Formation, fates and roles of catalytic precursors generated from the K_2CO_3 -carbon interactions in the K_2CO_3 -catalyzed CO_2 gasification of coal char

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Abstracts: A study was carried out in both inert and CO_2 atmosphere to investigate the interaction mechanism of K_2CO_3 with graphite and coal char during the catalytic gasification of coal char. The formation of K_2CO_3 catalytic precursors was identified by using series of different techniques. The results obtained in an inert atmosphere show that the interaction between K_2CO_3 and carbon readily took place at low temperature. For the K_2CO_3 loaded graphite, the intermediate of C_nK clusters formed by the interactions of K_2CO_3 with carbon prevented the evaporation of K at low temperature. At temperatures above 800 °C, however, the C_nK clusters were unstable, and decomposed to release K through vaporization. On the contrary, for the K_2CO_3 loaded demineralized coal char, due to the presence of oxygen groups, K was tightly bonded to carbon during heating, forming a complex precursor containing O and K with high thermal stability. The reaction pathway of carbon- K_2CO_3 interactions in an inert atmosphere are proposed for both char and graphite. The results of DRIFTS experiment suggest that CO_2 is chemisorbed by the K- catalytic precursors during CO_2 gasification to form potassium phenolate species and a covalently bound carbonate group (dimethyl carbonate). It is believed that these species act as active intermediates in the

gasification process.

Key words: Catalytic gasification; Coal char; Potassium carbonate; K_2CO_3 -carbon interaction; Catalytic precursor

1 Introduction

Currently, the proportion of coal consumption in China's energy generation is as high as 66%, and 35.8 % higher than the global average. Coal is believed to remain a major energy source in the future decades in China. In response to the increasingly strict emission standard of Chinese government for environmental protection, cleaner and more efficient coal utilization technologies are being exploited. Coal gasification has emerged as one of the most efficient and clean ways to convert coal, wherein, solid coal is converted to fuel gas or synthesis liquid fuel precursor. However, high temperature and pressure are required in the traditional coal gasification process. These requirements increase the capital and the operating expenses of the process considerably [1, 2]. Recently, catalytic gasification has been investigated intensively in view of its advantages of lower operating temperature, higher efficient throughput and better economical performance [3, 4].

Salts and oxides of alkali metals, especially potassium carbonate, have been widely employed for the gasification of carbon materials due to their superior catalytic properties and relative low cost [3-5]. It is well understood that the presence of catalyst enhances the reactivity of coal gasification by providing increased number of active intermediates on the carbon surface [6, 7]. Hamilton et al. [8] reported that the increase in the active surface area could be attributed to the interaction of catalyst with the solid carbon surface and to the resulting newly formed catalytic precursors. A comprehensive review of the published reports [9-11] indicates that the precursors are capable of dissociating oxygen containing gases (O_2 , CO_2 and H_2O) and producing oxidized intermediates that participate in the redox reaction. Wen [10] summarized the catalytic mechanism in the early published literature and concluded that the alkali metals can be firstly generated from the interaction between alkali carbonate and carbon (reaction (1)). The alkali metals then combine with aromatic carbonaceous material to form electron donor-acceptor (EDA) complexes (reaction (2)), which are specifically good electron donors, and proceed to catalyze the reactions of carbonaceous materials with various surrounding gases. This mechanism has received wide acceptance in a number of published literature [12, 13].

Table 1 summarizes some relevant past studies reporting on the gasification of carbonaceous materials in the presence of alkali carbonate catalyst. From the review, various types of intermediate (e.g. M_2O , M_2O_2 , C-O-M phenolate-type group) have been proposed as playing important roles in the gasification. Research techniques such as pulse reaction, temperature-programmed desorption/reduction (TPD/R) and isotope labeled reactants were mainly employed in the past to determine the composition of produced gases in order to speculate the specific reaction mechanisms. Substantial evidences emerge to show that alkali carbonates experience a redox cycle during gasification. However, there remains a lack of good understanding regarding the species of the resulting reduction state catalytic precursors and oxidation state active intermediates during the redox cycle, as well their fates/roles in the gasification process. Additionally, the forms and the distribution of catalyst on the solid-state products are also still poorly understood. Further investigations focusing on the above aspects are vital to an in-depth insight into the catalyzed gasification mechanism of carbonaceous materials and to the overall improvement of the process.

