

# Effect of carbon deposition over carbonaceous catalysts on $\text{CH}_4$ decomposition and $\text{CH}_4\text{-CO}_2$ reforming

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**Abstract** An investigation was made using a continuous fixed bed reactor to understand the influence of carbon deposition obtained under different conditions on  $\text{CH}_4\text{-CO}_2$  reforming. Thermogravimetry (TG) and X-ray diffraction (XRD) were employed to study the characteristics of carbon deposition. It was found that the carbonaceous catalyst is an efficient catalyst in methane decomposition and  $\text{CH}_4\text{-CO}_2$  reforming. The trend of methane decomposition at lower temperatures is similar to that at higher temperatures. The methane conversion is high during the initial of stage of the reaction, and then decays to a relatively fixed value after about 30 min. With temperature increase, the methane decomposition rate increases quickly. The reaction temperature has significant influence on methane decomposition, whereas the carbon deposition does not affect methane decomposition significantly. Different types of carbon deposition were formed at different methane decomposition reaction temperatures. The carbon deposition Type I generated at  $900^\circ\text{C}$  has a minor effect on  $\text{CH}_4\text{-CO}_2$  reforming and it easily reacts with carbon dioxide, but the carbon deposition Type II generated at  $1000^\circ\text{C}$  and  $1100^\circ\text{C}$  clearly inhibits  $\text{CH}_4\text{-CO}_2$  reforming and it is difficult to react with carbon dioxide. The results of XRD showed that some graphite structures were found in carbon deposition Type II.

**Keywords** carbon deposition, carbonaceous catalyst,  $\text{CH}_4\text{-CO}_2$  reforming

## 1 Introduction

Methane is the main component in natural gas and coke oven gas (COG). In coke oven gas the content of methane

reaches as high as 24%–28% [1,2]. As reforming is a reasonable way to convert methane and carbon dioxide into useful syngas ( $\text{CO} + \text{H}_2$ ) [3], the research on  $\text{CH}_4\text{-CO}_2$  reforming, especially that on carbon dioxide in coal gas from gasification reforming of the methane in COG, is becoming an active field [4]. However, the carbon deposition on the catalyst surface [5–9] is still a major problem, as it covers the active sites and pores of the catalyst and causes a decrease in catalytic activity [10,11]. To solve this problem, a kind of new catalyst—carbonaceous catalyst—for  $\text{CH}_4\text{-CO}_2$  reformation has been developed in our laboratory [12], which has the advantages of low cost, high activity and strong anti-carbon ability. However, there are still some unknowns such as the difference between the carbonaceous catalyst and carbon deposition, the characteristic of carbon deposition and so on. In this paper, both the characteristic of carbon deposition and the influence of carbon deposition on  $\text{CH}_4\text{-CO}_2$  reforming were investigated by GC and XRD.

## 2 Experiment

### 2.1 Experimental device and process

The experiment on  $\text{CH}_4\text{-CO}_2$  reforming was carried out with a self-made tubular reactor under atmospheric pressure. The catalyst was added to the horizontal corundum tube reactor which was 75 cm long and 2.2 cm diameter. The residence time was 3 s. The catalyst bed was in the constant temperature zone of the tube furnace. The methane decomposition and  $\text{CH}_4\text{-CO}_2$  reforming under  $900^\circ\text{C}$ ,  $1000^\circ\text{C}$  and  $1100^\circ\text{C}$  were investigated. First of all,  $\text{N}_2$  (99.99%) was fed into the experimental system at the rate of 50 mL/min before being heated to the reaction temperature, and then  $\text{CH}_4$  (99.99%) was fed into the reactor at the rate of 70 mL/min, and the product gas was analyzed by gas chromatography; methane conversion was

calculated using the balance of hydrogen. All experiments with larger errors in the material balances were rejected. The formulas for CH<sub>4</sub> and CO<sub>2</sub> conversion were as follows:

$$\text{conversion}(\text{CH}_4) = \frac{\text{content in feed} - \text{content in production gas}}{\text{content of CH}_4 \text{ in feed}},$$

$$\text{conversion}(\text{CO}_2) = \frac{\text{content in feed} - \text{content in production gas}}{\text{content of CO}_2 \text{ in feed}}.$$

After a 3 h decomposition, the mixture of CH<sub>4</sub> and CO<sub>2</sub> (CH<sub>4</sub> : CO<sub>2</sub> = 1 : 1, flow rate 140 mL/min) was fed into the reactor for reforming.

