



Short communication

# Effect of catalyst on coal char structure and its role in catalytic coal gasification

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## ABSTRACT

The structure of the coal chars with and without catalyst was characterized using X-ray diffraction and laser Raman techniques. The catalyst changes the structure of the organic unit in coal char. The mechanism by which the catalyst affects the structure of coal char in pyrolysis was investigated by X-ray photoelectron spectroscopy. For the first time, the direct evidence of electron transfer in catalyst–coal interactions was obtained, and a K-Char intermediate forms. This makes it easier for H<sub>2</sub>O to attack the K-Char intermediate, thus increasing the gasification reactivity of coal char.

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## 1. Introduction

Potassium carbonate is widely used in catalytic gasification of coal, biomass and other carbonaceous materials [1–4]. However, the mechanism of catalytic gasification is still obscure. Diverse and sometimes conflicting mechanisms have been proposed to account for the catalytic activity [5]. In general, the mechanism can be classified as oxidation-transfer theories and electron-transfer theories. The oxidation-transfer theory was proposed by Fox and White, in which alkali metal carbonate is first reduced by carbon to the metal and then the metal is oxidized by H<sub>2</sub>O as follows:



The mechanism was then modified by Mckee et al. [5,6]. However, the process is unfavorable because of the highly positive Gibbs free energy and the very low equilibrium constant for the reduction of alkali metal carbonate to the corresponding metal or metal oxide. The electron-transfer theory was postulated by Mims et al. [7,8]. They

considered the formation of active sites involving K-Char and K-Char-O complexes in catalytic gasification, but there was no direct evidence.

The objective of this study is to use X-ray diffraction (XRD), laser Raman technique, and X-ray photoelectron spectroscopy (XPS) to characterize the structure and nature of the coal char and the catalyst during pyrolysis, to further elucidate the detailed mechanism between the coal char and the catalyst during pyrolysis and steam gasification.

## 2. Experimental

### 2.1. Materials and devolatilization

Fugu bituminous coal was used in this study, as shown in Table 1. The samples were crushed to 0.4–0.8 mm and doped with K<sub>2</sub>CO<sub>3</sub> by impregnation with different amounts of K<sub>2</sub>CO<sub>3</sub> aqueous solutions. As a control study, KCl was added to the coal on an equal K molar basis as K<sub>2</sub>CO<sub>3</sub>. The samples were left to dry overnight in air at ambient temperature; then they were further dried at 105 °C in a vacuum oven for 6 h. The coal samples were devolatilized in a fixed-bed reactor without air. The temperature was increased from room temperature to 700 °C at a rate of 10 °C min<sup>−1</sup>, and the final temperature was maintained for 1 h. The coal chars (devolatilized coals) were then cooled and stored for use.

### 2.2. Steam gasification

Catalytic steam gasification was carried out in a stainless steel laboratory-scale fixed-bed flow reactor. The initial amount of the

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**Table 1**  
Ultimate, proximate and ash analysis of Fugu bituminous coal.

Sample	Fugu bituminous coal
<i>Ultimate analysis (wt.%, daf<sup>a</sup>)</i>	
Carbon, C	80.60
Hydrogen, H	4.47
Nitrogen, N	1.07
Sulfur, S	0.28
Oxygen, O (diff <sup>b</sup> )	13.58
<i>Proximate analysis (wt.%)</i>	
Moisture	8.66
Ash (db <sup>a</sup> )	4.70
Volatile (db)	35.27
Fixed carbon (db)	60.03
<i>Ash analysis (wt.%)</i>	
SiO <sub>2</sub>	47.09
Al <sub>2</sub> O <sub>3</sub>	36.08
Fe <sub>2</sub> O <sub>3</sub>	4.35
CaO	4.09
MgO	2.94
TiO <sub>2</sub>	1.35
Na <sub>2</sub> O	0.42
K <sub>2</sub> O	0.45
P <sub>2</sub> O <sub>5</sub>	0.39
SO <sub>3</sub>	2.22

<sup>a</sup> daf = dry and ash free, db = dry basis.

<sup>b</sup> Calculated by difference.

sample was  $\approx 10$  g. The temperature was 700 °C, and the pressure was 3.5 MPa. The water supply was carried out at a constant rate of  $24 \pm 0.5$  g h<sup>-1</sup>, and the N<sub>2</sub> supply was 14.4 L h<sup>-1</sup>. The product gas flow rate was measured using a wet gas meter, and the analysis of dry product gas was carried out using a gas chromatograph (GC) at 30 min intervals.

### 2.3. X-ray diffraction analysis

The samples were ground to the particles less than 0.075 mm. The structural characterization of the coal char was performed using a Rigaku Miniflex II powder X-ray diffraction-meter, using Cu K $\alpha$  radiation ( $\lambda = 0.154178$  nm). The tube voltage and current were 30 kV and 15 mA, respectively. For all the samples, the  $2\theta$  angle was scanned from 10° to 60° with a scanning speed of 1°min<sup>-1</sup> and 0.02° per step. The XRD patterns were analyzed for the structural parameters using the MDI Jade software package.

