Influence of Organic Sulfur on Low-Temperature Oxidation of Coal and its Transition Characteristics

Fei Gao,* Zhe Jia, Ya-fei Shan, Yifei Teng, Ying-di Li, and Xin-ge Pu

ABSTRACT: The low-temperature oxidation spontaneous combustion of coal was caused by the active groups in its structure. The oxidation mechanism of carbon and oxygen functional groups in coal had been extensively studied, but there were few reports on the study of sulfur functional groups initiating the coal spontaneous combustion. To investigate the influence of organic sulfur functional groups on the spontaneous combustion of high-sulfur coal and explore its transformation characteristics, the low-temperature oxidation experimental system was used to study the spontaneous combustion tendency of coal with similar metamorphic degrees and different organic sulfur contents. The variations of element forms and organic sulfur functional groups were analyzed by X-ray photoelectron spectroscopy and Fourier transform infrared spectroscopy during low-temperature oxidation of coal and model compounds. The results showed that the forms of organic sulfur in coal mainly included mercaptans, thioethers, thiophenes, sulfones (sulfoxides), and sulfates, and the low-temperature oxidation of coal was not only related to the content of organic sulfur but also related to its type. The coal samples, which possess a low content of total sulfur and a small proportion of active organic sulfur groups such as mercaptans and thioethers, had a lower concentration of indicator gas and a smaller tendency to coal spontaneous combustion. After low-temperature oxidation, the content of mercaptan, thioether, thiophene, methyl(methylene), and pyridine in coal decreased, and the content of oxygen-containing groups such as sulfone (sulfoxide), sulfate, carboxyl, and nitrogen oxide increased. The elements of S, C, and N all changed to a high-valent state. In the oxidation reaction of model compounds, mercaptans were more reactive than thiophenes in the low-temperature region, and the oxidation of thiophene could direct form sulfone (sulfoxide), while the oxidation of mercaptan formed disulfide first. It is speculated that low-valence sulfur migrated to a high-valent state by providing sulfhydryl radicals (•SH) and sulfur radicals (C−S•) combined with active oxygen atoms. After the low-temperature oxidation reaction of model compounds, some organic sulfur existed in the form of aromatic sulfur or sulfur oxides and a small part of sulfur escaped as SO₂ and H₂S gases in the solid oxidation product.

1. INTRODUCTION
Coal spontaneous combustion is a severe problem in coal mines. Due to the huge loss of high-quality coal caused by coal spontaneous combustion, scholars at home and abroad have carried out a great deal of research on the mechanism of coal spontaneous combustion.1−5 Since coal spontaneous combustion starts from the reaction of some active groups, many references have studied the activities of aliphatic chains and oxygen-containing functional groups such as −OH, −CHO, −COOH, C≡O, C−O, −CH₃, and −CH₂ in coal,6−12 but there are few studies on the coal spontaneous combustion caused by functional groups containing other elements in the coal structure. As a harmful element in coal, sulfur can not only produce H₂S and SO₂, which would cause environmental pollution during the combustion process, but also restrict the rational utilization of coking coal resources. The sulfur-containing components in coal are mainly divided into two categories:13 one is inorganic sulfur, which mainly exists in a
form of mineral sulfur such as pyrite; the other is organic sulfur, which generally exists in the molecular structure of coal by chemical bonds. According to the molecular orbital theory, it can be observed that sulfur atoms and other atoms could form $\pi$-bonds by utilizing $3p$ orbits of sulfur atoms. The valence electron shell is far away from the atomic nucleus and is less bound by the atomic nucleus, so $C-S$ bonds and $S-H$ bonds are prone to breakage. That is to say, the sulfur atom is more easily oxidized than carbon atoms.

As early as the 17th century, British Plot and Sweden Berzelius proposed the theory of pyrite causality, which indicated that coal spontaneous combustion was caused by the reaction of pyrite in coal seams with water and oxygen to release heat. When scholars studied the effect of sulfur on coal spontaneous combustion, they mainly focused on the influence of inorganic sulfur on the characteristics of coal spontaneous combustion; the role of organic sulfur groups is generally ignored during the coal spontaneous combustion process; thus, there are few reports related to the effect of organic sulfur groups on coal spontaneous combustion.\(^{15,16}\) Dark et al.\(^{17}\) found that free radicals could be generated during low-temperature oxidation, and the $C-S$ bond dissociation energy decreased significantly with the increase of aliphatic carbon atoms. Zhang et al.\(^{18}\) studied the influence of organic sulfur model compounds on coal spontaneous combustion. It was found that the oxidation activity of organic sulfur functional groups from high to low was mercaptan $>$ thioether $>$ thiophene. Despite the investigations of organic sulfur forms in coal before and after low temperature, the transition rule of sulfur forms is still in its infancy during low-temperature oxidation.\(^{19}\) Dai et al.\(^{20}\) used Gaussian to calculate the reaction mechanism of phenylthiophenol sulfur and thiophene sulfur in coal with $O_2$, but the calculation results were not verified by experiments.

