The characteristic of CH$_4$-CO$_2$ reforming catalyzed by
carbonaceous catalyst

Weidong Zhang, Yongfa Zhang*, Meng Zhang, Chengsheng Tian, Wei Zhao

Key Laboratory of Coal Sci. & Tec of Ministry of Education & Shanxi Province,
Taiyuan University of Technology, 030024 Taiyuan, China

Abstract

The performance of carbonaceous catalyst has been investigated for the carbon dioxide reforming of methane at 800-1000°C under atmospheric pressure. It was found that the carbonaceous catalyst is an efficient catalyst by which the initial transformation temperature of CH$_4$-CO$_2$ reforming is reduced from 950°C (under blank condition) to 650°C. There are three kinds of reaction in the system of CH$_4$-CO$_2$ — carbonaceous catalyst: CH$_4$-CO$_2$ reforming, CH$_4$ decomposition and gasification reaction between CO$_2$ and carbonaceous catalyst. In the temperature range of 700-900°C, the CH$_4$-CO$_2$ reforming is the dominating reaction. The mechanism of CH$_4$-CO$_2$ reforming is also deducted in this paper, it is thought that the H· decomposed from methane is the key reason for CO$_2$ dissociation. The results also indicate that the maximum methane conversion is reached in the initial stage and then gradually fallen to a stable stage along with the reaction time increasing, which shows that two kinds of yet unknown activity species — activity species I and activity species II are contained in the carbonaceous catalyst. High temperature is favorable to enhancing the initial conversion of CH$_4$ and CO$_2$, but unfavorable to the stability of carbonaceous catalyst.

* Corresponding author. Tel: +86 351 6018676
E-mail address: yongfaz@tyut.edu.cn (Y. Zhang)
1. Introduction

In the last few years, the catalytic reforming of methane with carbon dioxide (dry reforming) has stirred interest from both an environmental and an industrial perspective [1–4]. The dry reforming process offers several opportunities. Firstly, dry reforming could convert two abundant greenhouse gases (CH₄ and CO₂) into syngas (CO and H₂), which has a H₂/CO molar ratio typically lower than that of steam reforming, appropriate for several applications such as methanol synthesis [5], Fischer–Tropsch reaction and acetic acid synthesis [6-7]. Furthermore, the feed gas (CH₄ and CO₂) of dry reforming are two kinds of cheaper carbon-containing gases, especially CO₂ may be the cheapest one. In addition, the co-transformation of coke oven gas with gasification gas from coal into synthesis gas recently has attracted great attention since China has abundant resources of coke oven gas.

Considerable research efforts [8-12] have been directed towards the development of active and selective catalysts for CO₂ reforming of CH₄. Hansen[13] inspected the catalytic activity of Fe, No and Ni supported on Al₂O₃ and SiO₂, it was found that at the temperature of 400-800°C, the catalyst had the best catalytic activity and the longest catalytic life. Solymosi and his colleagues [14] did the research on the platinum metals, discovered that at 500°C methane already had remarkable reforming rate on precious metal. Asheroft [15] inspected the reforming activeness and carbon depositing situation by loading Ni, Pd, Ru, Rh and Ir on the supporter of Al₂O₃ and discovered that, the deposition carbon formed quickly to Ni/Al₂O₃ and 1% Pd/ Al₂O₃, but if added some O₂ to feed gas, the amount of deposition carbon would drop obviously. Shen Shikong et al. [16] investigated the CH₄-CO₂ reforming activeness in the bimetal/Al₂O₃ and Ni/Al₂O₃ catalyst. It was found that at 750°C the conversion of CH₄ and CO₂ reached 90.2% , 90.4% respectively with Pd bimetal/Al₂O₃ catalyst and 91.6% , 88.9% with
The research of metal catalysts have already made certain progress, but the developing speed of the research has been slowed because of the high cost (precious metal) and easy deactivation caused by carbon deposition. Coking and metal sintering are also the obstacles making the development of an industrially applicable catalyst a challenge. In order to solve the problems of metal catalysts, in this experiment, a kind of new catalyst- carbonaceous catalyst with low-cost, high-activity and strong ability of anti carbon deposition was developed, and the characteristics of the carbonaceous catalyst to CH$_4$-CO$_2$ reforming reaction were also studied.

