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Free radicals, apparent activation energy, and functional groups during low-temperature oxidation of Jurassic coal in Northern Shaanxi

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ABSTRACT

Correlations among free radicals, apparent activation energy, and functional groups during low-temperature oxidation of Jurassic coal in Northern Shaanxi were investigated by examining three coal samples collected from the Ningtiaota, Jianxin, and Shigetai coal mines. Free radical concentrations at less than 120 °C were investigated by electron spin resonance experiments while the thermogravimetric experiments were conducted to analyze apparent activation energies. In addition, Fourier transform infrared spectroscopy was employed to study the spectrum of functional groups generated in coal. The results indicated that, in decreasing order, the apparent activation energies were Shigetai > Jianxin > Ningtiaota, indicating that, from 50 to 120 °C, the Ningtiaota coal sample most easily absorbed and reacted with oxygen while the most resistant was the Shigetai coal sample. Free radical concentrations and line heights increased with increased temperature, and the line width and Lande factor showed irregular fluctuations. Functional group variations were different among these coals, and the phenol and alcohol-associated OHs, carboxyls, and aromatic ring double bonds might have had a major impact on free radical concentrations. These results were meaningful for better consideration and management of coal oxidation at low temperatures.

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1. Introduction

China is currently one of the major coal-producing countries in the world. However, low recovery results in numerous remaining coal deposits in goaf. Spontaneous combustion of coal is a serious problem in China [1]. This combustion is a very complex reaction process both physically and chemically, and many studies have sought to characterize this process. Xin et al. have investigated functional group variations during coal spontaneous combustion and re-oxidation [2–4]. Qi et al. have examined the influence of oxygen concentration on this combustion's characteristics [5,6]. Xia et al. have studied coal surface structure variations after oxidation at low temperature [7,8]. Li et al. have calculated the apparent activation energy during spontaneous coal combustion [9,10]. Baris et al. have analyzed gas production variations in such combustion [11–13]. Many types of free radicals have also been detected in coal that are related to coal-oxygen reactions; for example, methyne and carbon free radicals reacting with oxygen is the initial reaction during coal oxidation [14]. Carr et al. have

found that the free radical concentrations from coal increased with drying and that vacuum drying led to rapid radical concentration changes and is lower compared with results from flow drying [15]. Qiu et al. have found that free radical concentrations rose with increased temperature and retention in early combustion decrease when the vitrinite reflectance was higher than 1.75% [16]. Li have presented the mechanism for free radical reactions in spontaneous coal combustion, proposing that coal molecular structure is broken under the action of external forces to produce free radicals [17]. Meanwhile, based on electron spin resonance (ESR) experiments, free radical concentrations have been measured during oxidation, and free radical concentration increases corresponded with smaller particle size, higher temperature, and longer combustion time, while the linewidth showed irregular fluctuations [18]. Zhang et al. have investigated the correlations of the Lande factor, linewidth, and free radical concentration to coal metamorphic grade [19]. Liu et al. studied lignite and weathered coal, and by analyzing ESR spectra, concluded that the spin concentration of weathered coal is lower than that of fresh coal and that this phenomenon can be used to determine whether coal is weathered [20]. Guo et al. investigated the paramagnetic characteristics of tectonic coals and, further, explored the influences of

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dynamometamorphism and free radical concentration to develop the ability to predict methane outbursts [21]. Also, pulverization, illumination, oxidation, and ultraviolet radiation (UV) have been shown to influence coal free radical concentrations [22–24]. This indicated that the UV could cause free radical reactions while higher temperatures and smaller particle sizes lead to higher free radical concentrations, which is in agreement with results from the literature [18]. Furthermore, solvent extraction, as one of the means for determining coal structure, has been used to analyze free radical variation and it has been found that lowered radical concentrations, when temperatures are lower than boiling points, are caused by the coupling of free radicals dissolved from the coal. Meanwhile, increased radical concentrations at high temperatures are a result of solvent-caused cleavage of weak bonds in coal [25]. Zhou et al. considered that during pyrolysis, the variation of concentration, g value and linewidth of radicals in tars may be related to the condensation behavior of coke [26]. Liu et al. took lignite as the object and investigated the variation of free radical concentration during hydrothermal treatment, where the increase in free radical concentration was found [27]. Li et al. found that organic solvent has an effect on the behavior of free radicals in coal below 300 °C, which radical intensity would first increase and then decrease [28]. Green et al. investigated the weathering process of coal at low temperature, and the results showed that radical reactions on the coal surfaces were involved, whereas oxygen-derived radicals had more obvious influence on lower rank coals [29]. Retcofsky et al. studied several coal samples from America, suggesting that free radicals mainly exist in organic structures containing carbon, hydrogen, and oxygen [30].