The present study is aimed at investigating the interaction mechanism of carbon materials with potassium carbonate during the catalytic CO_2 gasification of coal char. The formation of intermediates from the K_2CO_3 -carbon interaction was firstly studied inside a thermogravimetric analyzer (TG) using graphite and coal char samples under an inert environment in order to obtain solid understanding of the mechanism without the complication of subsequent gasifying agent involvement in the interaction.

The occurrence, distribution and crystalline structure of the catalyst on the solid carbon residues were characterized using scanning electron microscopy coupled with the semi - quantitative energy dispersive X-ray spectra (SEM-EDX) and X-ray diffraction (XRD). The information regarding the absorption and desorption of CO_2 on the catalyst-loaded carbons surface during real gasification reaction was then obtained using in-situ diffuse reflectance infrared Fourier transformed spectroscopy (DRIFTS). The occurrence and evolution of catalytic precursors formed through different reaction pathways are also proposed.

2 Experimental

2.1. Materials

Powdered graphite (analytical reagent, purchased from Sinopharm Chemical Reagent Co., LTD, particle diameter of 120~180 μm) which has no minerals and pore structure, as well as two different rank coals (Xiaolongtan lignite (XLT), Gaoping anthracite (GP), particle diameter of 74~150 μm) were selected and dried in an oven at 105 °C for 24 h for experimental use. The proximate and ultimate analysis of the samples were respectively determined by EL-2 analyzer (Vario Company, Germany) and TGA-2000 (Las Navas Instruments, Spain), and the data were presented in Table 2.

2.2. Samples preparation

To eliminate the influence of inherent minerals on the reaction mechanism, the coal samples were firstly de-ashed by the usual method using 6 M HCl and 40% HF. The de-ashed procedure has been reported in details elsewhere [20]. In brief, 20 ± 0.01 g of coal powder was added into 300 mL, 6 M HCl solution, and the slurry was stirred for 24 h at ambient temperature. After vacuum filtration, the residue was then added into 300 mL HF solution (40 %). The mixture was also stirred for 24 h and vacuum filtered again at ambient temperature. The solid was washed with deionized water until no chloride ion was detected. Then the solid was dried at 105 °C in an oven for 48 h.

The detailed coal chars preparation procedure has also been described elsewhere [21]. Briefly, in each pyrolysis experiment, 1 ± 0.05 g of de-ashed coal sample was fed into a quartz fluidized bed reactor, and pyrolyzed at a temperature of 950 °C. After 10 min devolatilizing, the reactor was lifted out of the electric furnace. The fluidizing gas was then switched to high purity N₂ to quench the char particles to room temperature. Next, the collected chars were ground in an agate mortar and sieved to particle diameter of 74~150 μm . The results of proximate and ultimate analysis of the de-ashed coal char are also summarized in Table 2.

Finally, the powdered graphite and prepared coal chars were respectively mechanically mixed with anhydrous potassium carbonate (analytical reagent, purchased from Sinopharm Chemical Reagent Co., LTD). The mass ratio of catalyst and carbonaceous materials was 10:90 (wt. %). The mixtures were thoroughly blended in an agate mortar for interactions experiments use (as detailed below).

2.2. Interactions experiments

The mixture of catalyst with graphite and coal char was pyrolyzed in a TG (NETZSCH STA 449 F3) to investigate their interactions behavior in an inert atmosphere. In each run, 20 ± 0.2 mg of sample was loaded. The TG furnace was vacuumized and purged with high

purity N₂ three times to remove impurities, and it was then heated at a heating rate of 20 °C /min to a desired temperature in high purity nitrogen flow (20 ml/min). The resulting gases were analyzed on-line using a Fourier transform infrared spectrometer (Bruker EQUINOX 55/S, Germany).