2. Experimental

2.1. Experiment condition and equipment

The experiment was performed in the quartz tubular reactor with an inner diameter of 8mm, imbedded in an insulated electric furnace equipped with a programmable controller. A thermocouple was inserted into the catalyst bed to measure and control the reaction temperature. The length of the quartz tube filled with carbonaceous catalyst was 15cm, of which could be thought a constant temperature zone. The carbonaceous catalyst's granularity was controlled to 8-10 items, namely the size between 2.00-2.36mm, so as the feed gas CH$_4$ and CO$_2$ could pass over the catalyst smoothly, and contact fully with the carbonaceous catalyst. In the study, the resident time of the feed gas was 2 seconds. In the quartz tube, besides the carbonaceous catalyst in the constant temperature zone, other volume space was filled totally with quartz fragment, no more empty band left in order to avoid forming the short-circuit of the feed gas.

Before the experiment, the reactor was heated to the given temperature under nitrogen atmosphere, and the temperature was maintained for 5 hours to remove the moisture and residual gas in
carbonaceous catalyst.

2.2. Resident time

In the study, the resident time \( t \) refers to the time for the feed gas passing through the 15 cm constant temperature zone. Resident time \( t \) is determined as the formula (1).

\[
t = \frac{d \times s}{F} \times \frac{1}{273.15 + t_2} \times 60
\]

Where \( d \) is the length of constant temperature zone (cm), \( s \) is the cross-sectional area of quartz tube (cm\(^2\)), \( F \) is the total flow of \( \text{N}_2, \text{CH}_4 \) and \( \text{CO}_2 \) (ml/min), \( t_1 \) is the temperature of the constant temperature zone (°C), \( t_2 \) is the room temperature (°C).

2.3. Product analysis

The product was measured with gas chromatograph (GC). The conversion of methane \( X_{\text{CH}_4} \) and carbon dioxide \( X_{\text{CO}_2} \) were calculated using the formula as follows.

\[
X_{\text{CH}_4} = \frac{F_{\text{in}} \times C_{\text{in}, \text{CH}_4} - F_{\text{out}} \times C_{\text{out}, \text{CH}_4}}{F_{\text{in}} \times C_{\text{in}, \text{CH}_4}} \times 100\%
\]  

\[
X_{\text{CO}_2} = \frac{F_{\text{in}} \times C_{\text{in}, \text{CO}_2} - F_{\text{out}} \times C_{\text{out}, \text{CO}_2}}{F_{\text{in}} \times C_{\text{in}, \text{CO}_2}} \times 100\%
\]

Where \( F_{\text{in}} \) is the flow of feed gas (ml/min), \( C_{\text{in}, \text{CH}_4} \) is the concentration of methane in feed gas (%), \( F_{\text{out}} \) is the flow of product gas (ml/min), \( C_{\text{out}, \text{CH}_4} \) is the concentration of methane in product gas (%).

2.4. Catalyst preparation and analysis

The carbonaceous catalyst (c-catalyst) used in this study was prepared by pyrolyzing Datong coal (DT coal) at 900 °C for 12 hours. The proximate and ultimate analysis of Datong coal and the carbonaceous catalyst are shown in Table 1.

<table>
<thead>
<tr>
<th>Sample</th>
<th>Proximate analysis/ w %, ad</th>
<th>Ultimate analysis/ w %, daf</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>M</td>
<td>A</td>
</tr>
<tr>
<td>-----</td>
<td>-----</td>
<td>-----</td>
</tr>
<tr>
<td>DT Coal</td>
<td>3.10</td>
<td>12.20</td>
</tr>
<tr>
<td>C-catalyst</td>
<td>1.20</td>
<td>13.30</td>
</tr>
</tbody>
</table>

3. Result and discussion

3.1. The catalysis of carbonaceous on CH₄-CO₂ reforming

The comparison studies of CH₄-CO₂ reforming both uncatalyzed (blank condition) and catalyzed by carbonaceous catalyst have been done. The conversion of methane and carbon dioxide at different reaction temperature is shown in Fig. 1.

