Combustion Kinetics and Mechanism of Pre-Oxidized Coal with Different Oxygen Concentrations

Haohao Fan, Kai Wang, Xiaowei Zhai, and Lihong Hu

ABSTRACT: The phenomenon of spontaneous combustion of “oxidized coal” is common in mining processes of goafs, thick coal seams, and unsealing of closed fire areas. In order to study the reburning characteristics of coal with different oxidation degrees, the oxygen concentration in the pre-oxidation process was selected as the key influencing factor. Thermogravimetric analysis (TGA) and in situ Fourier-transform infrared (FT-IR) spectroscopy were used to study the macro- and microcharacteristics of raw and oxidized coal during the combustion stage. The results showed that the pre-oxidation treatment exhibited a dual effect on promoting and inhibiting the weight loss characteristics of oxidized coal. The apparent activation energy, $E_a$, of the combustion reaction for the utilized coal samples was calculated using the Flynn–Wall–Ozawa (FWO) and Kissinger–Akahira–Sunose (KAS) methods, and it was found that the average apparent activation energy ($E_a$) values of the oxidized coal samples were less in magnitude than that of the raw coal and that the coal sample with the pre-oxidized oxygen concentration of 15% was more prone to the combustion reaction. Using the correlation determination method of key active groups in the proposed coal combustion reaction, the key active groups affecting the weight change of the tested coal samples during the combustion stage were determined as $-\text{CH}_3$ and $\text{C}–\text{O}$. The results can be helpful to prevent and control coal spontaneous combustion during re-mining and unsealing of closed fire areas.

1. INTRODUCTION

When the coal body comes into contact with oxygen, an oxidation reaction occurs, resulting in the release of heat. If the heat cannot be dissipated in time, it causes a constant increase in the temperature of the coal body, which might even lead to spontaneous combustion. If the external conditions result in destroying the heat-storage capacity of the coal body during this process, coal cooling is promoted, resulting in “oxidized coal” formation. The problem of spontaneous combustion of oxidized coal is common in the process of coal mining and utilization such as mining or re-mining of the residual coal in the goaf; after anaerobic cooling in the closed fire zone, after the coalfield fire area is extinguished, around the burning area; in the process of slicing mining in thick coal seams, or for the upper-slice coal body exposed again under the influence of lower-slice mining. Therefore, it is of great significance to study the macroscopic and microscopic characteristics of the oxidized coal spontaneous combustion process for efficient prevention of reburning of the oxidized coal.

Various theoretical and experimental studies have been reported in the literature on the occurrence and development of the oxidized coal spontaneous combustion process. Li and Yin found that the thermophysical parameters of the oxidized coal were greater than those of the raw coal. Through experimental studies, these authors also expressed that the thermal diffusion coefficient of the oxidized coal increased linearly with an increase in the pre-oxidation temperature. Wang et al. concluded that the pre-oxidation temperature exhibited a significant dual impact of first inhibition and then promotion of the secondary coal oxidation through a temperature-programmed experimental system and a $C_{80}$ microcalorimeter, which was consistent with the research result of Jo. Wang et al. also discussed the influence of the pre-oxidation degree on the coal spontaneous combustion parameters, and their study revealed that the pre-oxidation process exhibited positive and inhibitive impact on the spontaneous combustion parameters during the initial and later stages of the coal–oxygen composite reaction, respectively.

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Deng\textsuperscript{16,17} and Li\textsuperscript{18} compared the physical and chemical properties of raw and oxidized coal using proximate analysis, element analysis, and thermogravimetric analysis–Fourier-transform infrared spectroscopy (TGA–FT-IR) combined testing method, and they realized that the number of aliphatic side chains, branched chains, and apparent activation energy of the oxidized coal was lower than those of the raw coal. According to the results obtained from FT-IR spectroscopy, Zhu\textsuperscript{19} et al. concluded that the number of aliphatic hydrocarbons and hydroxyl groups in the oxidized coal showed a decreasing trend with an increase in the pre-oxidation temperature, while the content of oxygen-containing functional groups as well as the free radical concentration significantly increased. Xiao et al.\textsuperscript{20} comprehensively compared the characteristic temperature, exothermic intensity, apparent activation energy, and microstructure of coal during the first and second oxidation processes and concluded that the oxidized coal samples were more prone to spontaneous combustion. The research results of Huang\textsuperscript{21} and Ma\textsuperscript{22} demonstrated that the absorption peak intensity of the active functional groups of the oxidized coal was generally greater than that of the raw coal, and that when the pre-oxidation temperature was 120 °C, the absorption peak intensity of the oxidized coal was significantly enhanced, while the hazardous risks of spontaneous combustion was at the highest level.

