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Effect of catalysts on the reactivity and structure evolution of char in petroleum coke steam gasification

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HIGHLIGHTS

- The effect of catalysts on petroleum coke reactivity in steam gasification was tested.
- Raman spectra and X-ray spectra analyzed the evolution of aromatic and crystallite structure of petroleum coke.
- The mechanism of catalytic gasification of petroleum coke was explored in depth.

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ABSTRACT

Petroleum coke was gasified using non-isothermal thermogravimetric analysis (TGA). The catalytic effects of $FeCl_3$, $CaCl_2$, KCl, K_2CO_3, K_2SO_4, KAC and KNO_3 were studied. It was found that the gasification of petroleum coke was inefficient at temperature <1000 °C. However, with the addition of catalysts, the efficiency greatly improved. In particular, with the addition of K_2CO_3, gasification was completed quickly in 10 min and the final temperature was about 900 °C. To further uncover the catalytic mechanism, the structures of char samples at various conversions were investigated with Raman spectra (Raman) and X-ray diffractometry (XRD). The Raman spectra showed that with K_2CO_3 catalyst, the formation of active intermediates C(O) and M–C–O were enhanced by the relatively small aromatic ring systems with 3–5 fused benzene rings, alkyl–aryl C–C structures and methyl carbon dangling onto an aromatic ring. K_2CO_3 could stimulate the crackdown of big aromatic ring systems into small aromatic ring systems. Thereby, the addition of K_2CO_3 could increase the steam gasification rate of petroleum coke. XRD analysis indicated that with char conversion increasing, char structure became more ordered with a large amount of aromatic ring formed in original samples, while the degree of graphitization was lowered with K_2CO_3 addition, which is favorable for char gasification.

1. Introduction

Petroleum coke is a byproduct of crude oil refining. In 2011, nearly 17 million tons of petroleum coke were produced, a 14.65% increase over the previous year [1]. The efficient use of petroleum coke for energy resource is strongly encouraged. Gasification is a promising technology and an attractive option, since it provides high quality fuel gases [2,3]. Particularly, steam gasification is an important technology of producing H_2-rich gas product from petroleum coke [3]. In order to obtain H_2-rich gas, high reactivity and high conversion of char are essential. The char conversion directly depends on the reactivity of char with gasifying agents (H_2O, CO_2 etc.). However, low reactivity remains an important obstacle for utilizing petroleum coke through gasification, due to the compactness of carbon structure, low volatile and low ash content [4,5]. Therefore, it is critical to improve the gasification reactivity of petroleum coke.

Many researchers have shown that gasification can be greatly enhanced by various metal compound catalysts (K, Na, Ca, Mg, Ba, Fe, Ni, etc.) [6–11]. Meanwhile, K-based catalysts could increase hydrogen production from steam gasification of petroleum coke [12,13]. It can be observed that the addition of catalysts, such as alkali (K), alkaline earth (Ca) and transition metal (Fe) can significantly improve the gasification reactivity of petroleum coke. Therefore, it is important to study the effects of various catalysts on steam gasification of petroleum coke.

Some researchers have recently reported the catalytic mechanism of the gasification reaction. They believed that there were some active intermediates in the gasification process, such as C(O) (active intermediates of carbon matrix) and M–C–O (active intermediates of carbon matrix with catalyst) [12,14–16]. The C(O) and M–C–O intermediates are active sites which react with the gasification agent such as steam, oxygen and/or carbon dioxide. Therefore, the catalysts increase the concentration of active intermediates

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(e.g. M–C–O intermediates) and enhance the gasification reactivity significantly. The change in carbonaceous structure is one of the key factors that affect the rate of gasification. However, the structure evolution of carbon matrix during steam gasification of coke is not clear yet.

Raman and XRD spectroscopy are the most powerful techniques for evaluating the structural features of carbonaceous materials. Oboirien, et al. [17] investigated the evolution of char properties during coal gasification with Raman and XRD and found that there was an increase in reordering of the amorphous carbon after gasification. While no significant growth of the crystalline component for Duhva and Matla chars was observed, the crystalline component was found to grow in Grootegeluk coal char. Cetin, et al. [18] studied the effects of pressure on the gasification reactivity of biomass char with XRD and found that the difference in gasification reactivity under different total pressures was mainly due to graphitization of biomass char structure at higher pressures. Li, et al. [19–23] introduced Gaussian peaking regression to analyze Raman spectra, and investigated semi-quantitatively the evolution of lignite and biomass structure with Na and K addition.

In this study, the evolution property of char structure during steam gasification of petroleum coke was investigated with Raman spectra combined with X-ray diffraction (XRD), and the influence of catalysts (e.g. $FeCl_3$, $CaCl_2$, KCl, KCO_3, K_2SO_4, KNO_3, CH_3COOK (KAC)) on the properties of coke structure was analyzed. Furthermore, the mechanism of catalytic gasification of petroleum coke was explored in depth.