![Fig. 1](image-url)

**Fig. 1** Effect of carbonaceous catalyst on CO₂ reforming of CH₄

It can be found from Fig. 1 that the initial conversion of methane and carbon dioxide increases with the temperature of CH₄-CO₂ reforming reaction both catalyzed and uncatalyzed increasing. In the reaction system, there are three main reactions.

\[
\begin{align*}
CH_4 + CO_2 & \rightarrow 2CO + 2H_2 \quad \Delta H^\circ = 248.0 \text{KJ/mol} \quad (4) \\
CH_4 & \rightarrow C + 2H_2 \quad \Delta H^\circ = 75.6 \text{KJ/mol} \quad (5) \\
C + CO_2 & \rightarrow 2CO \quad \Delta H^\circ = 151.7 \text{KJ/mol} \quad (6)
\end{align*}
\]
These reactions (4)-(6) are strong endothermic reactions, and the C-H bond energy in methane is as high as 435KJ/mol. The high temperature is favorable to the three reactions (4)-(6). Therefore, with the reaction temperature increasing, the conversion of methane and carbon dioxide increase correspondingly.

It can be seen from Fig. 1 that methane can be transformed for the uncatalyzed reaction. But the initial transformation temperature reaches as high as 950°C. However for the catalyzed reaction by carbonaceous catalyst, the initial transformation temperature of methane reduces to 650°C. At the reaction temperature of 1000°C, the conversion of methane and carbon dioxide for the catalyzed reaction achieves 87% and 98% respectively, while only 11% CH₄ conversion and 6% CO₂ conversion are achieved for the uncatalyzed reaction. Comparing to the blank condition, the conversion of methane and carbon dioxide under carbonaceous catalysis increase 76% and 92% respectively.

3.2 The transformation characteristic of CH₄ and CO₂ for different feed gas under blank condition

3.2.1 The transformation characteristic of CH₄ for the feed gas - single CH₄ or CH₄-CO₂ mixture

The transformation characteristic of CH₄ was investigated using the single CH₄ gas or the CH₄-CO₂ mixture as feed gas under the blank condition. The relationship between CH₄ conversion and reaction temperature is shown in Fig. 2.
Fig. 2  The relationship between CH₄ conversion in different feed gas and reaction temperature under blank condition

It can be found from Fig. 2 that when the feed gas - single CH₄ gas or the CH₄-CO₂ mixture is passed over the reactor separately, the tendency of methane conversion for the reaction of the single CH₄ gas used as feed gas is as same as that of the CH₄-CO₂ mixture. As shown in Fig. 2, at the temperature lower than 900°C, no methane conversion is found in the reactions using single CH₄ gas or CO₂-CH₄ mixture as feed gas respectively. In the temperature range from 900°C to 1200°C, the methane conversion for single CH₄ is also similar to that for the CH₄-CO₂ mixture.

Based on these results, it can be concluded that there no obvious carbon dioxide reforming of methane occur under the blank condition at the temperature lower than 1200°C, otherwise, when the CO₂-CH₄ mixture is used as the feed gas, CH₄ conversion should be greatly higher than that when the single CH₄ was used as the feed gas.

3.2.2 The transformation characteristic of CH₄ and CO₂ for the feed gas of CH₄-CO₂ mixture

The transformation characteristic of CH₄ and CO₂ were inspected using CH₄-CO₂ mixture as feed gas under the blank condition. The comparison of the conversion of methane and carbon dioxide at
different reaction temperature is shown in Fig. 3.

Fig. 3 The relationship between \( \text{CO}_2 \), \( \text{CH}_4 \) conversion and react temperature for the uncatalysed \( \text{CH}_4\text{-CO}_2 \) reforming

It can be found from Fig. 3 that the conversion of methane is higher than that of carbon dioxide in the whole reaction process. It can also be found that on the surface of the quartz fragments filled in quartz tube reactor some deposition carbon is formed and retained after the reaction.

