneous catalysis due to the large size surface area and controllable pore size as well as the enhanced mass transport rate of the products with less catalyst deactivations [1,2]. In order to prevent the catalyst deactivation by the sintering of iron nanoparticles or disintegration of structures during the reaction, ordered mesoporous iron oxide(Fe₂O₃) was synthesized by nano-casting method through an incorporation of irreducible ZrO₂ metal oxide as a structural promoter. The ZrO₂ promoter improved the structural stability significantly by forming the strong interactions and facile active iron carbide phases such as χ-Fe₅C₂ [3].

2. Experimental

Irreducible metal oxide ZrO₂ incorporated mesoporous Fe₂O₃ was synthesized with nano-casting replica method using a hard template of KIT-6 [4,5] at a different molar ratio of Zr/Fe from 0 to 1. The prepared catalysts were denoted as FeZr(x), where x represents the molar ratio of Zr/Fe. Catalytic activity test of the mesoporous FeZr catalysts was carried out in fixed bed reactor at the following reaction conditions: T = 300 °C, P = 2.0 MPa, weight hourly space velocity (WHSV) = 8000 L(mixed gas)/kg_cat/h and H₂/N₂/CO = 63.0/5.5/31.5. Before the FTS reaction, the catalyst was reduced under a flow of 5%H₂/N₂ at 500 °C for 12 h. The effluent gases from the reactor were analyzed by using an online gas chromatograph (YoungLin 6500 GC) connected with TCD (SUPELCO-12390-U) and FID (HP-PLOT/Q). To characterize the surface properties of FeZr(x), N₂ sorption, TEM, XRD, H₂-TPR, XPS, XAFS, H₂-TPSR, Raman spectroscopy, and ⁵⁷Fe Mössbauer spectra were carried out.

3. Results and discussion

The crystallite size of Fe₂O₃ was found to be in the range of 11.8 – 32.4 nm. As the amount of ZrO₂ was increased, the smaller Fe₂O₃ grains were formed due to the well-developed Fe₂O₃-ZrO₂ grain structures. However, the X-ray diffraction (XRD) peaks of ZrO₂ were not clearly observed due to its higher dispersion or intrinsic amorphous characters. As the amount of ZrO₂ metal oxide was increased, the specific surface area was also increased from 110.8 to 209.5 m²/g due to its structural promoting effect by generating ordered mesoporous structures [6]. The catalytic activities on FeZr(x) are summarized in Table 1. Compared with the FeZr(0), the catalytic activities were enhanced in all the ZrO₂ incorporated FeZr catalysts. Among them, FeZr(0.3) showed the most stable catalytic activity with a higher C₅+ and olefin selectivity with the values of 85.6 and 53.6%, respectively. The enhanced FTS activity and stability on the FeZr(0.3) seem to be attributed to an increased degree of reduction and the formation of active and stable iron carbide species instead of a waxy hydrocarbon or coke deposition [7].
Table 1. Physicochemical properties and activities of the mesoporous Fe₂O₃-ZrO₂ catalysts

<table>
<thead>
<tr>
<th>Catalysts</th>
<th>XRD</th>
<th>N₂ sorption</th>
<th>Activity</th>
<th>Product distribution</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Crystallite size of Fe₂O₃ (nm)</td>
<td>surface area (m²/g)</td>
<td>CO conv. (C-mol%)</td>
<td>Olefin sel. (C-mol%)</td>
</tr>
<tr>
<td>FeZr(0)</td>
<td>32.4</td>
<td>110.8</td>
<td>5.6</td>
<td>72.4</td>
</tr>
<tr>
<td>FeZr(0.1)</td>
<td>22.8</td>
<td>127.9</td>
<td>88.3</td>
<td>42.6</td>
</tr>
<tr>
<td>FeZr(0.3)</td>
<td>18.8</td>
<td>147.6</td>
<td>82.1</td>
<td>53.6</td>
</tr>
<tr>
<td>FeZr(0.5)</td>
<td>15.9</td>
<td>147.9</td>
<td>77.0</td>
<td>39.6</td>
</tr>
<tr>
<td>FeZr(1)</td>
<td>11.8</td>
<td>209.5</td>
<td>44.8</td>
<td>37.5</td>
</tr>
</tbody>
</table>

a) FTS reaction was carried out at the following reaction conditions; T = 300 °C, P = 2.0 MPa, WHSV = 8000 L/kg cat/h, and feed gas composition of H₂/N₂/CO = 63.0/5.5/31.5.
b) Olefin selectivity (C-mol%) was calculated in the C₂–C₄ light hydrocarbons.
c) Chain growth probability (α) values were obtained from the Anderson-Schulz-Flory (ASF) distribution in the range of C₁₂ - C₃₀ hydrocarbons.

As shown in Figure 1, the ZrO₂ incorporated FeZr catalyst preserved the ordered mesoporous structures without any significant structural disintegration after FTS reaction. This structural stability was well related with the suppressed aggregation of active components by stronger interactions with ZrO₂ promoters.

![Figure 1](image_url)

Figure 1. TEM image (20nm scale bar) of (A) fresh FeZr(0), (B) used FeZr(0), (C) fresh FeZr(0.3), and (D) used FeZr(0.3).

The structural disintegrations were also clearly verified by XAFS analysis, in which the co-presence of the larger Fe₂O₃ and metallic Fe phases were observed. In the Mössbauer analysis for the used FeZr catalysts, the content of χ-Fe₅C₂ was found to be higher on the most active FeZr(0.3) due to the stable and smaller iron carbide formation with the help of the strongly interacted FeO-ZrO₂ frameworks.

4. Conclusions

To prevent the structural disintegrations of the mesoporous structures during the reductive FTS reaction conditions, the ordered mesoporous Fe₂O₃ catalysts was synthesized with an incorporation of the irreducible ZrO₂ oxide via nano-casting technique. The stable and enhanced FTS activity on the FeZr(0.3) seem to be attributed to the stabilized mesoporous structures through the stronger interactions between Fe₂O₃ and irreducible ZrO₂ crystallites in the main frameworks of FeZr catalysts by facile formation of the well-known active iron carbide phases such as χ-Fe₅C₂ during FTS reaction.

References