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Catalytic Performance of Coal Char for the Methane Reforming Process

A new concept of combined coal gasification and methane reforming in a single reactor was proposed as an alternative path for syngas production using coal and coalbed methane. Here, the results of this process are summarized. The experimental work was carried out in a fixed-bed reactor. Methane cracking, CO₂/steam reforming of methane over coal char, and the effects of chars made from different types of parent coal on methane conversion were examined. The catalytic effect of coal char on methane cracking and reforming increased with decreasing coalification degree. A synergistic effect was observed in that, while the coal char catalyzed the methane reforming reactions, gasification of the coal char took place simultaneously, which counter-balanced the deposition of carbon especially for the methane-steam-char system.

Keywords: Carbon dioxide, Catalytic, Char, Methane, Reforming

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1 Introduction

Due to emerging industrial trends, methane cracking and reforming to syngas or H₂ has attracted research and development (R&D) interests from academia and industry in recent years [1–3]. Steam methane reforming is the most common process for the production of hydrogen and synthesis gas, but catalyst deactivation may occur during methane steam reforming with Ni catalysts since it promotes carbon deposition over the catalyst [4]. De Miguel et al. [5] used an Ni-Al₂O₃ catalyst for methane steam reforming. Roy et al. [6] found that a Pd-Rh/metal foam catalyst exhibited steady activity for methane steam reforming. CO₂ reforming of methane to produce CO-rich synthesis gas has gained growing interest, considering the chemical utilization of natural gas and CO₂. Dry reforming yields a low H₂/CO ratio (~1), which could be useful in the synthesis of valuable oxygenated chemicals. It is well known that two main kinds of catalysts are employed for this reaction: Ni- and noble metal-based catalysts. Mirzaei et al. [7] studied methane CO₂ reforming over nanostructure bimetallic Ni-Co-MgO catalysts and found that the stability of the catalysts seems to be related with the metal particle size and the production of a non-deactivating carbon deposition.

Considerable effort has been invested in studies for the production of high-purity H₂ and syngas [8–11]. However, catalyst deactivation due to carbonaceous deposition, metal sintering, and the high costs of noble metals are still serious problems so

that it would be more economical to develop low-cost and easy-to-get catalysts. In recent years, carbon catalysts have shown positive results; meanwhile, a new process combining coal gasification and methane reforming to produce syngas has been conceptualized and proven to be feasible in our laboratory, offering an economic means to utilize coalbed methane resources together with coal. The process is expected to have the following advantages: (i) The H₂/CO ratio of syngas is adjustable for the downstream synthesis process; (ii) there is no need for an expensive metal catalyst as coal char can serve as methane reforming catalyst; (iii) tolerance to sulfur and other potentially harmful impurities; (iv) there is no need for regeneration of the catalyst [12].

Preliminary results have been presented [13]. The present work summarizes and updates the results of our recent fundamental research on various aspects of this innovative process including methane cracking over coal char, CO₂ and steam reforming over coal char in the presence of methane, and the effects of chars made from different types of parent coal, including lignite, bituminous coal, and anthracite, on methane conversion.

2 Experimental

Three kinds of coal samples with different coalification degree, including a lignite, a bituminous coal, and an anthracite, were used in this work. The coal was crushed and sieved to a size fraction of 0.355–0.63 mm. Coal char was prepared by devolatilizing the coal in nitrogen in a fixed-bed reactor at 1173 K for 30 min. The results of the proximate and ultimate analyses of the coal chars are presented in Tab. 1.