Since it is difficult to remove organic sulfur groups in coal,\(^{20,21}\) the existing studies all added organic sulfur compounds to model compounds such as molecular sieves to simulate the coal samples with different organic sulfur contents and types. The effect of organic sulfur in coal on the coal oxidation spontaneous combustion was simulated by analyzing the oxidation exothermic characteristics and reaction paths of the model compounds.\(^{22}\) However, most of the organic sulfur groups in coal are bound to the macromolecular structure of coal by covalent bonds. Adding organic sulfur model compounds in coal cannot realistically reflect the organic sulfur structure in coal. In view of the above situation, three coal samples with a high organic sulfur content were selected, which have similar metamorphism degrees and different sulfur contents to investigate the influence of the type and content of organic sulfur groups on the coal oxidation spontaneous combustion. Two model compounds containing special organic sulfur groups were used to analyze the transition characteristics of organic sulfur groups during the low-temperature oxidation process, aiming to reveal the intrinsic relationship between the organic sulfur groups in coal and the low-temperature oxidation process of coal.

### 2. EXPERIMENT

#### 2.1. Sample Collection and Treatment

##### 2.1.1. Coal Preparation

To avoid the interference of inorganic sulfur in high-sulfur coal on the process of oxidation spontaneous combustion, the clean coal (which has removed most of the inorganic sulfur) after treating in the coal washery was selected as the research object. The remaining sulfur in coal is principally organic sulfur that cannot be removed by conventional washing and processing methods. In the experiment, the coal samples which are three fat coals with different sulfur contents were selected as the research objects. The three fat coals were, respectively, Lvinenghua clean coal (LLNH), Huipodi clean coal (HPD), and Shuiyu clean coal (SY).

Proximate analysis of the coal samples was based on China’s National Standard GB/T 212-2008. The total carbon, hydrogen, and nitrogen contents in coal were determined by China’s National Standard GB/T 30733-2014. The total sulfur of the coal samples was measured by China’s National Standard GB/T 214-2007. The oxygen content in the coal samples was calculated by subtraction. The proximate analysis and ultimate analysis of the three coal samples are shown in Table 1. As shown in Table 1, the three coal samples have similar metamorphic degrees. The various forms of sulfur in the coal sample were measured based on China’s National Standard GB/T 215-2003. The distribution result of the sulfur form is displayed in Table 2. The three coal samples were crushed and sieved to 100 mesh (about 0.15 mm) and were dried at 60 °C for 12 h in vacuum.

##### 2.1.2. Preparation of Organic Sulfur Model Compounds

By comparing the loading rate and adsorption rate of organic sulfur model compounds on activated carbon, silica, and activated trialumina, it was found that activated carbon was more suitable as a carrier.\(^{21}\) Therefore, to prepare organic

### Table 1. Proximate Analysis and Ultimate Analysis of Coal Samples
d

| coal sample | $A_d$ | $V_{daf}$ | $M_{daf}$ | $C_{daf}$ | $H_{daf}$ | $N_{daf}$ | $O_{daf}$ | $S_{daf}$ |
|-------------|-------|----------|-----------|----------|----------|----------|----------|----------|
| LLNH        | 9.68  | 21.6     | 0.89      | 83       | 4.12     | 1.12     | 9.33     | 2.43     |
| HPD         | 9.5   | 36.99    | 1.25      | 84.65    | 5.26     | 1.4      | 6.26     | 2.43     |
| SY          | 9.3   | 21.09    | 0.76      | 86.94    | 4.65     | 1.37     | 4.78     | 2.26     |

$d$ means dry basis, $daf$ means dry ash-free basis, $ad$ means air-dry basis, and the percentage of oxygen was calculated by difference.

### Table 2. Sulfur Forms Distribution and Organic Sulfur Proportion in Different Fat Coals

| coal sample | total sulfur $S_{daf}/\%$ | pyrite $S_{p,d}/\%$ | sulfate $S_{s,d}/\%$ | mercaptan (thioether) $S_{o,d}$ | thiophene sulfide (sulfone) $S_{t,d}$ | organic sulfur ratio (%) |
|-------------|--------------------------|-------------------|---------------------|-------------------------------|--------------------------------------|-------------------------|
| LLNH        | 2.43                     | 0.31              | 0.02                | 29.72                         | 37.24                                | 2.10                    | 86.24          |
| HPD         | 2.43                     | 0.44              | 0.02                | 18.68                         | 60.92                                | 20.4                    | 1.97           | 81.07          |
| SY          | 2.26                     | 0.25              | 0.05                | 12.22                         | 67.93                                | 19.85                   | 1.96           | 86.69          |
sulfur model compounds, activated carbon was selected as the coal-based of model compound, \( \text{l-cysteine (BGAS)} \) and thiophene (SF) were selected as the active structures to simulate the functional groups of coal such as the mercaptan (thioether) and thiophene, and anhydrous ethanol was selected as the solvent. All reagents used were from Aladdin (Shanghai) Co., Ltd., and the purity was AR grade. The preparation process was as follows: the activated carbon was placed in a vacuum drying oven at 60 °C for 12 h; a certain amount of model compound and anhydrous ethanol were evenly mixed and poured into a crystallization dish containing 5 g of activated carbon. After magnetic stirring for 60 min, the crystallization dish was ultrasonically treated for 60 min to ensure uniform mixing. The ethanol was volatilized after drying at room temperature for 24 h in the ventilation cabinet. The prepared model compounds were sealed and stored in a vacuum drying oven. The sulfur content in the sample can be calculated by the following formula. The proportion of organic sulfur model compounds is shown in Table 3.