The reaction temperature was controlled by a thermal sensor, the feed gas flow rate was controlled by the mass flow controller, the component content of the product gas was detected by gas chromatography, and the product gas flow was measured by a soap film flowmeter. The experimental apparatus is shown in Fig. 1.

## 2.2 Preparation and analysis of carbonaceous catalyst

The carbonaceous catalyst (C-catalyst) was prepared by pyrolyzing Datong coal (DT coal) at 900°C for 12 hours in the self-made tube furnace under a nitrogen atmosphere. The proximate and ultimate analysis of DT coal and the C-catalyst is shown in Table 1 [12].

## 2.3 Product gas analysis

Composition of raw gas and product gas was analyzed by GC-950TCD and GC-9890A. The GC-950TCD used hydrogen as the carrier gas, and the A-channel with a chromatographic column of 13X molecular sieve was used for detecting O<sub>2</sub>, N<sub>2</sub>, CH<sub>4</sub>, CO; the column length was 1 m and the column temperature was 40°C. The B-channel with a chromatographic column of GDX502 was used for detecting CO<sub>2</sub>, C<sub>2</sub>H<sub>4</sub> and C<sub>2</sub>H<sub>6</sub>; the column length was 2 m, and the column temperature was 40°C. The GC9890A used nitrogen as the carrier gas, and the B-channel with chromatographic column of GDX502 was used for detecting H<sub>2</sub>; the column length was 2 m and the column temperature was 40°C.

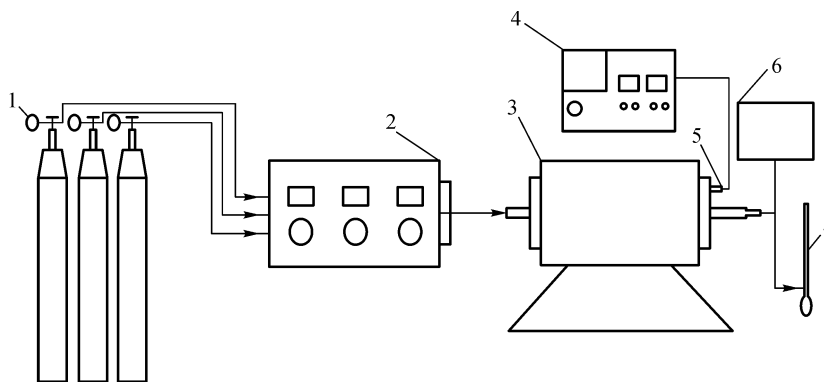
## 2.4 Analysis of XRD

XRD was used to analyze the C-catalyst before and after methane decomposition. A Y-4Q X-ray diffraction analyzer was used to analyze the surface structure of the C-catalyst using Cu as target, with a tube voltage of 35 kV at  $2\theta = 5^\circ\text{--}100^\circ$ .

# 3 Results and discussion

## 3.1 Effect of carbon deposition on CH<sub>4</sub> decomposition

The comparison studies on CH<sub>4</sub>-CO<sub>2</sub> reforming, both uncatalyzed (baseline condition) and catalyzed by the C-catalyst, were done in a fixed-bed reactor. The methane



**Fig. 1** Experimental apparatus

1 pressure gauge; 2 mass flow controller; 3 heating furnace; 4 temperature controller; 5 thermocouple; 6 gas chromatography; 7 soap film flowmeter

