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## Hydrogen production by methane cracking over different coal chars

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### ABSTRACT

Hydrogen production by methane cracking over a bed of different coal chars has been studied using a fixed bed reactor system operating at atmospheric pressure and 1123 K. The chars were prepared by pyrolysing four parent coals of different ranks, namely, Jincheng anthracite, Binxian bituminous coal, Xiaolongtan lignite and Shengli lignite, in nitrogen in the same fixed bed reactor operating at different pyrolysis temperatures and times. Hydrogen was the only gas-phase product detected with a GC during methane cracking. Both methane conversion and hydrogen yield decreased with increasing time on stream and pyrolysis temperature. The lower the coal rank, the greater the catalytic effect of the char. While the Shengli lignite char achieved the highest methane conversion and hydrogen yield in methane cracking amongst all chars prepared at pyrolysis temperature of 1173 K for 30 min, a higher catalytic activity was observed for the Xiaolongtan lignite char prepared at 973 K, indicating the importance of the nature of char surfaces. The catalytic activity of the coal chars were reduced by the carbon deposition. The coal chars had legible faces and sharp apertures before being subjected to methane cracking. The surfaces and pores of coal chars were covered with carbon deposits produced by methane cracking as evident in the SEM images. The results of BET surfaces areas of the coal chars revealed that the presence of micropores in the chars was not an exclusive reason for the catalytic effect of the chars in methane cracking.

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### 1. Introduction

The use of coal-bed methane (CBM) as a feedstock for hydrogen production presents an alternative pathway for utilization of the huge but largely un-tapped CBM resources. In a series of recent studies involving the present authors, hydrogen has proven to be the primary gas-phase product in methane cracking over coal chars [1]. Compared with the conventional hydrogen production methods using natural gas as a feedstock such as steam methane reforming (SMR), auto-thermal reforming (ATR) and partial oxidation reforming (POR) [2], cracking of coal-bed methane has many advantages in terms of process economy [3] as it can be easily integrated with existing coal conversion operations, avoiding the use of expensive metal catalysts and of course, eliminating the need of expensive new infrastructure. A detailed comparison of methane cracking and steam reforming reactors in hydrogen production showed that methane cracking can save about 40% of the unit energy consumption [4,5].

Many literature reports have focused on the catalytic decomposition of methane over transition metals, such as Ni, Fe, Co, which can be easily deactivated by carbon deposition [6]. Recently, the carbon-based catalysts for decomposition of methane to produce hydrogen were proposed. Muradov [7] investigated several types of carbon including activated carbon, carbon black, graphite, diamond, carbon fibers and carbon nanotubes as catalysts for methane cracking in a fixed bed reactor. It was shown that the best catalyst is the activated carbon prepared at 1123 K. The methane conversion over the carbon materials is much lower than that on the metal catalysts, but the use of carbon-based catalysts offers other advantages: being tolerant to sulfur and high temperatures, production of marketable byproduct carbon and no need of catalyst regeneration process [8]. Muradov et al. [7,8] considered that the carbon-based catalytic methane cracking can also produce valuable carbon byproduct, which can be used in several applications such as structural materials, power generation, soil amendment and environmental remediation [9]. Lee et al. [10] used carbon blacks as catalysts for methane decomposition with CO<sub>2</sub>-free hydrogen production which showed more stable catalytic activity and lower activation energies than activated carbons. Methane cracking studies have been performed over a bed of coal

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char in a laboratory-scale fluidized-bed [11] and a fixed bed reactor at temperatures ranging from 1073 K to 1273 K [1,12–15]. It has been demonstrated that the chars, rather than the ash, exert the catalytic effect on methane cracking [1]. Both the methane conversion and hydrogen yield increase with increasing reaction temperature but decrease with time on stream, indicating that the chars are deactivated with the exposure to methane cracking [1]. It has been shown [1,12–15] that the methane cracking over coal chars has a reaction order of 0.5 and the activation energies from 89 to 105 kJ mol<sup>-1</sup> which is lower than the methane C–H bond dissociation energy about 440 kJ mol<sup>-1</sup>. However, the mechanisms of methane cracking over the coal chars and the char deactivation have not been fully understood. The present work studied methane cracking on different coal chars with an aim to explain the changes in the catalytic activity of different coal chars for methane cracking and to speculate the mechanism of methane cracking.

## 2. Experimental

Four Chinese coals of different coal ranks were used in this work. They were Jincheng anthracite, Binxian bituminous coal, Xiaolongtan lignite and Shengli lignite. Each coal was crushed and sieved to a size fraction of 0.355–0.63 mm. Chars were prepared by devolatilising the coal samples, respectively, in nitrogen in a fixed bed reactor operating under different conditions: (i) a coal was placed in the reactor and heated at 30 K/min to a final temperature of 1173 K and maintained at the final temperature for 30 min; (ii) for Xiaolongtan lignite, char samples were also prepared at 1173 K for different pyrolysis times of 30 min, 60 min, 120 min and 240 min, respectively; (iii) Xiaolongtan lignite chars were also prepared at different final temperatures of 973 K, 1073 K, 1173 K and 1273 K for 30 min. Table 1 presents the proximate analysis data of the parent coals and their various chars and Table 2 shows the ash analysis data of the four coals.