Many researchers thought that free radicals exist in coal, which may play an important role in both oxidation and pyrolysis of coal. However, few studies focused on the correlation among free radicals, kinetics, and functional groups. In this paper, three coal samples were collected from Ningtiaota, Jianxin, and Shigetai mining areas whose contents include Jurassic coals. Based on ESR analysis, free radical concentration, linewidth, line height, and Lande factor, oxidation at <120 °C was measured. In addition, apparent activation energies were analyzed by thermogravimetric (TG) analysis from 50 to 120 °C. Meanwhile, the correlation between free radicals and functional groups was investigated by grey correlation analysis method. This study's goals were as follows: (1) to analyze the characteristics of free radicals for Jurassic coal, (2) to calculate apparent activation energies of Jurassic coal, and (3) to compare the characteristics of coal free radicals with apparent activation energy and functional groups, and explore their correlations.

2. Experimental and methods

2.1. Coal samples

Coal samples were collected from Ningtiaota, Jianxin, and Shigetai coal mines in Northern Shaanxi province, China, belonging to Jurassic period coal. The results of proximate and elemental analyses are shown in Table 1.

2.2. TG experiments

A thermal analysis instrument from Netzsch Company in Germany (Netzsch Instruments North America, LLC, Boston, MA, USA) was used to conduct TG experiments. Before an experiment, coal samples were crushed and screened for particle sizes of 0.075–0.109 mm and 10 mg samples tested. With a heating rate of 5 °C/min, samples were heated to 600 °C from room temperature while air was supplied at 100 mL/min.

2.3. ERS experiments

For ESR, 10 mg samples of coal particles, described above, were analyzed in a JES-FA200 spin resonance spectrometer (JEOL Ltd., Tokyo, Japan), with 60 mL of air per min. Related parameters were as follows: microwave frequency, 9034.47 MHz; microwave power, 1 mW; central field, 320.024 mT; scanning width, 5 mT; modulation frequency, 100 kHz; modulation width, 0.01 mT; time constant, 0.03 s; scanning time, 1 min; and amplification, 20-fold.

The method was calibrated using 4-hydroxy-tempo (tempol). The free radical concentrations in materials were proportional to the absorption curve intensity. In this experiment, tempol was used as standard sample. Based on Eq. (1) and measuring the spectra of Tempol and coal samples under the same conditions, free radical concentrations of coal samples were calculated using the following:

$$\frac{N_g}{N_s} = \frac{A_g}{A_s} \quad (1)$$

where N_g is the free radical concentrations of test sample, g^{-1} ; N_s the free radical concentration of standard sample, g^{-1} ; A_g the integral areas of test sample; and A_s the Integral areas of standard samples.

2.4. Fourier transform infrared spectroscopy (FTIR) experiments

An in situ diffuse reflectometer (Vertex 80 FTIR spectrometer, Bruker Corp., Billerica, MA, USA) was used to measure functional group changes during coal sample oxidations. Before an experiment, coal samples with particle size of 0.075–0.109 mm were mixed with KBr at a ratio of 1:1, and samples heated at 5 °C/min with an air flow rate of 100 mL/min. During continual collection of spectra, functional group absorption intensities fluctuated. Therefore, the temperature range was set to 30–350 °C for better observation of functional group changes.

3. Results and discussion

3.1. Kinetic parameters

TG and derivative-TG (DTG) curves were obtained from TG examinations of three coal samples (Fig. 1).

When the rate of mass loss of a sample reached a maximum, the temperature was considered as the critical temperature or the first accelerated temperature. The critical temperatures of three coal samples are shown in Table 2.

Table 1
Proximate and elemental analyses of coal samples.

| Coal sample | Proximate analysis (%) | | | Elemental analysis (% daf) | | | | | | |
|-------------|------------------------|------|-------|----------------------------|------|-------|------|------|------|-------|
| | Mad | Ad | Vdaf | C | H | O | N | S | C/H | H/O |
| Jianxin | 3.56 | 9.11 | 34.87 | 74.83 | 4.38 | 19.31 | 0.81 | 0.77 | 1.42 | 0.276 |
| Ningtiaota | 4.44 | 4.17 | 39.18 | 76.51 | 4.79 | 16.71 | 1.33 | 0.54 | 1.33 | 0.218 |
| Shigetai | 7.92 | 4.02 | 37.21 | 74.28 | 5.09 | 18.39 | 1.32 | 0.73 | 1.22 | 0.226 |

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