Effect of Tb promoter on catalytic performance of Ni/ZrO$_2$ catalysts in carbon dioxide reforming of methane

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Introduction

Dry reforming of methane is one of the most promising techniques to tackle the elimination/utilization of greenhouses such as CO$_2$ and CH$_4$ [1]. Efficient catalyst suitable for dry reforming can bring successful tools to achieve the required activity and stability for industrial applications. Nickel based catalysts are highly cost effective and very active for DRM reaction. However, Ni-based catalysts are prone to rapid deactivation due to low dispersion effect and carbon formation [2]. Therefore the search or development of suitable Ni based catalysts is still a challenge. It is reported in the literature that by incorporation of a proper support and/or promoter the performance of Ni-based catalysts could be enhanced both in terms of carbon resistance and stability [3]. In the present work, dry reforming of methane (DRM) was studied by investigating the effect of terbium (Tb) promoter upon nickel based catalysts supported on nano-sized zirconium oxide. The use of Tb promoter, in Ni/ZrO$_2$ catalyst, for dry reforming of methane has hardly been studied before.

Materials and Methods

The Ni-Tb/ZrO$_2$ catalysts were prepared by polyol method [3]. For each catalyst, the Ni loading was fixed to (5 wt%) while Tb loading was varied from 0.25–1.50 wt%. The prepared catalysts were calcined at 500°C for 4 h. The experiments were performed in a fixed bed micro tubular reactor at various temperature (500–700°C), atmospheric pressure and F/W= 60 mL/min.gcat. For each run the catalyst was first activated under H$_2$ flow (40 mL/min) at 500°C for 2 h. Catalysts were characterized by means of BET and TGA techniques.

Results and Discussion

The catalytic performance of promoted and un-promoted Ni/ZrO$_2$ catalysts, at 700°C for 6 h time-on-stream (TOS), in terms of CH$_4$ and CO$_2$ conversions, is presented in Figure 1. It is apparent from results that the un-promoted catalyst showed relatively high methane conversion as compared to Tb promoted catalysts. On the other hand all Tb promoted catalysts, except at 0.25wt% Tb loading, exhibited high CO$_2$ conversions than that of un-promoted catalyst. It is also worthwhile to note that for 0.5wt% and 1.0wt% Tb promoted catalysts the activity of methane increased on TOS; however, other catalysts showed relatively stable behavior. In fact the increase in CH$_4$ activity over these catalysts is probably resulted due to the occurrence of methane cracking side reaction [2]. The results of BET surface areas and amount of carbon deposition are summarized in Table 1. It is obvious from results that addition of Tb promoter in Ni/ZrO$_2$ catalyst has a notable effect on both textural properties and amount of carbon deposition. The highest surface area (38.6 m$^2$/g) and minimum carbon deposition (5.1 wt%) was observed over 1.5wt% Tb promoted catalyst. In fact the higher surface area for this catalyst facilitates the adsorption and dissociation of CO$_2$ (as evidenced from relatively high CO$_2$ activity) which in result favors the removal of carbonaceous species formed by reverse Boudouard reaction (2CO $\leftrightarrow$ C + CO$_2$).

![Figure 1](image_url)

**Figure 1.** Variations of (a) CH$_4$ (b) CO$_2$ conversions versus time on stream for Tb promoted and un-promoted catalysts at 700°C; (F/W= 60 mL/min.gcat).

<table>
<thead>
<tr>
<th>Wt. % Tb</th>
<th>0% Tb</th>
<th>0.25% Tb</th>
<th>0.50% Tb</th>
<th>1.0% Tb</th>
<th>1.5% Tb</th>
</tr>
</thead>
<tbody>
<tr>
<td>$S_{BET}$ (m$^2$/g)</td>
<td>22.8</td>
<td>25.5</td>
<td>28.7</td>
<td>28.9</td>
<td>38.6</td>
</tr>
<tr>
<td>Carbon Wt. loss %</td>
<td>12.5</td>
<td>10.2</td>
<td>12.8</td>
<td>13.2</td>
<td>5.1</td>
</tr>
</tbody>
</table>

Conclusion

The Tb promoted Ni/ZrO$_2$ catalysts were prepared by polyol method and tested in DRM. The results revealed that addition of Tb promoter in catalyst slightly reduces the CH$_4$ activity but improves the CO$_2$ activity which in turn suppresses the coke formation. The optimum amount of Tb loading in this study was found to be 1.5wt%.

References