In contrast to the above mentioned research results, Lu et al.\textsuperscript{23} determined that the spontaneous combustion tendency of the oxidized coal was lower than that of the raw coal when they comprehensively analyzed the determination indices for the coal spontaneous combustion tendency, velocity of producing gas, as well as functional group characteristics of gas—fat coal. Through a feasibility analysis study, Li et al.\textsuperscript{24} proposed a method of “pre-oxidation” to inhibit the risk of coal spontaneous combustion. Tang\textsuperscript{25} and Wang\textsuperscript{26} also found that excessively high pre-oxidation temperature resulted in the consumption of active functional groups such as aliphatic hydrocarbons and C–O structures in the coal samples, thereby reducing the possibility of spontaneous combustion of the oxidized coal.

In summary, oxidized coal with different oxidation degrees is obtained when the raw coal is affected by the initial oxidation conditions. In this process, the physical and chemical microstructure characteristics of the coal are changed, demonstrating the enhanced or weakened impact of the coal spontaneous combustion. The current state of research on the spontaneous combustion characteristics of the oxidized coal is mainly focused on the pre-oxidation temperature, and several important aspects of the combustion stage have attracted less attention for research such as thermal weight loss characteristics as well as microscopic mechanisms. In this study, the oxygen concentration in the process of pre-oxidation, referred to as “pre-oxidation oxygen concentration”, was selected as the key influencing factor for the process of the spontaneous combustion of the oxidized coal. From the perspective of macrokinetics and microfunctional groups, some qualitative and quantitative analysis methods were combined to explore the thermal weight loss characteristics as well as the microscopic mechanism during the coal combustion process under different pre-oxidation oxygen concentrations. The results obtained from this research will be beneficial for the prevention and control of coal reburning during mining of goafs and thick coal seams, as well as unsealing of closed fire areas.

2. RESULTS AND DISCUSSION

2.1. Thermogravimetric/Differential Thermogravimetric Analysis. 2.1.1. Thermogravimetric/Differential Thermogravimetric Curves. In the thermogravimetric (TG)
experiment, the TG curve directly reflects the mass change of coal during the oxidation and heating processes. The differential thermogravimetric (DTG) curve is the first derivative of the TG curve, and it represents the rate of mass change of coal at different temperatures.27 The TG–DTG curves for the tested coal samples at different heating rates are shown in Figure 1, which exhibits obvious segmentation characteristics. Combined with the characterization method of the characteristic temperature,28,29 the range of the weight loss stage of coal combustion can be defined from the temperature point at the end of the mass gain through oxygen chemisorption (i.e., the temperature corresponding to the local maximum mass value) to the temperature point at the end of the combustion reaction (i.e., the initial temperature at which the mass is basically unchanged after combustion). The characteristic temperature points for this stage include thermal decomposition temperature $T_d$, ignition temperature $T_i$, burnout temperature $T_b$, maximum mass loss rate temperature $T_m$, and inhibition temperature $T_p$.

Figure 1 shows the TG–DTG curve for the coal samples under different heating rates. As shown in Figure 1, the trends of TG curves for the coal samples are basically the same in the weight loss stage of combustion, showing a sharp decline in the mass of the coal. This is due to the fact that stable structures in coal such as aromatic rings are fractured and decomposed to a greater extent, and active functional groups are rapidly consumed because of the attack of the oxygen molecules, releasing CO, CO$_2$, and small molecular organic gases.30

It is also found that the weight loss rate for the tested coal samples is generally greater under a high heating rate, and the pre-oxidation oxygen concentration has a significant effect on the weight loss characteristics of the coal samples during the combustion stage, which is shown as a dual effect of promotion and inhibition. For instance, as the heating rate increases, the weight loss rate of the raw coal is gradually greater than that of the oxidized coal, while that of the Y-15% coal sample is generally lower at different heating rates. These phenomena may be related to the change of the functional group content in the coal samples.31,32