2. Experiment materials and methodology

2.1. Experimental materials

A sample of petroleum coke was obtained from the Shanghai Jinshan Petroleum Co., Ltd. in China. The sample was ground and sieved to collect the 0.25–0.5 mm fraction for experimental trials. The properties of Jinshan petroleum coke are summarized in Table 1. Compared to coal, Jinshan Petroleum coke is very clean, with trace ash content (<1%). However, it shows high fixed carbon, but low volatile content, indicating that the coke is too thermal stable for gasification. Furthermore, the high content of sulphur might be a critical issue during petroleum coke utilization and needs to be considered in near future. The ash component was analyzed with an X-fluorescence probe (XRF) and the results are listed in Table 2 on oxide basis. It is mainly SiO_2, Al_2O_3, Fe_2O CaO with some K and Mg, and other trace metals.

Alkali (K), alkaline earth (Ca) and transition metal (Fe) contained compounds were introduced as catalysts in petroleum coke steam gasification. $FeCl_3$, $CaCl_2$, KCl, K_2CO_3, K_2SO_4, KNO_3 and KAC were bought with analytical purity. They were mixed with petroleum coke particles through wet impregnation in aqueous solution separately, and the ratio of metal/carbon was 5 wt%. The mixture was stirred for 12 h at 30 °C, and then stirred for 12 h at 110 °C. Afterwards, it was dried for 24 h at 105 °C, and stored in a well-sealed container before analysis.

Table 1
Properties of Jinshan petroleum coke (wt%, db).

	Proximate analysis				Ultimate analysis				
	M	A	V	FC	C	H	N	S	O
JS	1.36	0.20	9.30	89.14	87.67	3.56	1.37	5.40	0.44

Table 2
Ash composition of Jinshan petroleum coke (wt%).

	SiO_2	Al_2O_3	Fe_2O_3	TiO_2	CaO	MgO	NaO	K_2O	MnO_2	SO_3
JS	43.76	27.04	11.82	0.57	11.65	1.65	0.72	2.04	0.01	0.20

2.2. Experimental method

2.2.1. Gasification reactivity

Steam gasification reactivity was evaluated in a STA 449F3 TGA (alumina sample crucibles (445.213) 3.4 ml). The gasification procedure was elaborated as follows: The sample (around 10 mg) was heated in a 50 vol.% N_2 and 50 vol.% H_2O (total 100 ml/min) stream up to 1000 °C at 10 °C/min, and kept isothermal at the final temperature for 30 min.

The specific reactivity (R) and the conversion fraction (X) of char were calculated with following equations:

$$R = -\frac{dm}{dt}\left(\frac{1}{m - m_{ash}}\right) \quad (1)$$

$$X = 1 - \frac{m - m_{ash}}{m_0 - m_{ash}} \quad (2)$$

where m is the instantaneous sample mass, m_0 is the initial mass, and m_{ash} is the sample ash content.

2.2.2. Char structure measurement

The raw sample and the sample with K_2CO_3 addition were used to investigate the char structure evolution in steam gasification. The sample (1 g) were gasified with 50 vol.% steam and 50 vol.% nitrogen (flow rate 900 ml/min) at 900 °C in fixed bed reactor (diameter 30 mm), and chars with various carbon conversions were collected.

The Raman of solid char was recorded using a Bruker VERTEX FT-IR/Raman spectrometer with a back-scattered configuration at room temperature and a Nd:YAG laser at 1064 nm as its light source. The laser power was 254 mW. An InGaAs detector was used, and each spectrum represents 1000 scans. The spectral resolution was 4 cm^{-1}. To minimize thermal emission, char particles were mixed with potassium bromide (KBr) powder with a ratio of 1:100.

Crystal structure was characterized by XRD (PANalytical B.V X'Pert PRO). 35 kV and 30 mA copper K (Cu K) radiation was used to scan over the angular 2 range of 5–85°. Microcrystalline sizes of char prepared at different conversions were calculated using the Bragg and Scherer equations [24].

All runs are repeated at least three times, the reproducibility of experimental data was very good with error below 5%. The data for the solid char are average values of three measurements.

3. Results and discussion

3.1. Catalytic gasification properties of petroleum coke

The conversion of petroleum coke steam gasification is shown in Fig. 1. The profile of specific gasification reactivity of different carbon conversion is shown in Fig. 2. Typical parameters are listed in Table 3. From Fig. 1, the thermal stability of Jinshan petroleum coke is very high, with almost no conversion occurring at temperatures lower than 600 °C. Beyond that, the conversion increased slowly with temperature increasing (600–900 °C), which might be mainly due to the release of volatiles. With temperature increasing further (>900 °C), the conversion was enhanced greatly as steam gasification of char occurred. 900 °C was the lowest temperature for the application of petroleum coke through steam gasification without catalysts. The gasification rate increased gradually with temperature increasing and reached the maximum gasification reactivity rate 0.025 min^{-1}, however it is quite low