The apparatus used in this study is schematically shown in Fig. 1. The fixed bed reactor was made of quartz which has a diameter of 25 mm (i.d.) and a height of 620 mm. In an experiment, the reactor was placed in an electrically heated furnace. A thermocouple with a quartz sheath was inserted into the coal (in pyrolysis) or char (in methane cracking) bed in the reactor to monitor the temperature. The flow rates of methane and nitrogen were controlled with mass flow controllers (MFC) being mixed and fed into the

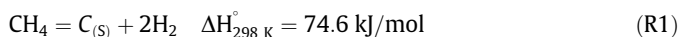
reactor. The gases used in this study were of the high purity analytical grade (>99.99%).

In a methane cracking experimentation, 10 g of a char was weighed and added to the fixed bed reactor, which was connected to a N<sub>2</sub> supply at a constant flow rate of 160 ml/min to prevent char oxidation. When the temperature reached the preset temperature for methane cracking, the gas was switched from N<sub>2</sub> to a CH<sub>4</sub>/N<sub>2</sub> mixture with a the total flow rate was 200 ml/min. All methane cracking experiments were performed at 1123 K unless specified otherwise.

The exit stream was analysed using a gas chromatograph (GC-14C) fitted with a thermal conductivity detector (TCD).

The surface structures of selected chars before and after being subjected to methane cracking were also examined using a NOVA NANO SEM 430 scanning electronic microscope (FEI, USA). The specific surface area and pore structure properties were determined using a TriStar 3000 physical adsorption apparatus using N<sub>2</sub> adsorption at 77 K.

Ideally, the methane cracking follows the reaction (R1) below:



The conversion of methane can be calculated using the following equation:

$$X_{\text{CH}_4} = \frac{V_{\text{in}}C_{\text{CH}_4,\text{in}} - V_{\text{out}}C_{\text{CH}_4,\text{out}}}{V_{\text{in}}C_{\text{CH}_4,\text{in}}} \quad (1)$$

and the hydrogen yield can be expressed as:

$$Y_{\text{H}_2} = \frac{V_{\text{out}}C_{\text{H}_2,\text{out}}}{2V_{\text{in}}C_{\text{CH}_4,\text{in}}} \quad (2)$$

The balance of hydrogen was used to check the quality of the experimental data and can be calculated according to:

$$\text{Ratio} = \frac{V_{\text{out}}(2C_{\text{H}_2,\text{out}} + 4C_{\text{CH}_4,\text{out}})}{4V_{\text{in}}C_{\text{CH}_4,\text{in}}} \quad (3)$$

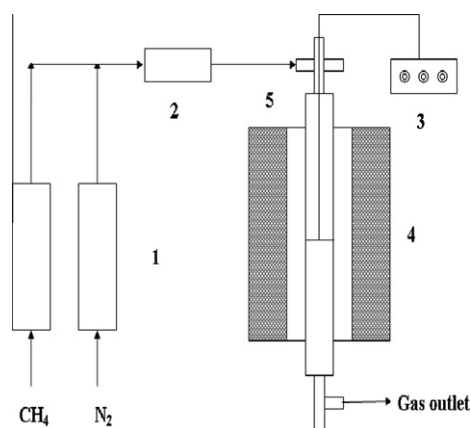
where “V” is the total volumetric flow rate, “C” is the concentration of CH<sub>4</sub> or H<sub>2</sub> and the subscripts “in” and “out” refer to the reactor inlet and outlet conditions, respectively. The flow rate at the exit of the reactor was determined using a soap bubble flowmeter.

**Table 1**  
Proximate analysis results of the parent coals and their chars prepared at 1173 K for 30 min.

Sample	Proximate analysis				Ultimate analysis				
	Moist (% ad)	VM	FC (% db)	Ash	C	H	S (% db)	N	O
Shengli coal	9.1	33.0	35.0	32.0	47.6	2.8	1.0	0.8	15.8
Shengli char	3.3	1.4	51	47.6	48.3	1.0	0.7	0.6	1.8
Xiaolongtan coal	24.8	51.6	26.7	21.7	52.8	2.4	1.7	1.3	20.1
Xiaolongtan char	1.7	3.4	53.3	43.3	64.8	1.3	2.2	0.7	3.2
Binxian coal	2.5	25.0	64.6	10.4	71.7	4.0	0.5	0.4	13.0
Binxian char	0.4	1.3	85.0	13.7	78.4	1.1	0.3	0.8	1.0
Jingcheng coal	1.3	9.5	68.1	22.4	69.6	2.8	1.1	0.9	3.1
Jingcheng char	0.4	0.9	74.6	24.5	65.9	1.0	1.3	0.7	1.0

**Table 2**  
Ash analysis data of the parent coals.

Sample	SiO <sub>2</sub> (%)	Al <sub>2</sub> O <sub>3</sub> (%)	Fe <sub>2</sub> O <sub>3</sub> (%)	CaO (%)	MgO (%)	TiO <sub>2</sub> (%)	SO <sub>3</sub> (%)	K <sub>2</sub> O (%)	Na <sub>2</sub> O (%)	P <sub>2</sub> O <sub>5</sub> (%)
Shengli	22.61	10.71	8.91	23.15	11.98	0.16	21.38	0.32	0.74	0.12
Xiaolongtan	11.40	36.22	9.34	28.71	1.40	1.24	10.04	0.68	0.08	0.82
Binxian	40.07	19.26	10.43	16.14	0.91	0.67	10.47	0.52	0.34	0.60
Jincheng	41.14	29.99	11.08	9.26	1.33	0.81	4.56	0.46	0.51	0.16

