ABSTRACT: To deeply explore the spontaneous combustion disaster of coal caused by air leakage and oxygen supply, low-temperature coal oxidation experiments under different oxygen concentrations (DOC) were carried out. Within the coal spontaneous combustion characteristic measurement system, a synchronous thermal analyzer (STA) and a Fourier transform infrared spectrometer (FTIR), the macro laws of gas and heat generation under DOC are analyzed, and the mechanism of the development of coal spontaneous combustion restricted by the lean-oxygen environment is also revealed. The results show that the change of oxygen concentration (OC) does not affect the critical temperature value and gas index change trend, but the lean-oxygen environment reduces the gas concentration and heat production rate very obviously. According to the temperature of the intersection, OC needs to be lowered to less than 5% when preventing spontaneous combustion of coal. The chain thermal reaction lags in the lean-oxygen environment, and the pyrolysis activity is significantly reduced. Meanwhile, the temperature points at $T_6$ and $T_7$ show significant differences. Furthermore, with increasing OC and temperature, the content of the aliphatic hydrocarbon presents an overall trend of first increasing, then decreasing, and continuously increasing after stage IV. It is concluded that $^\cdot$OH, aliphatic hydrocarbons, aromatic hydrocarbons, and carbonyl groups are the key groups for the coal spontaneous combustion evolution under DOC. To combine the spontaneous combustion reaction of coal in the DOC environment, the reaction path of the index gas in the macroscopic phenomenon and the reason for the concentration differences are revealed, the mechanism for exotherm varies caused by OC is clarified, and the microscopic inhibition affection on the chain reaction within the lean-oxygen environment is also explored. The results put forward the key groups evolution mechanism under the DOC for coal oxidation, which could provide the technical guidance for the fire prevention and control on coal mines.

1. INTRODUCTION

According to the BP Statistical Review of World Energy, the total coal consumption reached 15 786 million tonnes in 2019,¹ and the frequent occurrence of coal spontaneous combustion not only threatens the mineral resource deposits and life safety but also causes environmental pollution.² All coal-producing countries have problems with coal fires to varying degrees,³⁴ with China having the most frequent coal fires caused by spontaneous combustion.⁵

Currently, Northwest and North China, which account for more than 80% of China’s coal reserves, are facing severe challenges from coalfield fires. There are still 46 unmanaged in-combustion fire areas in Xinjiang, with a total fire area of 6 693 000 m² and 4.42 million tonnes of coal resources lost to combustion each year,⁶ while the emission of carbon oxides, hydrocarbons, and other harmful gases can cause serious atmospheric damage and geological disasters. In addition, there are more than 4000 fire hazards and 360 fires caused by spontaneous combustion of coal each year, nearly 100 working faces closed by fire each year, and more than 10 million tonnes of coal frozen due to fire area closure, bringing huge economic losses.⁷ Essentially, whether it is a large coalfield fire area burning, or a mine fire and other disasters caused by spontaneous combustion of coal left in the mining area, it is all due to the wind flow through the coal seam fissures creating a lean-oxygen environment and finally causing the coal to oxidation—combustion—diffusion. (Lean-oxygen, generally defined as an atmosphere with an OC of less than 18%.)

Therefore, research on the characteristics of coal oxidation and temperature rise in low-temperature and lean-oxygen
environment is extremely important for the prevention of coalfield fires. Many scholars have studied the effects of heating rate, moisture, and particle size on the process of coal spontaneous combustion in terms of macro characteristics. However, the macroscopic characteristics of coal spontaneous combustion are the macroscopic manifestations of the changes in the microscopic surface structure of coal. Many methods are used to describe the chemical structure of organic matter, including thermogravimetric analysis−infrared spectroscopy (TG-FTIR) method, pyrolysis-mass spectrometry (MS) method, and X-ray photoelectron spectroscopy (XPS). Among them, TG-FTIR has the characteristics of simple operation, low cost, and excellent effect. Many scholars have also made breakthroughs in the fields of coal pyrolysis characteristics and oxidation kinetics using this method. Xu et al. studied that CO produced by active groups during coal spontaneous combustion was analyzed by studying the reaction of free radicals and oxygen-containing functional groups. Song et al. studied the functional groups in the chemical structure of different low-level metamorphic coals and found that the decomposition characteristics and kinetics are closely related to its complex chemical structure. Qi et al. further analyzed and confirmed the thermodynamic parameters of coal basic reactions through quantum chemical methods. Tang et al. analyzed the relationship between active groups such as C=O, C≡O, °OH, and heteroatom functional groups in coal and coal permeability and porosity. Wang et al. analyzed the relationship between elementary reactions at
active sites in coal and their reaction sequence and secondary, including the construction of microstructures, quantum chemical analysis, and molecular dynamics simulations of various metamorphic coal types. In addition, Li et al., Shi et al., Bhai et al., and Chen et al. constructed a model of coal macromolecules and proposed the mechanism of initial oxidation at room temperature, the principle of gas production during pyrolysis, and the mechanism of hydrogen capture reaction. They refined the basic theory of coal spontaneous combustion from the level of coal surface microstructure.

