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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:

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

$$X = 1 - \frac{m - m_{ash}}{m_0 - m_{ash}} \tag{2}$$

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

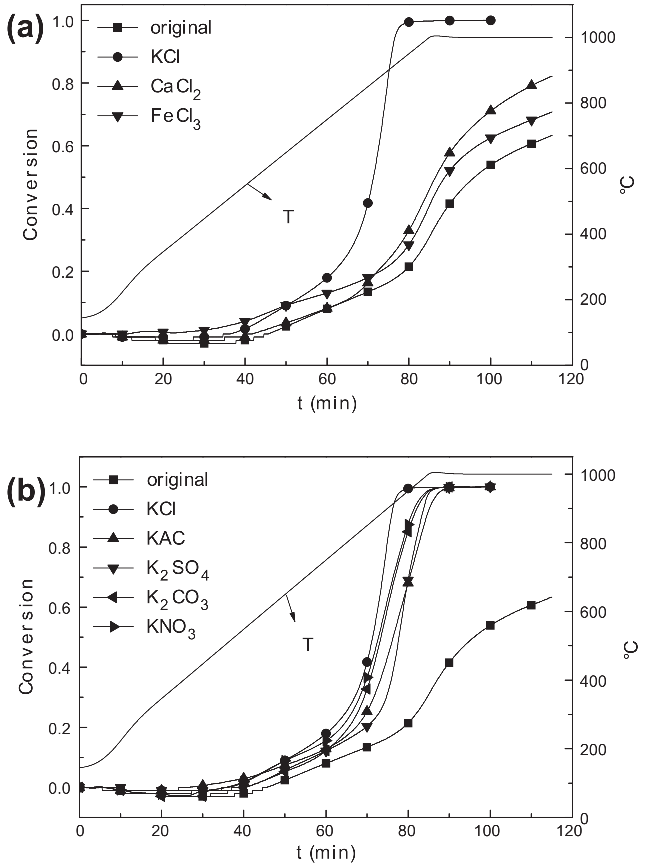

Fig. 1. TG curves corresponding to non-isothermal steam gasification. (a) different cation and (b) different anion.

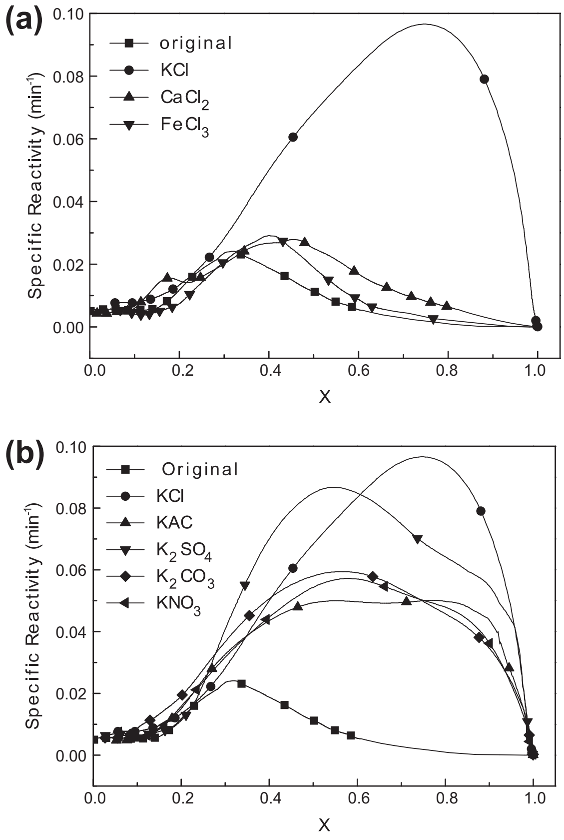

Fig. 2. Specific reactivity rate versus carbon conversion for steam gasification. (a) different cation and (b) different anion.

compared with that of coal gasification [20]. This indicates that the petroleum coke was difficult to gasify, and the industrial non-catalytic gasification of petroleum coke generally requires temperature over 1000 °C [6,7,12]. Relative to non-catalytic gasification, the gasification rate increases with the increase of conversion and then decreases after reaching a maximum rate when the carbon conversion is about 0.3. Zou, et al. [25] studied the kinetic characteristics of petroleum coke–CO$_2$ gasification, and found that the poor initial pore structure of petroleum coke was the main cause of the occurrence of the maximum gasification rate.

