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Original Research Paper

Chemical properties of superfine pulverized coal particles. Part 1. Electron paramagnetic resonance analysis of free radical characteristics

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ABSTRACT

Superfine pulverized coal combustion is a new pulverized coal combustion technology with lots of advantages. A mechanochemical effect exists during the comminution process, which changes the chemical properties of coal significantly. Free radical concentrations and certain functional groups would increase with the decrease of particle sizes. In this paper, we combined electron paramagnetic resonance (EPR) and ^{13}C solid-state nuclear magnetic resonance (NMR) techniques to study the free radical characteristics of superfine pulverized coal thoroughly. The final results indicate that the EPR spectra of coal are the superimpositions of several lines induced by different paramagnetic centers, which can be fitted by 1 Gaussian and 3 Lorentzian lines. The influences of coal maturities and particle sizes on EPR parameters, such as *g*-values, linewidths, and spin concentrations, are analyzed in detail. It is shown that with the decrease of particle sizes, more free radicals are induced through bond cleavages. Mechanical forces initiate the accumulation of free radicals in the fractures and inner pore surfaces of coal. Furthermore, the influence of particle sizes on oxygen-containing radicals (i.e., Lorentzian 1 types) is the greatest. This work provides a primary picture of the occurrence modes and spatial distributions of free radicals in superfine pulverized coal. The findings will help form the basis and provide guidance for further studies on revealing the correlations between the free radical reaction pathways and NO_x formation mechanisms.

1. Introduction

Energy and the environment are two global challenges that we are facing. China is the largest country on the aspects of producing and consuming coal. At present, 67% of the total Chinese energy needs are fulfilled by coal, and this situation will last for a long time in the future. The air pollutants released from coal combustion is one of the largest pollutive sources, and has caused serious damage to the environment [1–3]. This situation has been a serious restriction to the development of the global society and economy. The proposal of superfine pulverized coal particle combustion provided a new way to understand particle size's effect on combustion, and may become a useful and promising method on controlling CO_2 and NO_x emissions in the future. Through our previous research [4,5], it is found that after ultrafine grinding of coal particles, the combustion performances are significantly improved. Compared with using conventional particle sizes, superfine coal combustion has many advantages on stability, combustion efficiency, ignition and char burnout characteristics, pollutants emission, and comprehensive efficiency, etc.

The physical structure of pulverized coal particles is a crucial factor for the coal combustion process, because of the influence on heat transfer rate and reaction surface. Through our previous studies, several important parameters to characterize the physical properties of superfine coal particles have been studied, such as particle sizes by particle-size distribution [6], surface morphology by atomic force microscopy (AFM) [7], interfacial layers by small angle X-ray scattering (SAXS) [8], and pore structures by nitrogen adsorption [9]. Coal is a complicated compound with heterogeneous nature, which makes it hard to get a global picture of the coal chemical structure. The chemical properties of coal play a significant role in processes such as thermoplastic deformation, pyrolysis, liquefication, combustion, and pollutants emissions. Therefore, it is important to characterize the chemical properties of coal, which is useful for establishing the molecular modeling of coal, and further studying the microscopic mechanism of chemical reactions. Mechanochemical effects occur during the comminution process of superfine pulverized coal, and this makes it more interesting and necessary to learn the chemical properties of superfine pulverized coal.

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Radicals are chemical species that possess an unpaired electron, sometimes called a free spin. There is an appreciable concentration of stable free radicals in coal, presumably formed in the "coalification" process. Ever since Uebersfeld [10] and Ingram [11] discovered the electron spin resonance absorption in natural carbons, electron paramagnetic resonance (EPR) that is a well-established technique has been widely used in the study of coal [12]. Petrakis and Grandy [13] ascertained the presence, concentration and nature of free radicals in several coal, coal fractions, and pyrolyzed coal. Lineshapes, linewidths, *g*-value, and intensity of the EPR signals were measured. Results showed that the finer sieve fraction has a higher spin concentration than the coarse fraction, and significant changes in radical concentration were observed as the pyrolysis temperature increased. Silbernagel et al. [14] tested the EPR spectrum parameters of over 50 maceral samples from different coal rank, and found that radical densities increase with coal rank. Furthermore, there was a certain decrease in radical density upon comminution and an increase upon demineralization. Pilawa et al. [15] compared the influence of oxidation on the paramagnetic centers of demineralized coal and coal free of pyrite. Mutli-component lines were observed and divided into three groups, numerically analyzed using broad Gauss, broad Lorentz 1 and narrow Lorentz 3 separately. Additionally, Pilawa et al. [16] analyzed the EPR spectra of natural coal heated at 300–650 °C. The experimental spectra were approximated by the superposition of 1 Gauss and 3 Lorentz lines. Different behaviors of these unpaired electrons were observed during thermal decomposition of coal. Yokono et al. [17] studied the effect of heating rate on the change of radical concentration during coal pyrolysis. Results showed that the maximum radical concentration decreased with an increase in the heating rate. On the other hand, the effect of a catalyst on the change in radical concentration of coal/$ZnCl_2$ system was monitored. The maximum radical concentration showed a significant shift to temperature about 100 K lower. Korkmaz et al. [18] presented 12 Turkish coals in their raw state, applied the EPR study. They found that the linewidths of the samples were increased with the increase of the coal's carbon content, while the *g*-values showed the opposite trends. Wei et al. [19] took the fragmentation process as the key factor of producing and initiating free radical reactions. They proved coal can produce lots of active free radicals during the process of fragmentation using EPR. Dalal et al. [20] found that grinding produced more free radicals in anthracite coals than in bituminous coals. Fowler et al. [21] summarized some findings related with free radical concentrations during pyrolysis experiments, and pointed out limitations of EPR spectroscopy in evaluating the role of free radicals during coal reactions. They concluded that observed changes in spin concentrations were due to relatively stable char free radicals. Above all, it is generally recognized that free radicals play a crucial role in carbonization, gasification, pyrolysis processes and liquefaction reactions.