In summary, a large number of studies have been carried out by domestic and international scholars on the changes in the oxygen environments were analyzed and the effects of OC on coal spontaneous combustion gas production law, heat production, weight loss ratio, and other parameters were explored.

2. RESULTS AND DISCUSSION

2.1. Index Gas. By testing the change law of index gas with increasing temperature and the critical temperature point

Table 1. Characteristic Temperature

| OC (%) | $T_1/°C$ | $T_2/°C$ | $T_3/°C$ | $T_4/°C$ | $T_5/°C$ | $T_6/°C$ | $T_7/°C$ |
|--------|---------|---------|---------|---------|---------|---------|---------|
| 10     | 67.9    | 159.72  | 160.4   | 217.9   | 267.2   | 406.5   | 465.4   |
| 14     | 68.5    | 157.42  | 161.1   | 233.5   | 268.5   | 403.9   | 466     |
| 18     | 70.6    | 153     | 153     | 223.1   | 265.6   | 397.6   | 445.6   |
| 20     | 66.9    | 154.8   | 159.4   | 226.9   | 264.4   | 393.7   | 439.4   |

Figure 4. Characteristic temperature difference between OC-20% and coal under DOC.

under different oxygen concentrations (DOC) we can understand its spontaneous combustion characteristics of coal.

With the increase of temperature, the concentration of index gas C$_2$H$_4$ and CO produced by coal shows an exponential increase trend; 80 °C was the critical temperature of CO, after which the coal–oxygen reaction speeded up, and the CO concentration increased significantly. At this time, the concentration of C$_2$H$_4$ was extremely low, the rate of change was basically unchanged, and there was an obvious upward trend after the temperature increased to 120 °C. With the deepening of the lean-oxygen environment, the two indicator gases have obvious hysteresis. For OC-5%, it needed to reach 140 °C before there was a significant increase in concentration. This was because the active groups that produce C$_2$H$_4$ cannot be activated at low temperatures, and the lean-oxygen environment caused the hysteresis effect to occur. At the stage of 140–240 °C, the pyrolysis reaction was accelerated and the influence of OC on the concentration of C$_2$H$_4$ was obvious. With the increase of OC, the index concentration and release rate showed a more significant increase. The average change rate of OC-21% was 0.0008 ppm·s$^{-1}$ higher than that of OC-3%. After 240 °C, the change rate of the concentration of C$_2$H$_4$ generated at OC-21% decreased, indicating that the pyrolysis reaction gradually tended to equilibrium. The change of DOC to CO concentration changed obviously when the temperature is low. At 110–140 °C, the CO concentration was affected by the lean-oxygen environment, and it began to decrease significantly. After 140 °C, the coal–oxygen recombination reaction intensified and the concentration difference became more obvious. In particular, at around 200 °C, the rate of change of CO concentration at OC-21% was about 6 times that of OC-3%. However, judging from the law of curve growth in the low-temperature stage, DOC did not affect the critical temperature of every coal sample. It may be that the critical temperature was mainly determined by the exotherm of the oxygen-containing functional group with the highest activity.

As the lean-oxygen environment deepened, the strength of the coal–oxygen composite reaction was weakened, resulting in insufficient oxygen to activate the corresponding functional groups during the reaction. After a long period of temperature energy and oxygen molecule accumulation, it was activated at a higher temperature, the oxygen absorption capacity was accelerated, the macromolecular aromatic ring structure decomposed rapidly, the exposed active structure increased sharply, and the index gas concentration increased significantly. In addition, after the reaction between the molecular structure of coal and oxygen was completed under sufficient OC conditions, more coal–oxygen contact surfaces and pore structures would react with oxygen. Therefore, when the temperature increased, the index gas concentration in a lean-oxygen environment was always lower than OC-21%.

