Chemical Engineering Journal 156 (2010) 519–523

Contents lists available at ScienceDirect

Chemical Engineering Journal

journal homepage: www.elsevier.com/locate/cej

CO_2 reforming of CH_4 in coke oven gas to syngas over coal char catalyst

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ARTICLE INFO

Article history:
Received 25 September 2008
Received in revised form 16 March 2009
Accepted 2 April 2009

Keywords:
Methane
CO_2 reforming
Synthesis gas
Coal char

ABSTRACT

The CO_2 reforming of methane (in coke oven gas) on the coal char catalyst was performed in a fixed bed reactor at temperatures between 800 and 1200 °C under normal pressure. The effects of the coal char catalyst pretreatment and the ratio of CO_2/CH_4 were studied. Experimental results showed that the coal char was an effective catalyst for production of syngas, and addition of CO_2 did not enhance the CH_4 reforming to H_2. It was also found that the product gas ratio of H_2/CO is strongly influenced by the feed ratio of CO_2/CH_4. The modified coal char catalyst was more active during the CO_2–CH_4 reforming than the coal char catalyst based on the catalyst volume, furthermore the modified catalyst exhibited high activity in CO_2–CH_4 reforming to syngas. The conversion of methane can be divided into two stages. In the first stage, the conversion of CH_4 gradually decreased. In the second stage, the conversion of methane maintained nearly constant. The conversion of CO_2 decreased slightly during the overall reactions in CO_2–CH_4 reforming. The coal char catalyst is a highly promising catalyst for the CO_2 reforming of methane to syngas.

1. Introduction

The methane reforming process, for example CO_2–CH_4 reforming, produces synthetic gas that is the main route to convert methane to liquid fuels, ammonia, methanol, and other oxygenates in so-called gas to liquid (GTL) technologies [1–3]. The conversion of the two gases into a valuable synthesis gas would reduce emissions of CO_2 and CH_4 and also satisfy the requirement of many synthesis processes in the chemical industry. Furthermore, it has potential in the co-utilisation of coke oven gas and coal bed methane [3–5]. In view of these advantages, it is likely that CO_2 reforming of methane will become increasingly important in the future. With temperature range from 800 to 1200 °C, numerous supported catalysts studies on CO_2 reforming have been tested in fixed and fluidized bed reactors, especially nickel- and noble metal-based catalysts [6]. Although noble metals are more active, selective for CO_2 reforming and less sensitive to coking than Ni-based catalysts, but considering the high cost and limited availability of noble metals, these have discouraged their industrial application [7,8]. From the industrial standpoint, Ni-based catalysts have been employed as possible substitutes for precious metals as they are relatively cheap and exhibit high activity for the reaction [7,8]. However, the problem of CO_2–CH_4 reforming is carbon deposition on the nickel catalysts surface and cause the catalyst deactivation. Therefore, the search for suitable new catalysts is still a research priority. A possible alternative and a new kind of cheap catalyst is coal char, which has been reported to have significant potential [3,9,10].

Very recently, coal char as a highly promising catalyst for the carbon-free H_2O reforming of methane (in coke oven gas) has been reported [9,10]. This catalyst showed not only a high resistance to carbon formation, but also a high activity and selectivity in the H_2O reforming. In the present work, the CO_2 reforming of methane over the coal char catalyst at different process conditions (viz. reaction temperature and relative concentrations of methane and CO_2 in the feed) will be discussed.

2. Experimental

Three different catalysts composed of coal char were used in the experiment. The coal char catalysts were prepared by pyrolysis of coal at 1150 °C for 1.5 h, crushing the catalyst mass to 30–60 mesh-size particles. The modified catalyst was prepared by the impregnation method in a stirred sodium hydroxide aqueous solution at normal temperature for 3 h. The modified catalyst was dried in a drying oven for 12 h at 100 °C. The composition of the catalyst is provided in Table 1. The composition of coke oven gas used in the experiment was shown in Table 2.

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doi:10.1016/j.cej.2009.04.005

Table 1
Composition and specific surface area (SSA) pore specific volume (PSV)of catalysts.

