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Effect of temperature and stress on molecular structure and carbon monoxide generation of lignite from Kailuan mining area

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ABSTRACT

In order to analyze the origin of carbon monoxide (CO) in coal seams, stress–strain experiments under temperature of 50, 150 and 250 °C were conducted using lignite from Kailuan mining area. Fourier transform infrared spectroscopy and elemental analysis were carried out before and after deformation of the samples. The results indicated that CO generated at 150 and 250 °C; the gas component was mostly oxygen (O_2), with small amount of carbon dioxide (CO_2), methane (CH_4) and hydrogen (H_2). At 50 °C, O_2 and a little CO_2 were observed and no CO was found. The carbon content of the coal samples increased slightly after deformation, and the oxygen content, H/C ratio, and O/C ratio decreased. The molecular structure of coal displayed different evolution characteristics at various temperatures. At 50 and 150 °C, the falling off of side chains, broken of ether bond and directional realignment of the aliphatic chains resulting in the formation of long chains were the main performance of coal molecular structure evolution. While at 250 °C, the side chains fell off and short chains formed. Furthermore, at both 150 and 250 °C, condensed degree of aromatic ring increased. Under the action of temperature and pressure, CO forms in two ways. The first is that ether bond breaks, oxygen and carbon atoms combine together and forms CO, or O_2 forming in the broken of ether–oxygen bond leads to the oxidation of free radicals and resulting in the formation of CO. And the second is that CO derives from falling off of C=O group.

1. Introduction

Coal, one kind of organic rock, is very sensitive to temperature and pressure. In the process of the geological evolution, various tectonic-thermal events inevitably lead to a series of physical and chemical changes of coal. Aromatic structure, aliphatic structures, as well as oxygen containing functional groups in coal molecular structure perform different evolution characteristics, along with the generation of some kind gases. By employing fourier transform infrared spectroscopy (FTIR), X-ray diffraction (XRD), and X-ray photoelectron spectroscopy (XPS) methods to study the molecular structure of tectonic deformation coal, some researchers considered that tectonic deformation coal and primary structure coal with the same metamorphic degree are different in their chemical structure [1–10].

In recent years, carbon monoxide (CO) over safety standard has been detected from an increasing number of coal mines in China. Research shows that the origin of CO is not only due to the oxidation of coal in the open air, but also due to the primary deposition of CO in the coal seam [10,11]. Coal pyrolysis experiments show that CO is produced when the pyrolysis temperature reaches 300–800 °C [11]. CO is also produced in deformation experiments at temperature of 200 °C [12]. However, it is still not clear whether the original occurrence of CO in coalbed is caused by the side chain rupture of molecular structure at certain temperature at present.

In the past, deformation experiments at high temperatures and pressures usually concentrated on temperature, pressure, and strain rate. However, the chemical changes in the molecular structure has not been systematically studied in those experiments, and whether or not CO has been generated during the process of deformation have been received little attention in those experiments. In this study, coal samples were collected from the Cuijiazhai Coal Mine of the Kailuan Mining Group, where CO concentration has once exceeded the safety limitation during the year of 2012. The deformation experiments were performed at temperatures 50, 150, and 250 °C. The evolution of coal molecular structure and the CO generation mechanism has been studied. And the purpose of this is to find the origin of CO and provide a theoretical basis for the coal mining safety.

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2. Experimental

2.1. Sample collection and preparation

Samples in the study were obtained from E11510 working face of the Cuijiazhai Coal Mine, at depth of 835 m. Three columns with 40 mm length and 20 mm diameter were prepared. Then, following the national standard "GB474-2000", the remained samples were crushed and splitted for elemental, macerals component and industrial analysis, and for the measurement of vitrinite reflectance.

2.2. Stress–strain experiment

Experiments were conducted by using a high temperature and high pressure apparatus, which belongs to the institute of geology, China Earthquake Administration. The temperature was controlled by a set of device, which was used to adjust the power of the heating furnace. To ensure uniform pressure and safe heating of the samples, argon gas was used to apply the confining pressure. And the axial load was controlled with a digital hydraulic servo.