2.2. Heat Production Characteristics. The porosity of the coal sample is determined by the equation $\varphi = \frac{d - \varphi_a}{\varphi_a}$ (where $\varphi_t$ and $\varphi_a$ are the true density and apparent density, respectively), which gives $\varphi = 0.504$. In the low-temperature oxidation stage, the active group reacts physically and chemically with oxygen to generate gas and solid products accompanied by changes in heat. According to the conservation of energy, the heat production rate is obtained as eq 1:

$$Q_t = mC_p\frac{dT}{dt} - (s\lambda + Q_{in})(T_L - T)$$

where $m$ is the coal sample mass, kg; $C_p$ is the constant pressure specific heat coefficient, J·kg$^{-1}$·K$^{-1}$; $T$ is the coal temperature, K; $t$ is the heating time, s; $A$ is the outer surface area of the coal sample tank, m$^2$; $\lambda$ is the thermal conductivity of the test bituminous coal sample, W·m$^{-2}$·K$^{-1}$; $T_L$ is the furnace temperature, K; $Q_{in}$ is the mass flow of air at the
heat production rate, J

The temperature delay period in the initial stage of heating, which was due to the number of active groups in the molecular structure of coal, showed that the extremely low OC failed to activate a large number of active groups during the heating process. This resulted in no cross-point temperature between OC-5% and OC-3%. In particular, there was no cross-point temperature between OC-5% and OC-3%. Stage I, the initial heating phase (40–60 °C), was characterized by the heat transfer and oxygen absorption characteristics of coal at this time. The temperature difference between the control temperature and the coal temperature remained constant at this time, with no oxidation reaction occurring. At this time, the heat generation rate was close to zero. Stage II, endothermic process (60–140 °C), was characterized by the accelerated reaction of coal and oxygen, and the heat production rate was obviously separated when the OC is lower than 18%. Stage III, the rapid heat release stage (140–200 °C), was characterized by the oxygen supply capacity due to the heat release rate being highly dependent on the oxygen concentration. Stage IV, the rapid oxidation stage (200–300 °C), was characterized by the oxygen composite reaction, which limited the temperature rise of coal. Figure 2b was divided into stages according to the heating characteristics. Stage I, the initial heating phase (40–60 °C), was characterized by the heat transfer and oxygen absorption characteristics of coal at this time. The temperature difference between the control temperature and the coal temperature remained constant at this time, with no oxidation reaction occurring. At this time, the heat generation rate was close to zero. Stage II, endothermic process (60–140 °C), was characterized by the accelerated reaction of coal and oxygen, and the heat production rate was obviously separated when the OC is lower than 18%. Stage III, the rapid heat release stage (140–200 °C), was characterized by the oxygen supply capacity due to the heat release rate being highly dependent on the oxygen concentration. Stage IV, the rapid oxidation stage (200–300 °C), was characterized by the oxygen composite reaction, which limited the temperature rise of coal.

Figure 2a shows the relationship between coal temperature and control temperature with time. The heat generation rate characteristics of the coal sample during the heating process can be obtained by eq 1, as shown in Figure 2b.

It was observed from Figure 2a that there was a significant delay period in the initial stage of heating, which was due to the fact that coal was a depleted conductor of heat transfer. The temperature difference reached the maximum at 6800 s because the temperature increased to adsorb external oxygen and the endothermic reaction occurred. After 7700 s, most coal samples had temperature crossover points. In particular, there was no cross-point temperature between OC-5% and OC-3%. It showed that the extremely low OC failed to activate a large number of active groups in the molecular structure of coal, which limited the temperature rise of coal. Figure 2b was divided into stages according to the heating characteristics. Stage I, the initial heating phase (40–60 °C), was characterized by the heat transfer and oxygen absorption characteristics of coal at this time. The temperature difference between the control temperature and the coal temperature remained constant at this time, with no oxidation reaction occurring. At this time, the heat generation rate was close to zero. Stage II, endothermic process (60–140 °C), was characterized by the accelerated reaction of coal and oxygen, and the heat production rate was obviously separated when the OC is lower than 18%. Stage III, the rapid heat release stage (140–200 °C), was characterized by the oxygen supply capacity due to the heat release rate being highly dependent on the oxygen concentration. Stage IV, the rapid oxidation stage (200–300 °C), was characterized by the oxygen composite reaction, which limited the temperature rise of coal. Figure 2b was divided into stages according to the heating characteristics.