An electrically heated fixed-bed reactor made of quartz was employed for the methane cracking and reforming experi-

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Table 1. Proximate and ultimate analyses of coal chars. (ad = air dry)

Sample	Proximate analysis [wt %]			Ultimate analysis [wt %]				
	M _{ad} ^{a)}	A _{ad}	V _{ad}	S _{ad}	C _{ad}	H _{ad}	O _{ad}	N _{ad}
Lignite char	0.17	21.01	3.24	1.48	72.45	1.42	2.55	0.92
Bituminous char	0.38	18.31	1.32	0.27	78.11	1.13	1.04	0.76
Anthracite char	0.41	29.98	0.88	1.34	65.58	0.96	1.02	0.71

ments. A thermocouple was inserted into the reactor to monitor the temperature. High-purity gases (> 99.9 vol %) of methane, nitrogen, and carbon dioxide were used. The gas flow rate was controlled by a mass flow controller. The rate of steam was accurately controlled using a precise micro-flow pump to deliver distilled water, which was then heated and vaporized in an electric preheater prior to entering the reactor. The experiments were performed at temperatures from 1073 to 1223 K, and atmospheric pressure was maintained throughout the experiments; the typical experiment procedure has been described in [14].

The combined coal gasification and methane reforming process involves complex heterogeneous-homogeneous reactions. The major reactions involved are as follows:

Methane cracking:

Carbon dioxide and steam reforming of methane:

Carbon gasification by carbon dioxide and steam:

No notable other hydrocarbons were detected in the gas phase (less than 0.1 vol %). Nitrogen was used as a balance gas in the experiments and as a tracer for balance calculations. The balance of other species could be obtained by comparing their concentrations in the gas phase according to the following equations.

Methane conversion:

$$X_{\text{CH}_4} = \frac{V_{\text{in}}C_{\text{CH}_4\text{in}} - V_{\text{out}}C_{\text{CH}_4\text{out}}}{V_{\text{in}}C_{\text{CH}_4\text{in}}} \quad (6)$$

Carbon dioxide conversion:

$$X_{\text{CO}_2} = \frac{V_{\text{in}}C_{\text{CO}_2\text{in}} - V_{\text{out}}C_{\text{CO}_2\text{out}}}{V_{\text{in}}C_{\text{CO}_2\text{in}}} \quad (7)$$

Steam conversion:

$$X_{\text{H}_2\text{O}} = \frac{V_{\text{out}}(C_{\text{CO}_2\text{out}} + 2C_{\text{CO}_2\text{out}})}{V_{\text{in}}C_{\text{H}_2\text{Oin}}} \quad (8)$$

Hydrogen yield:

$$Y_{\text{H}_2} = \frac{V_{\text{out}}C_{\text{H}_2\text{out}}}{2V_{\text{in}}C_{\text{CH}_4\text{in}}} \quad (\text{for methane cracking and CO}_2 \text{ reforming}) \quad (9)$$

or

$$Y_{\text{H}_2} = \frac{V_{\text{out}}C_{\text{H}_2\text{out}}}{V_{\text{in}}(C_{\text{H}_2\text{Oin}} + 2C_{\text{CH}_4\text{in}})} \quad (\text{for steam reforming}) \quad (10)$$

Carbon monoxide yield:

$$Y_{\text{CO}} = \frac{V_{\text{out}}C_{\text{CO}_2\text{out}}}{2V_{\text{in}}C_{\text{CO}_2\text{in}}} \quad (\text{for CO}_2 \text{ reforming}) \quad (11)$$

or

$$Y_{\text{CO}} = \frac{V_{\text{out}}C_{\text{CO}_2\text{out}}}{V_{\text{in}}C_{\text{H}_2\text{Oin}}} \quad (\text{for steam reforming}) \quad (12)$$

Carbon dioxide yield in steam reforming:

$$Y_{\text{CO}_2} = \frac{V_{\text{out}}C_{\text{CO}_2\text{out}}}{V_{\text{in}}C_{\text{H}_2\text{Oin}}} \quad (13)$$

where C is the concentration of a gas component, V represents the gas flow rate (mL min^{-1}), and the subscripts in and out refer to the reactor inlet and outlet conditions, respectively.

3 Results and Discussion

3.1 Blank Experiments and Methane Cracking over Char

A set of blank experiments of methane cracking and steam and CO_2 reforming of methane over a bed of quartz with the same particle size as the char particles was performed in the temperature range from 973 to 1223 K. The results show that methane conversion increased with increasing temperature, but remained below 1.4%. Further, the methane cracking experiments with demineralized char and coal ash showed that the ash has hardly any catalytic effect [14].