**Table 1** The proximate and ultimate analysis of Datong coal and C-catalyst

sample	proximate analysis /wt-%, ad			ultimate analysis /wt-%, daf				
	M	A	V	C	H	N	S	O <sub>(dif)</sub>
DT coal	3.10	12.20	29.00	87.70	4.96	1.27	0.42	5.36
C-catalyst	1.20	13.30	4.50	94.60	1.47	0.99	0.17	2.36

conversion at different reaction temperatures is shown in Fig. 2. It can be seen from the figure that the methane conversion catalyzed by the C-catalyst is higher than that of uncatalyzed  $\text{CH}_4\text{-CO}_2$  reforming, and the methane conversion increases with increasing temperature. At temperatures of 900°C, 1000°C and 1100°C, the uncatalyzed methane conversions are 1%, 5% and 39% respectively, while catalyzed methane conversions by a C-catalyst reached 10%, 23% and 63%, respectively, indicating that the C-catalyst has a certain catalytic effect on methane decomposition. Owing to methane decomposition being an endothermic reaction, a higher reaction temperature is conducive to methane decomposition.

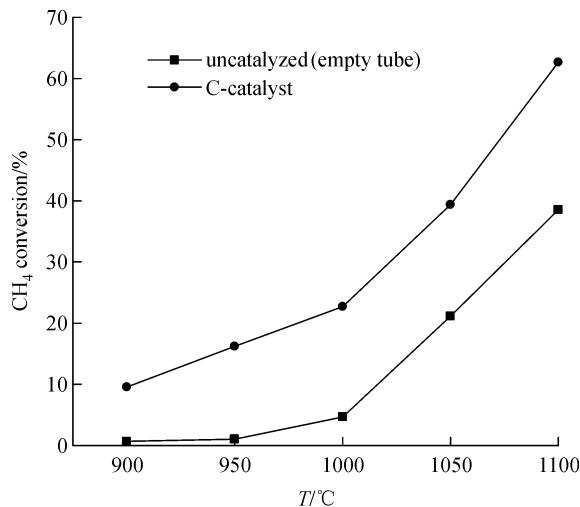


Fig. 2 Methane conversion over C-catalyst and uncatalyzed (empty tube)

The methane conversion at different temperatures of 900°C, 1000°C, and 1100°C (Fig. 3) shows that the methane conversion increases with increasing temperature. It can be seen from Fig. 3 that the methane conversion can be divided into two steps. The first step has the characteristic of high conversion and fast-speed decay, which is in contrast to the second step which is characterized by low conversion and slower deactivation. In the first step, the maximum conversion rates of methane at 1100°C, 1000°C and 900°C are 76%, 33%, and 18%, respectively, which take place at the early stage of the reaction. As the reaction time increases, the conversion rate of methane decreases gradually and enters the second step, in which the conversion rate of methane at 1100°C, 1000°C, and 900°C is maintained at about 61%, 20%, and 8%, respectively. It can be concluded that the reaction temperature has significant influence on methane decomposition, whereas the carbon deposition does not affect methane decomposition significantly.

