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Devolatilization behaviour and pyrolysis kinetics of coking coal based on the evolution of functional groups

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ABSTRACT

Knowledge of the mechanism of coking coal can improve coke and tar production in the coking industry. The evolution of six main functional groups in two coking coals with different ranks was investigated by in situ Fourier Transform Infrared Spectroscopy (FTIR) during non-isothermal pyrolysis in nitrogen gas flow. Different stages in various temperature ranges were proposed based on the evolution of functional groups during coking coal pyrolysis. The evolution of aromatic groups and C=O between the two coking coals had the largest difference because of the different coal ranks. The correlations among the evolution of the six functional groups during pyrolysis were also investigated to identify the possible reaction mechanism of coking coal pyrolysis. There were three processes, including evaporation of small molecules, decomposition of oxygen-containing groups, and devolatilization of aliphatic groups during pyrolysis. One-way transport and *n*th-order chemical reaction models were the main kinetic models of decomposition of the aliphatic groups, C=O, C–O, and OH. The activation energies of the functional group decomposition in two coking coals were in the range of 25.1–219.4 kJ/mol and 12.3–167.0 kJ/mol. The results that describe the pyrolysis process of coking coals with respect to functional groups can improve the understanding of the pyrolysis mechanism of coking coal and facilitate the development of clean coal technology.

1. Introduction

Coking coal is the main raw material for coke production, which is important for the metallurgy industry. However, because of the limited storage of coking coal and the increase of coking coal price, high carbon content materials, such as non-coking coal and biomass, have been considered to be added into the coking process [1–4], which would influence coke formation. For example, oxygen-containing groups in the additive could have a negative effect on coke formation [1], and some bituminous additives can partially recover the quality of coke from oxidation coal [5]. Deep investigation of the mechanism of coking coal pyrolysis appears necessary to solve this problem. Moreover, comprehensive understanding of the mechanism of coking coal pyrolysis facilitates the production of coal tar and limits pollutant emission during pyrolysis [6].

Studies on the coking process were performed in past decades. Krzesińska et al. investigated the coke formation process of three Polish coking coals and their blends with low rank coal, wooden char and industrial coke using thermogravimetric analysis (TGA), differential scanning calorimetry (DSC), and dynamic mechanical analysis (DMA

[7,8]. The weight loss and heat flow during pyrolysis, as well as the storage/loss elastic modulus measured as a function of the increasing temperature were related to the caking ability of coals. The caking properties of vitrinite concentrates and vitrain were also related to the coal rank and pyrolysis conditions [9,10]. However, the coal structure transformation was not involved in the discussion of coke formation. Hence, several semi-quantitative parameters of 11 coking coals derived from FTIR spectra were related to their caking properties. It was found that the characteristic of aliphatic groups, especially the length of aliphatic chain and branching degree, correlated closely with the caking property [11]. The condensation of coke formed in tar resulted from the removal of oxygen [12]. Nevertheless, the transformation of functional groups during coking coal pyrolysis was not explicitly investigated, especially by in situ FTIR.

The kinetic characteristics of coking coal and blends of coking coal and biomass during pyrolysis were also investigated under isothermal and non-isothermal condition according to the TGA curve [13,14]. The kinetics of pyrolysis in these studies were discussed based on the law of mass action, which requires an unchanged reaction characteristic of the remaining coal during pyrolysis; this is impossible. Hence, the kinetics

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based on the TGA curve are more similar to an empiric description [15]. Because the reaction characteristic of the functional groups in coal was invariable during pyrolysis, more precise kinetic characteristics can be obtained. The evolution of functional groups in coal during pyrolysis can be determined by in situ FTIR [16–20], which is more precise than the ex situ FTIR technique [21].

Solomon and colleagues conducted a series of studies on coal pyrolysis using both the in situ and ex situ FTIR technique [22–26]. The gas products were determined by multiple in situ analysis techniques, such as pyrolysis-FTIR, TG-FTIR, pyrolysis-MS, etc. The functional groups in coal char produced at successive stages were measured by an ex situ transmission FTIR spectrometer and carbon or proton NMR. The relationship between gas products and functional groups in coal was established, and the FG-DVC model was proposed for determining the mechanism and kinetics of coal pyrolysis. However, the online evolution and relationships of the functional groups during coal pyrolysis cannot be recognized because one of the important assumptions for the FG-DVC model is that most of the functional groups decompose independently to produce light gas species.

In this study, the evolution of six main functional groups in two coking coals with different ranks was investigated by in situ transmission FTIR. The kinetic characteristic was discussed based on the loss of four functional groups with the Coats-Redfern method. The purpose of this study was to gain an insight into the different structure transformation of two coking coals during low temperature pyrolysis, which would enhance understanding of coke formation process.