\[
s = \frac{s_1m + s_mC}{m + m_C} \times 100\%
\]

In the formula, \( s \) is the sulfur content of model compounds, %; \( s_1 \) is the sulfur content in the sulfur compound, %; \( s_C \) is the sulfur content in the activated carbon, %; \( m \) is the mass of the sulfur compound, g; and \( m_C \) is the mass of the activated carbon, g. The sulfur content in activated carbon was calculated at 0.5%.

2.2. Low-Temperature Oxidation Experiment. The coal low-temperature oxidation experiment was carried out with a self-made experimental system, which was mainly composed of an air intake system, a tubular furnace, and a gas detection system. Gas detection was completed using a 3420A gas chromatograph produced by North Branch. The inlet of the tube furnace was connected to the air intake system, and the outlet was directly connected with the gas chromatograph, which could detect the composition of gas products in real time. The experimental parameters for the low-temperature oxidation of the three clean coals were as follows: 2 g dried samples were programmed at the heating rate of 1 °C/min, and the air flow rate was set to 400 mL/min. The gas composition at the outlet of the tube furnace was analyzed every 20 °C, and the tubular furnace was closed after heating to 200 °C.

2.3. X-ray Photoelectron Spectroscopy Experiment. To analyze the change of sulfur element during the oxidation process, the oxidized coal samples and model compounds at different temperatures were tested by X-ray photoelectron spectroscopy (XPS).

SY coal was selected to repeat the above low-temperature oxidation experiment several times, and the coal samples were sequentially numbered according to the end temperature of the experiment, which were marked as SY40, SY60, SY80, SY100, SY120, SY140, SY160, and SY200. Similarly, thiophene model compounds were labeled as SF40, SF100, SF160, and SF220, and \( \text{l-cysteine model compounds were labeled as BGAS40, BGAS100, BGAS160, and BGAS220, respectively.} \)

The XPS test was carried out using an AXIS SUPPRA X-ray photoelectron spectrometer (Shimadzu). The analytical chamber was evacuated below the vacuum of 10\(^{-8}\) Pa. The X-ray excitation source was 150 W, and the monochromatic AlKα (1486.6 eV) was used. The analytical size was 300 \( \times \) 700 \( \mu \)m, and the fixed transmission energy of the full-spectrum energy analyzer was 160 eV. The fixed transmission energy of the narrow full-spectrum energy analyzer was 40 eV. The binding energy of standard C ls was 284.6 eV for correction. After the experiment, the results were processed by Casa XPS software.

2.4. Fourier Transform Infrared Spectroscopy Experiment. Fourier transform infrared spectroscopy (FT-IR) was used to characterize the functional groups of organic sulfur model compounds at different oxidation temperatures. In this

![Figure 1. Experiment system diagram (coal mill, gas chromatograph, XPS, and FT-IR photograph courtesy of Zhe Jia, Copyright 2021).](https://doi.org/10.1021/acsomega.2c03824)
paper, EQUINOX55-FTIR Fourier transform infrared spectrometer (Bruker, Germany) was used. The samples were mixed with KBr at the proportion of 1:100 in a mortar and thoroughly grinded to 200 mesh (about 0.071 mm). The samples were placed in the sample room and scanned 32 times at room temperature with 4.0 cm\(^{-1}\) spectral resolution in the spectral bands of 300–4000 cm\(^{-1}\). At the same time, the blank KBr tablet was used as the background for scanning to eliminate the influence of background on spectral quality. The experimental system diagram is shown in Figure 1.

3. RESULTS AND DISCUSSION

3.1. Analysis of the Indicator Gas Emission on Coal Spontaneous Combustion. CO, CO\(_2\), alkanes, alkenes, alkynes, and other indicator gases would be released during the coal oxidation and heating processes. The production of these gases changed regularly with the increase of coal temperature, which can predict and reflect the spontaneous combustion state of coal.\(^{24}\) The indicator gas concentrations of three clean coals in the low-temperature oxidation process are shown in Figure 2a–f. The variation trend of the concentration of all kinds of indicator gases was roughly similar during the coal low-temperature oxidation with different organic sulfur contents. It can be seen from Figure 2 that when the coal temperature increased to 80 °C, CO began to be produced. As the coal temperature increased, the concentration of CO increased slowly and increased sharply after 120 °C.