2.3. Thermogravimetric Characteristics. 2.3.1. Characteristic Temperature. In the coal–oxygen composite reaction, a series of reactions such as oxygen molecules attacking surface free radicals and organic carbon oxidation will cause quality changes. TG and differential thermogravimetric (DTG) curves were used to observe the change of quality with temperature under DOC conditions, and indirectly characterize the spontaneous combustion characteristics of coal by analyzing the characteristic temperature points of the curve, as shown in Figure 3.

At the beginning of the experiment, due to the evaporation of water, the quality of the coal sample decreased during the initial heating, and after reaching stage I at 110 °C, the quality was relatively stable. However, in stage II, the quality began to decrease significantly. At the same time, from the peak shape in Figure 3b, it can be observed that in stage 2, with the increase of OC, the weight loss temperature section shrunk. It was due to the coal–oxygen recombination reaction that the active
groups reacted faster in a sufficient oxygen environment and generate more gas. It can be observed from the DTG curve peak width that the higher the OC, the narrower the peak width, the faster the mass loss rate, and the easier it is for the coal–oxygen reaction to enter the combustion stage. During the weight loss process, the peak value of DTG increased significantly, and the TG curve was stable. The decrease of OC caused part of the temperature range to move to the high-temperature side, and thermal hysteresis occurred. For example, at OC-10%, the temperature needed to reach 550 °C before the TG curve showed no further change with temperature; however, at OC-20%, the temperature only needed to reach 500 °C afterward.

According to the TG and DTG curves, the critical temperature \( T_{1} \), dry cracking temperature \( T_{2} \), activation temperature \( T_{a} \), speed-up temperature \( T_{d} \), thermal decomposition temperature \( T_{g} \), ignition temperature \( T_{i} \) and maximum weight loss rate point temperature \( T_{7} \) of the coal sample at various oxygen concentrations are extracted, as shown in Table 1.

It can be seen from Table 1 and Figure 4 that comparing OC-20% and OC-18%, the difference in oxygen-poor environment \((T_{1}-T_{5})\) is not significant. It shows that starting from chemical adsorption of oxygen, some active groups such as oxygen-containing functional groups in coal can still be activated and react slowly with oxygen in advance. Although the reaction requires less temperature and energy from the outside than OC-20% and OC-18%, it still has a propensity for spontaneous combustion. Among them, the OC-20% slow reaction stage is significantly advanced, and \( T_{6} \) and \( T_{7} \) show a tendency to move to low-temperature point with the increase of OC, and the DTG curve peak appears earlier. It indicates that the lean-oxygen environment further affects the ignition point temperature and maximum weight loss rate point temperature of the coal on the basis of inhibiting the coal–oxygen complex reaction in the low-temperature oxidation stage, which changes the temperature point of coal combustion and firing.

As can be seen in Figure 4, the characteristic temperature change trend is consistent, and as the lean-oxygen degree deepens, the rising trend of \( T_{6} \) and \( T_{7} \) becomes more obvious. OC-10% \((T_{6}, T_{7})\) differ by 12.8 and 26 °C, respectively, indicating that the lean-oxygen environment inhibits the normal progress of the coal–oxygen composite reaction, causing the temperature point at the beginning of the spontaneous reaction phase to lag. In addition to the relationship between functional groups, it may be that in the low-temperature stage, sufficient OC makes the desorption of small molecules in the pores more complete, and the oxygen contact area on the coal surface is wider, making the reaction more rapid.

2.3.2. Thermal Effect Analysis. The combustion heat effect curve at OC-18% is shown in Figure 6a, and the histogram of the heat effect under DOC was obtained by Netzsch-T software, as shown in Figure 5b.

Figure 5a shows the equilibrium temperature \(^{24}\) point \( T_{E} \) and the sharply changing temperature point \( T_{R} \) under OC-18%. The temperature point under DOC is shown in Table 2. \( T_{E} \) and \( T_{R} \) decrease with the increase of OC. \( T_{E} \) was less than OC-20% in a lean-oxygen environment because the hydroxyl, C–
O, and carboxyl groups were more likely to react under suitable OC conditions, resulting in a backward equilibrium temperature point. The equilibrium temperature of OC-20% was 14.3 °C lower than that of the OC-10% coal sample. It was because that in the high-temperature oxidation stage, the specific surface area and pore structure of coal–oxygen contact with high OC were higher. In this case, a large number of functional groups reacted with oxygen at the same temperature. The complex reaction generated a large amount of heat, which made the oxidation reaction easier, and showed a macroscopic exothermic effect at a lower temperature.