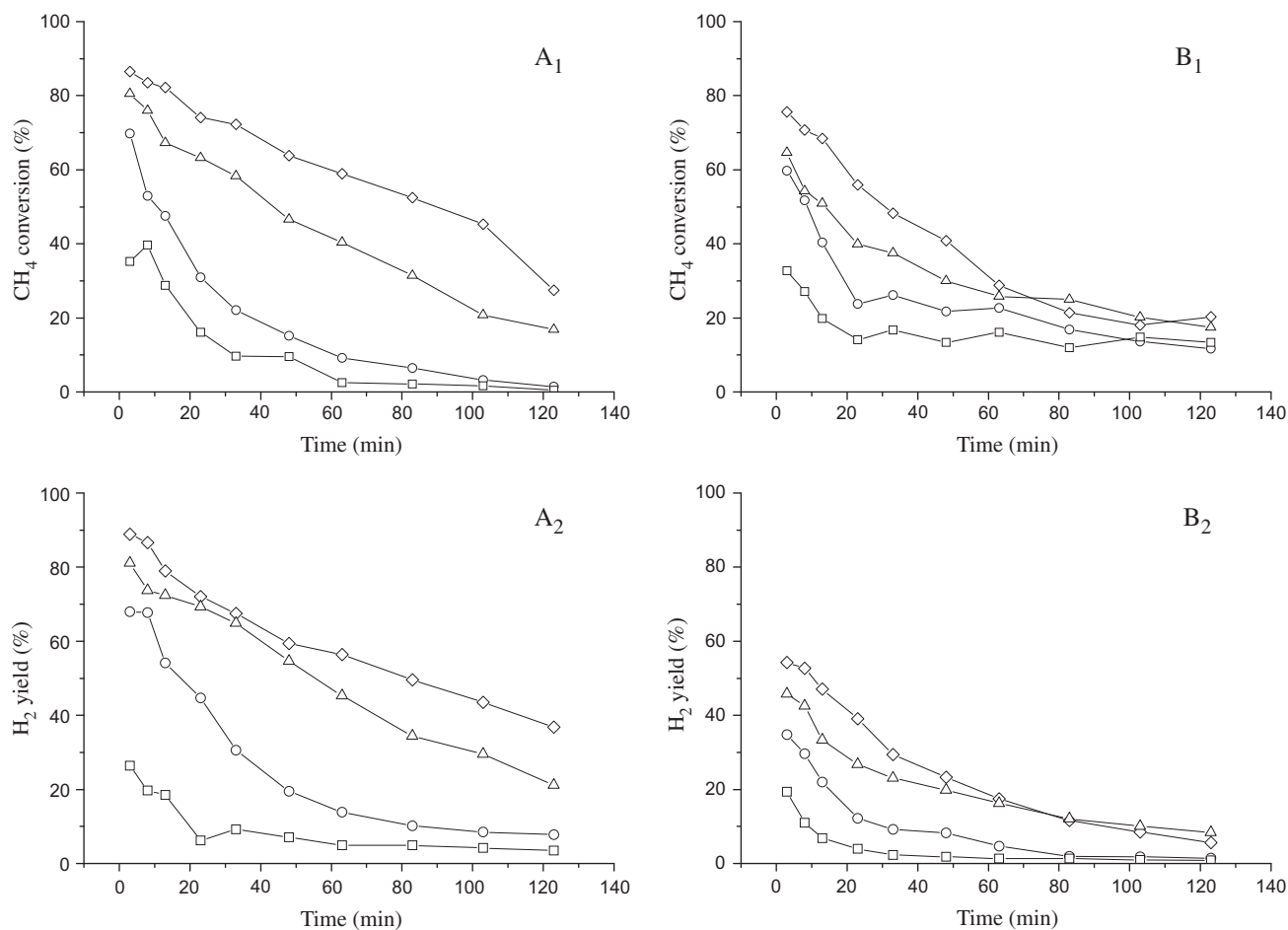


**Fig. 1.** A schematic diagram of the experimental system: (1) mass flow controllers, (2) mixing chamber, (3) temperature controller, (4) electrically heated furnace and (5) quartz tube reactor.

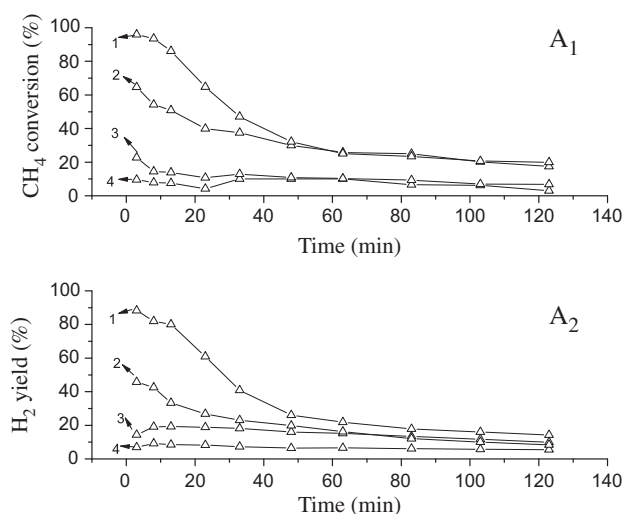
### 3. Results and discussion

In a blank experiment using a bed of quartz particles, also in the size fraction of 0.355–0.63 mm, the conversion of methane at 1123 K was negligible. This is in agreement with a previous report [14], suggesting that the temperature was not high enough to provoke thermal decomposition of methane and a catalyst would