Carbon catalysts	Ultimate analysis (%, ad)					Ash (%, ad)	SSA (m^2/g)	PSV (cm^3/g)	Modified
	C	H	O	N	S				
I	89.87	0.27	0.75	0.86	0.36	7.80	85.65	0.05	No
II	88.30	1.40	2.50	0.92	0.50	6.41	85.65	0.05	No
III	88.01	1.38	2.45	0.84	0.50	6.87	83.11	0.06	Yes

Table 2
The composition of coke oven gas.

	CH_4	CO	H_2	CO_2	N_2	O_2
Content (%)	25.4–26.3	3.6–4.5	59.3–62.8	3.2–5.0	2.5–3.7	0–0.3

The catalytic reforming reactions of CH_4–CO_2 over the catalyst were carried out at normal pressure in a continuous-flow quartz reactor (i.d. 20 mm) packed with 0.4–1.1 g catalyst and provided with a platinum–rhodium thermocouple located in the center of the catalyst bed. Before carrying out the reaction, the catalyst was heated in situ at 800 °C in a flow (50 $cm^3\,min^{-1}$) of moisture-free nitrogen for 1 h.

The catalytic reactions were carried out at different temperatures, and relative concentrations of CH_4, H_2, CO_2 in the feed were measured, at normal temperature and pressure. The feed gases and the product gases were analyzed by gas chromatography −960. The methane (in coke oven gas) intake can be measured by mass flow meter. And the output of product gas flow can be measured by soap liquid meter. The C, H, and O balance across the reactor was more than 97%. All experiments with larger errors in the material balances were rejected. The formula of H_2, CO, and CH_4 relative volume (to CH_4 in feed gas), CH_4 and CO_2 conversion, which were

$$\text{Relative Volume}(H_2\text{ or CO}) = \frac{\text{Content in production gas} - \text{Content in feed}}{\text{Content of } CH_4 \text{ in feed}}$$

$$\text{Relative Volume}(CH_4) = \frac{\text{Content in feed} - \text{Content in production gas}}{\text{Content of } CH_4 \text{ in feed}}$$

$$\text{Conversion}(CH_4) = \frac{\text{Content in feed} - \text{Content in production gas}}{\text{Content of } CH_4 \text{ in feed}}$$

$$\text{Conversion}(CO_2) = \frac{\text{Content in feed} - \text{Content in production gas}}{\text{Content of } CO_2 \text{ in feed}}$$

3. Results and discussion

3.1. Effects of coal char catalyst on CH_4 (in coke oven gas) pyrolysis and CO_2–CH_4 reformation

Fig. 1 shows the CH_4 pyrolysis and CO_2–CH_4 reforming conversion change during the reactions at different temperature. It also can be seen obviously that the coal char had apparent catalyzation to CH_4 (in coke oven gas) pyrolysis in the temperature range from 800 to 1200 °C. Compared with blank test, CH_4 pyrolysis takes place at 950 °C with coal char catalyst and has more CH_4 conversion during pyrolysis. With the reaction temperature increasing, the conversion of CH_4 gradually increases. When the reaction temperature arrived at 1050 °C, the conversion of CH_4 is about 50% with coal char catalyst, and the conversion of CH_4 is about 35% without coal char catalyst. The data shows that the coal char could promote some of CH_4 conversion.

Based on the data of experiment as Fig. 1, it could be also concluded that the coal char had apparent catalyzation to CO_2–CH_4 (in coke oven gas) reforming in the temperature range from 800 to 1200 °C. During reforming of CO_2–CH_4 the following reaction may take place

