Study of synthesis gas production via CO$_2$ reforming of CH$_4$ over supported cobalt catalysts

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Introduction
Catalysts based on transition elements like Co can play dramatic role by consuming and transforming the greenhouse gases (CH$_4$ & CO$_2$) into synthesis gas through dry reforming processes [1, 2]. Synthesis gas is the basis for most of the chemical industries. Nevertheless, the need for efficient catalysts is indispensable to achieve long-term operation of the process [3, 4]. The primary reaction for CO$_2$ reforming of methane process is: CH$_4$ + CO$_2$ → 2CO + 2H$_2$ ($\Delta$H° = +61.1 kcal/mol). In this paper the catalytic performance of cobalt catalyst supported on TiO$_2$P25, Al$_2$O$_3$, SiO$_2$ and CeO$_2$ for synthesis gas production was studied experimentally.

Materials and Methods
The Co based catalysts were prepared with TiO$_2$-P25, Al$_2$O$_3$, SiO$_2$ and CeO$_2$ supports by the incipient wet impregnation method. The samples were calcined at 500°C for 3 h. Catalysts were characterized by BET and TG/DTA techniques. The experiment was carried out in a micro tubular reactor (PID Eng&Tech) at atmospheric pressure, using CO$_2$:CH$_4$:N$_2$ feed ratio of 17:17:2 and a total flow rate of 36 ml/min, at 700°C reaction temperature.

Results and Discussion
Study of cobalt based catalyst was conducted at 700°C reaction temperature for the carbon dioxide reforming of methane to produce synthesis gas. Catalyst activities toward synthesis gas and stability tests and their corresponding results of catalyst characterization were presented. To highlight the effect of deactivation due to carbon deposition on the catalysts and to gain significant reference data for industrialization, the stability tests for the catalysts were performed. The synthesis gas was recorded at different time intervals for a total of 360 minutes as shown in Fig. 1. Co/TiO$_2$-P25 catalyst gave the highest synthesis gas ratio (1.04) of almost unity. This overcomes the limitations of high ratio of synthesis gas that was unsuitability for methanol and Fischer-Tropsch synthesis. The catalyst exhibited good stability for 6 h time of reaction. Similarly, Co/Al$_2$O$_3$ catalyst showed good values of synthesis gas ratio close to the optimum i.e., unity and good stability. On the other hand, the Co/CeO$_2$ catalyst gave decreasing synthesis gas ratio for the first 4 h as result of deactivation due to carbon deposition. After that the ratio increased by the transformation of formed carbon to carbon monoxide as the result of the reverse Boudouard reaction (2CO ↔ C + CO$_2$). Co/SiO$_2$ catalyst provided the lowest synthesis gas ratio (0.17). The synthesis gas ratio decreased continuously. Catalyst sintering was ascribed to this loss of activity instead of carbon deposition. The absence of carbon formation substantiated this as shown by the TGA results in Table 1. The results of specific surface areas and amount of coke deposits over spent catalysts are shown in Table 1. The BET surface area of fresh Co/TiO$_2$-P25 and Co/Al$_2$O$_3$ diminished after reaction as result of carbon deposition. The carbon formation also increased the BET surface area of used Co/Co$_2$O catalyst. Alternatively, no significant variation of BET surface area was obtained for Co/SiO$_2$ catalyst as result of lack of carbon deposition.

**Figure 1.** Variations of synthesis gas (H$_2$/CO) ratios versus time on stream for supported cobalt catalysts at 700°C; (F/W= 60 mL/min.g$_{cat}$).

**Table 1.** BET surface areas and amount of coke deposition (estimated by TGA).

<table>
<thead>
<tr>
<th>Support type</th>
<th>Fresh catalyst BET (m$^2$/g)</th>
<th>Used catalyst BET (m$^2$/g)</th>
<th>Carbon Wt. loss %</th>
</tr>
</thead>
<tbody>
<tr>
<td>TiO$_2$-P25</td>
<td>53.0</td>
<td>37.9</td>
<td>32.3</td>
</tr>
<tr>
<td>Al$_2$O$_3$</td>
<td>128.2</td>
<td>119.8</td>
<td>11.2</td>
</tr>
<tr>
<td>CeO$_2$</td>
<td>7.4</td>
<td>17.8</td>
<td>18.1</td>
</tr>
<tr>
<td>SiO$_2$</td>
<td>6.6</td>
<td>4.7</td>
<td>&lt;1</td>
</tr>
</tbody>
</table>

Significance
The results revealed that Co supported catalysts produced synthesis gas ratios of one and below and therefore suitability for methanol and Fischer-Tropsch syntheses. Cobalt catalysts supported with TiO$_2$-P25 and Al$_2$O$_3$ gave better synthesis gas ratios and stability performances.

References