be needed. Fig. 2 shows that the methane conversions ( $A_1$ ,  $B_1$ ) and hydrogen yields ( $A_2$ ,  $B_2$ ) of methane cracking over the different coal chars with two mixtures of 5%  $\text{CH}_4$  in  $\text{N}_2$  ( $A_1$ ,  $A_2$ ) and 20%  $\text{CH}_4$  in  $\text{N}_2$  ( $B_1$ ,  $B_2$ ), respectively. For all of the chars, the methane conversion was higher for the experiments with the mixture of 5%  $\text{CH}_4$  in  $\text{N}_2$  and than with the mixture of 20%  $\text{CH}_4$  in  $\text{N}_2$  and was as high as 86% over the Shengli lignite char at 1123 K. Hydrogen was the only gas phase product detected in the experiments. It is certain that the chars do exert a catalytic effect on methane cracking and the catalytic activity is dependent on the type of the char. Fig. 2 shows that the most active char is the Shengli lignite char, and the least active char is the Jincheng anthracite char among the chars prepared from the four types of coals. It is clearly seen from Fig. 2A<sub>1</sub> and B<sub>1</sub> that the methane conversions over all types of the chars also decreased with increasing time on stream. The catalytic effect of the char, as reflected by the methane conversion level, reduced very rapidly with time on stream, indicating rapid deactivation of the chars due to carbon deposition [1,14,15]. Fig. 2A<sub>2</sub> and B<sub>2</sub> display the results of hydrogen yields over the different coal chars at the same reaction temperature. Clearly, the hydrogen yields also decreased with the time on stream. It is evident that the methane conversion and hydrogen yield increased with a decrease in the rank of the parent coal. The catalytic activity of these four chars follow the order of Jincheng anthracite char < Binxian bituminous char < Xiaolongtan lignite char < Shengli lignite char. Note that between the two lignites, Shengli lignite has a higher ash and Fe contents, which may have contributed to the slightly higher catalytic activity of its



**Fig. 2.** Methane conversions (upper figures) and hydrogen yield (lower figures) over a bed of 10 g of various types of coal chars:  $\diamond$  Shengli lignite char;  $\Delta$  Xiaolongtan lignite char;  $\circ$  Binxian bituminous char;  $\square$  Jincheng anthracite char. Experimental conditions: (A) 5%  $\text{CH}_4$  and 95%  $\text{N}_2$ ; and (B) 20%  $\text{CH}_4$  and 80%  $\text{N}_2$ ;  $T = 1123$  K; and the total flow rate 200 ml/min.



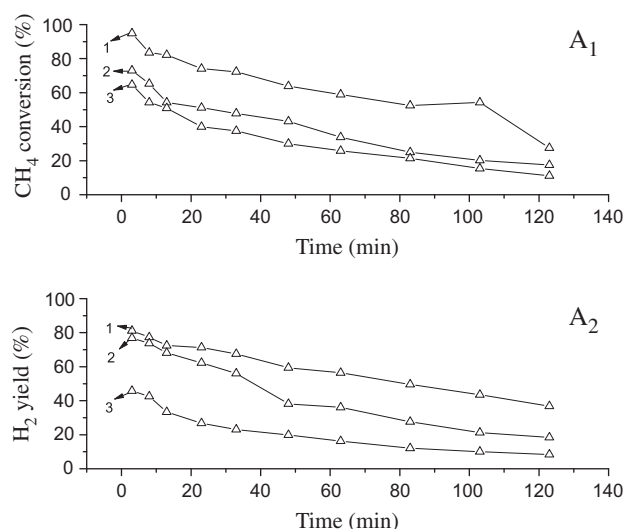
**Fig. 3.** Methane conversions and hydrogen yields over the Xiaolongtan char prepared at 1173 K for 30 min at different methane cracking temperatures: line 1: 1273 K, line 2: 1123 K, line 3: 973 K, and line 4: 873 K. Experimental conditions:  $\text{CH}_4:\text{N}_2 = 1:4$ , the total flow rate: 200 ml/min.

char towards methane cracking than the Xiaolongtan lignite char. Given everything else being equal, the lower the coal rank, the greater the catalytic activity in methane cracking [1,14,15]. The higher Fe contents in the two lignite chars may have played a minor role in their higher catalytic activity in methane cracking than the bituminous and anthracite coal chars. However, considering the very low levels of methane conversion (<2.5%) in cracking over the Binxian coal ashes (prepared by combusting the coal in air and gasifying the coal in steam, respectively) [1], neither the ash, nor its Fe content, is the main reason for the observed difference in the catalytic activity of the four different coal chars.

Fig. 3 displays the results of methane conversions and corresponding hydrogen yields at different reaction temperatures over the Xiaolongtan char prepared at 1173 K for 30 min. It is seen that the initial methane conversion and hydrogen yield increased sharply with increasing reaction temperature. Note that the highest initial methane conversion of 96% and hydrogen yield of 88.3% were achieved at 1273 K and the least initial methane conversion and hydrogen yield were obtained at 873 K, at about 9.5% and 7%, respectively.

The methane conversion and hydrogen yield over a char decreased with an increase in methane concentration in the feed stream, as shown in Fig. 4. The highest methane conversion was about 95% for the mixture of 5%  $\text{CH}_4$  and 95%  $\text{N}_2$ . The corresponding hydrogen yield was about 81%. The lower the methane concentration, the higher the methane conversion and hydrogen yield. This observation suggests that methane cracking over the char is a surface reaction and becomes more dependent on the diffusion of methane from the gas phase to the char surface as the methane concentration increases.