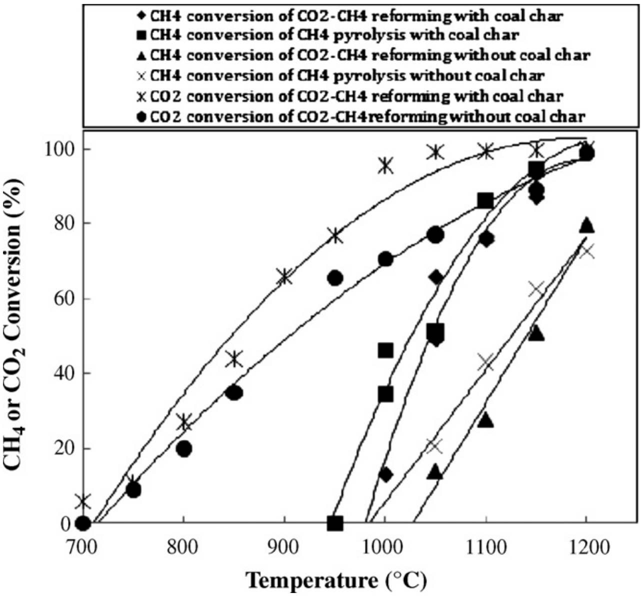

Fig. 1. Conversion change of overall reactions in CH_4-CO_2 reforming or CH4 pyrolysis (reaction condition: catalysts: coal char catalyst II or quartz powder catalyst, residence time: 3 s, $CO_2/CH_4 \approx 1{:}1$, CO_2:12 mL/min, coke oven gas:50 mL/min).

$$CH_4 \rightarrow C + 2H_2 \tag{1}$$

$$CH_4 + 2CO_2 \rightarrow 2CO + 2H_2 \tag{2}$$

Addition of CO_2 does not enhance the CH_4 reforming to H_2, because of a great amount of H_2 in feed (coke oven gas). This indicates, under H_2 atmosphere, adding CO_2 is disadvantageous to the transformation of CH_4 during reforming process.

3.2. Effects of temperature on distribution of the product gas

The CO_2 reforming of methane (in coke oven gas) was carried out by passing a mixture of CO_2 and CH_4 (in coke oven gas) over coal char catalyst, while keeping CO_2/CH_4 ratio (1.0) constant in the feed, under the temperature range from 700 to 1200 °C. Results showing the influence of temperature on the conversion and product gas relative content are presented in Fig. 2. It can be found that the relative content of CH_4 nearly unchanged when the reforming temperature is below 900 °C. However, from Fig. 1, it can be seen obviously that H_2 and CO_2 are consumed, and CO are formed. It can be interpreted as follows:

$$CO_4 + H_2 \rightarrow H_2O + CO \tag{3}$$

$$C + CO_2 \rightarrow 2CO \tag{4}$$

After the produce gas was condensated, a slight amount of water was found, which indicated the reaction (3) had taken place.

When the reforming temperature is higher than 1065 °C, the conversion of CO_2 was basically 100%, the relative volume of H_2

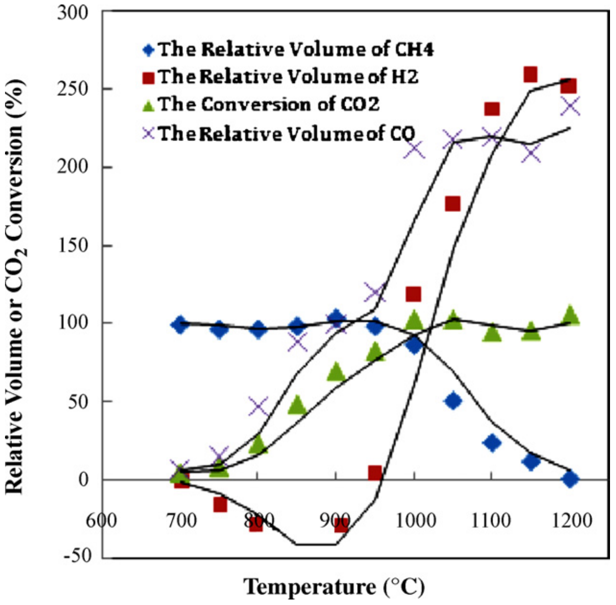

Fig. 2. The distribution diagram of production gas in the experiment of CO_2/CH_4 reforming (reaction condition: coal char catalyst II, residence time: 3 s, $CO_2:CH_4 \approx 1:1$, CO_2:12 mL/min, coke oven gas:50 mL/min, the relative volume of CH_4, H_2 and CO is to CH_4 in feed gas).

