

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 CO₂-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⁻¹ which is lower than the methane C–H bond dissociation energy about 440 kJ mol⁻¹. 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

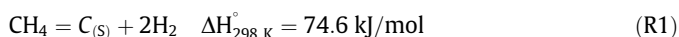
reactor. The gases used in this study were of the high purity analytical grade (>99.99%).

In a methane cracking experimentation, 10 g of a char was weighed and added to the fixed bed reactor, which was connected to a N₂ 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 N₂ to a CH₄/N₂ 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 N₂ 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 CH₄ or H₂ 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 ₂ (%)	Al ₂ O ₃ (%)	Fe ₂ O ₃ (%)	CaO (%)	MgO (%)	TiO ₂ (%)	SO ₃ (%)	K ₂ O (%)	Na ₂ O (%)	P ₂ O ₅ (%)
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

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