2.3 Residues structural characterization

Due to the limited amount of residues available after TG experiments, it was inconvenient to conduct the subsequent structural characterization by using SEM-EDX, XRD and DRIFTs. Therefore, the same pyrolysis procedure as that of TG experiment was conducted in a vertical quartz reactor, of which the inner size was similar with that of the TG. 100 ± 5mg of sample was loaded in each run. The same flow rate of 20 ml/min high purity nitrogen was purged into the quartz reactor until the impurity gas was not detected. The quartz reactor was then heated at a heating rate of 20 °C /min to the same temperature (as that of the TG experiment) to obtain residues for structural characterization. The sample of K₂CO₃ with graphite heated at the temperature of 950 °C was labeled as graphite-K-950; K₂CO₃ with XLT demineralized char heated at the temperature of 950 °C was labeled as XLT-K-950, and so on.

The obtained residue was further characterized using SEM-EDX and XRD. SEM-EDX analysis was conducted on a FEI Company Nova NanoSEM 450 SEM equipped with Oxford X-Max 50 EDX. XRD analysis was conducted on a PANalytical B.V. X' Pert PRO X-ray diffractometer (40 mA, 40 kV, Cu Ka). The XRD spectra were recorded in the scan range of 2θ = 0°~90°.

2.4. In-situ DRIFTs experiment

The DRIFTs analysis was conducted using a VERTEX 70 FTIR spectrometer. The vacuum chamber was connected to a gas-handling unit for sample treatment where temperature can be kept constant at any temperature between room temperature to 600 °C by a thermostat. In each run, the DRIFTs cell at which the sample was located was firstly vacuumized by a vacuum pump (vacuity below 8×10⁻⁴ Pa) to eliminate impurity gas. Then, a flow of CO₂ (100 ml/min) was introduced to the cell at desired temperature until the spectra stabilized. After adsorption process, desorption started when the cell is vacuumized again. A background spectrum was collected before each test and subtracted from the sample spectrum. 0 min was set as the starting time to purge CO₂ into the reactor, and about 30 min following the purging, the vacuum desorption began. Spectra were recorded in the range of 2000-800 cm⁻¹ (the

chemical structure of species produced by CO₂ located in this range) by accumulating 128 scans at a resolution of 4 cm⁻¹.

3. Results and discussion

3.1 TG-FTIR analysis

Figure 1 shows the TG/DTG curves obtained by heating the samples in an inert atmosphere. As expected, under this condition, pure graphite certainly did not show any weight loss (Figure 1a). Conversely, a notable weight loss of pure K₂CO₃ could be observed when the temperature reached its melting point of 891 °C (Figure 1b). The weight loss of pure K₂CO₃ reached about 40 wt. % when the temperature was increased to 1050 °C. Accompanying this weight loss was the emergence of CO₂ in the product gas. The CO₂ releasing profile (shown in supplemental Figure S1) indicates that CO₂ appeared only after the temperature reached the melting point of K₂CO₃, and its amount increased with further increases in temperature. Thermodynamically, K₂CO₃ can hardly decompose before reaching its boiling point (~1689 °C). The CO₂ production and the resulting weight loss might be due to the reaction of liquid carbonate with corundum holder; similar to what has been observed by Saber et al [17] during the heating of pure alkali carbonate.

Figure 1c shows the correlation between weight loss and the release of CO_x during the interaction of graphite with 10 wt.% K₂CO₃ in an inert atmosphere. It is clearly shown that majority of the samples' weight loss appeared between the temperature of 709 °C and 950 °C, (with the maximum weight loss occurred around 884 °C), indicating that the graphite - K₂CO₃ interaction had already taken place before reaching the K₂CO₃ melting point, and the presence of carbon accelerated the decomposition of the carbonate.

Figure 1c also indicates that a minor weight loss, accompanied with the release of a small amount of CO₂ (as detected by the FTIR), took place slightly above 320 °C. This implies that K₂CO₃ reacted with carbon and decomposed at temperature far below the onset temperature of gasification. Contrarily, CO was not observed until around 709 °C, and the maximum concentration of CO was recorded at the temperature of 884 °C. It can be concluded that the reaction (3) K₂CO₃ took place slowly at lower temperature (<709 °C) to result in the evolution of CO₂. On the other hand, the formation of CO above the temperature of 709 °C could be caused by either the Boudouard-reaction with CO₂ or the graphite attack by the catalyst (reaction (4)). It was also noted that excluding the minor weight loss of moisture evaporation

