EFFECT OF MN PROMOTER ON NI-BASED CATALYSTS SUPPORTED ON γ-Al₂O₃

Ahmed S. Al–Fatesh*, Anis H. Fakeeha and Ahmed E. Abasaeed
Chemical Engineering Department, College of Engineering, King Saud University, P.O. Box 800, Riyadh 11421, Saudi Arabia

Dry reforming reactions have important environmental and economical implications, since they can utilize both methane & carbon dioxide which are considered as greenhouse gases that cause global warming and produce useful chemical products such as H₂ and CO commonly known as synthesis gases. These gases can be used as feedstock for numerous chemicals and fuels as well as being sources for pure hydrogen and carbon monoxide. An experimental investigation was carried out to prepare suitable catalysts for dry reforming reaction using Nickel based catalyst prepared by impregnation method. Alumina, specifically, γ-Al₂O₃ with high surface area were used as support. The catalysts were dried at 120°C and calcined at 700°C. The reforming reactions were carried out using CO₂/CH₄/N₂ feed ratio of 17/17/2, F/W=60 ml/min.gcat and reaction temperature range 500-700°C. The presented study focuses on the experimental investigation the effect of addition of Mn promoter on 5%Ni/Al₂O₃ support. The performance of the developed catalyst was quantified by determining CH₄ and CO₂ conversions and synthesis gas ratio (H₂/CO). Time on stream stability tests of the promoted catalyst showed that the addition of Mn promoter increased carbon formation.

Keyword: CH₄, CO₂, Dry reforming, Ni/γ-Al₂O₃, catalysts, Mn and H₂/CO

Introduction

There are different methods for the conversion of methane into syngas namely; steam reforming using steam (CH₄ + H₂O ↔ CO + 3 H₂), Carbon dioxide reforming of methane (CH₄ + CO₂ ↔ 2CO + 2H₂), Partial oxidation using oxygen (CH₄ + 1/2O₂ ↔ CO + 2H₂). Methane is one of the as greenhouse gases that contributes to global warming (~4-9% of greenhouse gases). The other greenhouse gases are CO₂ (~9-26% of greenhouse gases) and water-vapor (~36-70% of greenhouse gases)[1].

The production of syngas (CO and H₂) by catalytic CO₂ reforming of methane which is also called dry reforming has attained a great attention in this decade due to the advantage it offers in simultaneous utilization and reduction of two major greenhouse gases.

The other advantage of dry reforming is that it results in a lower H₂/CO ratio, near unity, which is required for the synthesis of methanol and other valuable higher hydrocarbons (Fischer Tropsch synthesis)[2-8].

Mostly group VIII metals (Ru, Ir, Pd, Pt) and Ni- based catalysts in combinations with various supports and promoters have been used for CO₂ reforming of methane[5]. It was found that the Boudouard reaction (2CO → C...
+ CO₂) and/or methane decomposition (CH₄ → C + 2H₂) is the main hindrance to the successful industrial application of the process. This side reaction also gives rise to the deactivation due to coke formation and breakdown of the catalyst. In order to overcome this side reaction i.e to develop a coke resistant catalyst several studies has been considered.

The Nobel metal based catalysts were found to be more active and exhibit higher coke resistance than nickel based catalysts but the main drawback of Nobel metal is high cost and less abundance. It is also found that the addition of sulfur in Ni- based catalyst reduces the coke formation but it lowers the activity of catalyst [6-7]. Consequently it is lucrative to develop improved Ni- based catalysts which are coke resistant, highly active and exhibits stable operation for a long period [2- 6]. Alumina supported nickel which is the usual component of commercial steam reforming catalyst, had been tested for CO₂ reforming of methane that showed high initial activity but encountered severe carbon deposition in the end [9-10].

Different modifiers e.g Co, Cu, Zr, Mn, Ti, and Ag were investigated by adding them in Ni/Al₂O₃ catalyst. The major objective to use these modifiers is to reduce the carbon deposition and increase activity. The best results with high stability and activity was found when Mn was used as a modifier. During the reactions MnO undergoes oxidation reduction cycles due to which it changes its oxidation state. [2,3,11-13]

In the present study, a set of γ-Al₂O₃ supported Mn-Ni catalysts, with varying Ni/Mn molar ratio were designed, developed and tested for carbon dioxide reforming of methane as the main reaction in order to determine an effective catalyst with optimum Ni/Mn metal ratio assuring high activity and stability.

**Experimental**

**Catalyst preparation**

Supported 5 wt.% nickel catalysts were prepared by incipient wetsness impregnation as follows: the promoter x wt.% Mn (x = 0, 0.25, 0.5, 1 and 4) were prepared by impregnating γ-Al₂O₃ (BET area = 196 m²/g). After drying at 120 °C overnight and calcining at 700 °C for 3 h, The catalysts obtained are xwt%Mn-5wt%Ni/γ-Al₂O₃ BET area are reported in the table given below.