The trend of the DSC curves showed that the exothermic power of the OC-20% and OC-18% coal samples changed sharply at 219.8 and 220.6 °C, respectively, due to the fact that at this point, the macromolecular structure began to break down and the reaction absorbs a large amount of thermal energy, resulting in a sharp change in exothermic power. For OC-14% and OC-10%, the corresponding temperature points appeared at 251.9 and 252.3 °C, and the heat release power was also weaker than that of coal samples under OC-20% and OC-18%, which was due to the macromolecular structure unspoiled. Moreover, part of it was decomposed into small molecular structures, causing the temperature point of the rapid change of exothermic power in a lean-oxygen environment to be delayed or even not to occur.

Figure 8. Curve-fitted spectra in the 2200–3000 cm⁻¹ region for coal with DOC: (a) OC-21% to 40 °C, (b) OC-21% to 150 °C, (c) OC-10% to 40 °C, and (d) OC-10% to 150 °C.

Figure 9. Variation of functional groups in DOC. (a) Aliphatic hydrocarbons and (b) aromatic hydrocarbons.
It can be seen from Figure 5b that the heat absorption and heat release do not change significantly before the equilibrium temperature. Mainly because at this stage the number of activated functional groups was small, the oxygen supply was in a state of surplus and the oxygen consumption rate and the coal–oxygen composite strength were weak, which offset the low heat loss caused by coal thermal diffusion and moisture evaporation. However, as the temperature increased, the size of OC limits the amount of heat released and the difference between the heat release of OC-10% and OC-20% was 36 280 mJ. Because of the increase in temperature, the number of activated functional groups increased, the coal–oxygen reaction increased, and the rate of oxygen consumption increased. At this time, the influence of OC was more prominent. There is no suitable OC in the lean-oxygen environment at this time, so the heat release was small, which further indicated that the thermal effect was closely related to the high-active groups and OC.

2.3.3. Pyrolysis Activity. To better study the influence of DOC on coal pyrolysis reaction activity, the correlation between average reaction rate, maximum reaction rate, maximum weight loss, pyrolysis initial temperature and thermal decomposition temperature range, and coal pyrolysis reaction activity is comprehensively analyzed. Combined with the pyrolysis characteristic index \( P \), as shown in eq 2:

\[
P = \frac{\left( \frac{dW}{dt} \right)_{\text{max}} \left( \frac{dW}{dt} \right)_{\text{mean}} \Delta W_{\text{max}}}{T_d(T_e - T_d)}
\]

where \( T_d \) is the initial temperature of pyrolysis, °C; \( T_e \) is the end temperature of thermal decomposition, °C; \( \left( \frac{dW}{dt} \right)_{\text{max}} \) is the maximum weight loss rate; \( \left( \frac{dW}{dt} \right)_{\text{mean}} \) is the average weight loss rate; and \( \Delta W_{\text{max}} \) is the maximum weight loss, %.

According to Figure 5 and eq 2, the data were extracted and the \( P \) value was calculated, as shown in Table 3.

The calculation method of the pyrolysis characteristic index \( P \) integrates the entire pyrolysis process such as dry degassing, thermal decomposition, and secondary degassing, and therefore, can reflect the pyrolysis activity of the whole process. From Table 3, it was found that as the OC decreased, \( P \) decreased. Combining the changes of \( T_j \) and \( T_{\text{fl}} \), it was found that the compound reaction of OC-21% is the most intense. It is because part of the macromolecular aromatic ring structure in coal decomposed under sufficient oxygen, a large number of free radicals are generated, resulting in a larger \( \left( \frac{dW}{dt} \right)_{\text{max}} \) and \( \left( \frac{dW}{dt} \right)_{\text{mean}} \) and faster reaction.