CO\(_2\) gas is released at 40 °C because CO\(_2\) is adsorbed in coal samples. Some of the CO\(_2\) monitored in the experiment came from desorbing the coal sample when the coal sample was heated, and the others came from the oxidation reaction when the coal temperature increased. Therefore, there is no evident regularity in the release of CO\(_2\) before 100 °C. After 100 °C, the coal sample began to react, and the CO\(_2\) concentration gradually increased. Comparing three coals, LLNH coal produced the highest concentration of CO and CO\(_2\), the second highest was HPD coal, and SY coal produced the lowest. It can be seen from Table 2 that the order of total sulfur content in the three coals is LLNH = HPD > SY. It is basically in line with the fact that the lower the sulfur content in coal, the less the gas concentration produced at the same temperature.

The common hydrocarbon gases include CH\(_4\), C\(_2\)H\(_4\), C\(_3\)H\(_6\), and C\(_3\)H\(_8\). The release of the four hydrocarbon gases mainly comes from the thermal cracking of coal,\(^{25}\) in which CH\(_4\) is generated by the methyl branched chain at low temperature and aromatic rings and cyclic hydrocarbons at high temperature. C\(_2\)H\(_4\) is the product of coal fat side-chain fracture, and its production usually indicates that coal begins to enter the stage of deep oxidation.\(^{26}\) When the temperature reached 100 °C, CH\(_4\) began to precipitate from HPD coal. However, the
releasing temperatures of CH\textsubscript{4} from LLNH and SY coal were gradual after 120 °C. At this time, the CH\textsubscript{4} concentration of HPD coal increased sharply, indicating that HPD coal contained more methyl branched chain structures. The releasing temperature of C\textsubscript{2}H\textsubscript{4} from the three coal samples was 120 °C, indicating that the samples entered the deep oxidation stage at this time. When the coal temperature gradually increased to 180 °C, the concentration of C\textsubscript{2}H\textsubscript{4} increased exponentially with the increase of temperature, indicating that the coal samples began to oxidize rapidly after 180 °C. LLNH coal began to release C\textsubscript{3}H\textsubscript{6} at 120 °C, when HPD and SY coal were at 140 and 180 °C, respectively. When release started, the concentration of C\textsubscript{3}H\textsubscript{6} released by LLNH coal and HPD coal began to increase rapidly and the rate increased sharply.

The release rule of four hydrocarbon gases was similar to that of CO and CO\textsubscript{2}. At the same temperature, the concentration of hydrocarbon gases produced by SY coal is the smallest; that is, the lower the sulfur content, the lower the concentration of the indicator gas and the slower the release rate. It is noteworthy that the amounts of CO and CO\textsubscript{2} produced by LLNH coal are obviously larger than that by HPD coal and SY coal, and the change trend of the latter two is almost the same; this is because although LLNH and HPD have the same sulfur content, the organic sulfur of HPD coal is mainly composed of thiophene sulfur; the stable thiophene structure in coal reduces the reactivity of coal−oxygen composite reaction due to the existence of conjugated π-bonds. Therefore, HPD shows a poorer tendency to spontaneous combustion than LLNH.

In summary, the low-temperature oxidation process of coal is not only affected by the organic sulfur content but also related to the proportion of active sulfur functional groups in coal. That is, the less the active sulfur functional groups in coal, the slower the spontaneous combustion oxidation process of coal.

3.2. Analysis of Element Form Characteristics during Coal Spontaneous Combustion. 3.2.1. Analysis of Sulfur Forms in SY Coal. XPS fitting curves of SY coal at different oxidation temperatures are shown in Figure 3. Taking SY40 as
an example, the peak positions of organic sulfur 2p$_3/2$ are mercaptan, thioether sulfur 162.1–163.6 eV; thiophene sulfur 164.0–164.4 eV; sulfoxide sulfur 165.0–166.0 eV; and sulfate sulfur more than 169.1 eV. The fitting spectrum shows that the main forms of organic sulfur in SY coal are mercaptan, thioether, thiophene, sulfone, and sulfoxide. There is no significant difference in the forms of organic sulfur at each experimental temperature.

The distribution of sulfur forms in SY coal at different oxidation temperatures is shown in Figure 4. It can be seen from the XPS fitting graphs (Figures 3 and 4) that the content of C and N elements in coal were also studied. Carbon in coal contains functional groups with oxygen can more intuitively reflect the carbon-containing functional groups are generally divided into the following four bands: C–C (284.4 ± 0.5 eV), C–H (285.0 ± 0.3 eV), C–O (286.1 ± 0.2 eV), and COO$^-$ (288.8 ± 0.2 eV), respectively. The N-containing functional groups were divided into the following four bands: 398.8 ± 0.4 eV for pyridine nitrogen (C$_5$H$_4$N), 400.2 ± 0.3 eV for pyrrole nitrogen (C$_5$H$_5$N), 401.4 ± 0.3 eV for protonated pyridine (C$_6$H$_6$N$^+$), and 402.9 ± 0.5 eV for nitrogen oxides (NO$_x$). The changes of C and N functional groups during low-temperature oxidation are shown in Table 4.