2.1.2. Characteristic Temperature. Figure 2 shows the change of characteristic temperature of the tested coal samples in the combustion reaction process. It can be seen that the characteristic temperature presents a hysteresis phenomenon with the heating rate increase. The explanation is that the temperature of the coal body increases rapidly under the action of a high heating rate, but the oxygen in the atmosphere is limited, and the active structure in coal cannot be oxidized and decomposed in time, which causes the characteristic temperature to move backward. On the other hand, because of the poor thermal conductivity of coal, the oxidation and spontaneous combustion characteristics of coal cannot be accurately reflected when the heating rate is very high. Therefore, the heating rate of 5 °C/min is taken as an example for analysis.

As shown in Figure 3, the thermal decomposition temperature $T_d$, ignition temperature $T_i$, maximum weight loss rate temperature $T_m$, and burnout temperature $T_b$ for the tested coal samples are in the range of 276~289 °C, 418~435 °C, 480~490 °C, and 592~604 °C, respectively, indicating that the pre-oxidation oxygen concentration has a certain effect on the characteristic temperature, but the difference is not significant. $T_5$ is the dynamic equilibrium point between the oxygen absorption of the coal sample and the consumption mass of the oxidation reaction. $T_5$ of the oxidized coal is smaller than that of the raw coal, indicating that the oxidized coal has entered the rapid combustion reaction stage in advance. $T_6$ is an important parameter that affects the ignition characteristics of the coal sample. Beyond this temperature, the coal samples are pyrolyzed and burned rapidly, the active functional groups are consumed rapidly, and the weight loss rate of the coal sample is increased significantly.33,34 Through a comparative analysis, it is found that the ignition temperature of the oxidized coal sample is smaller in value than that of raw coal, and $T_8$ of the Y-15% coal sample is at minimum, that is, 16.4 °C lower than that of the raw coal and is more prone to ignition. $T_7$ is the temperature at the point of maximum weight loss rate of the coal sample. At the same time, an aggressive chemical reaction takes place inside the coal molecules, and the concentration of pre-oxidized oxygen has both the promoting and inhibiting effects on $T_7$. At $T_8$, the combustion reaction of the coal sample is basically completed, and $T_9$ of the oxidized coal is increased to a certain extent compared with the raw coal, which indicates that the pre-oxidation treatment can increase the temperature range of the oxidized coal.

2.2. Oxidation Kinetics. Under the condition of heating, coal reacts with oxygen and decomposes to produce oxidized coal and gas-phase products. The reaction can be simply expressed as follows:

$$\text{Coal} + \text{O}_2 \rightarrow \text{CO}_2 + \text{H}_2\text{O}$$
Coal (s) + oxygen (g) → oxidized coal (s) + gas (g)

The coal–oxygen complex reaction is a dynamic oxidation kinetic process. According to the basic assumption of oxidation reaction kinetics and assuming that the reaction is irreversible, the relationship between temperature and reaction rate in the oxidation process of coal can be described using the Arrhenius equation under nonisothermal conditions

\[
\frac{\mathrm{d}\alpha}{\mathrm{d}t} = \left(\frac{A}{\beta}\right) \exp\left(-\frac{E_a}{RT}\right)f(\alpha)
\]

where \(t\) is the reaction time in min; \(\alpha\) is the mass-conversion rate of coal at time \(t\); \(A\) is the pre-exponential factor in min\(^{-1}\); \(\beta\) is the heating rate in °C/min; \(E_a\) is the apparent activation energy in kJ/mol; \(R\) is the universal gas constant (8.314 J/(mol·K)); \(T\) is absolute temperature in K; and \(f(\alpha)\) is the differential mechanism function.

According to the TG curve, the conversion of coal during the spontaneous combustion reaction process is as follows:

\[
\alpha = \frac{m_0 - m_t}{m_0 - m_\infty}
\]

where \(m_0\) is the initial sample mass in g; \(m_t\) is the sample mass at time \(t\) in g; and \(m_\infty\) is the sample mass at the end of the reaction in g.