Methane is very stable; it exhibits a high C–H bond strength (434 kJ mol^{-1}) and a large ionization energy. Without an effective catalyst, it could only be thermally cracked at high temperatures, usually higher than 1473 K [15, 16]. Methane cracking over a bed of coal char was studied and the results are shown in Fig. 1. All three types of coal char exerted a significant catalytic effect on methane cracking. The lignite char showed the highest catalytic activity; the initial methane cracking conversion rate reached 98.7% at 1223 K while the catalytic activity decreased with increasing coalification degree. However, all the chars lost their initial activity rapidly after 30 min on stream and then maintained relatively low activity values. The deactivation is mainly due to carbonaceous deposition and blockage of active centers [4, 14].

Figure 1. Methane conversion versus time during methane cracking over different coal chars (CH_4 10%, N_2 90%, total flow rate 250 mL min^{-1} , 1223 K).

Regarding the different catalytic activities of chars, most of the prior studies [17–19] concluded that the active centers for methane decomposition are high-energy sites (HES), such as surface defects, low-coordination sites, and other energetic abnormalities. Low-rank coal with a lower degree of crystallinity

has a larger number of HES. Thus, the catalytic activities of amorphous carbon catalysts are better than the activities of more ordered carbon catalysts.

3.2 CO_2 Reforming of Methane over Coal Char

Fig. 2 and Tab. 2 show the experimental results of CO_2 reforming of methane over a bed of bituminous char at different temperatures. The coal char greatly promoted the reforming reaction compared to the blank experiment. Methane/ CO_2 conversions and H_2/CO yields increased with increasing temperature, and the highest initial methane conversion reaches 90% at 1223 K . This can be expected as both the methane reforming reaction and the char gasification reaction are endothermic. It is also notable that the methane conversion decreased rapidly in the first 30 min and then leveled off and maintained at a certain value. It has been reported that there are two routes for the formation of carbon deposits: one is CH_4 decomposition and the other is CO disproportionation. CO disproportionation is thermodynamically favored in the low-temperature region of $773\text{--}873 \text{ K}$ while CH_4 decomposition is favored in the high-temperature zone at $\sim 1173 \text{ K}$ [20]. In the experimental temperature range, CH_4 decomposition should be the dominant reaction for deactivation. The initial carbonaceous deposition from methane cracking on the coal char surface led to the decrease in catalytic activity; at the same time, the gasification reaction consumed some of the deposited carbon and produced fresh pore surface and new active sites. This helped to maintain the char activity at a higher level compared with methane cracking in which the deposited carbon accumulated and was not consumed. The trend of the H_2 yield was similar to that of the methane conversion; however, the CO_2 conversion rate and the CO yield remained relatively constant for each given temperature. Particularly, at 1223 K , both the CO_2 conversion rate and the CO yield reached almost 100% . It is also a proof of the concept of combined coal gasification and methane reforming that, while the coal char catalyzes the methane reforming reaction, the gasification of carbon takes place simultaneously and produces CO .

Figure 2. Conversion of gas reactants versus time during methane carbon dioxide reforming over bituminous coal char at different temperatures (CH_4 10%, CO_2 10%, N_2 80%, total flow rate 250 mL min^{-1}).

Table 2. Product yields versus time during methane reforming over the bituminous coal char at different temperatures. Reaction conditions: CH₄ 10 %, CO₂ 10 %, N₂ 80 %, total flow rate 250 mL min⁻¹.

Time [min]	H ₂ yield [%]				CO yield [%]			
	1223 K	1173 K	1123 K	1073 K	1223 K	1173 K	1123 K	1073 K
5	91.70	67.54	38.68	18.88	101.16	76.77	48.87	29.63
10	81.76	58.67	34.95	13.10	102.72	73.98	50.08	26.39
15	69.69	51.24	28.07	10.67	101.38	77.33	41.09	26.32
25	56.73	36.99	23.81	8.77	103.28	72.04	50.26	24.72
35	48.31	36.28	16.78	5.94	101.18	71.94	44.78	23.45
50	44.99	32.28	15.55	4.91	91.00	77.12	47.98	22.76
65	54.80	32.74	13.99	4.01	102.72	78.84	48.30	19.17
100	47.21	35.62	11.95	3.66	101.57	80.39	48.34	21.69
120	53.46	38.69	10.86	2.81	93.11	81.25	43.55	21.67