at the initial stage, the total weight loss in the whole process was ca. 11 wt. %; exceeding the amount of catalyst added in the original sample. Although liquid K_2CO_3 could react with corundum holder, as concluded above, this reaction would be limited because almost all the K_2CO_3 had already been consumed by graphite before the melting point of K_2CO_3 was reached. From mass balance calculation, it is apparent that Boudouard reaction alone cannot cause such significant mass loss as well as such large amount of CO production. Therefore, most of the CO production and mass loss must be associated with the occurrence of reaction (4) at high temperature. Huhn et al [13], who studied the steam gasification of coal with carbonate catalyst also observed the evaporation of elemental potassium (leading to its condensation in the cooling zone of the reactor) during the thermal treatment at 900 °C.

Figure 2 shows the TG-DTG curves of XLT/GP demineralized coal char with 10 wt. % K_2CO_3 , obtained in an inert atmosphere, together with their corresponding CO_x releasing profile. Three peaks appeared in the DTG of both coal char samples: the first peak was attributed to the evaporation of absorbed moisture; the second peak corresponded to the release of residual volatiles and the last peak was mainly attributed to the char- K_2CO_3 interaction. A calculation of weight loss in the temperature range of 150~1050 °C was made to elucidate the reaction pathway of char- K_2CO_3 interaction. It was found that the total weight loss of XLT and GP coal char was 7.00 wt.% and 6.93 wt.%, respectively, and their respective volatile content was 3.49 wt.% and 2.95 wt.%. Obviously, the char- K_2CO_3 interaction contributed only to a weight loss of less than 4 wt. %; a significant difference from 10 wt.% weight loss of graphite- K_2CO_3 interaction under the same heating conditions. It is therefore postulated that the interactions of char- K_2CO_3 and that of graphite- K_2CO_3 followed a different reaction pathway.

To get further insights into the different mechanisms of K_2CO_3 interaction with char/graphite, the CO_x releasing profile of coal char samples was further analyzed. As shown in Figure 2, two distinct peaks appeared for both XLT and GP coal chars: the first peak at low temperature due to the devolatilization of residual volatiles, and the second peak at high temperature caused by char- K_2CO_3 interactions (reaction (3)). The amount of CO_2 released was found to be much larger than CO in most of the temperature range; a significant

difference from the result shown in Figure 1c. CO did not show up in the low temperature range, and its release only started around 660 °C and 783 °C, respectively. This CO releasing could also be related to Boudouard reaction or char-K₂CO₃ interactions (reaction (4)). However, the amount of CO released from XLT and GP coal char heating process was significantly less than that in the graphite heating process. Thus, considering the remarkable differences in weight loss and CO₂/CO releasing pattern, it can be concluded that the release of CO at high temperature was mainly due to Boudouard reaction, and that the reaction (4) could hardly take place in the coal char heating process.

Based on the above discussions, the following mechanisms (as shown in Scheme 1) are proposed to explain the plausible reactions taking place during the interactions of K₂CO₃ and char/graphite during heating in an inert atmosphere. Firstly, in both graphite and coal char heating process, K₂CO₃ catalyst interacted with carbon surface at low temperature to form -COK intermediates, resulting in the production of gas-phase CO₂. At high temperature, however, graphite and coal char followed a different reaction pathway. With high graphitization degree graphite underwent route (1), where the cross-linking reaction between -COK intermediates and C matrix occurred, forming C_nK clusters and producing gas-phase CO. With further heating, C_nK clusters cleaved to form elemental K which in turn vaporized under high temperature condition. On the other hand, for the low graphitization degree of coal char, in which oxygen-containing functional groups were present, the interaction followed route (2). The presence of oxygen groups helped to stabilize potassium on the carbon surface [22, 23]. Thus, the cross-linking reaction between -COK intermediates and C matrix took place, forming a tightly-bonded O-C-K complex which is thermally stable under high temperature condition. These explain why the weight loss and CO production of coal char in this study were significantly lower than that of graphite. To further prove the above speculated pathways, the occurrence, distribution and crystalline structure of the catalyst were determined by SEM-EDX and XRD. These will be further discussed below.

