



Full Length Article

Study on the change of organic sulfur forms in coal during low-temperature oxidation process



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ARTICLE INFO

Keywords:

Organic surface functional groups
Coal spontaneous combustion
Low-temperature oxidation
Acid treatment
XPS

ABSTRACT

Organic sulfur functional groups in coal not only have certain oxidation characteristics at low temperature and but also can break to produce free radicals, which is bound to have a considerable effect on coal spontaneous combustion. However, this area has not been reported yet. There are relatively few studies on variation laws of organic sulfur functional groups in coal in the coal spontaneous combustion process (especially low-temperature oxidation stage), and the release of SO₂, the gaseous product of organic sulfur during the low-temperature oxidation, is also rarely reported. Therefore, it is necessary to systematically obtain the change laws of organic sulfur forms in coal during low-temperature oxidation. In this paper, the morphological changes of organic sulfur in coal during low-temperature oxidation were studied first, and then the changes of organic sulfur forms in coal before and after low-temperature oxidation and the release of the low-temperature oxidation product SO₂ were studied by using the X-ray photon spectroscopy (XPS) technique and the XLZ-1090 infrared gas analyzer. The XPS analysis results show that the relative contents of mercaptan and sulfide are reduced; the content of thiophene sulfur decreases slightly or remains unchanged; and the contents of sulfone, sulfonate and sulfate all increase. This verifies that the low-temperature oxidation process of active organic sulfur functional groups in coal is: sulfide → sulfoxide → sulfone, mercaptan → disulphide → sulfoxide → sulfone → sulfonic acid. The study reveals that the release of gaseous SO₂ is not detected during the low-temperature oxidation of the raw coal samples, whereas it is detected during the low-temperature oxidation of the acid-treated coal samples. This is because the acid treatment can remove alkaline minerals in coal, weakens the inhibitory effect of alkaline minerals on SO₂ and enable SO₂ to escape almost completely. In addition, the study also discovers that the time and amount of SO₂ gas release during the low-temperature oxidation process are directly related to the metamorphic degree and organic sulfur content of coal.

1. Introduction

As a very complex physical and chemical process covering turbulent flow, phase change, heat transfer, mass transfer and complex chemical reactions, coal spontaneous combustion is a three-dimensional, multi-phase, unsteady, non-linear and non-equilibrium dynamic process involving the interaction among material, momentum, energy and coal chemical structure. The research on it which involves interdisciplinary integration is a major scientific and technical problem that has not been solved yet at home and abroad [1,2]. All kinds of coal contain a certain amount of sulfur which can be divided into two categories, namely, inorganic sulfur and organic sulfur according to their occurrence forms in coal. As sulfur in coal is directly linked with the characteristics of

coal spontaneous combustion, it is of great importance to study the effect of sulfur on coal spontaneous combustion. At present, there are many researches on the spontaneous combustion characteristics of inorganic sulfur coal, especially pyrite. However, a considerable proportion of organic sulfur exists in coal in addition to inorganic sulfur, and their oxidation properties and action mechanisms in coal spontaneous combustion process are different. In the study of coal spontaneous combustion, the effect of organic sulfur is often neglected. The changes of organic sulfur functional groups of coal in low-temperature oxidation process in air are relatively less studied [3], and there is basically no research on the effect of organic sulfur on the spontaneous combustion characteristics of coal.

Organic sulfur is a general term for many organic sulfur-containing

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<https://doi.org/10.1016/j.fuel.2018.02.157>

Received 6 September 2017; Received in revised form 12 February 2018; Accepted 24 February 2018

Available online 23 March 2018

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functional groups. Consisting mainly of some sulfur-containing functional groups combined with organic matters, organic sulfur in coal is generally bound as C–S bond in coal macromolecule skeleton, and its chemical structure and composition are very complex [4]. It can be known from the knowledge of modern chemistry that sulfur atoms can form π bonds using 3p orbit, but the π bonds in different orbits have narrow overlaps and the electrons of a π bond are far from the nucleus, so C–S and S–H bonds are prone to break. Besides, the large size of sulfur atom determines that its electronegativity is small, and the valence electron layer is less bound by the nucleus due to its large distance from the nucleus, so it is oxidized more easily compared with carbon atom [5]. Therefore, the organic sulfur functional groups in coal often show higher activity, but the oxidation characteristics of organic sulfur in different forms still differ remarkably. For example, due to the strong reducibility of thiol group in mercaptan, it can be oxidized into disulphide by low-temperature air just in mild conditions, and the disulphide can be further oxidized into sulfonic acid [6]. Thioether and other sulfides can also be oxidized by air to form sulfoxide and sulfone, while the $-\text{SO}_2$ bonds connected to aliphatic and aromatic functional groups tend to undergo C–S bond breakage to release SO_2 gas. In addition, in the presence of β hydrogen, sulfoxide and sulfone can be further oxidized into sulfinic acid and sulfonic acid at higher temperature [7]. Among different kinds of organic sulfur, thiophene is very stable, as it remains stable when the temperature of air gets up to 500 °C [8]. Borah et al. held that the removal of organic sulfur in coal mainly resulted from the release of sulfur free radicals when the temperature was lower than 50 °C, while the removal mechanism was influenced by both free radicals and volatile sulfides when the temperature was over 50 °C. After the oxidation pretreatment, the organic sulfur in coal will be decomposed into small molecular structures which were easier to be removed. They also believed that low-temperature oxidation can transform organic sulfur in coal into S=O and $-\text{SO}_2$ [3,9,10]. Gorbaty et al. carried out oxidation experiments on Raša and other two coal samples in air under the temperature condition of 125 °C. The XPS and XANES test results showed that aliphatic sulfides were more easily oxidized in air than aromatic sulfides and that they could be transformed into sulfoxide, sulfone and sulfonic acid and other oxidized sulfur [11]. Grzybek et al. who used oxidants such as $\text{O}_2/\text{Na}_2\text{CO}_3$ and PPA to oxidize coal of different metamorphic degrees inferred via XPS test and analysis that the oxidation process of organic sulfur in coal was unoxidized sulfur \rightarrow sulfoxide \rightarrow sulfone [12,13]. The aforesaid studies were mostly aimed at removing organic sulfur in coal, and the variation laws of organic sulfur in coal in the coal spontaneous combustion process (especially low-temperature oxidation stage) were rarely reported [14–16]. In fact, SO_2 , the gas product of organic sulfur during coal oxidation, can hardly be detected among indicator gases of coal spontaneous combustion, which is why the role of organic sulfur in the low-temperature oxidation process of coal is often neglected. The organic sulfur functional groups in coal possess certain oxidation characteristics at low temperature, which is bound to have a considerable impact on coal spontaneous combustion. Hence, it is necessary to systematically conclude the change laws of organic sulfur forms in coal during low-temperature oxidation. In this paper, the changes of organic sulfur forms in coal before and after low-temperature oxidation and the release of the low-temperature oxidation product SO_2 were studied by using the X-ray photon spectroscopy (XPS) technique and the XLX-1090 infrared gas analyzer. Meanwhile, the form change and variation law of organic sulfur in coal during the low-temperature oxidation process were obtained, which can provide a valuable basis for further understanding the influence mechanism of organic sulfur on coal spontaneous combustion and the development of low-temperature oxidation desulfurization technology.