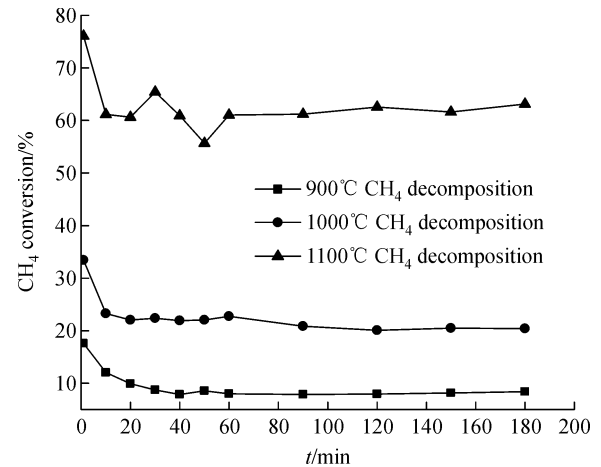


Fig. 3 Methane conversion over C-catalyst

### 3.2 Effect of carbon deposition on $\text{CH}_4\text{-CO}_2$ reforming

Two different processes (process I and II) were carried out to examine the effect of carbon deposition on  $\text{CH}_4\text{-CO}_2$  reforming. Process I: after 3 hours of methane decomposition reaction over the C-catalyst (900°C, 1000°C, 1100°C), the C-catalyst with carbon deposition was prepared, then the mixture of  $\text{CH}_4$  and  $\text{CO}_2$  was fed into the reactor for  $\text{CH}_4\text{-CO}_2$  reforming; Process II: the mixture of  $\text{CH}_4$  and  $\text{CO}_2$  was fed into the reactor for  $\text{CH}_4\text{-CO}_2$  reforming directly over a fresh C-catalyst. From the conversions of methane and carbon dioxide under different processes in Figs. 4 and 5, it can be seen that at 900°C, the methane conversion over the C-catalyst with carbon deposition fluctuates in a similar range as the conversion over a fresh C-catalyst, while the carbon dioxide conversion over the C-catalyst with carbon deposition increases to 64% (increased about 10%). At 1000°C and 1100°C, after the carbon deposited on the C-catalyst, the catalytic activity for  $\text{CH}_4\text{-CO}_2$  reforming decreased. When the  $\text{CH}_4\text{-CO}_2$  reforming reaction reached the stable stage after about 150 min reforming reaction, the methane conversions were 47% and 65%, respectively. Compared to the C-catalyst with carbon deposits, the methane conversions over the fresh C-catalyst were 58% and 75%, respectively. During the  $\text{CH}_4\text{-CO}_2$  reforming, different types of carbon deposition were formed at different reaction temperatures. Carbon deposition Type I generated at 900°C reacted with carbon dioxide easily, and had a little effect on  $\text{CH}_4\text{-CO}_2$ ; Carbon deposition Type II generated at 1000°C and 1100°C obviously inhibited  $\text{CH}_4\text{-CO}_2$  reforming and is difficult to react with carbon dioxide [13]. The effect of carbon deposition generated at different temperatures on  $\text{CH}_4\text{-CO}_2$  reforming increased in the order of 900°C < 1000°C < 1100°C.