Although the catalytic effect of the chars on methane cracking has been ascertained, it is not known if the pyrolysis time and temperature in the char preparation would alter the catalytic activity of the char. For this reason, different Xiaolongtan lignite chars were prepared for various pyrolysis times at 1173 K and at different temperatures for 30 min, and their effects on the methane conversion and hydrogen yield at a constant temperature of 1123 K were examined. The results are presented in Fig. 5. Fig. 5A<sub>1</sub> and A<sub>2</sub> show the methane conversions and hydrogen yields, respectively, at 1123 K over the Xiaolongtan chars prepared with the different pyrolysis times (30, 60, 120 and 240 min, respectively) at 1173 K.

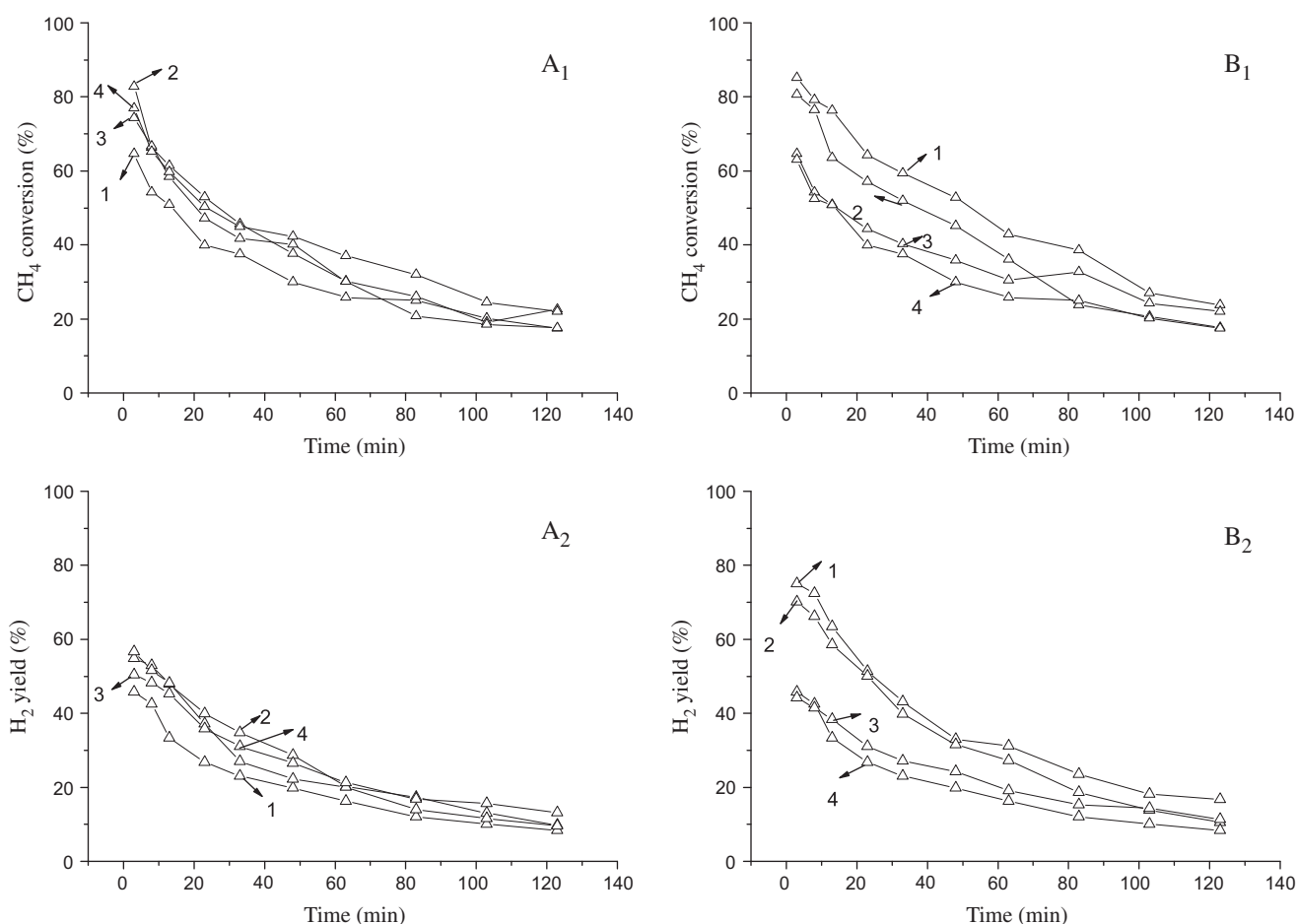


**Fig. 4.** Methane conversions and hydrogen yields over the Xiaolongtan char prepared at 1173 K for 30 min with different methane concentrations: line 1: 5%  $\text{CH}_4 + 95\% \text{N}_2$ , line 2: 10%  $\text{CH}_4 + 90\% \text{N}_2$ , and line 3: 20%  $\text{CH}_4 + 80\% \text{N}_2$ . Experimental conditions:  $T = 1123 \text{ K}$ ; the total flow rate 200 ml/min.

The results do not show a profound trend in the effect of the pyrolysis time and the observed methane conversions and hydrogen yields were within a relatively narrow range (Fig. 5A<sub>1</sub> and A<sub>1</sub>). Perhaps varying the pyrolysis time from 30 to 240 min at 1173 K did not cause sufficient changes in the char surface properties to show a clear trend of the effect of the pyrolysis time. In order to gain an insight into why the effect of the pyrolysis time did not show an emerging trend, these chars were analysed for the BET surface areas and pore properties with the results presented in Table 3. It can be seen that, indeed, for pyrolysis times between 30 and 240 min at 1173 K, the BET surface areas and pore properties did not incur significant changes.