For the determination of \(E_a\), the Flynn–Wall–Ozawa (FWO) method based on the multiheating rate experimental conditions was used. In this method, it is not needed to assume the reaction mechanism function, which avoids the error caused by the selection of the mechanism function and the result is more accurate. By calculating the \(T\) parameter at the same \(\alpha\) (i.e., equal conversion rate method), the change of \(E_a\) values under different conversion rates can be intuitively obtained. In order to verify the accuracy of the FWO method in calculating the apparent activation energy, Kissinger–Akahira–Sunose (KAS) method was selected for comparison. The expressions of FWO and KAS methods are as follows:

\[\text{Figure 4. FWO fitting curves for the Y-0% coal sample (a), Y-5% coal sample (b), Y-10% coal sample (c), Y-15% coal sample (d), Y-20% coal sample (e), and raw coal sample (f).} \]
\[ \alpha = -i_k \]

\( \beta = -i_k \)

\[ AE = \text{RT} \]

\[ \ln \beta = \ln \left( \frac{AE}{G(\alpha)} \right) = 2.315 - 0.4567 \frac{E}{RT} \]  

(3)

KAS method:

\[ \ln \left( \frac{\beta}{T^2} \right) = \ln \frac{AR}{EG(\alpha)} - \frac{E}{RT} \]  

(4)

where \( G(\alpha) \) is the integral mechanism function.

According to eqs 3 and 4, it can be obtained that \( \ln \beta \) and \( \ln \left( \frac{\beta}{T^2} \right) \) are linearly related to \( 1/T \). The calculation results are plotted and fitted to a straight line, and the \( E_a \) corresponding to each determined \( \alpha \) can be calculated according to the slope of the straight line. Take \( \alpha \) as 0.05, 0.1, 0.15, 0.2, 0.25, 0.3, 0.35, 0.4, 0.45, 0.5, 0.55, 0.6, 0.65, 0.7, 0.75, 0.8, 0.85, 0.9, and 0.95. The fitting curves for the tested coal samples under the FWO and KAS methods are shown in Figures 4 and 5, and the change curves of \( E_a \) and \( \alpha \) in the coal combustion reaction are shown in Figure 6.

As shown in Figure 6, the \( E_a \) of the tested coal samples obtained using the FWO method and the KAS method is basically consistent with the change of \( \alpha \). For \( \alpha < 0.25 \), the change trend of \( E_a \) is different with an increase in \( \alpha \); however, for \( \alpha > 0.25 \), \( E_a \) decreases continuously, and the decrease rate shows a characteristic of rapid change at first, followed by slower change. Wang\(^\text{39}\) and Lu\(^\text{40}\) showed that coal spontaneous combustion is a self-accelerating heating process in which different functional groups are gradually activated and react.
with oxygen. Before the ignition temperature $T_{i0}$, the energy of the reaction system increases with the increase in temperature, and stable structures such as aromatic hydrocarbons are thermally cracked and gradually participate in the reaction. However, variations of $E_a$ for the oxidized coal with $\alpha$ are different because of the differences in the degree of initial oxidation. When the temperature exceeds the ignition temperature $T_{i0}$ that is, $\alpha > 0.25$, the coal samples enter the stage of intense combustion, the activity of the coal–oxygen complex reaction increases rapidly, and a large amount of heat is released, which causes a gradual decrease in the apparent activation energy.

As shown in Figure 7, the average apparent activation energy ($E_a$) values obtained using the FWO and KAS methods are relatively close, which mutually verifies the accuracy of the results. According to this figure, $E_a$ of the tested coal samples increases first and then decreases, followed by an increase with the increase in the pre-oxidation oxygen concentration. The $E_a$ values of the oxidized coal samples are lower than those of the raw coal, which is shown as Raw > Y-20% > Y-5% > Y-0% > Y-10% > Y-15%. The apparent activation energy can reflect the energy threshold required for coal to reach a certain oxidation state, and its value determines the degree of difficulty in the chemical reaction between coal and oxygen. The smaller the $E_a$ value is, the easier the oxidation reaction of coal is, which indicates that oxidized coal exhibits stronger combustion reactivity than the raw coal. Among them, the $E_a$ value of the Y-15% coal sample is the smallest in the combustion reaction, which is more prone to ignition and should be paid more attention.