With the addition of chloride catalyst, it can be observed that devolatilization and gasification occured at a lower temperature (<900 °C) (Fig. 1(a)), and the reaction rate also increased clearly (Fig. 2(a)). However, there were some differences among KCl, CaCl$_2$ and FeCl$_3$ in terms of catalytic effects. Firstly, KCl and FeCl$_3$ could accelerate the devolatilization, but CaCl$_2$ could not. In addition, the devolatilization occurred at lower temperature with FeCl$_3$ catalyst, but the reaction rate of FeCl$_3$ was lower than that of KCl. Thirdly, the addition of KCl can enhance gasification reactivity more significantly than the addition of CaCl$_2$ or FeCl$_3$ (Fig. 1(a)). The addition of KCl enabled the petroleum coke to react with steam vigorously, even at lower temperature, and the conversion of KCl sample was completed before the temperature reached 950 °C. As shown in Fig. 2(a), the gasification rate of KCl was about 4–5 times that of the CaCl$_2$ and FeCl$_3$ samples. This suggested that catalytic gasification could effectively lower the gasification temperature. However, catalytic gasification occurred slowly when the temperature was less than 750 °C, suggesting a significant change in the effect of the gasification temperature on catalysts activity [12,13,26].

Table 3
Characteristic parameters of Petroleum coke steam gasification.

Catalytic and non-catalytic	T_{max} °C	R_{max} min^{-1}	C_{max} –
Original sample	1000	0.0248	0.314
KCl	882	0.0966	0.745
K$_2$SO$_4$	932	0.0867	0.462
K$_2$CO$_3$	892	0.0594	0.551
KNO$_3$	890	0.0572	0.429
KAC	921	0.05	0.463
FeCl$_3$	997	0.0293	0.399
CaCl$_2$	998	0.0284	0.465

T_{max}: The temperature corresponding to the maximum reaction rate.
R_{max}: The maximum reaction rate.
C_{max}: Char conversion corresponding to the maximum reaction rate.

As shown in Fig. 1(b), as all K-based catalysts displayed significant catalytic effects on petroleum coke pyrolysis and gasification, all samples with K-based catalysts complete reaction before 1000 °C. However, there were some differences among these catalysts in terms of catalytic effects in the steam gasification reactions. During pyrolysis process, the catalytic effects of K-based materials may be ordered: K$_2$CO$_3$ < K$_2$SO$_4$ < KAC < KNO$_3$ < KCl. The catalytic effects of the K-based materials for char gasification may be ordered: KAC < K$_2$SO$_4$ < K$_2$CO$_3$ < KNO$_3$ < KCl. Lang [27] investigated the anion effect in alkali catalyzed steam gasification of coal chars, and found that alkali salts of weak acids were good gasification catalysts, while those of strong acids were poor. Some anions could compete with carbon material for the alkali cations and thus inhibit the formation of an alkali-carbon complex (M–O–C).

In Fig. 2(b), the instant mass gasification rate for both non-catalytic and catalytic gasification increased during carbon gasification. When the carbon conversion was between 0.2 and 0.6, the catalytic gasification rate rose continuously. On the other hand, when the carbon conversion was 0.3, the non-catalytic gasification rate started to decrease clearly. As char gasification was completed, the instant mass gasification rates for both cases decreased rapidly. Gasification rates differ greatly for various catalysts. For example, the maximum rates for KCl and K_2SO_4 samples were higher than for the other samples. The KCl sample reached the maximum gasification rate at around $x = 0.75$, whereas the samples of K_2SO_4, K_2CO_3 and KNO_3 reached the maximum at about 0.5 (Table 3).