Fig. 5B<sub>1</sub> and B<sub>2</sub> present the methane conversions and corresponding hydrogen yields over the different Xiaolongtan coal chars prepared at different pyrolysis temperatures (973, 1073, 1173 and 1273 K, respectively) for 30 min. It can be seen that the initial methane conversion increased with decreasing pyrolysis temperature. The trend of hydrogen yield is similar to that of methane conversion. These results imply that the low pyrolysis temperature of the char induced a high char catalytic activity for the methane cracking, while the BET surface areas and the pore properties did not show great variations due to the different pyrolysis temperatures employed in the present study (Table 3). It is therefore speculated that it is not just the char surface area and pore structure but also the chemical nature of the char surface (e.g. the surface functional groups) that have played a key role in the catalytic effect on methane cracking. It is also deduced that the stability of the surface functional groups is more dependent on the temperature, rather than the pyrolysis time at a given temperature, which explains why there was not a clear trend in the effect of pyrolysis time as shown in Fig. 5A<sub>1</sub> and A<sub>2</sub>. Identification of the surface functional groups on the char surfaces and their role in the methane cracking is beyond the scope of the present work but certainly warrants further investigation.

Methane cracking involves carbon deposition. The char characteristics before and after being subjected to methane cracking at 1123 K with a mixture of  $\text{CH}_4:\text{N}_2 = 1:4$  for 123 min were analyzed using SEM imaging. Significant carbon deposition was found on the chars after methane cracking as shown in Fig. 6. The chars before methane cracking (A–D) have clear surface with sharp edges. The Shengli (A) and Xiaolongtan (B) lignite chars have abundant pores



**Fig. 5.** Methane conversions and hydrogen yields over the different Xiaolongtan lignite chars. (A) Effect of pyrolysis time in the chars preparation at the constant temperature of 1173 K; line 1: 30 min, line 2: 60 min, line 3: 120 min, line 4: 240 min; (B) effect of pyrolysis temperature in the char preparation; line 1: 973 K, line 2: 1073 K, line 3: 1173 K, line 4: 1273 K. Experimental conditions:  $T = 1123$  K,  $\text{CH}_4/\text{N}_2 = 1:4$ , total flow rate 200 ml/min.

**Table 3**

Variations in the surface properties of the different Xiaolongtan lignite chars.

	Pyrolysis time at 1173 K			
	30 min	60 min	120 min	240 min
Total surface area ( $\text{m}^2/\text{g}$ )	212.2	221.6	222.1	221.9
Micropore area ( $\text{m}^2/\text{g}$ )	167.8	189.1	186.3	185.6
Total pore volume ( $\text{cm}^3/\text{g}$ )	0.131	0.147	0.143	0.142
Micropore volume ( $\text{cm}^3/\text{g}$ )	0.074	0.088	0.082	0.080
Average pore diameter (nm)	2.4	2.3	2.3	2.3
	Pyrolysis temperature for 30 min			
	973 K	1073 K	1173 K	1273 K
Total surface area ( $\text{m}^2/\text{g}$ )	219.3	223.8	212.2	201.1
Micropore area ( $\text{m}^2/\text{g}$ )	187.7	195.5	167.8	141.2
Total pore volume ( $\text{cm}^3/\text{g}$ )	0.124	0.124	0.131	0.137
Micropore volume ( $\text{cm}^3/\text{g}$ )	0.087	0.091	0.074	0.066
Average pore diameter (nm)	2.3	2.2	2.4	2.7

and the surfaces are very rough and floppy, with the Shengli lignite char being more porous which explains why Shengli lignite char incurred a high catalytic activity in methane cracking than the Xiaolongtan lignite char. The Binxian bituminous char image (C) clearly shows that the surface had experienced a liquid phase or “plastic” transformation during the pyrolysis, characteristic of bituminous coal. The surface is smooth with random cracks and pores. The Jincheng anthracite char (D) is the least porous amongst all types of chars and its surface is very rigid. Comparing the surface structures of the four chars, the roughness and porosity

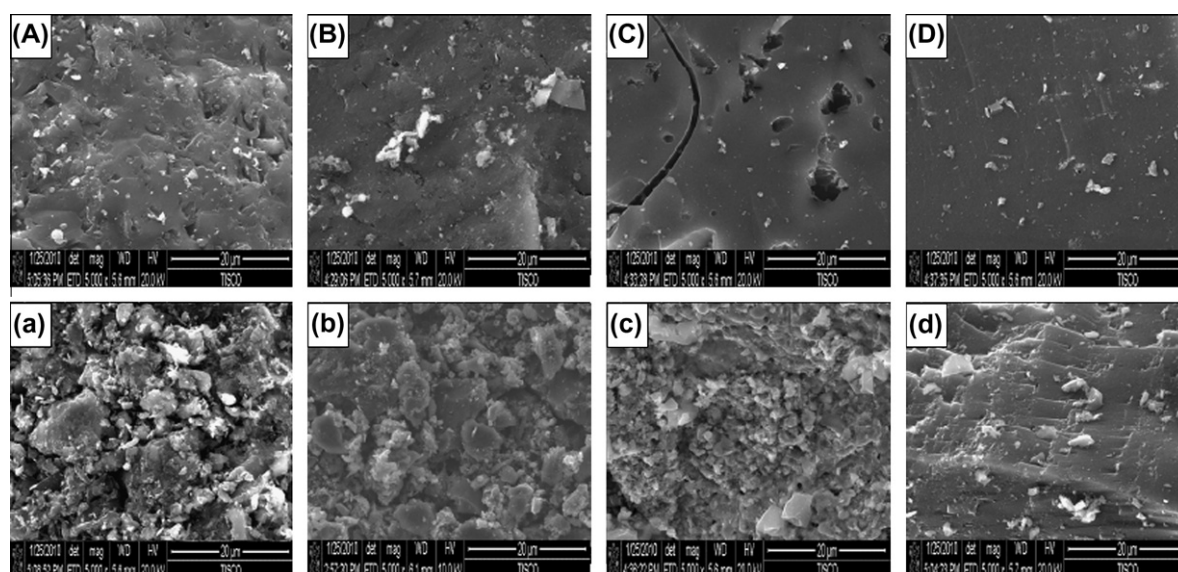
clearly follow the order of Jincheng anthracite char < Binxian bituminous char < Xiaolongtan lignite char < Shengli lignite char, which corresponds to the order of their catalytic effect on methane cracking as observed in Fig. 2. Clearly, the surface area and porosity is a factor in determining the char activity in methane cracking.