### 2.3. FT-IR Analysis

#### 2.3.1. Analysis of Three-Dimensional In Situ FT-IR Spectra

According to the experimental results, the three-dimensional (3D) in situ FT-IR spectra of the molecular structure for each coal sample during the oxidation heating process is obtained (Figure 8). The X-axis is the wavenumber of the infrared spectrum, the Y-axis is the absorbance of the spectral peak, and the Z-axis is the temperature.

The reactivity of different functional groups for the tested coal samples varies with temperature. Among them, the hydroxyl group belongs to a kind of oxygen-containing functional group, which is more active in the oxidation process and plays a leading role in the release of water vapor, and it is often discussed as a separate type of the functional group. Hydroxyl groups usually appear in three forms: free hydroxyl groups, intramolecular hydrogen bonds, and intermolecular hydrogen bonds, and the peak positions are in the range of 3697–3625 cm$^{-1}$, 3625–3613 cm$^{-1}$, and 3550–3200 cm$^{-1}$, respectively. Aliphatic hydrocarbon series exhibit the highest reaction rate among all other functional groups, and they are the main molecular structures that directly and indirectly produce hydrocarbon and carbon–oxygen gases. It usually exists in the form of short-chain alkanes $\text{CH}_n$ and $\text{CH}_i$, 2945–2915 cm$^{-1}$ and 2870–2845 cm$^{-1}$ showed the stretching vibration of methylene, and 1470–1430 cm$^{-1}$ showed the deformation vibration of methyl. Aromatic hydrocarbon series are relatively stable in the oxidation process, and their peak positions are mainly located at 3056–3030 cm$^{-1}$ (stretching vibration of aromatic C$\equiv$C), 1625–1575 cm$^{-1}$ (stretching vibration of C$\equiv$C), 1150–990 cm$^{-1}$, and 900–700 cm$^{-1}$ (bending vibration of aromatic C$\equiv$H). The stretching vibration of C$\equiv$C is an important basis for judging the existence of benzene rings in substances. All the tested coal samples contain this functional group, indicating that coal is a macromolecular compound composed of benzene rings. The peak positions of the oxygen-containing functional groups are mainly in the ranges of 1790–1690 cm$^{-1}$ (stretching vibration of carbonyl) and 1230–1015 cm$^{-1}$ (stretching vibration of aromatic ether). The attribution of functional groups of coal molecules corresponding to the infrared spectra is shown in Table 1.

#### 2.3.2. IR Spectra Analysis at Characteristic Temperatures

The Lambert–Beer law states that the absorbance is positively correlated with the molecular composition or the content of

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**Figure 6.** Change curves for $E_a$ of the FWO method (a) and KAS method (b).

**Figure 7.** $E_a$ values of the combustion reaction for the tested coal samples.
chemical groups; therefore, it can be used as an index to analyze the number of functional groups. The FT-IR spectroscopy data for different coal samples at $T_5$, $T_6$, $T_7$, and $T_8$ are extracted (Figure 9), and the changes in trends associated with the microstructure at characteristic temperatures are discussed.

As shown in Figure 9, the characteristic peaks of the free hydroxyl group, intramolecular hydrogen bond, and intermolecular hydrogen bond are 3668 cm$^{-1}$, 3624 cm$^{-1}$, and 3525 cm$^{-1}$, respectively. The free hydroxyl groups and intramolecular hydrogen bonds of each coal sample are relatively stable and exist during the combustion process, which indicates that these two active groups are consumed, while the other functional groups participate in the reaction to form hydroxyl molecules. The peak of the intermolecular hydrogen bond gradually narrows, and the content decreases with an increase in the characteristic temperature. By comparison, it is found that the hydroxyl content of the Y-15% coal sample is significantly greater than that of other coal samples. In addition, the infrared spectra of the Y-15% coal sample show several continuous absorption peaks of intermolecular hydrogen bonds, and the characteristic peaks also include 3446 and 3303 cm$^{-1}$.

In aliphatic hydrocarbon series, the corresponding characteristic peak positions are the asymmetric stretching vibration of methylene of 2929 cm$^{-1}$, symmetric stretching vibration of methylene of 2855 cm$^{-1}$, and deformation vibration of methyl of 1447 cm$^{-1}$. The aliphatic hydrocarbon structure of each experimental coal sample is rapidly consumed in the combustion reaction, and oxygen-containing functional groups such as hydroxyl and carbonyl groups are continuously generated. After the ignition temperature $T_6$, the absorbance of the methylene group approaches zero. While the methyl group is continuously consumed, it exists during the whole combustion stage. Moreover, the consumption of methylene is greater than that of methyl groups, which indirectly indicates that the reactivity of methylene is greater.