reached more than 200%. In the CO_2–methane reforming process, both the CO_2 and H_2O may be converted simultaneously by the reactions as follows[9]:

$$CH_4 + CO_2 \rightarrow 2CO + 2H_2 - 247.39\ \text{kJ/mol} \qquad (5)$$
$$\Delta G^0 = 61770 - 67.32T$$

$$CH_4 + H_2O \rightarrow CO + 3H_2 - 206.37\ \text{kJ/mol} \qquad (6)$$
$$\Delta G^0 = 189982 - 142.09T$$

The CO_2 reforming of methane (in coke oven gas) was studied over quartz powder, while keeping CO_2/CH_4 ratio (1.0) constant in the feed under the temperature range from 900 to 1200 °C. The results as Fig. 3 shown, there is almost no influence on the CH_4 conversion when the reforming temperature is below 1000 °C, but H_2 and CO_2 consumed, which could be explained by reactions (3) and (4). The CO_2–CH_4 reforming reaction begin about 1000 °C over quartz powder, CO and H_2 are produced.

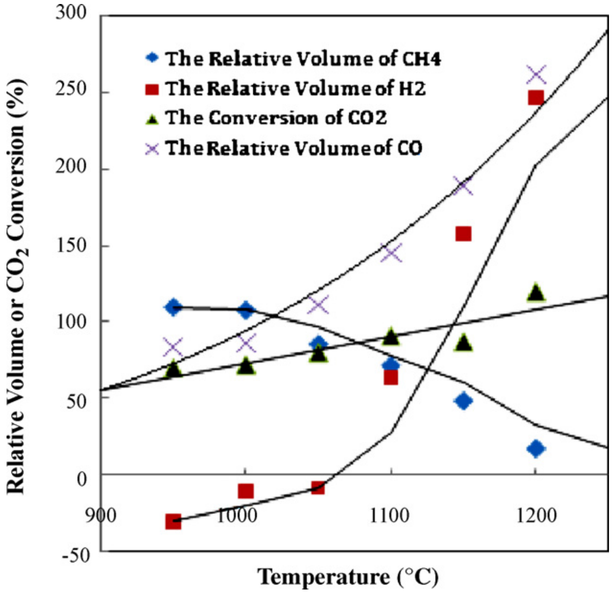

Fig. 3. The distribution diagram of production gas in the experiment of CO_2/CH_4 reforming (reaction condition: Quartz powder, residence time: 3 s, $CO_2:CH_4 \approx 1:1$, CO_2:12 mL/min, coke oven gas: 50 mL/min, the relative volume of CH_4, H_2 and CO is to CH_4 in feed gas).

When the reforming temperature arrived at 1050 °C, the results show that the formation rate of H_2 is far higher than its consumption rate, which indicates that reactions (5) and (6) play a leading position at the latter stage (1065–1200 °C). At 1200 °C, the conversion of CO_2 seems complete. The higher temperature is favored to CO_2–CH_4 reforming reaction. Compared the distribution diagram of production gas of CO_2–CH_4 reforming over coal char catalyst with quartz powder, it can be seen that the starting reaction temperature differences compared with quartz powder is lower than about 100 °C for coal char catalyst.

3.3. *Effects of different coal char catalyst on CO_2–CH_4 reformation*

To investigate the effect of different coal char catalyst on CO_2 reforming of methane, several experiments were conducted, both in the presence and absence of the char catalyst and the results are presented in Fig. 4. It can be seen that the methane conversion both over the quartz powder and catalyst II is about 10%, furthermore, the methane conversion over catalyst I is about 30% at temperature 1000 °C. At the same temperature, the conversion over catalyst III is some 50%. Clearly, the catalyst III displayed a significant higher catalytic activity than catalyst I and II, catalytic activity sequence of the catalysts is catalyst III > I > II.

The temperature has an evident influence on catalytic activity. The catalyst III has higher catalytic activity at the temperature 950 °C, however catalytic activity is very weak for catalyst I and II. Fig. 4 also shows the negligible difference in performance of catalyst I and II before 1000 °C. After temperatures above reaching 1050 °C, the acivty of catalyst I is much higher than catalyst II. After temperature reaching 1100 °C, there is no discernable difference between coal char catalyst I and III. At higher temperature 1200 °C, the catalytic activity of three kinds of catalyst is same. This suggests that different coal char materials have an evident influence on CH_4–CO_2 reforming reaction at different temperature.