Base on the above phenomenon, it can be concluded that both reaction (5) and (6) occur in the \( \text{CH}_4\text{-CO}_2 \) system and the amount of reaction (5) is more than that of (6), which causes the conversion of methane always higher than that of carbon dioxide and has the residual deposition carbon formed.

3.2.3 The reaction mechanism of \( \text{CH}_4\text{-CO}_2 \) reforming under blank condition

Based on the phenomenon mentioned above, the mechanism of uncatalyzed \( \text{CO}_2\text{-CH}_4 \) reforming is assumed as follows.

\[
\text{CH}_4(\text{g}) \rightarrow \text{C} + 2\text{H}_2(\text{g}) \quad (7)
\]

\[
\text{C} + \text{CO}_2(\text{g}) \rightarrow 2\text{CO}(\text{g}) \quad (8)
\]

In the \( \text{CH}_4\text{-CO}_2 \) reforming, the methane decomposition occurs first and produces the hydrogen and the carbon deposition (7), then the reaction between carbon dioxide and carbon deposition occurs
directly in gas phase to produce carbon monoxide (8). It is thought that the methane decomposition is the rate limiting reaction, carbon dioxide has little effect on the methane decomposition.

3.3 The transformation characteristic of \( \text{CH}_4 \) and \( \text{CO}_2 \) for catalyzed \( \text{CH}_4\text{-CO}_2 \) reforming by carbonaceous catalyst

3.3.1 The transformation characteristic of \( \text{CH}_4 \) for the feed gas - single \( \text{CH}_4 \) or \( \text{CH}_4\text{-CO}_2 \) mixture

The catalyzed \( \text{CH}_4\text{-CO}_2 \) reforming by carbonaceous catalyst was inspected using single \( \text{CH}_4 \) or the \( \text{CH}_4\text{-CO}_2 \) mixture as the feed gas. The relationship between \( \text{CH}_4 \) conversion and reaction temperature is shown in Fig. 4.

![Fig.4 The relationship between \( \text{CH}_4 \) conversion and react temperature in different feed gas under the carbonaceous catalysis condition](image)

It can be found from Fig. 4 that when single \( \text{CH}_4 \) gas or \( \text{CH}_4\text{-CO}_2 \) mixture passes over the reactor respectively under the carbonaceous catalysis condition, the conversion of methane for the former is greatly higher than that for the latter. The results indicate that when methane and carbon dioxide exist simultaneously, methane not only takes part in the reaction (5), but also takes part in the reaction (4) simultaneously. For example, at the temperature of 800 °C, when only single \( \text{CH}_4 \) gas is used as feed
gas, the conversion of methane is only 5%, but using the mixture of CH₄ and CO₂ as feed gas, the conversion of methane quickly rises to 50%. It can be deducted that the increased 45% of the methane conversion is responsible for the CH₄-CO₂ reforming reaction (4). In another words, when the mixture (methane and carbon dioxide) passes over the reactor, the majority percentage of methane are transformed through the reforming reaction (4), only a few of methane are transformed through the methane decomposition.

### 3.3.2 The CO₂ transformation characteristic for the feed gas - single CO₂ or CH₄-CO₂ mixture under carbonaceous catalysis condition

The transformation characteristic of CO₂ was inspected using single CO₂ gas or the CH₄-CO₂ mixture as feed gas under the carbonaceous catalysis condition. The relationship between CO₂ conversion and reaction temperature is shown in **Fig. 5**.

![Fig.5 The relationship between CO₂ conversion and reaction temperature in different feed gas under the carbonaceous catalysis](image)