3.2 Solid residues structural characterization

3.2.1 SEM-EDX analysis

The main elemental contents of solid residues treated at different temperatures were semi-quantified by SEM-EDX, and the results are summarized in Table 3. As can be seen, the concentration of K on graphite surface increased significantly when the temperature was elevated from 500 to 800 °C (the result at 950 °C will be discussed later). It is believed that

within this temperature range, reaction (3) took place to result in the release of CO_2 , and thus increasing the relative content of metal catalyst. Likewise, the K/C mole ratio was also observed to increase within the same temperature rise. Conversely, however, the O/C mole ratio showed somewhat a different trend where it started to decrease when the temperature was further increased beyond 600 °C. As mentioned before, reaction (4), wherein elemental K and gas-phase CO are produced, started at 709 °C. The release of O-containing gas at higher temperature was therefore responsible for the observed decrease in O/C mole ratio. The increased K/C mole ratio within 500 – 800 °C, on the other hand, can be related to the occurrence of reaction (2) where the elemental K, produced from the initial interaction of K_2CO_3 with carbon (reaction (1)), formed a C_nK type bonding with carbon surface. The newly formed C_nK clusters, consequently, prevented the vaporation of K [1, 24], resulting in the increased K/C mole ratio. Nevertheless, at 950 °C, K concentration and K/C mole ratio decreased drastically. It is believed that the intermediate of C_nK cluster is thermally unstable at elevated temperature in which they cleave to produce elemental K that subsequently vaporized. This postulation is consistent with the conclusion obtained from the TG results shown in Section 3.1.

In complete contrast to graphite, both XLT and GP demineralized coal chars showed a significant increase in both the elemental K composition and the K/C mole ratio at 950 °C. To gain further information, the morphology and the elemental distribution of solid residues obtained at 950 °C were examined with SEM at high magnification. Figure 3a shows carbon and K distributions in the GP solid residue obtained from the SEM micro area compositional analysis (the magnification and the scale bar was respectively $\times 200$ and 300 μm). It is evidently shown that K element existed on the surface of coal char, and well-distributed. Figure 3b shows the existence of many small flakes that were well distributed and anchored to the particle surface. Several representatives of flake particles such as spot 'a' were then selected to be analyzed by EDX (the mean data are shown in Table 3). Evidently, these small flakes also contained mainly C, O and K. Therefore, combining with the results discussed in Section 3.1, a conclusion can be drawn that at the temperature of 950 °C, coal char and K_2CO_3 reacted to release O-containing products (CO and CO_2), leading to the weight loss of the sample. Meanwhile, K was anchored to the particle surface to form intermediate complex containing O and K.

3.2.2 XRD analysis

Figure 4(a) shows the XRD patterns of K_2CO_3 loaded graphite powder before and after heat treatment at 950 °C. It can be seen that, unlike the fresh sample, no distinct crystalline peak of inorganic metal was detected from the sample heated at 950 °C. This is in agreement with the conclusions drawn from the TG-FTIR and SEM data discussed above. The XRD results indicate that the K_2CO_3 was consumed completely. In other words, the reaction (4) took place thoroughly, and the resulting elemental K vaporized completely at this temperature (950 °C).

Figure 4(b) shows the XRD patterns of K_2CO_3 loaded coal chars heated at 600 °C and 950 °C. Numerous peaks corresponding to K_2CO_3 crystalline phase were detected from the XLT coal char heated at 600 °C. When the same coal char was heated at 950 °C, several peaks (identified and unidentified) with lower intensities were observed in the XRD spectrum, indicating that some K_2CO_3 were consumed, and that some K-containing crystalline compounds (which could not be determined by the PDF standard card of XRD) were formed due to the interactions of K_2CO_3 and coal char at high temperature. Similarly, crystalline peaks of K_2CO_3 were also detected with the GP coal char sample, but their peak intensity and amount were much lower. Nevertheless, it provides a further evidence that the reaction of K_2CO_3 and coal chars occurred.