2. Materials and methods

2.1. Coal sample

Two coking coal samples collected from Qujing, Yunnan Province (QJ), and Huainan, Anhui Province (HN), China were used in this study. The coal particles were ground and sieved to less than 0.094 mm in size. Proximate analyses were performed according to the Chinese National Standard Method (GB/T 212–2008) and the ultimate analyses were determined in an elemental analyser (Vario EL cube in Hefei National Laboratory for Physical Science at Microscale). The results are presented on an air-dried (ad) and dry ash free basis (daf), respectively (Table 1). QJ coal has a higher rank and contains higher level of carbon and fixed carbon, lower content of hydrogen, oxygen and volatile materials than HN coal, which was assigned to 1/3 coking coal. The term 1/3 coking coal is a kind of coking coal with a rank between coking coal and gas or fat coal. It contains a high or medium level of volatile matters (28%–37%, daf), has good caking ability and can produce high intensity cokes [27,28].

2.2. In situ FTIR analysis

The in situ FTIR instrument was an FTIR spectrometer (Thermo Nicolet 8700) coupled with a pressurized in situ transmission sample cell (TOPS-IR02, Xiamen Tops Equipment Development Co. Ltd.). Approximately 1 mg of coal was finely ground in an agate mortar with dried KBr at a mass ratio of approximately 1:50 (coal to KBr) under an infrared lamp to minimize the contribution of water to the spectrum,

Table 1

The ultimate and proximate analyses of HN and QJ coals.

Sample	Proximate analyses (ad, %)				Ultimate analyses (daf, %)					H/C	O/C
	M	A	VM	FC	C	H	N	S	O ^a		
HN	1.40	25.4	37.1	45.0	86.0	5.01	1.45	0.78	6.76	0.70	0.059
QJ	0.62	14.0	20.0	68.4	89.2	4.46	1.64	0.46	4.19	0.60	0.035

^aby difference; M: moisture; A: ash content; VM: volatile matter; FC: fixed carbon.

and pressed into a pellet in an evacuated die under 10 MPa of pressure for 1 min. The detailed introduction of this device and the sample preparation process can be found elsewhere [18].

The coal samples were pyrolyzed at a heating rate of 10 °C/min under N₂ gas flow. The FTIR spectra at 25 temperature points in the range of 20–500 °C were recorded on the spectrometer at a resolution of 4 cm⁻¹ by co-adding 8 scans, as shown in Fig. A1. Because the window of the sample cell was made of CaF₂, the available wavenumber range was 1000–4000 cm⁻¹. The 25 temperature points for in situ FTIR determination were chosen based on the TG analysis result. The faster the weight loss of the sample proceeded, the denser the temperature points were set. To distinguish the absorption peaks for each functional group in coal, the Peakfit software was employed to deconvolve the FTIR spectra. The procedure of the deconvolution was described in our previous work [19]. The normalized area used for semi-quantification of each functional group was obtained by defining the integral area of the peak at 20 °C as 1.0.

2.3. TG analysis

TG analysis of the two coal samples were performed using a Q5000IR TGA instrument (TA Instruments). Approximately 11–14 mg of sample was added to an alumina sample pan and heated at 10 °C/min in the range of 20–900 °C, under N₂ gas with a flow rate of 75.0 mL/min. The TG and derivative thermogravimetric (DTG) curves are shown in Fig. 1.

3. Results and discussion

3.1. TG analysis

The TGA and DTG curves (Fig. 1) showed that the weight loss and rate of weight loss of QJ coal during pyrolysis was lower than for HN coal due to the higher coal rank. The DTG curve of HN coal exhibited two peaks in the range of 350–550 °C and 620–720 °C, respectively. The peak centred at approximately 459 °C represented the principal pyrolysis stage of HN coal, while the minor peak centred at approximately 665 °C was for the second cracking stage attributed to the production of gas materials at higher temperature [29]. However, the primary peak in the DTG curve of QJ coal was centred at approximately 494 °C, which was higher than that of HN coal, while the height of the primary peak was much weaker than that of HN coal. In addition, there was no obvious peak for the production of the gas stage.

3.2. Thermal characteristics of functional groups

The weight loss during pyrolysis indicates the evaporation of small molecules and decomposition of functional groups, but the loss of functional groups does not necessarily result in weight loss. For instance, the decomposition of some functional groups, such as –O–, and –CH₂–, which exist as bridges in coal structure, does not always produce fragments that are released. Sometimes, the cracked groups reconnect to the net structure by chemical reactions. Nevertheless, the evolution of the functional groups can reflect more detailed information on the pyrolysis process. Furthermore, the decomposition of functional

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