Since the volatile matter content in petroleum coke is very low, the conversion of pyrolysis is quite limited for the whole gasification process. Therefore, char gasification is the key step to produce the synthesis gas in the steam gasification of petroleum coke. When the carbon conversion was lower than 0.2, the catalytic and non-catalytic gasification rates were similar. Some researchers [12,28] showed that the formation of active intermediates from char sample and gasifying agent was necessary for gasification to occur. Therefore, the contact area between char and steam was critical for gasification rates; however, the structure of raw petroleum coke is compact, without rich pores. An increase in gasification rate was attributed to an increase in the concentration of the intermediate (C(O)) for both non-catalytic and catalytic gasification [13,26]. When catalyst-coke mixture was heated, the metal cations were combined with the edge C atom of char surface to form the intermediate M–O–C (where M is a metal) in the steam atmosphere. Meanwhile, the distribution of the electron cloud in C atom of char surface was changed with the structure of M–O–C. Consequently, the intensity of C–C was weakened. As a result, the concentration of the intermediate (C(O)) and (M–C–O) increased rapidly, leading to a rapid increase in the gasification rate [12,13]. However, in the end, when gasification is almost finished, the instant gasification rates for both cases decreased rapidly.

3.2. Char structure analysis

3.2.1. Raman analysis

Fig. 3 shows a typical Raman spectrum of char from steam gasification of petroleum coke. The spectrum is similar to that of brown coal, but quite different from that of mallee wood [19,21–23]. In all Raman spectra the G and D bands were dominant, which were found at 1300 cm^{-1} and 1600 cm^{-1}, respectively. The G bands of all chars were weaker than D bands. 10 bands were fitted in Fig. 3, each of which is explained in the literatures [22,23]. There were six bands (D, G, G_R, V_L, V_R, and S) in the dominant positions. I_x was the area of band x, where x is D, G, G_R, V_L, V_R or S.

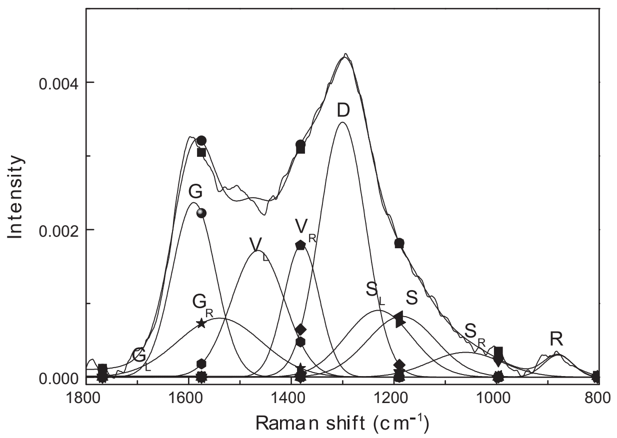

Fig. 3. Curve-fitting of a Raman spectrum of the char from steam gasification.

D band represents medium-to-large sized (⩾6) aromatic ring systems, while G band represents the molecular vibration of aromatic quadrant ring breathing [23]. Therefore, the I_D/I_G ratio can represent the degree of aromatic ring growth. A decrease in I_D/I_G ratio indicates the growth of aromatic ring, i.e. the structure of the sample is closer to that of graphite. Fig. 4(a) shows that the I_D/I_G of the original petroleum coke decreased rapidly with char conversion increasing. It indicates that the aromatic ring grew during steam gasification of original petroleum coke, which may result from the dehydrogenation of hydro-aromatics and the growth of

