Effect of WO₃ on the nickel-based sulfur-resistant methanation catalyst

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Introduction
As being acknowledged, the production of synthetic natural gas (SNG) from coal or biomass is becoming of interest nowadays, especially in the areas which are lack of the natural gas resource [1]. The methanation is the main reaction that converts the syngas produced from gasifier to SNG. The commercial methanation catalyst is the nickel-based catalysts prepared by impregnation or precipitation methods which can be poisoned by ppm-level sulfur [2]. So the feedstock must be treated by the fine desulfuration which is an expensive process. Increasing the sulfur resistant ability is an interesting target to survive the nickel catalyst with the ppm-level H₂S feedstock [3].

In this work, we prepared a series of Ni-based methanation catalysts doped WO₃. The results of methanation activity and sulfur-resistant ability show that WO₃ can increase the CO conversion and promote the sulfur-resistant ability of the catalyst. Adding WO₃ ranging from 1-3 wt% can significantly increase the CO conversion. But when the metal oxide content exceed 4 wt%, the catalyst will be inferior to the catalyst which no promoter. Appropriate WO₃ can play a positive role in the development of sulfur-resistant methanation catalyst.

Materials and Methods
The catalysts were prepared by the successive impregnation method. All the reagents used for the catalyst preparation were in analytical grade (AR) and used as received without further purification. The γ-Al₂O₃ support was aged at 650 °C for 5 h before the impregnation. Typically, the γ-Al₂O₃ was first impregnated with an aqueous solution of ammonium tungstate, and dried at 60 °C. The impregnated sample was heated at 100 °C for 10 h and calcined in air at 650 °C for 5 h. Then the sample was impregnated with a solution of nickelous nitrate as the same way with the WO₃. After calcined in air at 650 °C for 5 h, the catalysts loading NiO, WO₃ were obtained.

The catalysts were characterized by N₂ physisorption measurements, XRD, and H₂ temperature-programmed reduction (H₂-TPR).

Results and Discussion
As shown in Table 1, adding WO₃ ranging from 1-3 wt% does not cause significant changes in surface area, pore volume and pore diameter of the NiO/Al₂O₃ catalyst. This can ensure the catalytic activity of the catalyst is not caused by the texture property of the catalysts, but caused by the addition of promoter WO₃. H₂-TPR profiles of the different catalysts show two reduction peaks, as shown in Figure 1. The low temperature peak is attributed as the reduction of alloy of NiO and WO₃ while high temperature peak is due to the reduction of NiAl₂O₆. With the increase of WO₃, the alloy peak shift to the low temperature.

As shown in Figure 2, adding WO₃ to the Ni/Al₂O₃ catalyst can increase the H₂S-resistant of the NiO catalyst. The optimal content of the WO₃ is from 1 wt% to 3 wt%. When the WO₃ exceeds 4 wt%, the activity and H₂S-resistant ability will decrease compared with NiO/Al₂O₃ catalyst.

Table 1. Texture properties of WO₃-NiO/Al₂O₃ catalysts

<table>
<thead>
<tr>
<th>Samples</th>
<th>BET surface area (m² g⁻¹)</th>
<th>Pore volume (cm³ g⁻¹)</th>
<th>Average pore diameter (nm)</th>
</tr>
</thead>
<tbody>
<tr>
<td>NiO-1WO₃/Al₂O₃</td>
<td>143.9</td>
<td>0.34</td>
<td>6.8</td>
</tr>
<tr>
<td>NiO-3WO₃/Al₂O₃</td>
<td>143.2</td>
<td>0.32</td>
<td>6.5</td>
</tr>
<tr>
<td>NiO-4WO₃/Al₂O₃</td>
<td>143.8</td>
<td>0.33</td>
<td>6.5</td>
</tr>
<tr>
<td>NiO-5WO₃/Al₂O₃</td>
<td>142.4</td>
<td>0.33</td>
<td>6.5</td>
</tr>
</tbody>
</table>

Significance
In this study, the experimental results demonstrated that the WO₃ is an efficient promoter of the nickel-based catalyst to promote the catalytic activity and sulfur resistant ability. This provides a new approach to develop new methanation catalyst which can work with ppm level H₂S, and save the desulfuration cost in the SNG production process.

![Figure 1 H₂-TPR profile of the NiO-WO₃/Al₂O₃ catalysts](image1)

![Figure 2 Activity H₂S-resistant ability comparison of the NiO-WO₃/Al₂O₃ catalyst with different WO₃ loadings](image2)

References