Methane Decomposition over Ni/α-Al₂O₃ Promoted by La₂O₃ and CeO₂

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Abstract: The decomposition of methane on Ni/α-Al₂O₃ modified by La₂O₃ and CeO₂ with different contents has been investigated and the relationship between methane decomposition and removal of carbon by CO₂ over these catalysts has also been studied by pulse-chromatography. The catalysts were characterized by TPR and XRD. It was shown that Ni/α-Al₂O₃ could be promoted by adding La₂O₃, and the carbon species produced over this catalyst was activated and eliminated by CO₂. But CeO₂ would suppress the decomposition of methane over Ni crystallite. Both La₂O₃ and CeO₂ can inhibit aggregation of the Ni particles. Decomposition of methane over the Ni-based catalysts is structure sensitive to a certain extent.

Key words: methane, carbon dioxide, nickel, lanthana, ceria

1. Introduction

Recently, Ni-based catalysts or noble metal catalysts such as Pt, Rh, Ru, etc. have been used in the reforming of methane with carbon dioxide. Taking cost into consideration, many researchers tend to investigate the supported Ni-based catalysts [1,2]. Most Ni-based catalysts exhibit high activity for reforming reaction but with poor stability. Adding promoter to improve the properties of Ni-based catalysts has become an important measure in this field [3]. Usually, alkaline-earth metal oxide and rare-earth oxides have been used as the promoter [4]. The properties of Ni/α-Al₂O₃ catalysts have been improved by rare-earth oxides, such as La₂O₃ and CeO₂ [5,6].

In this study, decomposition of methane over La₂O₃ and CeO₂ modified Ni/α-Al₂O₃ has been investigated. The mechanism of methane reforming with carbon dioxide was analyzed on the basis of experiments of two-step pulse reaction. The effect of the rare-earth promoters on the properties of Ni/α-Al₂O₃ has also been discussed.

2. Experimental

2.1. Preparation of catalysts

The catalysts were prepared by routine impregnation of nitrates. The industrial α-Al₂O₃ with wheel-shape was smashed into particles with diameter in the range of 0.85–1.41 mm, and then calcined in air at 800 °C for 2 h. α-Al₂O₃ was impregnated with a nickel nitrate solution in a certain concentration. After drying at 120 °C for 2 h, the sample was calcined at 400 °C for 2 h to obtain the Ni/α-Al₂O₃ catalyst. The promoted catalysts were prepared by the same procedure. The α-Al₂O₃ was impregnated with nitrates of rare earth elements La and Ce first, then dried and
calcined before it was impregnated with nickel nitrate. In this work, the content of nickel was 8% in weight and the promoter of rare-earth oxides added was 1%, 2%, 3% in weight, respectively.

2.2. Evaluation of catalyst by pulse reaction

The catalysts were reduced by hydrogen for 30 min before use. About 50 mg catalyst was embedded in the reactor connected with a gas chromatograph (103G, made in Shanghai). The single-component gas (CH₄, or CO₂) was fed by carrier gas (Argon) into the reactor.

Temperature programmed reduction was carried out in a stainless steel reactor, in which about 50 mg unreduced catalyst was filled. The catalyst in the reactor was purged with Argon at 500 °C for 30 min to remove the impurity. While the reactor was cooled to room temperature, the mixture of H₂-Ar (7%H₂ in volume) was fed into reactor at a flow rate of 30 ml/min. The reactor was raised to 900 °C by program-controlled heating at a rate of 10 °C/min. The crystalline phases of the catalysts were analyzed by an X-ray diffractometer (D/max-rB, CuKα, Made in Japan).

3. Results and discussion

3.1. Effect of temperature on methane decomposition

The decomposition of methane can be accelerated as the reaction temperature is elevated due to endothermic feature of the reaction. The results of decomposition of methane over Ni/α-Al₂O₃, Ni/La₂O₃/α-Al₂O₃ and Ni/CeO₂/α-Al₂O₃ are shown in Figure 1. It can be seen that the conversion of methane was increased as the temperature was elevated up to 800 °C. However, at 850 °C the conversion of methane over Ni/α-Al₂O₃ decreased. Ni particles easily aggregated into larger particles at the elevated temperatures, leading to decrease of active sites for methane decomposition. Consequently, the conversion of methane decreased appreciably. But this tendency can be prevented by the addition of rare earth oxide. At 850 °C, the conversion of methane increased with the content of rare-earth oxide promoter. It is suggested that the rare earth oxide can inhibit the aggregation of Ni crystallite, and maintain the catalytic activity.