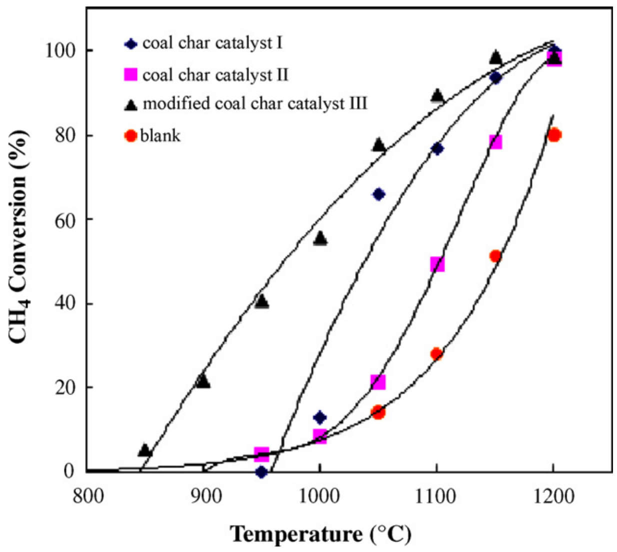

Fig. 4. CH_4 Conversion in CH_4–CO_2 Reforming Catalyzed by Different Coal char Catalyst (reaction condition: different coal char catalyst, residence time: 3 s, $CO_2:CH_4 \approx 1:1$, CO_2:12 mL/min, coke oven gas:50 mL/min).

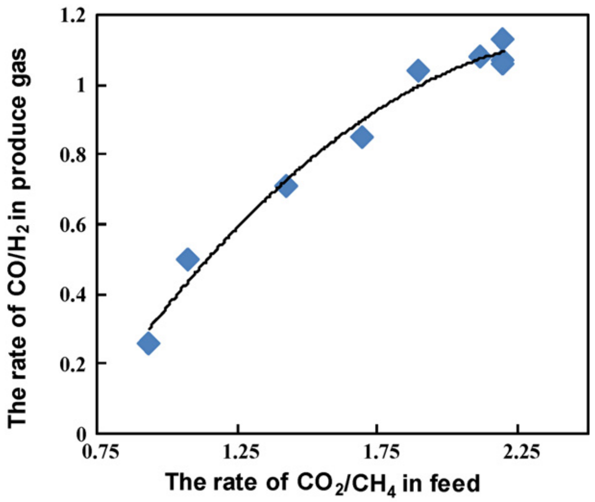

Fig. 5. Effect of CO_2/CH_4 ratio on CO/H_2 ratio in the CO_2 reforming of methane over coal char catalyst (reaction condition: coal char Catalyst II, temperature: 1050 °C, coke oven gas:50 mL/min).

3.4. *Effects of CO_2/CH_4 ratio on the rate of CO/H_2 in produce gas*

The influence of CO_2/CH_4 feed ratio on the catalyst performance in the CO_2 reforming of methane was also studied at temperatures 1050 °C over coal char Catalyst II. The results (Fig. 5) show a strong influence of the CO_2/CH_4 feed ratio on the process performance. With the CO_2/CH_4 feed ratio increasing, the CO/H_2 ratio is also increased. When the feed ratio of CO_2/CH_4 arrived at 1:1, the conversion of CH_4 was about 97.35%, the ratio of CO/H_2 is about 1:3 in produce gas. While the feed ratio of CO_2/CH_4 arrived at 2:1, the CO/H_2 ratio is approximately 1:1.1. Hence, the CO/H_2 ratio of CO_2–CH_4 reforming could be adjusted by means of adjusting the feed ratio of CO_2/CH_4.