Moreover, the pyrolysis characteristic index gradually decreased as the degree of oxygen depletion deepened, reflecting that only part of the active groups was consumed in the lean-oxygen environment, and the chemical adsorption rate became slow as a result, leading to a higher temperature required for the slow reaction stage. From the thermogravimetric analysis of the specific impact of the lean-oxygen environment on the oxidation of bituminous coal, it can be found that the lean-oxygen environment reduced the pyrolysis reaction activity and had a significant inhibitory effect in the high-temperature section. However, it had no inhibitory effect on the low-temperature oxidation stage gradually entering the severe oxidation stage, which can be proved without changing the critical temperature. In general, the higher the temperature, the more prominent the OC influence.

2.4. FT-IR Analysis. Coal spontaneous combustion is a complex cyclic chain reaction process,26 during which different functional groups are oxidized and decomposed, and correspondingly generated and converted into various free radicals. Through the study of the molecular structure of coal,27 the functional groups and their spectral peak positions mainly studied in this paper are determined.28,29

2.4.1. Effect of Oxygen Concentration on FT-IR. To study the change law between the activity control group and temperature under the influence of DOC, many precious studies have pointed out that hydroxyl is the key group in coal spontaneous combustion,30 so here we analyze the changes of other groups. The infrared spectrum curve of the raw coal

Figure 10. Relative content difference of functional groups under DOC. (a) Aliphatic hydrocarbons and (b) aromatic hydrocarbons.

Figure 11. Mechanism of coal spontaneous combustion under DOC.
sample under the DOC was selected for analysis, as shown in Figure 6.

It can be seen from Figure 6 that 2911 and 2851 cm\(^{-1}\) belonged to \(-\text{CH}_3\), \(-\text{CH}_2\), and \(-\text{CH}\) in aliphatic hydrocarbons; 2362, 2330 and 1694 cm\(^{-1}\) belonged to \(-\text{COOH}\); 1601 cm\(^{-1}\) belonged to C\(=\text{C}\) stretching vibration in aromatic hydrocarbons; 1440 cm\(^{-1}\) belonged to \(-\text{CH}_3\) antisymmetric deformation vibration and \(-\text{CH}_2\) shear vibration; 1375 cm\(^{-1}\) belonged to \(-\text{CH}_3\) symmetric deformation vibration; and 1223 cm\(^{-1}\) belonged to a phenol, alcohol, ether, and ester oxygen bond. On the whole, it can be seen from the change of peak shape that relative to the lean-oxygen environment, the \(-\text{CH}_3\), \(-\text{CH}_2\), C\(=\text{C}\) peak intensity under OC-21% has a significant increase, indicating that the lean-oxygen environment will inhibit the activation of functional groups to a certain extent.

### 2.4.2. Content of Main Functional Groups

The structure of coal is very complicated. During the test, the peaks of different functional groups are superimposed at the same position. The fitting results of the coal spectrogram are obtained from the peak fitting analysis, as shown in Figures 7 and 8.

Figures 7 and 8 show one of the curve-fitting results, samples at OC-21% and OC-10%. As OC increased, alkylic and aromatic hydrocarbons exhibited higher activity and the carbon—oxygen double bonds in R—CO—R and R—CHO produced CO indicator gas, while causing a gradual decrease in C—O. The alkylic counterpart peak shape started to decrease significantly at 150 °C, while the decrease deepened with increasing OC. Related literature\(^{32,33}\) pointed out that \(\text{CH}_3\) and \(\text{CH}_2\) have similar production mechanisms. They were both produced by oxygen attacking the aliphatic hydrocarbons on the side chain of the benzene ring, and at the same time, the original hydrocarbon side chain was oxidized to \(-\text{CH}_3\)\(=\text{COOH}\). This process was confirmed by the increase in \(-\text{COOH}\) peak shape. The oxidation of \(-\text{CH}_3\) and \(-\text{CH}_2\) in aliphatic hydrocarbons produced unstable \(-\text{OH}\) which then decomposed hydrocarbon gas (\(\text{C}_x\text{H}_y\)) and produced carboxyl \(-\text{COOH}\).\(^{34}\) And because \(-\text{COOH}\) has a peak shape at low temperatures, as the oxidation reaction deepened, the increase in peak shape was positively correlated with OC and temperature. Due to the decarboxylation reaction, the peak shape decreased slightly at a temperature of 210 °C. In particular, the carboxyl group can be oxidized to CO and \(\text{CO}_2\).

We selected 3, 5, 10, 14, 18, and 21% OC, aliphatic hydrocarbons, and aromatic hydrocarbons with temperatures of 40 °C, 80, 150, and 210 °C for analysis, as shown in Figure 9.