![Figure 1. The effect of temperature on methane decomposition](image-url)
3.2. The carbon species from methane decomposition

First, methane was passed through the fresh catalyst at 750 °C for 30 min then the reactor was purged with Argon. About 72 ml of carbon dioxide was injected into the reactor at this temperature. Due to methane decomposition over the Ni-based catalyst at this elevated temperature, active carbon species were formed on the surface of catalyst, which would react with carbon dioxide pulsed into the reactor. The conversion of carbon dioxide to carbon monoxide may imply that the deposited carbon species reacted with carbon dioxide.

The conversion of CO$_2$ over Ni/La$_2$O$_3$/$\alpha$-Al$_2$O$_3$ was higher than those over Ni/$\alpha$-Al$_2$O$_3$ and Ni/CeO$_2$/$\alpha$-Al$_2$O$_3$ (shown in Figure 2). Moreover, there was little tendency of descent in the conversion of carbon dioxide over Ni/La$_2$O$_3$/$\alpha$-Al$_2$O$_3$ after six pulse-reactions especially as the content of La$_2$O$_3$ was over 2%. However, for the case of Ni/CeO$_2$/$\alpha$-Al$_2$O$_3$ this was different: the conversion of carbon dioxide over Ni/CeO$_2$/$\alpha$-Al$_2$O$_3$ descended faster than that over Ni/$\alpha$-Al$_2$O$_3$ as the pulse number increased.

Figure 2. Deposited carbon from methane decomposition (a) La-promoted Ni/$\alpha$-Al$_2$O$_3$, (b) Ce-promoted Ni/$\alpha$-Al$_2$O$_3$

It is suggested that after decomposition of methane over Ni/La$_2$O$_3$/$\alpha$-Al$_2$O$_3$, many active carbon species were formed on the surface of this catalyst. It can be assumed that during the reduction of NiO in the catalyst, the aggregation of Ni particles was inhibited by the presence of La$_2$O$_3$, which led to homogeneous dispersion of tiny-sized Ni particles on the surface of the catalyst. Consequently, there were many active sites for methane decomposition. Over this kind of catalyst, the carbon species formed can easily move away from the active sites and then may be exposed again for further methane decomposition.

With respect to Ni/CeO$_2$/$\alpha$-Al$_2$O$_3$, the carbon produced from methane quickly covered the surface of catalyst. Thus, the amount of carbon species on the surface of these catalysts was less than that over Ni/La$_2$O$_3$/$\alpha$-Al$_2$O$_3$. It has been thought that CeO$_2$ acted as an electronic promoter in methane reforming with carbon dioxide [7,8]. In a reductive atmosphere, CeO$_2$ can be converted into Ce$_2$O$_3$. Electrons in the 4f sub-orbit of cerium may increase the density of electron cloud around the Ni atom, which can retard the decomposition of methane on the surface of Ni particles. Thus, the amount of carbon species formed over the Ni/CeO$_2$/$\alpha$-Al$_2$O$_3$ was less than that over Ni/$\alpha$-Al$_2$O$_3$.

It has been assumed that in the methane reforming with carbon dioxide, decomposition of methane
is a first step and removal of carbon species by CO$_2$ the second [9]. According to this mechanism, the experiment has been performed as follows: (1) a certain amount of methane was fed into the reactor filled with fresh catalyst, and the hydrogen produced during this process was determined by a gas chromatograph; (2) the same amount of carbon dioxide was pulsed into the reactor to remove the carbon species formed from methane decomposition, and the carbon monoxide formed during this process was also quantitatively analyzed by the chromatograph. The ratio of H$_2$/CO reflects the relationship between the methane decomposed and the carbon species removed by CO$_2$.

After CH$_4$ was fed into the reactor, carbon species and hydrogen in the gas phase were formed according to the following scheme:

\[
CH_4 \rightarrow C^* + 2H_2 \quad (1)
\]

As CO$_2$ was pulsed into the reactor, assuming all carbon species reacted with this CO$_2$ as shown in equation (2) and no side-reactions took place, the amount of CO should be equal to that of hydrogen produced in the first reaction.

\[
CO_2 + C^* \rightarrow 2CO \quad (2)
\]

The ratio of H$_2$/CO can be represented as $R_{H_2/CO}$. The results are shown in Table 1. If $R_{H_2/CO}>1$, it is then suggested that the carbon species from methane decomposition reacted with carbon dioxide incompletely. On the other hand, when $R_{H_2/CO}<1$, it may imply that not only the carbon species have been removed by carbon dioxide thoroughly, but also the following reactions (3) and (4) may occur:

\[
CO_2 \rightarrow CO + O_{(ads)} \quad (3)
\]

\[
CO_2 + 2H_{(ads)} \rightarrow CO + H_2O \quad (4)
\]