3.5. *Reaction activity and life of catalyst*

The life of catalyst of the CO_2 reforming of CH_4 was shown in Fig. 6. It can be found that the conversion of methane can be divided into two stages. In the first stage, the conversion of CH_4 is about 95.2% at the beginning, then with the reaction time extend, the conversion of CH_4 obviously decreases, reaches the lowest at 210 mins, about 38.3%. Then the second stage, the conversion of CH_4 maintain nearly constant, about 40%.

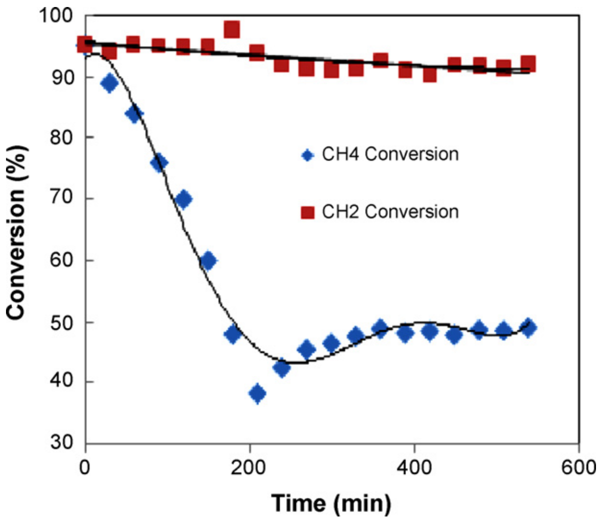

Fig. 6. The life of the coal char catalyst during CO_2/CH_4 reforming (reaction condition: coal char catalyst III, temperature:950 °C, $CO_2:CH_4 \approx 1:1$, CO_2:12 mL/min, coke oven gas:50 mL/min).

Table 3
The change of oxygen-bearing functional group in c-catalyst.

Item	The content of oxygen-bearing functional group (%)				
	C–C	Phenolic hydroxyl	Carbonyl	Carboxyl	Lactone
Before reaction	56.60	28.66	6.08	6.04	2.62
After reaction	82.14	4.20	9.79	3.67	0.20

Through X-ray photoelectron spectra, four oxygen-bearing functional group can be detected on the surface of catalyst: phenolic hydroxyl, carbonyl, carboxyl and lactone. The content of oxygen-bearing functional group in catalyst is shown in Table 3.

It can be found from Table 3, after CO_2–CH_4 reforming, the content of oxygen-bearing functional group in catalyst declined fiercely, especially the phenolic hydroxyl and lactone, decreases from 28.66% and 2.62% to 4.2% and 0.2%, respectively. Based on the phenomenon mentioned above, it can be concluded that the phenolic hydroxyl and lactone play an important role in CO_2–CH_4 reforming, and promote the conversion of CH_4 efficiently. However, with the phenolic hydroxyl and lactone consuming, the conversion of CH_4 drop off. When the phenolic hydroxyl and lactone is consumed completely, the conversion of methane maintains nearly constant.

It also can be seen from Fig. 6, the tendency of carbon dioxide conversion is different from methane, the conversion of CO_2 decreases slightly during the overall CO_2–CH_4 reforming reactions. This indicates that the coal char catalyst during reforming process has high activity for CO_2, and better catalyst stability for CO_2–CH_4 reforming at 200 min later, which is promising new catalyst for transforming coke oven gas to syngas.

4. Conclusions

The coal char catalyst is a highly promising catalyst for the CO_2 reforming of methane to syngas. The CO/H_2 ratio in the CO_2 reforming of methane can be adjusted by means of adjusting by feed ratio of CO_2/CH_4, which rang from 0.2 to 1.1. The modified coal char catalyst has more active than coal char catalyst I and II in CO_2 reforming of CH_4. For the modified coal char catalyst, the conversion of methane can be divided into two stages. In the first stage, with the reaction time extend, the conversion of CH_4 gradually decreases. In the second stage, the conversion of methane maintains nearly constant. The conversion of CO_2 decreases slightly during the overall CH_4- CO_2 reforming reactions.

Acknowledgements

This work was supported by the National Basic Research Program of China (2005CB221202), Innovation Team Funds Scheme and the youth fund of School Funds of Taiyuan University of Technology (TYUT).

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