Tab. 3 shows the Brunauer-Emmett-Teller (BET) surface areas of the bituminous char samples after different exposure times. The surface area of the raw char was 213.09 m²g⁻¹; after 30 min and 2 h of exposure to a methane and CO₂ atmosphere at 1123 K, its surface area was more than doubled to 541.06 and 583.94 m²g⁻¹, respectively. The scanning electron microscopy (SEM) images taken for the raw char and the used chars as shown in Fig. 3 verify the BET surface area results: after a period of reaction, some new pores were created and fresh surface appeared. It can be seen that there are no obvious fluffy carbon deposits on the char surface. This can be attributed to the gasification reaction in Eq. (4), which is responsible for eliminating the deposited carbon and keeping the surface bright.

Table 3. BET surface areas of bituminous char samples after different residence times at 1123 K during the reaction of methane and carbon dioxide on coal char. Reaction conditions: CH₄ 10 %, CO₂ 10 %, N₂ 80 %.

Sample	Raw char	Sample after 30 min	Sample after 2 h
Surface area [m ² g ⁻¹]	213.09	541.06	583.94

Figure 3. SEM images of coal char samples. (a) Fresh coal char (treated in N₂ at 1173 K for 30 min, temperature increasing at 10 K min⁻¹), (b) coal char after 15 min of exposure to CH₄ and CO₂ reaction (CH₄ 10 %, CO₂ 10 %, N₂ 80 %, total flow rate 250 mL min⁻¹, 1123 K).

3.3 Steam Reforming of Methane over Coal Char

Steam reforming of methane and steam gasification of coal char are the two most important reactions in the combined coal gasification and methane reforming process. Fig. 4 and Tabs. 4 and 5 show the results of steam reforming of methane over a bed of the bituminous char expressed in terms of CH₄ conversion, H₂O conversion, H₂ yield, CO yield, and CO₂ yield, as a function of the reaction time at different temperatures. Compared with the results of steam reforming of methane over quartz, it is clear that the coal char exhibited a strong catalytic activity for methane steam reforming. High temperature favored the methane conversion and syngas (H₂, CO) yield, and CO₂ was not detected in the high-temperature range of 1173 and 1223 K. This is because the water-gas shift reaction is exothermic and high temperature favors the CO yield. At 1223 K, the initial methane conversion rate reached 80 %; meanwhile, both the H₂O conversion rate and the syngas yields reached almost 100 %. Moreover, CH₄ conversion remained at a higher level and did not decrease as much as in the case of methane CO₂ reforming, indicating that the coal char catalytic activity is relatively stable under steam atmosphere. It was measured that the rate of H₂O gasification of coal char (Eq. (5)) is generally faster than that of CO₂ gasification (Eq. (4)) under the present experimental conditions, with an activation energy of 223 kJ mol⁻¹ for Eq. (5) and 283 kJ mol⁻¹ for Eq. (4). Thus, it can be reasonably speculated that the deposited carbon on the char surface from methane cracking is consumed more easily under the H₂O atmosphere and that the gasification of char continuously regenerates the active centers, resulting in the high catalytic activity.

Figure 4. Conversion of gas reactants versus time during methane steam reforming over bituminous coal char at different temperatures (CH_4 10 %, H_2O 10 %, N_2 80 %, total flow rate 250 mL min^{-1}).

Table 4. H_2 yields versus time during methane reforming over bituminous coal char at different temperatures. Reaction conditions: CH_4 10 %, H_2O 10 %, N_2 80 %, total flow rate 250 mL min^{-1} .