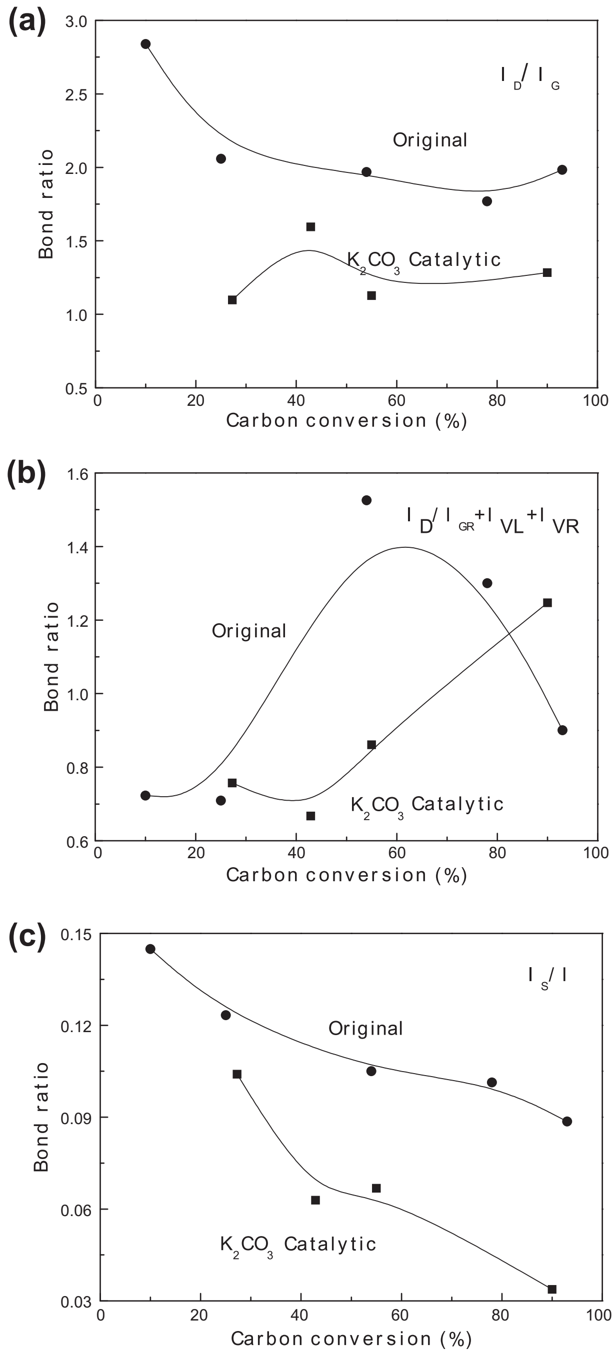

Fig. 4. The band ratio changed with the increasing char conversion during steam gasification. (a) I_D/I_G, (b) $I_D/I_{(GR+VL+VR)}$ and (c) I_S/I.

aromatic rings during char gasification [23]. However, the I_D/I_G ratio of catalytic sample increased gently or remained unchanged during gasification reaction. It suggested that no obvious change in the amount of aromatic rings was found during the catalytic gasification. It can be inferred that the catalyst K_2CO_3 might reduce the formation of large aromatic rings during steam gasification.

The G_R, V_L and V_R bands between the G bands and D bands (Fig. 3) represent the relatively small aromatic ring systems with 3–5 fused benzene rings. The D bands represent medium to large ($\geqslant 6$) aromatic ring systems. Therefore, the $I_D/I_{(GR+VL+VR)}$ ratio could reflect the proportion of big rings relative to small fused rings in chars from petroleum coke gasification [20,23]. Fig. 4(b) shows that the ratio $I_D/I_{(GR+VL+VR)}$ in the non-catalytic sample first increased in the wide range of char conversion and then decreased. It indicated that the small aromatic rings would tend to react with the steam or change to big ones. Tay, et al. [29,30] found that the smaller aromatic ring structures were more selectively consumed and/or converted into big ones in steam gasification. Steam could be dissociated into oxygen-containing species and separate hydrogen radical species which attached to neighboring sites on char surface [31]. Hydrogen radicals absorbed on the char surface may be rather active and able to penetrate into the char matrix [32,33]. Therefore, it may activate the inner structure of char, especially the aromatic ring structures, to induce the aromatic ring condensation (i.e. for the rings to grow) [29]. Compared with the decrease of I_D/I_G shown in Fig. 4(a), it was the preferential consumption of small aromatics that reacted with steam. In other words, the relatively small aromatic ring systems with 3–5 fused benzene rings represented by the G_R, V_L and V_R bands were the active sites reacting with the steam in the gasification of petroleum coke.