As shown in Figure 9, temperature and OC had different effects on the functional group content. Highly active aliphatic hydrocarbons existed in the side chains of coal molecules. As the preoxidation temperature increased, the side chains accelerated oxidation to generate small molecular structures, such as methyl and methylene. Then, these small molecular structures participated in the oxidation reaction. When the preoxidation temperature was low, because the generation of methyl and methylene was greater than the consumption, the overall trend was increasing.

Because coal samples at 80, 120, and 150 °C have been preoxidized, many groups have reacted to produce indicator gases and other substances, resulting in fewer active groups. With the increase of OC, the aliphatic hydrocarbon content showed a trend of first increasing and then decreasing. However, the continuous increase at 210 °C was due to the oxygen absorption and weight gain stage at this time. At higher OC, a large number of various active functional groups in the molecular structure of coal were activated. Moreover, the primary adsorbed gas in the coal pores was desorbed and a large amount of coal—oxygen contact surface was generated after partial structural reaction, which made the coal—oxygen composite reaction become very violent.

Comparing the coal sample under DOC with OC-3%, the change trend of aliphatic and aromatic hydrocarbons can be clearly observed. As shown in Figure 10, relative to OC-3%, OC-5% coal samples had no obvious change, which was caused by the extremely deep lean-oxygen environment. With the increase of OC, the difference was gradually obvious. Compared with the OC-21% coal sample, the relative content of aliphatic and aromatic hydrocarbons in coal samples under other OC had a very obvious separation. From the change trend of aliphatic hydrocarbons, it can be seen that from the perspective of the influence of OC on the micro-groups of coal spontaneous combustion, aliphatic hydrocarbons changed significantly. The variation between aromatic hydrocarbons was small, but there was also a significant separation under DOC. Aromatic hydrocarbons were similar in structure to coal cores, had high stability, and changed little under different conditions. As OC increased, it showed a trend of first decreasing, then increasing, and then decreasing. The reason for the increase is that as the OC increases, the active structure of the side chain of the benzene ring and the side chain of the alkyl group in the molecular structure of the coal reacted in a large amount, resulting in a relative increase of the content of the main aromatic ring structure. Later, as the OC continued to increase, the coal—oxygen reaction became increasingly more intense and the main aromatic ring structure began to pyrolyze and oxidize, resulting in a decrease in its content.

### 2.4.3. Microscopic Reaction Mechanism of Coal Sample under DOC

In the process of low-temperature oxidation in a lean-oxygen environment, the covalent bonds of the macro-molecular structure of coal can still be destroyed and various active groups react with oxygen to form peroxide radicals. From Section 2.3.2, this process is an exothermic reaction and produces gas at the same time. The heat released by the reaction is used to break new bonds, producing more active groups.\(^{35}\) Active aliphatic hydrocarbons can still generate a small amount of peroxides (\(-\text{C—O—O}\)) in a lean-oxygen environment and generate heat at the same time. And because \(\text{H}_2\text{O}\) is mainly derived from the hydroxyl groups of aliphatic hydrocarbons combined with a large amount of hydrogen, during the development of coal spontaneous combustion, most of the oxygen-containing functional groups are consumed to generate carbon radicals (R).

Combining the pore structure and OC change with related literature\(^{17}\) on coal spontaneous combustion mechanism, the coal—oxygen reaction mechanism under DOC was obtained, as shown in Figure 11. Compared with the conventional oxygen concentration, the lean-oxygen environment would reduce the concentration of heat and free radicals and reduced the activity of the chain reaction. At the same time, this environment did not have a high OC and a large number of coal molecular structures reacted to generate more pore structures and abundant active sites. As the lean-oxygen environment deepened, this change became more obvious.
3. CONCLUSIONS

This paper analyzes the index gas and thermal properties of bituminous coal under DOC by the macro and micro test, reveals the key groups evolution of coal oxidation by FTIR, and indicates coal oxidation mechanism affected by the lean-oxygen environment. The conclusions are given as follows:

(1) Lean-oxygen environment could inhibit the progress of coal oxidation reaction. The index gas concentration under DOC presents the same rising trend as increasing temperature. After 120 °C, the lower the OC, the more obvious the hysteresis effect of the thermal reaction. As the oxygen concentration decreases, the heat production is greatly suppressed and there is no cross-point temperature appearing below 5%. However, the critical temperature does not change significantly.