Time [min]	H_2 yield [%]			
	1223 K	1173 K	1123 K	1073 K
5	84.17	80.83	57.13	44.80
10	94.07	81.87	57.13	43.63
15	94.28	84.08	57.27	41.04
25	85.32	72.88	61.08	38.43
35	85.41	69.33	53.40	38.97
50	87.84	70.38	48.64	37.55
65	74.54	75.57	50.79	35.03
100	82.62	65.27	47.71	34.59
120	81.15	68.89	49.41	34.48

Table 5. CO_x yields versus time during methane reforming over bituminous coal char at different temperatures. Reaction conditions: CH_4 10 %, H_2O 10 %, N_2 80 %, total flow rate 250 mL min^{-1} .

Time [min]	CO yield [%]				CO_2 yield [%]	
	1223 K	1173 K	1123 K	1073 K	1123 K	1073 K
5	82.89	72.56	37.76	20.46	7.65	3.31
10	95.10	92.76	37.76	26.65	8.54	17.59
15	98.35	90.56	46.92	25.16	11.81	22.99
25	97.67	77.60	57.37	25.31	12.77	26.50
35	100.00	76.06	51.86	32.65	14.18	22.74
50	98.87	84.67	54.03	26.78	12.87	19.65
65	96.63	89.20	53.53	25.83	11.71	25.95
100	93.55	75.18	51.07	24.57	13.80	17.54
120	93.30	86.32	53.50	25.04	15.34	23.99

3.4 Effect of the Coalification Degree on the Reforming Reaction

Many researchers agree with the hypothesis that the methane reforming reaction catalyzed by carbon materials occurs as a combination of CH_4 decomposition and gasification of the carbonaceous deposits by $\text{CO}_2/\text{H}_2\text{O}$ [18, 21]. The physical and chemical properties of the char that influence the catalytic activity and the causes of deactivation are presumably the same as those involved in methane cracking (Sect. 3.1).

The effect of the coalification degree on the catalytic activity of char was examined in CO_2 and steam reforming of methane at 1123 and 1223 K, and the results are shown in Figs. 5 and 6, respectively. It can be seen that the catalytic activity of char for CO_2 and steam reforming of methane follows the order of lignite > bituminous coal > anthracite, i.e., the younger the parent coal, the higher the catalytic activity of the char will be. The catalytic activities of carbon materials have been found to be

proportional to the concentration of oxygen surface groups, mainly the groups that desorbed as CO in temperature-programmed desorption (TPD) experiments [18, 22]. As is known, the low-rank coal lignite containing more amorphous carbon has a higher oxygen content, which possibly generates more oxygen surface groups on the char surface, and this will provide unsaturated atoms of carbon that can react with the CH_4 . With increasing coalification degree, the oxygen content decreases dramatically and the carbon structure becomes more ordered; therefore, the high energy sites decrease accordingly.

4 Conclusions

Coal char has significant catalytic activity for methane cracking and reforming with CO_2 or H_2O . In methane cracking, the catalytic activity of the char rapidly decreases due to carbonaceous deposition and active center blockage. The reforming experi-

Figure 5. CH₄ conversion versus time during methane carbon dioxide reforming over different coal chars. At (a) 1123, (b) 1223 K (CH₄ 10 %, CO₂ 10 %, N₂ 80 %, total flow rate 250 mL min⁻¹).

Figure 6. CH₄ conversion versus time during methane steam reforming over different coal chars. At (a) 1123 K, (b) 1223 K (CH₄ 10 %, H₂O 10 %, N₂ 80 %, total flow rate 250 mL min⁻¹).

ments demonstrate that the process is more likely to follow the succession of CH₄ decomposition/gasification regeneration cycles. That is, in CO₂ or H₂O reforming, while the coal char catalyzes the methane decomposition reaction, the gasification of deposited carbon and char also takes place simultaneously. The carbon-consuming gasification reaction contributes to the resistance to carbonaceous deposition, thus maintaining the catalytic activity of the char for the reforming reaction, especially for the case of steam gasification. Furthermore, it was also found that char from the low-rank parent coal has a higher catalytic activity in the methane cracking and reforming reaction, due to the different carbon structure and surface chemistry.

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Symbols used

X	[-]	conversion rate
Y	[-]	yield
C	[-]	volume concentration of a gas component
V	[mL min ⁻¹]	gas flow rate

Sub-/superscripts

in	inlet stream
out	outlet stream

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