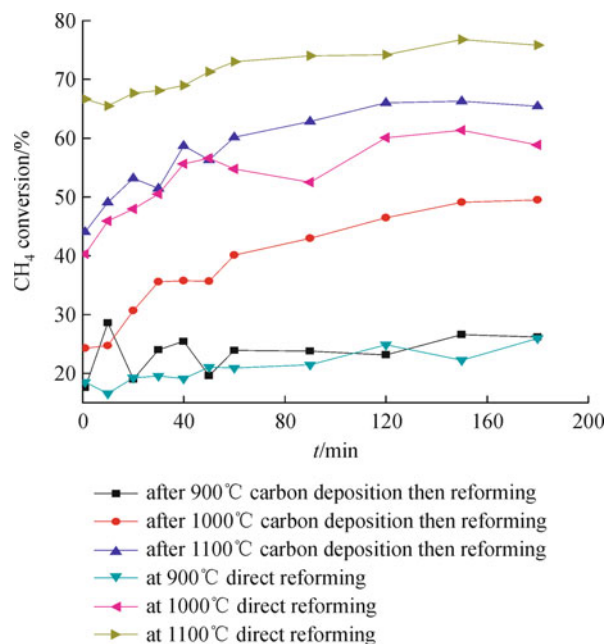


Fig. 4 Effect of carbon deposition on methane conversion

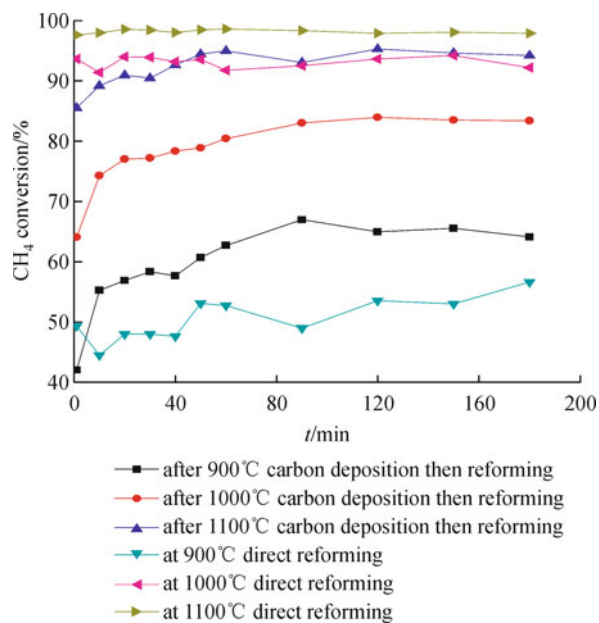


Fig. 5 Effect of carbon deposition on carbon dioxide conversion

### 3.3 Analysis of C-catalyst by XRD

The XRD profiles analysis of the C-catalyst before and after the methane reforming is shown in Fig. 6. The C-catalyst diffraction peaks significantly changed before and after the  $\text{CH}_4\text{-CO}_2$  reforming. The C-catalyst after the methane reforming has obvious diffraction peaks at diffraction angles  $2\theta = 26^\circ$  and  $54^\circ$ , which is close to the ideal graphite crystal diffraction peak ( $2\theta = 26.6^\circ$  and  $54^\circ$ )

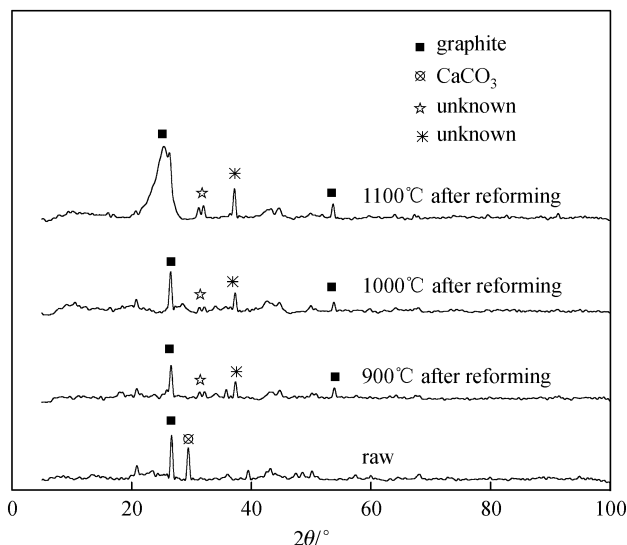


Fig. 6 C-catalyst surface analysis of XRD

[14]. From the intensity of the diffraction peaks, it suggests that the micro crystal structure of graphite in the C-catalyst was enhanced in an orderly manner with the increasing temperature. Based on the discussion above, it can be concluded that the gasification activity of carbon deposition Type II with carbon dioxide is lower because it has a higher degree of graphitization. Diffraction angles  $2\theta$  at  $31^\circ$  and  $37^\circ$  have a marked change, which may be caused by compounds of Ca and Si.

## 4 Conclusions

The trend of methane decomposition at lower temperatures is similar to that at high temperatures. The  $\text{CH}_4$  conversion is high during the initial stages of reaction, and then decays to a relatively fixed value after about 30 min. As the temperature increases, the methane decomposition rate increases quickly. The temperature plays a significant role in the methane decomposition.

The carbon deposition I does not affect the methane decomposition significantly. Different types of carbon deposition were formed at different methane decomposition reaction temperatures. Carbon deposition I generated at lower temperature has a minor effect on  $\text{CO}_2\text{-CH}_4$  reforming and it easily reacts with carbon dioxide. It is also the intermediate during carbon dioxide reforming of methane, which improves the conversion of carbon dioxide. At  $900^\circ\text{C}$ , 180 min, the carbon dioxide conversion is 56.6%, and the carbon dioxide conversion reaches to 64.1% with deposited carbon on the C-catalyzer. However, it does not have obvious impact on methane conversion, carbon deposition generated at higher temperature obviously inhibits  $\text{CO}_2\text{-CH}_4$  reforming and is difficult to react with carbon dioxide.

The result of XRD analysis shows that the carbon deposition II is composed of some graphite structure. The carbon deposition II almost has no catalytic activity and is difficult to react with carbon dioxide. The active sites of the catalyst are covered by carbon deposition II, which causes a loss of catalytic activity.

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