2. Experiment

2.1. Sample processing method

The experimental coal samples were Anning anthracite (AN) from Guizhou, Taifeng fat coal (TF) from Guizhou, Xingcheng fat coal (XC) from Guizhou, Datong weakly caking coal (DT) from Shanxi and Chifeng lignite (CF) from Inner Mongolia, respectively. As can be judged according to the Chinese national standard GB/T15224.2-2004 [17], AN, XC and CF belong to low-sulfur coal, while TF and DT belong to high-sulfur coal. It can be seen from literatures [18,19] that minerals especially pyrite in coal will affect the reliability of XPS test results. Hence, in order to avoid the interference of pyrite with the results, this paper also treated the samples with hydrochloric acid and hydrochloric acid/nitric acid and then made a comparative analysis on the acid-treated samples. The acid treatment was carried out according to the method described in literature [20]. The specific procedure was as follows. First, 30 g of raw coal (60–80 meshes) was placed in a 500 ml beaker, and then 250 ml (4.8 N) hydrochloric acid solution was poured into the breaker. Next, they were heated in water bath at 70 °C and stirred with a glass rod. After being heated for 30 min, the mixture was vacuum filtered and washed repeatedly with distilled water until the pH of the filtrate became neutral. After the coal residue had been dried in a vacuum oven at 50 °C for 12 h, it was sealed for the next treatment. Then, the coal treated by hydrochloric acid was taken for the second treatment, namely, nitric acid treatment. In the same way, 30 g of coal treated by hydrochloric acid was placed in a 500 ml beaker, and then 250 ml (2N) nitric acid solution was poured into the breaker. Next, they were heated in water bath at 70 °C and stirred with a glass rod. After being heated for 30 min, the mixture was vacuum filtered and washed repeatedly with distilled water until the pH of the filtrate became neutral. After the coal residue had been dried in a vacuum oven at 50 °C for 12 h, it was sealed for the next treatment. After the acid treatment, 10 samples were prepared. They are labeled according to the following method. An “H” was added at the end of the codes of samples treated by hydrochloric acid, whereas an “N” was added to those treated by hydrochloric acid/nitric acid. The proximate analysis, elemental analysis and sulfur form analysis were made on raw coal samples and the acid-treated in accordance with Chinese national standards GB/T 212-2008 [21], GB/T 476-2001 [22], GB/T 214-2007 [23] and GB/T 215-2003 [24], respectively. The detailed results of coal quality and sulfur form analysis are listed in Tables 1 and 2.

2.2. Experimental steps and instrument parameter setting

The main steps of this experiment are as follows. First, 30 g of experimental coal sample was taken from the sealed bag and ground to 180–250 μm . The experiment was performed on the self-made low-temperature oxidation experimental device used by literature [13] which was mainly composed of an air intake system, a coal sample tank, a temperature-programmed furnace, a temperature control system, a gas chromatograph and an infrared gas analyzer. The sample was placed in the sample tank, and then the sample tank was put into the temperature-programmed furnace with the air flow rate set as 50 ml/min and the temperature range as 30–180 °C. Next, the temperature-programmed furnace and temperature controller were turned on to raise the furnace temperature at an interval of 10 °C. After the temperature of the tank reached the set value, the temperature was kept unchanged for 20 min. In the whole experimental process, an XLX-1090 infrared gas analyzer was used to monitor SO_2 , the oxidation product of samples. The temperature-programmed furnace was turned off when the tank temperature reached 180 °C. After the sample cooled to room temperature, 2 g of the oxidized coal sample was taken and ground to smaller than 74 μm for the XPS test. The XPS test results of organic sulfur on the coal surface before and after the oxidation were comparatively analyzed. The XPS test was performed on an ESCALAB250 X-

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