As shown in Fig. 5, when the CH₄-CO₂ mixture or the single CO₂ is used as the feed gas under the carbonaceous catalysis condition respectively, the conversion of carbon dioxide for the former feed gas is greatly higher than that for the later, especially in the temperature range of 700-900 °C. After the
temperature is increased to above 900°C, the CO₂ conversion for the two kinds of feed gases become about the same. It is thought that during the temperature of 700-900°C, when CH₄-CO₂ mixture passes over the reactor filled with carbonaceous catalyst, carbon dioxide participates in the reaction (6)
\[ \text{C} + \text{CO₂} \rightarrow 2\text{CO} \]
and the reaction (4) \[ \text{CH}_4 + \text{CO₂} \rightarrow 2\text{CO} + 2\text{H₂} \] simultaneously, and the amount of the reacted carbon dioxide in the reaction (4) is much greater than that in the reaction (6). For example, at the reaction temperature of 800°C, using single CO₂ as feed gas, the CO₂ conversion is only 10%, however, using the CH₄-CO₂ mixture as feed gas, the CO₂ conversion is as high as 60%. It is inferred that the increased 50% conversion is attributed to the reaction (4). After the temperature over 900°C, the CO₂ conversion for single CO₂ as feed gas is similar to that for CH₄-CO₂ mixture, which indicates that the amount of the reacted carbon dioxide in the reaction (4) tends to be same as that in the reaction (6) after the reaction temperature is higher than 900°C.

3.3.3 Reaction mechanism of catalyzed CH₄-CO₂ reforming by carbonaceous catalyst

Based on the characteristics of CH₄-CO₂ reforming under carbonaceous catalysis, it can be assumed that the carbonaceous catalyst can provide an activity species which could effectively promote the reaction of CH₄-CO₂ reforming. The mechanism of CH₄-CO₂ reforming under carbonaceous catalysis could be thought as follows:

Firstly, there are some activity species M in the carbonaceous catalyst, and the activity species M causes methane decomposing under a lower temperature and producing the H· (9).

\[ \text{CH}_4 + \text{M} \rightarrow \text{CH}_x \cdot \text{M} + (4-x)\text{H} \cdot \]  \hspace{1cm} (9)

The H· produced from methane decomposition makes carbon dioxide activated and produces activity species OH·(10), then the OH· reacts with CHₓ-M to produce another activity species
CH₃O· (11), from which CO is produced (12) further.

\[ \text{CO}_2 + \text{H} \rightarrow \text{CO} + \text{OH}· \] (10)

\[ \text{CH}_X\cdot\text{M} + \text{OH} \rightarrow \text{CH}_X\text{O} + \text{H}·\text{M} \] (11)

\[ \text{CH}_X\text{O} \rightarrow \text{CO} + \text{XH}· \] (12)

At last, hydrogen atom forms to hydrogen (14), and activity species M is dissociated (13) to be reused in the reaction.

\[ \text{H}·\text{M} \rightarrow \text{M} + \text{H}· \] (13)

\[ \text{XH}· \rightarrow \text{X}/2\text{H}_2 \] (14)

It can be concluded that, under carbonaceous catalysis, the reaction (9) is promoted by the activity species M, and the hydrogen atom produced from (9) is the main reason to carbon dioxide activation. Activity species M reduces the activation energy of CH₄-CO₂ reforming, and allows the reaction to occur at a lower temperature. It can be seen that under the condition of carbonaceous catalysis, the reaction (9) and (10) are promoted mutually, both contributes as the rate limiting reaction.

3.4. The catalytic activity of carbonaceous catalyst in CH₄-CO₂ reforming

Keeping the reaction temperature at 800°C, 900°C and 1000°C, the feed gas (CH₄:CO₂=1:1) was passed over the quartz reactor which was loaded with carbonaceous catalyst. After the reaction became stable, the composition of the product was examined at different reaction time, and the conversion of methane and carbon dioxide were calculated according to the formula (2) and (3). The comparison of the conversion of methane and carbon dioxide at different reaction time is shown in Fig. 6.
a: 800 °C  b: 900 °C  c: 1000 °C
The relationship between CO$_2$, CH$_4$ conversion and reaction time at different temperature

It can be seen from Fig. 6 that the conversion of methane can be divided into two time stages. The first stage has the characteristic of high conversion and fast-speed deactivation, in contrast to the second one which is characterized with low conversion and slow-speed deactivation. In the first stage, the maximum conversion of methane at 800°C, 900°C and 1000°C reached 38%, 55% and 87% respectively at the beginning of the reaction. With the time increasing, the conversion of methane reduces gradually and enters the second stage in which the conversion of methane is maintained at about 10%, 30% and 50% respectively. Because the gasification reaction between carbon dioxide and carbonaceous catalyst at 900°C and 1000°C, the tendency of carbon dioxide conversion are different from that of methane, which reflects that after the temperature is higher than 900°C, the reaction between carbon dioxide and carbonaceous catalyst will become the dominating reaction, namely that high temperature is unfavorable to the stability of carbonaceous catalyst.