(2) The spontaneous combustion tendency of coal is changed by the lean-oxygen environment, and the characteristic temperature shows obvious variation in the high-temperature stage. The change law of $T_1 - T_5$ indicates that the oxygen-poor environment reduces the tendency of coal to spontaneous combustion. As OC increases, the temperature points of $T_6$ and $T_7$ move forward, and the ignition temperature point changes accordingly.

(3) Lowering OC would inhibit the pyrolysis process. The lean-oxygen environment lags the temperature of the coal pyrolysis stage, reducing the pyrolysis activity and heat release. The low oxygen concentration could defer the oxidative exothermic reaction of active functional groups and restrain the exotherm progress of the oxidative exothermic stage. The heat release of OC-20% is 1.1 times that of OC-10%.

(4) The OC would play a significant role in the microscopic groups for coal low-temperature oxidation so that the development of coal spontaneous combustion could be inhibited by limiting the content of peroxides. The free radical *OH is the key to connect primary groups and secondary free radical active groups. Simultaneously, the *OH would generate index gas and release the heat to promote the chain reaction. As the OC increases, the content of the aliphatic hydrocarbon presents an overall trend of first increasing, then decreasing (at 80–150 °C), and continuously increasing after 210 °C. But the content of aromatic hydrocarbons only changes a little, that is, first increasing and then decreasing with the increase of OC. Therefore, hydroxyl, aliphatic hydrocarbons, and –COOH are the key groups for the evolution of coal spontaneous combustion.

4. EXPERIMENTS AND METHODS

4.1. Coal Samples. Fresh coal samples were collected from the working face and wrapped in cling film in time to arrive at the laboratory for crushing to take internal coal samples, which were crushed with a coal crusher, sieved to a particle size of 0.3–0.45 mm, packed into glass jars, and placed in a vacuum-drying oven for pretreatment. The dried coal sample and KBr were mixed and ground at a mass ratio of 1:100 and placed in a drying oven for pretreatment. The dried coal sample and KBr were crushed with a coal crusher, sieved to a particle size of 0.3–0.45 mm, packed into glass jars, and placed in a vacuum-drying oven for pretreatment.

| $\rho$ (kg·m$^{-3}$) | proximate analysis (W/%) | ultimate analysis (W/%) |
|---|---|---|
| 1400 | $M_{ad}$ 6.43 | $A_{ad}$ 15.71 | $V_{ad}$ 41.51 | $F_{daf}$ 36.35 | $C_{daf}$ 70.86 | $H_{daf}$ 5.44 | $N_{daf}$ 0.69 | $O_{daf}$ a 15.32 | $S_{daf}$ 7.69 |

| cas reg. no. | suppliers | mass fraction | T/K | analysis method |
|---|---|---|---|---|
| coal sample | 65996-77-2 | Bulianta Coal Mine, Inner Mongolia | ≥0.990 | 303.15 | PA”&UA” |
| KBr(SP) | 7785-02-3 | Tianjin Komiou Chemical Reagent Co., Ltd. | ≥0.995 | 303.15 | FTIR |
| oxygen | 132259-10-0 | Jiaozuo Xibolong Gas Co., Ltd. | 0.999 | 303.15 | GC df |
| nitrogen | 7727-37-9 | Jiaozuo Xibolong Gas Co., Ltd. | 0.999 | 303.15 | GC df |
| hydrogen | 1333-74-0 | Jiaozuo Xibolong Gas Co., Ltd. | ≥0.990 | 303.15 | GC df |

“Proximate analyzer. ”Ultimate analyzer. ”Fourier transform infrared spectrometer. ”Gas chromatograph. ”The temperature at the beginning of the experiment. The experiments all started at 101.325 kPa.
the heating rate is 10 °C-min⁻¹, and the end temperature is 800 °C. Figure 12c shows a TENSOR-37 Fourier transform infrared spectrometer (Bruker company). The wave number ranges from 400 to 4000 cm⁻¹, the resolution is 4 cm⁻¹, and the cumulative number of scans is 32. The test result uses professional infrared analysis software OMNIC, the peak fitting method of Gaussian function, and the baseline is linear. The gaseous products generated from the coal sample are separately analyzed by the gas chromatograph with an accuracy of 10⁻⁴ ppm. The temperature accuracy of the thermogravimetric analyzer is 0.1 °C, and the gas flow rate is 0.01 mL-min⁻¹.

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**Notes**

The authors declare no competing financial interest.

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