It can be seen from the data in Table 4 that at 40 °C, the functional groups in coal samples mainly exist in the form of C–C and C–H, and there is a small amount of C–O and COO$^-$. Among them, the contents of C–C and C–H were more than 80%; after 100 °C, the content of C–O and COO$^-$ increased relatively, and C–C and C–H decreased. This was basically consistent with the temperature at which the indicator gas began to be released. With the increase of temperature, the content of C–O and COO$^-$ in coal samples increased by about 7% at 200 °C. At the temperature, the released indicator gas concentration increased significantly. This indicates that with the low-temperature oxidation process, the side chains and the bridge bonds of the polycyclic aromatic system began to crack, and the carbon atoms exposed to the air were oxidized to C–O, COO$^-$, CO, CO$_2$, and so on.

The proportion of pyrrole in the coal samples at different temperatures was the largest, and the relative content was the highest, up to 43.49%, followed by the content of pyridine. At 40 °C, there was 30.57% pyridine, while the content of protonated pyridine and nitrogen oxides was the lowest, and the peak proportion was also the smallest. With the increase of temperature, the content of protonated pyridine decreased, and the content of pyridine, pyrrole, and nitrogen oxide increased. The reason is that the C–C and C–C bonds in coal are destroyed so that the protonated pyridine is exposed and oxidized to pyrrole and pyridine on the edge of the aromatic ring in the coal molecule. The content of nitrogen oxide increased gradually, indicating that with the increase of temperature, nitrogen in coal is oxidized and existed in a higher-valence state. This is consistent with the rule reflected by the sulfur and carbon spectra.

3.2.2. Analysis of Other Element Forms in SY Coal. While studying the form changes of S element in coal, the changes of C and N elements in coal were also studied. Carbon in coal exists in the form of functional groups such as C–C, C–H, C–O, and COO$^-$. According to the carbon spectrum of XPS, the

![Figure 4. Change of organic sulfur forms in SY coal with different oxidation temperatures.](https://doi.org/10.1021/acsomega.2c03824)
Figure 5. Sulfur XPS peak fitting graphs for different temperatures of SF and BGAS model compounds.

Figure 6. Changes of sulfur in various forms at different temperatures: (a) thiophene and (b) cysteine.

Figure 7. Infrared spectra of sulfur model compounds at different temperatures: (a) thiophene and (b) cysteine.
fitting results of SF and BGAS model compounds are exhibited in Figure 5. Taking SF40 and BGAS40 as examples, at room temperature (40 °C), only thiophene sulfur and sulfate sulfur were found in SF model compounds, and only mercaptan sulfur and sulfate sulfur were found in BGAS model compounds. After oxidation, it can be seen from the fitting spectra that the sulfur content in SF model compounds mainly included thiophene, sulfoxide, sulfone, and sulfate and BGAS model compounds mainly included mercaptan, sulfoxide, sulfone, and sulfate.

As shown in Figure 6, before 100 °C, the content of thioether in BGAS decreased from 67 to 45%, the sulfoxide increased from 0 to 35%, and the sulfone increased from 0 to 11%, indicating that aliphatic sulfur (thioether) in coal reacted with oxygen to form sulfoxide and sulfone; however, the content of thiophene in SF did not change significantly, only decreasing from 55 to 51%, and sulfoxide increased from 0% to about 4%, indicating that most of the aromatic sulfur (thiophene) did not react with oxygen at low temperature. With the increase of temperature to 220 °C, the content of thioether and thiophene in SF and BGAS decreased continuously, the content of sulfoxide (sulfone) and sulfate increased, and the content of sulfone in SF increased to 37%, indicating that both aromatic sulfur and aliphatic sulfur could gradually react with oxygen to form sulfoxide and sulfone during the oxidation process. This is basically consistent with the change trend of organic sulfur form in SY coal.

3.4. Transition Rule of Functional Groups during Oxidation Spontaneous Combustion of Model Compounds. The infrared absorption peaks of SF and BGAS model compounds were roughly divided into four regions, namely, hydroxyl (3700–3200 cm⁻¹), fatty structure (3000–2800 cm⁻¹), oxygen-containing functional groups (1800–1000 cm⁻¹), and aromatic structure (900–400 cm⁻¹). The stretching vibration peaks of sulfur-containing functional groups are mainly concentrated in the 1800–400 cm⁻¹. Figure 7 shows the change of sulfur-containing functional groups at different oxidation temperatures. It can be seen from Figure 7a that the stretching vibration peak of aromatic C=–C in the SF model compound was at 1620 cm⁻¹, and the vibration positions of hydroxyl and carbonyl were at 1122 and 1402 cm⁻¹, respectively. The stretching vibration of C–S–C in thiophene was located at 538 cm⁻¹. After the low-temperature oxidation, the stretching vibration absorption peaks of sulfone at 1152 cm⁻¹ and sulfoxide at 1044 cm⁻¹ became stronger, indicating that sulfone and sulfoxide were generated during oxidation.