<table>
<thead>
<tr>
<th>Catalysts</th>
<th>Promoter content (%)</th>
<th>$R_{H_2/CO}$</th>
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<tr>
<td></td>
<td></td>
<td>700 °C</td>
</tr>
<tr>
<td>Ni/$\alpha$-Al$_2$O$_3$</td>
<td>—</td>
<td>1.33</td>
</tr>
<tr>
<td>Ni/La$_2$O$_3$/-$\alpha$-Al$_2$O$_3$</td>
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<td>1.27</td>
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<td></td>
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<tr>
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<td>3</td>
<td>1.43</td>
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Although the conversion of methane increased as the temperature was raised, the ability of carbon dioxide to remove carbon species was enhanced more quickly than the methane decomposition. Because the bond of C=O in carbon dioxide molecular is too strong to be broken at lower temperatures, less CO$_2$ molecules can be activated. Therefore, the reaction of CO$_2$ with carbon species on the surface of catalyst is not sufficient. At higher temperatures, the C=O bond will vibrate more easily and the number of activated carbon dioxide molecules will thus be increased, which may lead to complete removal of carbon species on the surface of catalyst.

As the temperature was above 800 °C, $R_{H_2/CO}$ was almost equal to unity in the case of Ni/La$_2$O$_3$/-$\alpha$-Al$_2$O$_3$, while this value was lower than unity over Ni/$\alpha$-Al$_2$O$_3$ and Ni/CeO$_2$/-$\alpha$-Al$_2$O$_3$. It can be suggested that the reactions (3) and (4) occurred over the latter two catalysts and La$_2$O$_3$ was able to inhibit two reactions. It has also been found that the value of $R_{H_2/CO}$ increased with the content of promoter.

### 3.3. Temperature programmed reduction

The temperature programmed reduction (TPR) profiles of the catalysts are shown in Figure 3. It can be seen that all nickel oxide in the catalyst was reduced to metallic nickel completely far below 700 °C. However, there are obvious differences among these peak temperatures. As for lanthanum promoted catalyst, the peak for consumption of hydrogen was higher than that of Ni/$\alpha$-Al$_2$O$_3$. La$_2$O$_3$ is a kind of structural promoter, which can inhibit the aggregation of Ni particles during reduction by hydrogen. To keep the tiny size of Ni particles, more energy was needed. As a result, Ni particles can be dispersed evenly to form many active sites for the decomposition of methane.
In the cerium promoted catalyst, the electrons can transfer via $4f$ sub-orbit during either reduction or catalytic reaction. For this reason, the cerium containing catalyst can be reduced at lower temperature than the promoter-free catalyst. Though CeO$_2$ can inhibit aggregation of Ni particles, the electrons of $4f$ sub-orbit of cerium may strongly influence the catalytic properties of the Ni-base catalyst. Due to electrons in the $4f$ sub-orbit of cerium, the methane decomposition was inhibited as previously mentioned.

3.4. Crystalline phases of catalysts

The XRD patterns of the three fresh catalysts, which are shown in Figure 4, indicate that there was elementary nickel in each catalyst. During reduction by hydrogen, nickel oxide in catalyst was converted into metallic nickel that tended to aggregate into particles with various diameters. This tendency can be hindered in the presence of rare-earth oxide. Usually, the principal planes of a nickel crystal are (100), (110) and (111). Because nickel crystal possesses an FCC structure, not (100) and (110) planes but (200) and (220) planes are detected by X-ray diffraction. It has been suggested that the decomposition of methane occurs more easily on (110) plane and (100) plane than on (111) plane [10].

It can be seen from the figure that the intensities of the peaks corresponding to metallic nickel on the catalysts promoted by La are noticeably weaker than those on the other two catalysts. It is suggested that the particles of nickel catalysts on the Ni/La$_2$O$_3$/α-Al$_2$O$_3$ are smaller than those on the Ni/α-Al$_2$O$_3$ and Ni/CeO$_2$/α-Al$_2$O$_3$ catalysts and dispersion of the former is better than that of the latter [6]. This would preferentially expose the catalytically more active (110) plane and (100) plane of the Ni particles as revealed by the x-ray diffraction patterns. It is thought that, for this reason, the La-promoted catalyst can provide more active sites for methane decomposition than the other two.

4. Conclusions

When La$_2$O$_3$ and CeO$_2$ are added to Ni/α-Al$_2$O$_3$, while they can both inhibit the aggregation of Ni particles, they are different types of promoter for the Ni-based catalyst. La$_2$O$_3$ is largely a structural promoter, which can accelerate the decomposition of methane and keep the carbon species formed active even at higher temperatures. CeO$_2$, acted as an electronic promoter more often than as a structural promoter, may even retard the decomposition of methane under different conditions.
References