Firstly, 30 min of vacuating was conducted, and then 20 MPa confining pressure was applied. The airtightness was detected. If the entire system was completely sealed, another 15 min of vacuating was applied. Secondly, let the system heating be the experiment temperature. The heating rate was set at 5 °C per minute. After the temperature reached the desired value, the experimental confining pressure was set to 30 MPa. Thirdly, the axial pressure was added. The axial deformation rate was set to 0.001 mm per second until the deformation displacement reached 3–3.5 mm, then kept the temperature at 50, 150 and 250 °C, deformation and axial pressure were stable for 7 h and ended the experiment. During the experiment, the temperature was strictly controlled to ensure the accuracy of the experimental results. Meanwhile, a vacuum bag was used to collect the gas generated in the process of deformation. The deformed samples were broken and ground to 200 mesh for infrared spectroscopy and elemental analysis. The detection of gas composition was performed in the Beijing Coal Chemical Research Branch of the China Coal Science and Technology Research Institute, using an Agilent 7890 meteorological chromatograph.

2.3. Fourier transform infrared spectroscopy

A Vertex 70 Fourier transform infrared spectrometer of Bruker Dalton was used in the infrared spectrum analysis. Each sample was cut into thin slices with a diameter of about 13 mm. For the test sample, KBr ratio was 1:160, in the range of 400–4000 cm^{-1} for collecting spectral information, and the resolution was 4 cm^{-1}. FTIR spectrum was obtained after 32 cumulative scans. In addition, the above experiment was conducted for both samples before and after stress–strain experiments.

3. Results analysis

3.1. Coal quality

The values listed in Table 1 show that the sample represents a low-degree metamorphism of lignite.

3.2. Deformation feature and gas composition

In order to analyze the molecular structure changes of the sample under different temperatures, the deformation experiments were performed at 50, 150, and 250 °C. Fig. 1 shows the results of the experiments.

To ensure purity of the collected gas, the impact of the air and gas adsorbed in coal were minimized. Before the experiment, the air collecting-bag was connected directly to the experimental equipment. And it was vacuumed through the vacuum system together with the whole system simultaneously. Coal samples were kept under vacuum state and significant amount of adsorbed gas was desorbed, and only little part of the adsorbed gas in the confined pores was difficult to expel. This little amount of adsorbed gas had insignificant effect on the experimental results, thus the collected gas mostly came from the deformation experiment. The gases detected in the experiment are listed in Table 2.

The values listed in Table 2 indicate that CO is not collected at 50 °C; and CO is collected at both 150 and 250 °C. Similar performance is observed for other gases, such as H_2 and CH_4. Other observations show that the concentration of O_2 content is the highest at 50 and 150 °C, while the CO_2 concentration is the highest at 250 °C.

3.3. Elemental analysis

Coal is mainly composed of five elements: carbon, hydrogen, oxygen, nitrogen and sulfur. Carbon is of the highest concentration of all elements in coal. Carbon is mainly present as aromatic nucleus and aliphatic side chains, such as C—C, C—O, and C—H bonds. Hydrogen is also present in coal mainly as C—H bonds. Oxygen in coal is represented by molecular bridge bonds and functional groups, mainly in the form of C—O, COO, and C═O bonds. In order to analyze the effect of deformation on the coal macromolecular composition, elemental analysis of the deformed samples was performed.

Elemental analysis before and after deformation was performed using an Elementar Vario MACRO Cube test at the Chemical Engineering Department of the China University of Mining and Technology (Table 3).

Deformation led to the increase in the carbon content of all three samples; however, the oxygen content decreased. The percentage of O reduces, which leads to a material basis for the collection of CO and O_2 during the experiment. This indicated the formation of the oxygen gas as a result of the deformation.

The C/H atom ratio in coal is 3:2 (Table 1), which is greater than the ratio 1:1 in the benzene ring. This value of ratio indicates that the aromatic structure, with at least two substituents on the benzene ring, represents the main part of the coal molecular structure. Moreover, the aliphatic structure, with the average of three substituents, is relatively less, indicating the presence of many aliphatic side chains in coal macromolecular structure.

Compared to undeformed coal, the O/C ratios decreased at 50 °C while H/C ratio kept stable. O_2 and a small amount of CO_2 were collected, which might be attributed to that after the falling off of the oxygen atom from oxygen containing functional groups, carbon atoms combined directly with each other to form C—C bonds, resulting in O/C decrease. And only small amount aliphatic side

Table 1
Coal quality data.

Sample	Industrial analysis (%, by weight)			Elemental analysis (%, by weight)					Maceral composition (%, by weight)				R_0 (%)
	M_{ad}	A_d	V_{daf}	C_{daf}	H_{daf}	O_{daf}	N_{daf}	S_{daf}	V	I	E	M	
CJZ	18.36	5.54	55.58	73.14	4.38	21.31	0.86	0.31	47.37	38.21	0.78	13.64	0.41