The formations of free radicals are, in essence, homolysis of covalent bonds. Bond breaking must occur under intense external forces during the comminution process of superfine pulverized coal, which provides large amount of free radicals. However, few studies focused on the influence of fragmentation on free radicals in pulverized coal particles. There are no systematic studies about the characteristics of free radicals in superfine pulverized coal particles. In this paper, we recorded the *g*-values, lineshapes, linewidths, and integrated intensities of EPR spectra from several superfine pulverized coal samples. The heterogeneity and variability of coal indicate the complex character of its paramagnetic centers. The roles of individual groups of free radicals in different chemical processes are not well known so far [15]. The deconvolution of the EPR spectra was conducted through numerical analysis, applying computer techniques. EPR spectra are the superposition of several lines [22,23], and the individual component lines in the multi-component EPR spectra are studied thoroughly.

2. Material and methods

2.1. Preparation of raw superfine pulverized coal samples

Three different kinds of coal with the distinct extent of coalification were chosen for the experiments. Shenhua (SH), Nei Monggol (NMG), and Tiefa (TF) coal samples from China were pulverized into different mean particle sizes using a QLM-80K fluidized bed jet mill (China). The detailed preparation process was depicted in previous work [7]. The particle-size distribution of the particles was analyzed by the Malvern MAM5004 Laser Mastersizer (U.K.). The resulting equivalent mean particle sizes for TF samples are 6.9, 11.3, 18.9, and 33.6 μm. The sizes of SH samples are 14.7, 17.4, 21.3, and 44.2 μm, while NMG samples are 12.5, 14.9, 25.8, and 52.7 μm. The properties of the coal (i.e., the ultimate and proximate analysis) are listed in Table 1. The ultimate analysis data were recorded in Vario ELIII (Elementar, Germany), and the oxygen content was obtained by difference. The proximate analysis was obtained in LECO MAC 500 (America).

2.2. Free radical analysis methods

The free radical characteristics of superfine pulverized coal particles were investigated utilizing EPR spectroscopy analysis. The EPR experiments were carried out in a Bruker EMX-8 spectrometer (Germany), operating at a frequency of 9.87 GHz. A measured amount of the samples was placed into a 2 mm quartz EPR tube, and then sealed. The magnetic field strength was swept using the standard continuous wave method, in which the microwave frequency is held constant. EPR scan parameters were kept the same during all the experiments: modulation frequency, 100 kHz, X-band; modulation amplitude, 1 G; microwave frequency, about 9.87 GHz; attenuation, 40 dB; time constant, 5.12 ms; scan time, about 20 s; receiver gain, 2500; scan range, 200 G. All the observations were accomplished in air, at ambient temperature and atmospheric pressure. EPR spectroscopy scans were performed with the Bruker computer software WinEPR Acquistion. The main parameters that characterize the EPR spectra are *g*-value, linewidth, lineshape, and spin concentration (radical intensity, i.e., concentrations of paramagnetic centers). The detailed calculation procedures of the parameters and the numerical method of multi-component EPR spectra analysis are summarized in the supplementary material.

Table 1
The ultimate and proximate analysis of tested coal samples.

	Proximate analysis (wt %) (ad)		Ultimate analysis (wt %) (ad)	
SH	Moisture	11.5	C	63.13
	Volatile	24.22	H	3.62
	Ash	10.7	O	9.94
	Fixed carbon	53.58	N	0.70
			S	0.41
NMG	Moisture	14.72	C	54.82
	Volatile	35.69	H	4.39
	Ash	10.64	O	14.58
	Fixed carbon	38.95	N	0.63
			S	0.22
TF	Moisture	5.82	C	55.69
	Volatile	30.30	H	3.88
	Ash	22.65	O	10.62
	Fixed carbon	41.23	N	0.75
			S	0.59