The images (a–d) of all the chars after being subjected to methane cracking for 123 min at 1123 K clearly show that the char surfaces were covered with varying degree of carbon deposition in accordance with the char catalytic activity in methane cracking.

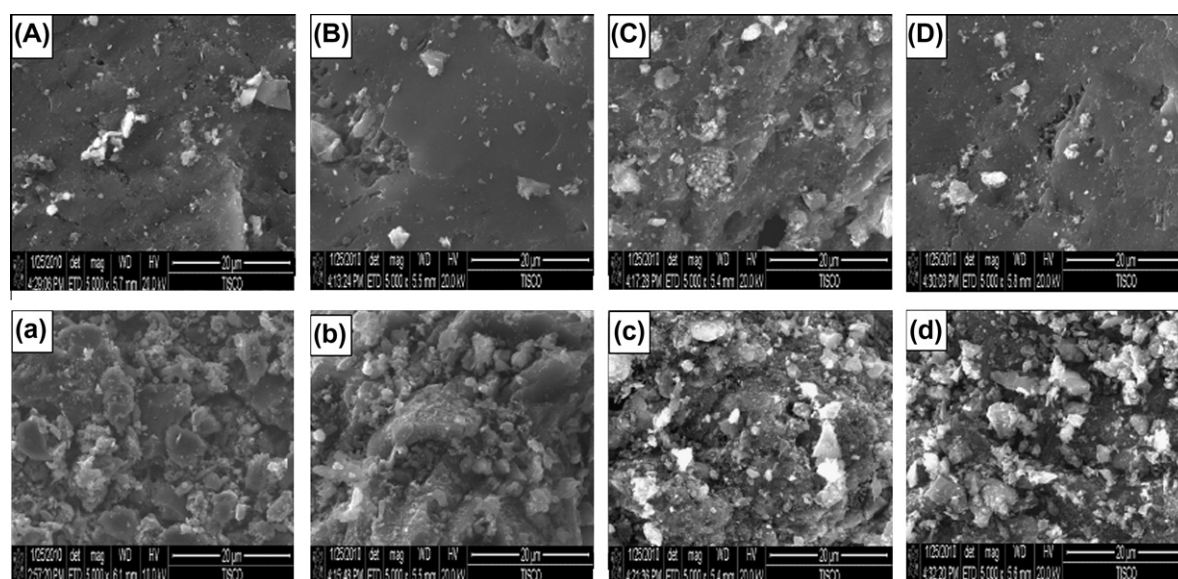
Fig. 7 presents the SEM images of the Xiaolongtan lignite chars prepared with different pyrolysis time, before and after being subjected to methane cracking at 1123 K. From these SEM images, it can be seen that the fresh chars have clean surfaces and sharp-edged porous structures. It is also evident that varying the pyrolysis time from 30 to 240 min induced some but insignificant differences in the char surfaces. This explains the less profound effect of pyrolysis time on the catalytic activity in methane cracking as observed in Fig. 5. The surfaces of chars after being subjected to methane cracking are covered with carbon deposits from the methane cracking. The brighter appearance of the carbon deposits on the chars is seen on the SEM images. It is clear that the deactivation of the chars can be attributed to carbon deposition following methane cracking.

Fig. 8 shows the SEM images of the Xiaolongtan lignite chars prepared at different final pyrolysis temperatures, before and after being subjected to methane cracking. Again, it can be seen that the fresh chars have obvious porous structures and the chars after being subjected to methane cracking are covered with carbon





**Fig. 6.** SEM images of various chars before (A–D) and after (a–d) being subjected to methane cracking for 123 min (A and a: Shengli lignite char; B and b: Xiaolongtan lignite char; C and c: Binxian bituminous char; D and d: Jincheng anthracite char. All chars were prepared at 1173 K for 30 min). Experimental conditions:  $\text{CH}_4:\text{N}_2 = 1:4$ ,  $T = 1123$  K; and the total flow rate 200 ml/min.



**Fig. 7.** SEM images of Xiaolongtan lignite chars before (A–D) and after (a–d) being subjected to methane cracking 123 min on chars prepared with different pyrolysis times at 1123 K (A and a: time 30 min, B and b: time 60 min, C and c: time 120 min, D and d: time 240 min). Experimental conditions:  $\text{CH}_4:\text{N}_2 = 1:4$ ,  $T = 1123$  K; and the total flow rate 200 ml/min.