### 2.4. Raman spectroscopy

The Raman scattering measurements were performed using a Labram-HR800 spectrometer. The 514.5 nm line of the Spectra Physics Ar laser was used for excitation. The laser power was 20 mW. The samples were scanned in the range 800–2000 cm<sup>-1</sup>. For all the spectra, a linear baseline correction was used, and the peaks were analyzed using OriginLab Pro 7.5G.

### 2.5. X-ray photoelectron spectroscopy

The XPS data were acquired using a KRATOS XSAM800 system equipped with monochromatic Al K $\alpha$  radiation (photon energy = 1486.6 eV). The samples were mounted on a gold mesh net attached to the sample holder. The spectra were acquired at a pressure of  $\sim 10^{-7}$  Pa. The X-ray gun was operated at 12 kV and 10 mA, corresponding to a power of 120 W. The analysis area was  $8 \times 8$  mm<sup>2</sup>. The detecting depth is about 5 nm. In most cases, the uncertainty in peak position was  $\pm 0.2$  eV. Curve fitting analysis was performed using the Gaussian/Lorentzian (80%/20%) curve fitting function in the Xps peak 41 software.

## 3. Results and discussion

### 3.1. Gasification reactivity of coal char

The gasification reactivity of the coal char pyrolyzed from coal impregnated with different amounts of K<sub>2</sub>CO<sub>3</sub> and KCl is shown in Fig. 1. It is apparent that K<sub>2</sub>CO<sub>3</sub> increases the gasification rate. The carbon conversion of coal char without catalyst is only 34%; when 8 wt.% K<sub>2</sub>CO<sub>3</sub> was added to the coal, the carbon conversion increased to 90%. The K<sub>2</sub>CO<sub>3</sub> works well in catalytic coal gasification. While 8.64 wt.% KCl (equal K molar basis as 8 wt.% K<sub>2</sub>CO<sub>3</sub>) was added to the coal, the carbon conversion is only 41%.

### 3.2. Carbonaceous structure characterization

Fig. 2 demonstrates the XRD spectra of coal chars pyrolyzed from coal impregnated with different amounts of K<sub>2</sub>CO<sub>3</sub>. In contrast to the profiles of crystals, the diffraction peaks of coal char are low and broad. In the XRD profile of coal, the 100 peak can be attributed to the degree of aromatic ring condensation, and the 002 peak can be attributed to the ordering of aromatic rings [9]. Fig. 2 shows the two main diffraction peaks around 20–30° and 40–50°, which are close to the 002 peak ( $2\theta = 26.6^\circ$ ) and 100 peak ( $2\theta = 43.4^\circ$ ) of graphite. For the coal char without catalyst, the peak corresponding to the 002 plane is  $2\theta = 24.836^\circ$  with high intensity, and the full width at half maximum (FWHM) of the diffraction peak is 9.336. Compared to the raw coal char, the peak corresponding to the 002 plane of the coal char with catalyst shifted to a small angle ( $2\theta = 24.547^\circ$ ), the peak intensity reduced clearly, and the diffraction peak became broad. With increasing amounts of catalyst, the 002 peak shifted to a smaller angle, the peak intensity decreased, and the diffraction peak became broader.

XRD is routinely used to determine the crystallite sizes (carbon crystallite site  $L_a$ , average stacking height  $L_c$ , and interplanar spacing  $d_{002}$ ) in carbonaceous materials [10–11]. The structural parameters of the coal char were calculated using the Scherrer formula as shown in Table 2. Because the diffraction peaks of amorphous materials are characterized by low intensity, broad peak shape, and a high and variable background, the profiles should be fitted to obtain the parameters of the coal char. In this study, the XRD background was removed using a cubic spline, and the broad hump in this region was determined by whole pattern fitting. Compared to the raw coal char, as shown in Table 2, the  $d_{002}$  of the coal char with catalyst increased slightly, while the  $L_a$  and  $L_c$  of the coal char with catalyst decreased significantly. All the above results indicate that the addition of K<sub>2</sub>CO<sub>3</sub> makes the carbon lattice unit grow

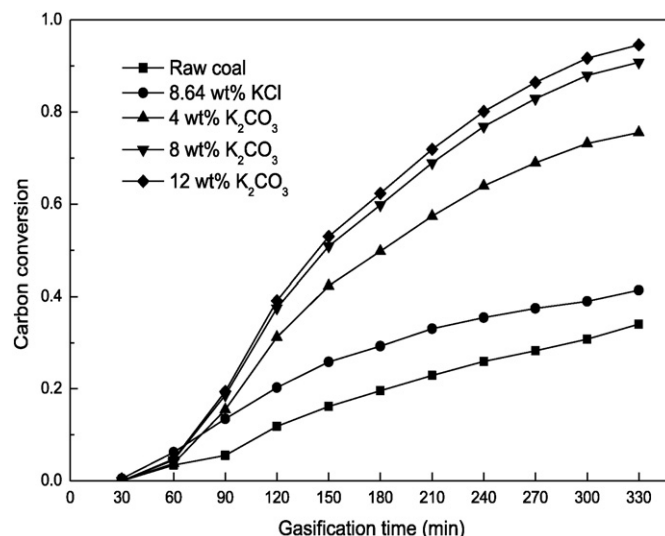


Fig. 1. Reactivity of coal char pyrolyzed from coal impregnated with catalyst.

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