The infrared spectra of BGAS model compounds are shown in Figure 7b. The stretching vibration of mercaptan C–SH and disulfide –S–S– were located at 540 and 454 cm⁻¹, respectively. With the deepening of oxidation, C–SH was rapidly oxidized and the vibration intensity was weakened, the absorption peak of sulfoxide at 1045 cm⁻¹ was significantly enhanced, and the absorption peak of sulfone at 1296 cm⁻¹ is also increased. This manifests that with the increase of temperature, C–SH continuously combined with oxygen to form sulfone and sulfoxide.

The proportion of sulfur-containing functional groups to all functional groups in the model compound at the different oxidation temperatures is shown in Figure 8. At 100 °C, the mercaptan C–SH decreased from 7.64 to 2.65% and that of thiophene C–S–C decreased from 9.06 to 6.10%, and the disulfide –S–S– in BGAS increased sharply. The downward trend of mercaptan C–SH was higher than that of thiophene C–S–C, indicating that the chemical structure of thiophene C–S–C was relatively stable, while mercaptan C–SH showed
strong reactivity. When the temperature increased to 160 ºC, the downward trend of mercaptan C−SH became slow, and the downward trend of thiophene C−S−C became obvious. At 220 ºC, the proportion of mercaptan C−SH decreased to 0.74%; that is, mercaptan C−SH reacted with oxygen almost completely throughout the reaction, but there were still some stable thiophene C−S−C that did not react with oxygen. The changes of these functional groups also further illustrate the activity of sulfur-containing functional groups in coal and their influence on coal spontaneous combustion from the micro perspective.

3.5. Reaction Mechanism Analysis. Changes of organic sulfur in coal during low-temperature oxidation are closely related to its speciation state. Combined with XPS and FT-IR results, most of the sulfur initially existed in the form of active organic sulfur. At the beginning of oxidation, aliphatic sulfur was more easily bound with oxygen and changed to higher-valence sulfur due to its chemical activity; the chemical structure of aromatic sulfur is stable, and it will not easily react with oxygen. With the increase of oxidation temperature, the activity of aromatic sulfur gradually increased, and the high-valent sulfur content in coal increased. Combined with references and previous studies, the reaction mechanism of organic sulfur functional groups during low-temperature oxidation is shown in Figure 9.

As shown in Figure 9, sulfur-containing active functional groups in coal can trigger and transfer free radicals in chain reaction during low-temperature oxidation. In the initial stage of coal oxidation, aliphatic sulfur and aromatic sulfur existed in coal. Under the continuous impact of oxygen molecules, R−SH in coal begin to decompose, providing sulfur free radicals (C−S°) or sulfdryl (SH) for coal-oxygen reaction. Sulfdryl free radicals (SH) can combine with hydroxyl free radicals (HO•) to produce H2S, two sulfur free radicals (C−S°) react to form disulfide bonds (S−S−), and sulfur free radicals (C−S°) and sulfdryl free radicals (SH) react with other free radicals such as hydroxyl radicals (OH•) to produce sulfur−oxygen free radicals (S−O°). Some sulfur−oxygen free radicals (S−O°) combine with oxygen free radical species to form sulfone (sulfoxide), and the others can directly react with oxygen to form SO2. Some of sulfone can be decomposed into alcohol and SO2 at high temperature. Under the double impact of temperature and oxygen, the concentration of active free radicals in the reaction increases continuously, and S atoms migrate from coal to gaseous products.

4. CONCLUSIONS

Three different sulfur contents of coal and two model compounds were selected for low-temperature oxidation experiments, XPS test, and FT-IR test. The influence of organic sulfur on low-temperature oxidation of coal and its transition characteristics were analyzed. The conclusions were summarized as follows:

1. During the coal low-temperature oxidation, the coal with a low content of total sulfur and a small proportion of active organic sulfur groups had a lower concentration of indicator gas and a smaller tendency to coal spontaneous combustion. The influence of organic sulfur in the coal spontaneous combustion process not only was related to the sulfur content in coal but also had a great correlation with the form distribution of organic sulfur.

2. After low-temperature oxidation, the content of mercaptan, thioether, thiophene (methylene), pyridine, and other groups in coal decreased; the content of sulfone, sulfate, carboxyl, nitrogen oxide, and other groups increased; and the elements of S, C, and N in coal changed to a high-valent state. Most of the sulfur in coal initially existed in the form of active organic sulfur and existed in solid oxidation products in the form of stable aromatic sulfur or sulfur oxides after oxidation.