In the aromatic hydrocarbon series, the stretching variations of the aromatic Ar$-\text{CH}$ bond of 3053 cm$^{-1}$ and the in-plane bending vibration of aromatic C$-\text{H}$ of 1029 cm$^{-1}$ exhibit little change, which represents the stability of the aromatic ring structure. The C$=\text{C}$ double bond of 1597 cm$^{-1}$ is relatively stable before the maximum weight loss rate temperature $T_7$, and then, the absorbance and the content gradually decrease. The continuous out-of-plane bending vibration of aromatic C$-\text{H}$ appears at the peak position of 900–700 cm$^{-1}$, which is an
3. CORRELATION ANALYSIS OF OXIDATION KINETICS AND MICROSTRUCTURES

In order to further reveal the microscopic mechanism of coal oxidation reaction kinetics, a method is proposed in this study to determine the key active groups that affect the weight loss during the coal combustion process. According to the calculation results of oxidation kinetics, the \( E_k \) of the combustion reaction for the tested coal samples decreases with the increase in temperature, and the change in weight loss becomes easier. Therefore, the active groups with a good and positive correlation with the apparent activation energy can promote the kinetic process of the coal sample and can be identified as the key active groups during the weight loss stage of coal combustion.

The Pearson correlation coefficient method is used to measure the degree of linear correlation between the two variables X and Y, and its value is between \(-1\) and 1, which is denoted by \( r \). The calculated result is 1, meaning that X and Y are completely positively correlated, and the calculated result is \(-1\), if the parameters are completely negatively correlated. The greater the absolute value of \( r \), the stronger the correlation is. It is generally believed that \( |r| > 0.6 \) is a strong correlation. The calculation formula is as follows:

\[
\rho = \frac{n \cdot \sum XY - (\sum X)(\sum Y)}{\sqrt{(n \cdot \sum X^2 - (\sum X)^2) \cdot (n \cdot \sum Y^2 - (\sum Y)^2)}}
\]

where \( r \) is the Pearson correlation coefficient; X and Y are the data aggregates of variables and dependent variables; \( n \) is the number of variables.

Gray relational analysis is a quantitative description and comparison method for the development and change trend of a system. The basic idea is to determine whether the connection is close by determining the geometric shape of the similarity degree between the reference data column and several comparison data columns. The value range of the gray relational coefficient \( \xi(k) \) is \([0,1]\). The formula is as follows:

\[
\xi(k) = \frac{\min_{i} \left| x_{0i} - x_{ki} \right| + \rho \cdot \max_{i} \left| x_{0i} - x_{ki} \right|}{\max_{i} \left| x_{0i} - x_{ki} \right|}
\]

where \( \xi(k) \) is the gray relational coefficient; \( i \) is the number of parameters; \( k \) is the number of coal samples; \( x_{0i}(k) \) is the normalized reference sequence; \( x_{ki}(k) \) is the normalized comparative sequence; and \( \rho \) is the distinguished coefficient, where \( \rho \in [0,1] \). Generally speaking, the stability of the coefficient is the most moderate when \( \rho \) is equal to 0.5.

The Pearson correlation coefficient method and gray relational analysis have their own advantages in correlation analysis. The Pearson correlation coefficient method can characterize the contribution of different active groups in the process of coal oxidation reaction, but it cannot characterize the degree of correlation between variables and dependent variables. On the other hand, gray relational analysis cannot characterize the positive and negative correlations between variables and dependent variables, but it can truly characterize the degree of correlation between the data columns. Therefore, the key active groups can be determined more accurately by combining these two methods. The results of the Pearson correlation coefficient and the gray relation coefficient between the active groups and activation energy for the tested coal samples are shown in Figure 10.
As shown in Figure 10a, the intermolecular hydrogen bonds (−OH), C=C, −CH₃, and C−O of the tested coal samples are roughly positively correlated with the change of $E_a$ with a Pearson correlation coefficient of more than 0.6. Because coal combustion is a weight loss process and $E_a$ decreases with the increase in temperature, it is speculated that the decrease in the
content of these abovementioned functional groups may contribute to the decrease in activation energy. According to the calculation results shown in Figure 10b, it can be found that the gray correlation coefficients of different active groups and \( E_a \) are quite different, and the value ranges from 0.35 to 0.94. Similarly, when the gray correlation coefficient is greater than 0.6, it indicates that the active group has a good correlation with \( E_a \). On this basis, the active groups with high correlation with the change in \( E_a \) are identified. As shown in Table 2, the key active groups affecting the weight loss stage of coal combustion can be determined more accurately by combining the two correlation analysis methods.