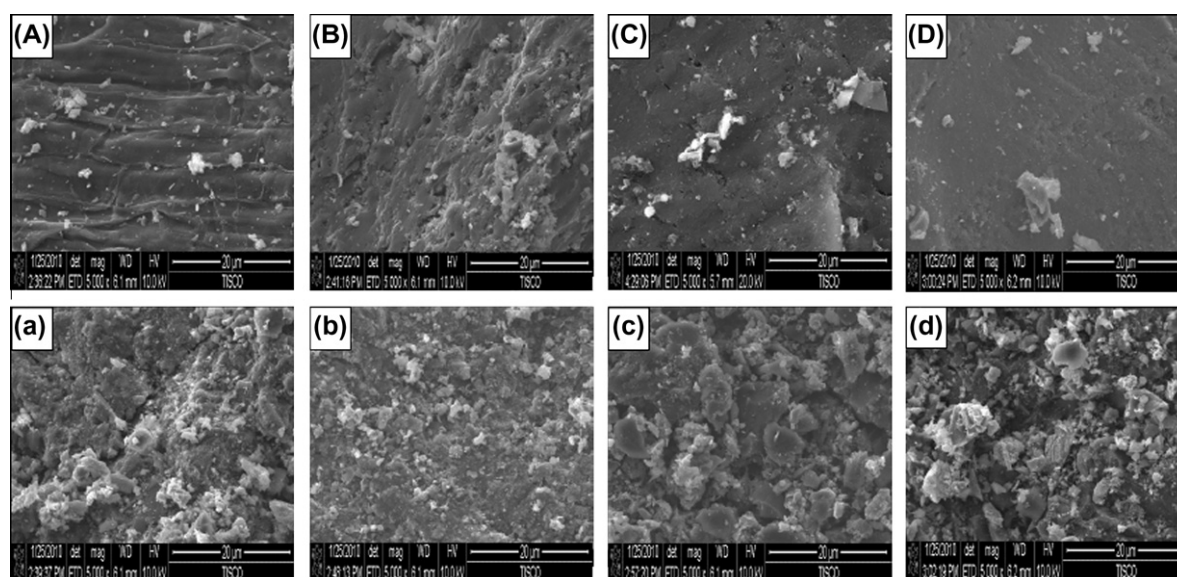
deposits on the surfaces. It is evident that the fresh chars prepared at 973 K have abundant pores and clear porous structure, while the coal chars prepared at 1173 K and 1273 K have lower total surface areas and micropore areas than the chars prepared at 973 K. This observation is consistent with the BET surface area and porosity analyses of the chars as shown in Table 3 and also supported by the trend of methane cracking as shown in Figs. 3 and 5. These observations suggest that the methane cracking is not only related to the physical nature of the surface (including the total surface area, micropore area, and total pore volume), but also depends on the chars' surface functional groups.

Table 4 shows that surface areas and pore properties of the Xiaolongtan lignite char prepared at 1173 K for 30 min, before and after the methane cracking with different times on stream (15 min, 1 h and 2 h). The total surface areas and micropore areas

after methane cracking decreased with time on stream. This explains the methane conversion and hydrogen yield, and therefore, the catalytic effect of the char, decreased with increasing the time on stream as shown in Figs. 2–5. This also explains that the differences in the methane conversions and in the hydrogen yields for different chars became less significant with increasing times on stream as the char surface was covered with more carbon from methane cracking.

#### 4. Conclusion

Methane cracking over different coal chars in a fixed bed reactor has been studied. The chars have a profound catalytic effect on the methane cracking, with the catalytic activity varying with different



**Fig. 8.** SEM images of Xiaolongtan lignite chars before (A–D) and after (a–d) being subjected to methane cracking for 123 min on coal chars prepared at the different final pyrolysis temperature (A and a: 973 K, B and b: 1073 K, C and c: 1173 K, D and d: 1273 K). Experimental conditions:  $\text{CH}_4/\text{N}_2 = 1:4$ ,  $T = 1123 \text{ K}$ ; and the total flow rate 200 ml/min.

**Table 4**

Variations in the surface properties of the Xiaolongtan lignite chars before and after being subjected to methane decomposition at 1123 K for different times.

Sample	Xiaolongtan lignite char	After reaction for 15 min	After reaction for 1 h	After reaction for 2 h
Total surface area ( $\text{m}^2/\text{g}$ )	214.5	75.4	42.4	7.2
Micropore area ( $\text{m}^2/\text{g}$ )	170.0	40.3	17.6	1.5
Total pore volume ( $\text{cm}^3/\text{g}$ )	0.134	0.074	0.052	0.026
Micropore volume ( $\text{cm}^3/\text{g}$ )	0.079	0.018	0.008	0.001
Average pore diameter (nm)	2.5	3.9	4.9	14.3

types of coal chars. The catalytic activity of char in methane cracking decreases with increasing coal rank, with the Shengli lignite char being the most active and the Jincheng anthracite char being the least active. Methane conversion and hydrogen yield decrease with the time on stream as the coal char becomes deactivated and the carbon deposition from methane cracking is primarily responsible for the loss of catalytic activity of the chars with the time on stream. The methane cracking is a surface reaction controlled by the gas phase diffusion and therefore is influenced by both reaction temperature and methane concentration. The methane conversion increases with increasing temperature and decreasing methane concentration. The catalytic effect of char decreases with increasing pyrolysis temperature in the char preparation but is less affected by the pyrolysis time indicating that the catalytic activity depends not only on the porous structures but also on the chemical nature of the char surface.

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