As shown in Fig. 6, the conversion of methane is decreasing in the initial stage. It is assumed that there are two kinds of catalytic activity species - activity species I and activity species II in the carbonaceous catalyst. Activity species I has high catalytic activity in the initial stage, but it is easy to become deactivated, which makes the conversion of methane reduce rapidly in the initial stage. In contrast, activity species II shows excellent stability, no sign of deactivation is shown in the experiment time of about 240 minutes. But it is weaker in the catalytic effect on CH$_4$-CO$_2$ reforming. The composition and structure of the two activity species are under study.

From these experimental results showed from Fig. 6, it also can be concluded that the catalytic activity of activity species I and activity species II increase with increasing temperature, and that the deactivation of activity species I also increase with temperature increasing. High temperature is favorable to enhancing the initial conversion of methane, but unfavorable to the stability of activity
species I.

3.5 Product analysis

Table 2  Syngas distribution (mol%) for the CH₄/CO₂ reforming under carbonaceous catalyst

<table>
<thead>
<tr>
<th>Temperature/℃</th>
<th>CO/%</th>
<th>H₂/%</th>
<th>CO+H₂/%</th>
<th>H₂/CO</th>
</tr>
</thead>
<tbody>
<tr>
<td>800</td>
<td>22.26</td>
<td>19.02</td>
<td>41.28</td>
<td>0.85</td>
</tr>
<tr>
<td>900</td>
<td>40.23</td>
<td>28.97</td>
<td>69.20</td>
<td>0.72</td>
</tr>
<tr>
<td>1000</td>
<td>53.76</td>
<td>38.27</td>
<td>92.03</td>
<td>0.71</td>
</tr>
</tbody>
</table>

Table 2 shows the syngas distribution for the CH₄/CO₂ reforming under carbonaceous catalyst at different temperature. It can be found from table. 2 that the content of syngas in total gas is increased with the temperature. At the temperature of 1000℃, the content of syngas reaches to 92.3%, which indicate that most of feedgas (CH₄ and CO₂) is converted to CO and H₂.

4  Conclusions

(a) The initial transformation temperature of CH₄-CO₂ reforming catalyzed by carbonaceous catalyst can be reduced from 950℃(under blank condition) to 650℃.

(b) In the CH₄-CO₂ reforming catalyzed by carbonaceous catalyst, three reactions: CH₄-CO₂ reforming, CH₄ decomposition and gasification reaction between CO₂ and carbonaceous catalyst exist simultaneously. When the reaction temperature is lower than 700℃, the conversion of the above three reactions are all small. In the temperature range of 700-900℃, the CH₄-CO₂ reforming becomes the dominating reaction. After the reaction temperature is higher than 900℃, both the CH₄-CO₂ reforming and the gasification reaction become dominating reaction.

(c) High temperature is favorable for enhancing the initial conversion of methane and carbon dioxide, but as the temperature increase, the reaction rate between carbon dioxide and carbonaceous catalyst is also accelerated, causing high temperature to be unfavorable to the stability of the carbonaceous catalyst.
(d) For the system of CH₄-CO₂ reforming catalyzed by carbonaceous catalyst, the maximum methane conversion is reached during the initial stage and then gradually reducing and stabilizing to a stable stage along with the reaction time increasing.

(e) There are two kinds of activity species - activity species I and activity species II in the carbonaceous catalyst. Activity species I has high catalytic activity and plays a key role in the initial stage of CH₄-CO₂ reforming, but it is easy to become deactivate. In contrast, activity species II shows excellent stability and longer life, but its effect on CH₄-CO₂ reforming is weaker than that of the activity species I. The composition and structure of the two activity species are being studied.

Acknowledgement

The authors are grateful to the National Basic Research Program(973) of China (2005CB221202) and Shanxi Provincial Natural Science Foundation (20051020) for financial support of the present study.

References