Based on the above discussions, the following conclusion is made regarding the reaction between K_2CO_3 and carbon materials. For graphite sample, which has lower porosity and higher graphitization degree, the graphite could react with K_2CO_3 at increasing temperature under inert atmosphere. Up to 800 °C, the cross-linking reaction between K and C takes place, resulting in the formation of C_nK clusters that prevent the volatilization of K. Further increasing the temperature beyond 800 °C will result in the dissociation of C_nK clusters which eventually allows the vaporization of K and thus lead to the deactivation of K_2CO_3 catalyst. For the coal char with higher porosity and plenty of active functional groups, the coal char could react with K_2CO_3 to form K- and O-containing complexes which are thermally stable even at the temperature of 950 °C. This is evidenced from the detection of small peaks corresponded to K crystalline compounds in Figure 4(b).

Wigmans et al. [14, 25], who investigated alkali metal-catalyzed gasification of activated carbon and coal char, proposed a mechanistic interpretation that three types of active catalyst species can be formed on the surface of solid particles during heat treatment: (i) the loosely bonded metal - oxygen complexes; (ii) the intercalated metal - carbon complexes that make

certain part of the catalyst is accessible for the gaseous reactant; and (iii) the tightly-bonded metal - oxygen complexes. The formation of these catalyst species is dependent on the graphitization degree of the samples. It is known that graphite has a much more complete graphitization degree than the coal char, and comparatively, its oxygen content is much lower. Therefore, Type 1 and Type 3 catalysis would be more predominant in coal char; while Type 2 (C_nK cluster) catalysis would be more predominant in graphite. Clearly, the results of our SEM-EDX and XRD analysis provide a strong support to the proposed reaction pathway shown in Scheme 1.

3.3 CO₂ chemisorption in DRIFTS experiments

The interaction of carbonaceous materials and K₂CO₃ as well as the formation of resulting active intermediates in an inert atmosphere have been discussed above. To further understand their implications in an active/CO₂ atmosphere, the vibrational modes of the above solid residues in CO₂ atmosphere were analyzed in DRIFT experiments.

Figure 5 shows the DRIFT spectra of graphite-K-950 and pure XLT demineralized char in CO₂ atmosphere for various times at 300 °C. After subtracting the background spectrum, the obtained original spectrum without CO₂ flow in the reactor was almost a flat line. With increasing adsorption time in CO₂ atmosphere, all the spectra remained as a flat line along the x-axis, suggesting that no obvious chemisorption of CO₂ happened. The above findings indicate that the newly formed C_nK cluster intermediate, which is thermally unstable at 950 °C, has cleaved to produce elemental K. The absence of catalyst in the solid residue has resulted in the observation of no chemisorption of CO₂.

DRIFT spectra of the XLT-K-950 exposed to CO₂ at 300 °C are shown in Figure 6. As can be seen, after 30 min of CO₂ adsorption, several new bands were observed in the spectra. After vacuum desorption, the small bands located at 1084, 1048 and 973 cm⁻¹ disappeared. According to Cerfontain et al.[26], these small bands, which are always observed at high temperatures in CO₂ atmosphere, are associated with the gas-phase CO₂. Thus, these bands can be considered as weak chemisorption of CO₂. In contrast, the broad bands remaining after desorption at around 1579, 1438, 1112 and 940 cm⁻¹ undoubtedly can be considered as strong chemisorption of CO₂ (resulting from the strong withholding of CO₂ molecule by the K catalytic precursor[27]). Further analysis on the characteristics of the formed strong chemisorption are discussed below.

The broad band at around 1438 cm⁻¹ appeared only in the XLT-K-950 adsorption

(comparing with the results of other catalysts not related to the present work), indicating that it was related with the potassium-char system. Mul et al.[28] also observed the band located at around 1400-1800 cm⁻¹ in the DRIFT spectra of partially oxidized Na-, K-, Rb-, and Cs-impregnated carbon black samples at 300 °C in 10% O₂ /90% Ar atmosphere. They pointed out that this band corresponds to the carbonato stretching vibrations of the anhydrous alkali metal carbonates due to the simultaneous appearance of bending vibrations of free carbonate ion around 880 cm⁻¹ in the same spectra. In addition, the absence of band at 880 cm⁻¹ in Figure 6 indicates that the surface complex at around 1438 cm⁻¹ formed in CO₂ atmosphere belongs to another species. Actually, species such as carboxylate and potassium benzoate ( ) formed on an electron-donor centrum of the alkali-carbonate system with the frequency at around 1440 cm⁻¹, can reasonably explain the band at around 1438 cm⁻¹ observed in this study. They could be formed when the incorporation of CO₂ with potassium phenolates occurs in the so-called Kolbe reaction[26]:

In respect to the broad band at around 1112 cm⁻¹, Mims et al.[15] used methylation by CH₃I to test the K₂CO₃-catalyzed carbon surface after partial gasification (solid-state ¹³C NMR detection), and they pointed out that surface phenolate salt ( ) was formed in the partially gasified sample. In another study, Mul et al.[28] measured the spectrum of synthesized potassium phenolate. They found that the strong vibrations occurring around 1320, 980, 780 and 550 cm⁻¹ in the spectrum of synthesized phenolate were not observed in the spectra of alkali-catalyzed carbon black oxidation, although the 1110-1153 cm⁻¹ band appeared. As analyzed above, an active precursor containing O and K can be formed in the char-catalyst system after heat treatment. Thus, it is believed that the 1112 cm⁻¹ band was resulted from CO₂ adsorption by the precursor. In addition, the bands at around 1438 cm⁻¹ were also resulted from the incorporation of CO₂ with potassium phenolates. Therefore, the assumption that the band at around 1112 cm⁻¹ in this study belongs to the potassium phenolates seems reasonable.

Using isotope labeled method, Meijer et al.[29] found that CO₂, which strongly adsorbed on the preheated alkali metal impregnated activated carbon, did not desorb in helium below 402 °C, but it can be exchanged with the gas phase CO₂ at an extremely high rate. This

suggests that the strongly chemisorbed CO₂ had a special interaction with the newly formed surface precursor which could also result in some vibration bands in the spectra. Davydov[30] investigated the IR wave numbers of chemisorbed CO₂ and proposed different vibrational modes of a covalently bound carbonate group. They assigned adimethyl carbonate

configuration ($\text{H}_3\text{CO}-\overset{\text{O}}{\parallel}{\text{C}}-\text{OCH}_3$) to represent the 969 cm⁻¹ adsorption of chemisorbed CO₂, which is in well agreement with the observation of 840-1060 cm⁻¹ vibration in this study.

Figure 7 shows the DRIFT spectra of XLT-K-950 exposed to CO₂ at 200~500 °C. Similar spectral features (except for a slight band position offset at 1408 and 876 cm⁻¹) were observed at 200 °C and 300 °C. At 400 °C and 500 °C, however, the band located around 1400 cm⁻¹ disappeared from the spectra, but instead, an additional absorption band at around 1201 cm⁻¹ was observed. The results signify that potassium benzoate(attributed to the band at 1400 cm⁻¹) tend to decompose during the heating process[26], and not stable enough to be present in the gasification process. Meanwhile, it is clear that potassium phenolate and the strongly chemisorbed CO₂ (dimethyl carbonate), represented by the remaining bands at around 1100 and 940 cm⁻¹, can act as active intermediates in the gasification process. It should also be noted that an assignment of 1201 cm⁻¹ band to the surface oxygen complexes has been proposed in the past by Mul et al.[31]. The presence of this band at higher temperature in this study proves the catalytic effect of K₂CO₃. Clearly, the active precursors formed during the heat treatment process would chemisorb CO₂ and react with it at a relatively higher temperature (higher than 400 °C).

4. Conclusions

The interaction mechanism of K₂CO₃ with graphite and coal char in inert and CO₂ atmosphere was investigated by multi-techniques. The main conclusions from this study are:

- The interactions mechanism is significantly affected by the presence of oxygen groups. Coal char-K₂CO₃ and graphite-K₂CO₃ interactions undergo a different reaction pathway.
- The interaction of graphite and K₂CO₃ creates a C_nK cluster, which is thermally unstable and tend to cleave at high temperature to cause an evaporation of elemental K.
- The interaction of coal char and K₂CO₃ forms a tightly bonded -COK precursor with high thermal stability. It stabilizes the K on the coal char even at high temperatures.
- The DRIFTs results of coal char shows that CO₂ can be chemisorbed by the K- catalytic precursors at 200~500 °C to form potassium phenolate species and a covalently bound

carbonate group (dimethyl carbonate). These two intermediates participate actively in the gasification process.