3. The low-temperature oxidation experiment of organic sulfur model compounds showed that the reaction activity of mercaptan was higher than that of thiophene at low temperature, and the reaction of mercaptan with oxygen occurred with disulfide to form sulfoxide, and thiophene reacted with oxygen to form sulfide directly. Mercaptans, thioethers, and thiophenes combined with active oxygen atoms by providing sulfur free radicals (C−S°) or sulfdryl free radicals (SH) so that the organic sulfur groups in coal changed to a high-valent state, and part of sulfur escaped in the way of generating small gas molecules such as H2S and SO2.

AUTHOR INFORMATION

Corresponding Author
Fei Gao – School of Safety Science and Engineering, Liaoning Technical University, Fuxin 123008, China; orcid.org/0000-0001-6565-2243; Email: ggfg2001@163.com

Authors
Zhe Jia – School of Safety Science and Engineering, Liaoning Technical University, Fuxin 123008, China
Ya-fei Shan – School of Safety Science and Engineering, Liaoning Technical University, Fuxin 123008, China
Yifei Teng – School of Safety Science and Engineering, Liaoning Technical University, Fuxin 123008, China; orcid.org/0000-0001-5321-3243
Ying-di Li – School of Safety Science and Engineering, Liaoning Technical University, Fuxin 123008, China
Xin-ge Pu – School of Safety Science and Engineering, Liaoning Technical University, Fuxin 123008, China

Complete contact information is available at: https://pubs.acs.org/10.1021/acsomega.2c03824

Author Contributions
The paper was a collaborative effort among the authors. F.G. and Z.J. conceived and designed the experiments and wrote the paper; Y.-f.S. proposed the idea; X.-g.P. performed the experiments; Z.J. and X.-g.P. analyzed the data; F.G., Y.T., and Y.-d.L. modified the paper.

Notes
The authors declare no competing financial interest. The data used to support the findings of this study are available from the corresponding author upon request.

ACKNOWLEDGMENTS
This work was supported by the National Natural Science Foundation of China (51874161).

REFERENCES

1. Deng, J.; Xiao, Y.; Li, Q.; Lu, J.; Wen, H. Experimental studies of spontaneous combustion and anaerobic cooling of coal. Fuel 2015, 157, 261–269.
(2) Hu, X.; Yang, S.; Zhou, X.; Yu, Z.; Hu, C. Coal spontaneous combustion prediction in gob using chaos analysis on gas indicators from upper tunnel. *J. Nat. Gas Sci. Eng.* 2015, 26, 461–469.

(3) Avila, C.; Wu, T.; Lester, E. Estimating the spontaneous combustion potential of coals using thermogravimetric analysis. *Energy Fuels* 2014, 28, 1765–1773.

(4) Chou, C. L. Sulfur in coals: A review of geochemistry and origins. *Int. J. Coal Geol.* 2012, 100, 1–13.

(5) Onifade, M.; Genc, B. Spontaneous combustion of coals and coal-shales. *Int. J. Min. Sci. Technol.* 2018, 28, 933–940.

(6) Liang, Y.; Tian, F.; Luo, H.; Tang, H. Characteristics of coal re-oxidation based on microstructural and spectral observation. *Int. J. Min. Sci. Technol.* 2015, 25, 749–754.

(7) Deng, J.; Zhao, J.; Zhang, Y. N.; Wang, C. P. Micro-characteristics of spontaneous combustion of second oxidation with different rank coals. *J. China Coal Soc.* 2016, 41, 1164–1172.

(8) Gündaral, G.; Hosgörümen, H.; Örcan, D.; Li, X.; Liu, H.; Song, W. The properties of Çanakkaale coal (Çanakkale-Turkey): Spontaneous combustion and combustion by-products. *Int. J. Coal Geol.* 2015, 138, 1–15.

(9) Wang, D. M.; Xin, H. H.; Qi, X. Y.; Dou, G. L.; Qi, G. S.; Ma, L. Y. Reaction pathway of coal oxidation at low temperatures: a model of cyclic chain reactions and kinetic characteristics. *Combust. Flame* 2016, 163, 447–460.

(10) Li, K.; Khanna, R.; Zhang, J.; Barati, M.; Liu, Z.; Xu, T.; Yang, V.; Sahajwalla, V. Comprehensive investigation of various structural features of bituminous coals using advanced analytical techniques. *Energy Fuels* 2015, 29, 7178–7189.

(11) Qi, X.; Xue, H.; Xin, H.; Wei, C. Reaction pathways of hydroxyl groups during coal spontaneous combustion. *Can. J. Chem.* 2016, 94, 494–500.

(12) Qi, X.; Chen, L.; Xin, H.; Ji, Y.; Bai, C.; Song, R.; Xue, H.; Liu, F. Reaction mechanism and thermodynamic properties of aliphatic hydrocarbon groups during coal self-heating. *Energy Fuels* 2018, 32, 10469–10477.

(13) Calkins, W. H. The chemical forms of sulfur in coal: a review. *Fuel* 1994, 73, 475–484.