According to the distribution of the key active groups shown in Table 2, it can be seen that the key active groups affecting the coal combustion process for the tested coal samples are mainly \( -CH_3 \) and \( C=O \). These structures are largely involved in the combustion reaction and are the main reason for the weight loss of coal. However, the kinds of key active groups for various tested coal samples are different.

### 4. CONCLUSIONS

The effects of pre-oxidation oxygen concentration on the macroscopic and microscopic characteristics of the coal samples during the weight loss stage of the combustion process were studied by TG analysis and FT-IR measurements. The main conclusions of this study are as follows:

1. The pre-oxidation treatment has double effects of promoting and inhibiting the weight loss characteristics. The \( E_a \) values of the combustion reaction for the tested coal samples were calculated using the FWO and KAS methods, and it was found that after the ignition temperature of \( T_{so} \), \( E_a \) decreased with the increase in the conversion rate \( \alpha \). Compared with the raw coal, the \( E_a \) of the oxidized coal combustion reaction was lower, showing as \( Raw > Y-20% > Y-5% > Y-0% > Y-10% > Y-15% \), indicating that the coal sample with the pre-oxidation oxygen concentration of 15% was more prone to the combustion reaction.

2. During the weight loss stage of the coal combustion process, the changes of functional groups for the tested coal samples were basically consistent. The difference was that the hydroxyl content of the coal sample with a pre-oxidation oxygen concentration of 15% was significantly higher than those of other coal samples, and there were several continuous absorption peaks of intermolecular hydrogen bonds, and the contents of \( C=O \), \( Ar=CH_3 \), and \( C=O \) of the coal sample were relatively higher at the burnout temperature.

3. A correlation method for determining the key active groups during the coal combustion process was proposed. The correlation between the \( E_a \) and active groups were calculated by combining the Pearson correlation coefficient and the gray relational analysis. Using the correlation values, it was found that the key active groups for the tested coal samples were mainly \( -CH_3 \) and \( C=O \), but the kinds of key active groups for various tested coal samples were different.

### 5. MATERIALS AND METHODS

#### 5.1. Preparation of the Oxidized Coal

The Jurassic coal from western China, easily combusted spontaneously with a low-medium ash content and high caloric value, was selected as materials for this study. Under a nitrogen atmosphere, the unoxidized part at the center of the original coal block was crushed and ground, and the fresh coal samples with the particle size of 180–200 mesh were sieved and then placed in a vacuum drying oven at room temperature for sealed storage. The results of proximate and elemental analyses are shown in Table 3.

Five samples of fresh coal with similar mass were slowly oxidized under the oxygen atmosphere of 0, 5, 10, 15, and 20% concentrations, respectively, with the temperature range of 30–155 °C. When the temperature reached 155 °C, it was maintained constant for 3 h to ensure full oxidation of the coal samples; then, nitrogen was introduced for anaerobic cooling. The coal samples taken out after the temperature was lowered to room temperature were the “oxidized coal” samples, marked as Y-0%, Y-5%, Y-10%, Y-15%, and Y-20%, respectively. These samples were then placed in a vacuum drying box for sealed storage. The experimental atmosphere was matched with \( N_2 \) and \( O_2 \), and the flow rate was 50 mL/min.

#### 5.2. Experimental Procedure and Conditions

TG experiments: the TG curves for the tested raw and oxidized coal samples were prepared using a German NETZSCH STA409PC simultaneous thermal analyzer, with the raw coal samples as the reference group. During the experiment, the simulated air with a flow rate of 50 mL/min \((V(O_2):V(N_2) = 1:4)\) was continuously introduced, and the coal samples were heated from 30 to 700 °C at different heating rates of 5, 10, 15, and 20 °C/min. The mass of each tested coal sample was 5 mg.