In addition, with the increase of char conversion in the catalytic sample, the small aromatic ring systems could no longer be consumed and the big aromatic ring systems started to dissociate, leading to the decrease of the $I_D/I_{(GR+VL+VR)}$ ratio. However, in the catalytic samples, the $I_D/I_{(GR+VL+VR)}$ ratio increased more slowly, suggesting that the catalyst K_2CO_3 can enhance the breakdown of the big aromatic ring systems into small ones. Therefore, the $I_D/I_{(GR+VL+VR)}$ ratio increased more slowly, while the small aromatic ring systems increased significantly, which would accelerate the gasification rate. According to previous literatures [12,14–16], the mechanism of steam gasification is that the char first forms the intermediate (C(O)) and (M–C–O) in the catalytic samples, and then the intermediate matter reacts with gasifying agent (steam). Therefore, it was easier for the small aromatic ring system to form the intermediate (C(O)) and (M–C–O) in the steam gasification of petroleum coke. The amount of intermediate (C(O)) and (M–C–O) increased as more active sites appeared, leading to an increase in the gasification rate.

The S bands represent sp^3-rich structures such as alkyl–aryl C–C structures and methyl carbon dangling to an aromatic ring. The I_S/I ratio refers to the ratio of the S band peak area to the total peak area (I) between 800 cm^{-1} and 1800 cm^{-1}. Fig. 4(c) shows that the relative S band intensity decreased with char conversion increasing. These results suggested that the S band was where the active sites react with steam. In other words, the sp^3-rich or sp^2–sp^3 mixed structures as alkyl–aryl C–C structures and methyl carbon dangling onto an aromatic ring were the active sites in petroleum coke steam gasification [22,23]. The I_S/I ratio was about 0.09 with 90% char conversion in the non-catalytic samples, but about 0.03 with 90% char conversion in the catalytic samples. This implies that the alkyl–aryl C–C structure and methyl carbon dangling onto an aromatic ring should have a concentration above 9% to react with steam in the non-catalytic gasification of petroleum coke. However, in the presence of K_2CO_3 catalysts, the concentration could be less than 3%.

3.2.2. Char crystallite property

XRD spectra for the different char conversions during steam gasification of petroleum coke are shown in Fig. 5. Two peaks are observed as 2θ at 25° and 43°, which correspond to the peaks 002 and 100 in diffuse graphite. The most prominent feature in XRD patterns in all samples is peak 002, which is generally attributed to the stacking of the graphitic basal plans of char crystallites. The high angle (about 43°) corresponds to peak 100, which is generally attributed to graphite-like atomic order within a single plane [34,35]. In XRD spectra for char particles, the broad peak 002 implies that petroleum coke char has a highly disordered structure. The fraction of disordered carbon includes amorphous carbon and aliphatic branched chains. The background intensity of the XRD spectrum is caused by amorphous carbon in the char. While peak 002 should be symmetric in theory, the apparent asymmetry of this peak is due to the presence of γ peak on its left side, which is associated with the packing of saturated structures such as aliphatic branched chains[36–38]. With the increase of char conversion, the (002) peak intensity of the XRD spectra for the original samples in Fig. 5(a) became stronger, and the (002) peak shape became more symmetric and sharper. It can be concluded that the content of amorphous carbon and aliphatic branched chains in char particle decreases and the degree of orientation of aromatic lamellae becomes higher, suggesting that the char structure becomes more ordered and aromatic. Therefore, the gasification rate is much lower in the original petroleum coke steam gasification. However, peak 002 for the catalytic samples in Fig. 5(b) became weaker and its shape became more symmetric and broader. It can be concluded that the content of aliphatic branched chains in