(14) Mracek, A. Towards an understanding of the coal structure: a review. *Fuel Process. Technol.* 2002, 77-78, 25–32.

(15) Deng, J.; Ma, X.; Zhang, Y.; Li, Y.; Zhu, W. Effects of pyrite on the spontaneous combustion of coal. *Int. J. Coal Sci. Technol.* 2015, 2, 306–311.

(16) Li, X.; Shang, Y. J.; Chen, Z. L.; Chen, X. F.; Niu, Y.; Yang, M.; Zhang, Y. Study of spontaneous combustion mechanism and heat stability of sulfide minerals powder based on thermal analysis. *Powder Technol.* 2017, 309, 68–73.

(17) Dack, S. W.; Hobday, M. D.; Smith, T. D.; Pilbrow, J. R. Free-radical involvement in the drying and oxidation of victorian brown coal. *Fuel* 1984, 63, 39–42.

(18) Zhang, L.; Li, Z.; He, W.; Li, J.; Qi, X.; Zhu, J.; Zhao, L.; Zhang, X. Study on the change of organic sulfur forms in coal during low-temperature oxidation process. *Fuel* 2018, 222, 350–361.

(19) Dai, F.-W.; Deng, C. B.; Deng, H. Z.; Wang, X. F.; Gao, F.; Zhang, X. Theoretical study on the mechanism of the thiophene structure with O₂ reaction. *J. China Coal Soc.* 2014, 39, 699–704.

(20) Mu, X.; Liu, J.; Gao, F.; Deng, C.; Jin, Z.; Gong, L.; Peng, Y. Microwave-assisted removal of sulfur in large particle size coal by bromine water. *Fuel* 2021, 289, 119838.

(21) Gonsalvesh, L.; Marinov, S. P.; Stefanova, M.; Carleer, R.; Yperman, J. Organic sulphur alterations in biodesulfurized low rank coals. *Fuel* 2012, 97, 489–503.

(22) Tang, Y. B.Low Temperature Oxidation of Coal Surface Active Groups based on Model Compounds: China University of Mining and Technology: Xu Zhou, 2014; pp 61–66.

(23) Liu, F.; Xie, L.; Guo, H.; Xue, M.; Hu, R.; Hu, H. Sulfur release and transformation behaviors of sulfur-containing model compounds during pyrolysis under oxidative atmosphere. *Fuel* 2014, 115, 596–599.

(24) Lu, X. X.; Zhao, H. B.; Zhu, H. Q.; Han, Y.; Xue, X. Characteristic rule of spontaneous combustion tendency of oxidized coal at recrudescence stage. *J. China Coal Soc.* 2018, 43, 2809–2816.

(25) Wang, J.; Chen, Q.; Deng, C.; Deng, H.; Wang, X. Reaction mechanism of coal spontaneous combustion producing methane. *J. China Coal Soc.* 2009, 34, 1660–1664.

(26) Zheng, H.; Li, Y.; zhang, W.; He, Y.; Han, D.; Xu, D. Study on the effect of organic sulfur on coal spontaneous combustion based on model compounds. *Fuel* 2021, 289, 119846.

(27) Ma, L. L.; Qin, Z. H.; Zhang, L.; Liu, X.; Chen, H. Peak fitting methods and parameter settings in XPS analysis for organic sulfur in coal. *J. Fuel Chem. Technol.* 2014, 42, 277–283.

(28) Ge, T.; Ma, X. M. XPS study on occurrence characteristics of carbon, oxygen, nitrogen and sulfur in coking coal. *Coal Technol.* 2018, 37, 293–295.

(29) Mu, X. G. Study on Oxidation Exothermic Characteristics and Reaction Mechanism of High Organic Sulfur Coking Coal. Diss. Liaoning Technical University, 2021.

(30) Shriner, R. L.; Hermann, C. K.; Morrill, T. C.; Curtin, D. Y.; Fusan, R. C. Infrared spectroscopy. *The Systematic Identification of Organic Compounds*, 7th ed.; John Wiley & Sons: Beijing, Chemical Industry Press, 2007; Chapter 7, pp 165–170.

(31) Liu, S. L.; Kong, J.; Shen, Y. F. Study on sulfur occurrence form and thermal change behavior of separated components of high organic sulfur coking coal. *J. Fuel Chem. Technol.* 2019, 47, 915–924.

(32) Gao, F.; Jia, Z.; Qin, M. L.; Mu, X. G.; Teng, Y. F.; Li, Y. D.; Bai, Q. H. Effects of organic sulfur on oxidation spontaneous combustion characteristics of coking coal. *Energy Explor. Exploit.* 2022, 40, 193–205.

(33) Li, G. Y.; Wang, F.; Wang, J. P.; Li, Y. Y.; Li, A. Q.; Liang, Y. H. ReaxFF and DFT study on the sulfur transformation mechanism during the oxidation process of lignite. *Fuel* 2016, 181, 238–247.