FT-IR experiments: the test was carried out using a German Bruker VENTEX70 in situ diffuse reflectance IR spectrometer. The set values for the heating rate, scanning wave number

### Table 2. Key Active Groups of the Tested Coal Samples

| coal samples       | Y-0%     | Y-5%     | Y-10%    | Y-15%    | Y-20%    | raw   |
|--------------------|----------|----------|----------|----------|----------|-------|
| key active groups  | C=C      | C=C      | intermolecular hydrogen bond | \(-CH_3\) | \(-CH_3\) | intermolecular hydrogen bond |
|                    | C=O      | C=O      | \(-CH_3\) | C=O      | C=O      | \(-CH_3\) |
|                    |          |          | C=O      |          |          | C=O   |

### Table 3. Proximate Analysis and Elemental Analysis of Fresh Coal

| proximate analysis/% | elemental analysis/% |
|----------------------|----------------------|
|                      |                      |
| \( M_{ad} \)         | \( A_{ad} \)         | \( V_{ad} \)       | \( FC_{ad} \)     |
| C                    | H                    | O                    |
| N                    | S                    |
| 5.06                 | 13.45                | 33.34                | 48.15               | 80.62      | 4.82  | 13.15 | 1.05 | 0.36 |

\(^aM\): moisture; \(A\): ash; \(V\): volatile matter; \(FC\): fixed carbon; \(ad\): air dry.
range, and resolution were 5 °C/min, 4000∼650 cm⁻¹, and 4.0 cm⁻¹, respectively, and the coal samples were scanned 32 times in order to synthesize a spectrum. The experimental temperature range, atmosphere, flow rate, and the quality of the coal samples were consistent with those used in the TG experiment. In order to decrease the influence of the diffraction peaks on the results, KBr powder was mixed with the coal samples at a ratio of 1:150.

5.3. Experimental Methodology. In order to clarify the relationship between the experiments in this study, a flowchart showing methods and results is shown in Figure 11. Through the TG and FT-IR experiments, the changes in the macro and microcharacteristics of the oxidized coal during the combustion stage with different pre-oxidation oxygen concentrations were discussed from the perspectives of TG characteristics, oxidation kinetic parameters, and functional group characteristics. By combining the apparent activation energy with the active groups, the correlation analysis method was used to determine the key active groups that affect the weight loss during the coal combustion stage.

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Notes
The authors declare no competing financial interest.

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■ NOMENCLATURE

A  Pre-exponential factor, min⁻¹
DTG  Derivative thermogravimetry
Eₐ  Apparent activation energy, kJ/mol
Eₐ  Average apparent activation energy, kJ/mol
FT-IR  Fourier-transform infrared spectroscopy
FWO  Flynn–Wall–Ozawa
f(α)  Differential mechanism function
G(α)  Integral mechanism function
i  Number of parameters
k  Number of coal samples
KAS  Kisseringer–Akahira–Sunose
m₀  Initial sample mass, g
m₁  Sample mass at time t, g
mₐ  Sample mass at the end of the reaction, g
n  Number of variables
r  Pearson correlation coefficient
t  Reaction time, min
T  Absolute temperature, K
T₄  Thermal decomposition temperature, K
T₆  Ignition temperature, K
T₇  Maximum weight loss rate temperature, K
T₈  Burnout temperature, K
TG  Thermogravimetry
TGA  Thermogravimetric analysis
xᵢ(k)  Normalized reference sequence
x₁(k)  Normalized comparative sequence
X, Y  Data aggregate of variables and dependent variables
Y-0%  Coal sample pre-oxidized at 0% oxygen concentration
Y-5%  Coal sample pre-oxidized at 5% oxygen concentration
Y-10%  Coal sample pre-oxidized at 10% oxygen concentration
Y-15%  Coal sample pre-oxidized at 15% oxygen concentration
Y-20%  Coal sample pre-oxidized at 20% oxygen concentration

Greek Symbols
α  Mass-conversion rate of coal
β  Heating rate, °C/min
ξ  Gray relational coefficient
ρ  Distinguished coefficient

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