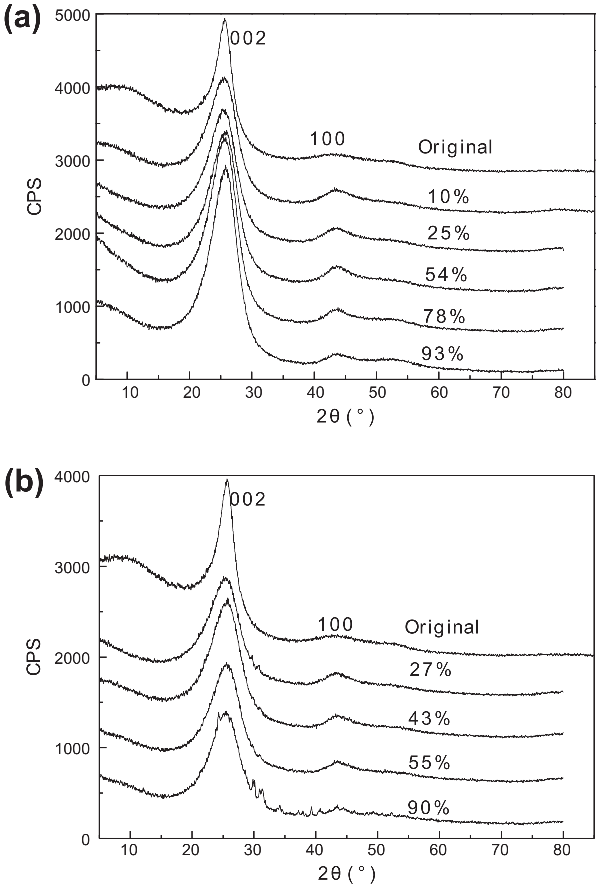

Fig. 5. XRD spectrum of different char conversion during steam gasification. (a)original sample and (b) with K_2CO_3 catalyst.

Table 4
Characteristic parameters of XRD.

Sample	Carbon conversion(%)	d_{002} (nm)	L_c (nm)	L_a (nm)
Original	0	0.35	2.71	3.98
	10	0.35	1.82	4.50
	25	0.35	1.83	5.04
	54	0.35	1.85	5.09
	78	0.35	1.87	6.66
	93	0.35	1.93	6.37
Catalytic(K_2CO_3)	27	0.35	1.66	5.67
	43	0.35	1.83	6.21
	55	0.35	1.76	6.90
	90	0.35	1.73	7.50

the char decreased and amorphous carbon with the char increased, and the degree of orientation of the aromatic lamellae became lower. In other words, the addition of K_2CO_3 reduced the degree of graphitization of petroleum coke.

The XRD patterns of the petroleum coke chars were also analyzed to obtain their structure parameters. The d_{002} (interplanar distance of two aromatic layers of microcrystalline (nm)) remained essentially unchanged during steam gasification (Table 4). As the char conversion increased from 10% to 93% in the original samples, L_c (the thickness of microcrystalline (nm)) slightly increased from 1.81 nm to 1.92 nm (Table 4) due to the tendency of the defects of longitudinally aromatic layer to disappear. The longitudinally aromatic structure began to condense and distort, increasing the thickness of microcrystalline. This indicates that the char structure became more ordered and aromatic during the gasification of the original sample. However, L_c first increased and then decreased during the catalytic gasification process and was lower than for the original samples (Table 4). This might be attributed to the fact that in the catalytic process the longitudinally aromatic structure condensed and distorted, and occurred simultaneously with catalytic cracking. However, L_a (the microcrystalline diameter) increased during petroleum coke steam gasification with or without catalyst. It is expected that the growth of crystallites in chars was promoted with char conversion increasing, leading to the increase in crystallite size.

4. Conclusions

The gasification reactivity and the feature of char structural evolution in steam gasification of petroleum coke with and without catalysts were studied using TGA, Raman and XRD spectra. The conclusions can be drawn as follows:

(1) Petroleum coke is very difficult to be gasified as temperature lower than 1000 °C, while catalyst promotes the gasification obviously. The following chloride catalysts were listed in decreasing order in terms of their catalytic effects: alkali metal (K) > alkaline earth metal (Ca) > transition metal (Fe) > Original sample. All K-based catalysts with different anions had a significant effect on the efficiency of the steam gasification, and all the gasification reactions were completed below 1000 °C.

(2) The degree of aromatic ring growth of original samples increased rapidly during the process of petroleum coke steam gasification, but that of catalytic samples remained unchanged or decreased. The proportion of big rings increased more slowly in catalytic samples. K_2CO_3 catalyst can stimulate the breakdown of the big aromatic ring systems into small ones. K_2CO_3 catalysts can enhance the formation of active intermediates C(O) and M–C–O, increasing the gasification reactivity of petroleum coke.

(3) Petroleum coke chars have a highly disordered structure, which becomes stronger and its shape becomes more symmetric and sharper with char conversion increasing, while it becomes weaker and its shape becomes more symmetric and broad for the catalytic samples.

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