Table 1. Specific surface area of the catalysts

<table>
<thead>
<tr>
<th>Catalyst</th>
<th>BET area (m²/g )</th>
</tr>
</thead>
<tbody>
<tr>
<td>5wt% Ni/γ-Al₂O₃</td>
<td>189.9</td>
</tr>
<tr>
<td>0.25 wt% Mn -5wt%Ni/γ-Al₂O₃</td>
<td>189.8</td>
</tr>
<tr>
<td>0.5 wt% Mn -5wt%Ni/γ-Al₂O₃</td>
<td>190.7</td>
</tr>
<tr>
<td>1.0 wt% Mn -5wt%Ni/γ-Al₂O₃</td>
<td>189.2</td>
</tr>
<tr>
<td>4.0 wt% Mn -5wt%Ni/γ-Al₂O₃</td>
<td>187.2</td>
</tr>
</tbody>
</table>
Catalytic activity

Catalytic tests were performed under conditions in fixed bed reactor. The activity measurements performed on 0.6 g of catalyst with feed mixture consisted of CH$_4$/CO$_2$/N$_2$ = 17/17/2 and total space velocity of 60 ml/min. g$^{-1}$. Prior to the reaction the catalyst was reduced in H$_2$ at 650 °C for 2 h (30 ml/min). The reforming activity was studied in the temperature range of 500 °C to 700 °C with the stabilization of 2 h at each temperature.

Results and discussion

It was found that Mn has a promoter effect on the activity of the Ni catalysts supported on modified γ-Al$_2$O$_3$ in the reaction of the reforming of methane with CO$_2$. It was established that the catalytic system requires an optimum ratio between the quantity of Mn and its capacity of affecting catalytic behavior. Thus, with nominal values close to 0.25% the maximum conversion Fig.1 & 2. On the other hand, it was shown that the Mn does not have any effect with regard to the surface area in the catalysts.

The main products of the reaction are H$_2$ and CO, and the measured H$_2$/CO ratios were always less than unity Fig. 3. CO$_2$ conversion is higher than the corresponding CH$_4$ conversion, which means that the DRM reaction is influenced by the simultaneous occurrence of the usual RWGS reaction.

Fig.1 & 2 shows the results of catalyst activity, maximum conversion reached and the final conversion at 700 °C. Also, it is important to point out that the catalysts with 0.25 wt% of the promoter, registered the highest conversions which are found to be between 11 and 20.8% for the CH$_4$ and CO$_2$ respectively at 500 °C and 40.4 and 56.1% at 600 °C. The catalysts with 0.5% Mn registered conversions that were equal to or, in some cases, lower than those obtained for the catalysts with 0.25% Mn.

![Figure 1. CH$_4$ conversion over xwt%Mn-5wt%Ni/γ-Al$_2$O$_3$ at different temperatures](image)
Table 2 presents the stability behavior of the catalyst in terms of the conversion of CH$_4$ with time on stream at 700 °C. The initial and final conversions of methane and carbon dioxide for the 5%Ni/γ-Al$_2$O$_3$ catalyst changed from 80.7% to 79.7% and 86.2% to 79.5%, respectively. The calculated deactivation factor (DF) were −1.7%. For the catalysts promoted with 0.25% Mn there was no significant enhancement in the conversions of methane and carbon dioxide. A significant drop in the deactivation factor −2.2% however, upon increasing the amount of promoter to 4% the conversions of methane and carbon dioxide dropped by 7.4% (from 74.7% to 70.3%) and by 12.6% (from 74.7 % to 70.3%), respectively. The calculated deactivation factor were 5.9%.
Table 2: Catalytic performance of the Mn-promoted 5%Ni/γ-Al₂O₃ catalyst

<table>
<thead>
<tr>
<th>wt% Mn-5%Ni/γ-Al₂O₃</th>
<th>Conversion</th>
<th>% DF</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Initial</td>
<td>After 7 h</td>
</tr>
<tr>
<td></td>
<td>CH₄(%)</td>
<td>CO₂(%)</td>
</tr>
<tr>
<td>0.0</td>
<td>80.7</td>
<td>86.2</td>
</tr>
<tr>
<td>0.25</td>
<td>80.9</td>
<td>86</td>
</tr>
<tr>
<td>4</td>
<td>74.7</td>
<td>79.5</td>
</tr>
</tbody>
</table>

Reaction Temperature = 700 °C Calcination temperature= 700°C.

DF = [(Final CH₄ conversion _ initial conversion CH₄)/initial conversion of CH₄] * 100.

Conclusions

The following conclusions can be drawn on the basis of the catalytic activity data. The different activity levels of the catalysts clearly showed that the catalytic performances of Mn-Ni samples strongly depended on the metal loading and Ni/Mn ratio. Among all the catalysts, 0.25 wt% Mn - 5wt%Ni catalyst with the lowest Mn/ Ni ratio exhibited the highest catalytic activity in the DR reaction.

References