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Appendix. Supplementary Figure

Supplementary Figure associated with this article can be found in the online version at
supplemental Figure S1.docx

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Table list

Table 1 Published alkali metal compounds catalyzed gasification mechanism

Table 2 Proximate and ultimate analysis of coal and char samples

Table 3 Percentages of elements in heating treated samples analyzed from EDX results

Figure list

Scheme 1. The reaction pathway of carbon- K_2CO_3 interactions in an inert atmosphere

Figure 1 TG-DTG curves of the samples heating in inert atmosphere. Samples: (a) pure graphite, (b) pure K_2CO_3 , (c) graphite + 10 wt. % K_2CO_3 , TG-DTG curve correlated with gas released

Figure 2 TG-DTG curve correlated with gas releasing in inert atmosphere. (a)XLT+10 wt. % K_2CO_3 , (b) GP+10 wt.% K_2CO_3

Figure 3 SEM-EDX images of solid residues after GP demineralized char interact with K_2CO_3 in inert atmosphere at 950 °C

Figure 4 The XRD patterns of K_2CO_3 with carbonaceous materials in inert atmosphere at different temperature. (a) graphite with 10% K_2CO_3 ; (b) XLT/GP coal char with 10% K_2CO_3

Figure 5 DRIFT spectra of (a) graphite-K-950 and (b) pure XLT demineralized char in CO_2 atmosphere at 300 °C

Figure 6 DRIFT spectra of XLT-K-950 in CO_2 atmosphere at 300 °C

Figure 7 DRIFT spectra of XLT-K-950 in CO_2 atmosphere at 200~500 °C

Table 1

Catalyst type	Measuring techniques	Active intermediates	Reference
Alkali Carbonate	Thermogravimetry (TG)	Loosely bonded metal-oxygen complexes, intercalated metal-carbon complexes and tightly-bonded metal-oxygen complexes	[14]
K ₂ CO ₃	Solid-state ¹³ C NMR	Phenolate group	[15]
K ₂ CO ₃	Molecular orbit calculation	C-O-K phenolate-type group	[7, 16]
Na ₂ CO ₃	Isotope labeling, temperature programmed desorption / reduction (TPD/R)	Na ₂ O-Na ₂ O ₂ cycle	[17, 18]
Na ₂ CO ₃	Pulse reaction, isotope labeling, TPD/R	Sodium cluster (Na _n -C) and cluster containing oxygen (Na _n (O)-C)	[19]

Table 2

Sample	Proximate analysis (wt.%, ad)				Ultimate analysis (wt.%, ad)				
	M	V	A	FC	C	H	N	S	O*
XLT	4.66	47.18	8.74	39.41	57.42	5.08	1.70	1.47	25.59
GP	1.32	13.30	21.25	64.14	70.28	2.41	1.51	0.30	4.25
XLT-DC	2.29	3.49	1.55	92.68	92.95	1.77	1.26	0.45	2.02
GP-DC	1.87	2.95	1.68	93.49	93.89	1.74	1.18	0.28	1.23

O*: by difference; XLT: Xiaolongtan lignite; GP: Gaoping anthracite; XLT-DC/GP-DC: XLT/GP demineralized coal char

Table 3

Sample	Temperature	C	K	O	K/C	O/C
		(At%)	(At%)	(At%)	(mol/mol)	(mol/mol)
Pure Graphite	500 °C	93.18	0.66	5.18	0.007	0.056
	600 °C	92.82	1.11	5.59	0.012	0.060
	800 °C	94.76	1.88	2.14	0.020	0.023
	950 °C	97.74	0.29	1.59	0.003	0.016
XLT-DC	600 °C	93.61	0.78	4.53	0.008	0.048
	950 °C	89.96	2.45	6.65	0.027	0.074
GP-DC	600 °C	87.53	1.71	9.97	0.020	0.114
	950 °C	69.87	7.48	21.79	0.107	0.312
	spot 'a' mean	74.72	5.61	19.67	0.075	0.263

Scheme 1

Figure 1

Figure 2

(a) Catalyst distribution in the solid residues

(b) SEM images of the solid residues (several representative flake particles such as spot 'a' was selected to analyze by EDX)

Figure 3

Figure 4

Figure 5

Figure 6

Figure 7