Study on the Oxidation Kinetics and Microreactivity of Water-Immersed Coal

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ABSTRACT: Both the macroscopic reaction and microscopic characterization of water-immersed coal have been studied. The methods of thermogravimetric analysis via Fourier transform infrared spectroscopy (TG-FTIR) and diffuse reflectance infrared Fourier transform spectroscopy (DRIFTS) are used. The apparent activation energy of water-immersed coal was significantly lower than that of raw coal. For the same coal sample, the production of CO in water-immersed coal is significantly higher than that in raw coal. The analysis shows that after water immersion, the content of hydroxyl and aromatic hydrocarbons in the coal increases significantly and the temperature at which fat-based and oxygen-containing functional groups participate in the reaction decreases. This indicates that the functional groups are unstable after water immersion and react violently. When the immersion time is 60 days, the activation energy is the lowest, the production of CO reaches its maximum, and the variation of each functional group is most obvious.

1. INTRODUCTION

With the large-scale development of coal resources and the mining of extra-thick coal seams, mines are facing the dual disasters of spontaneous combustion and water disasters.1–4 In the mining of lower layers, water exploration and drain measures are usually used to prevent water disasters in goafs.5,6 However, with the drainage and leakage of upper goafs, air leakage and oxygen supply channels easily form, which leads to residual coal accumulation in goafs under water for long periods.7 This makes coal not only absorb water and expand but also dissolve organic and inorganic compounds on the surface of coal molecules, resulting in changes in the coal structure.8,9 At the same time, a large amount of air leakage dries the coal body with water, which provides the oxygen needed for the oxidation of residual coal in goafs, also increasing the possibility for the spontaneous combustion of residual coal in goafs. Thus, it is easy to cause the spontaneous combustion of coal. For example, in June 2012, a serious fire occurred in the Shendong Bulianta Coal Mine due to the spontaneous combustion of coal seams in goaf areas,10 and such major disasters have also occurred in the goaf area of the 1101 fully mechanized mining face of the Barapukuria Coal Mine in Bangladesh.11,12

Coal is a porous medium13 that has a large internal surface area due to its molecular structure characteristics. Because of Van der Waals force and hydrogen bonding,14 there is always a certain amount of water in coal. According to the occurrence characteristics of water in coal, Wang15 divided water in coal into internal water and external water. He pointed out that the point of evaporation and loss of temperature of external water is between 40 and 50 °C, while the complete evaporation of internal water requires a temperature above 100 °C. Therefore, moisture has an important influence on coal spontaneous combustion.16–19 However, there are a few studies on the influence of water on coal spontaneous combustion and oxidation characteristics. Yang14 found that long-term water immersion can lead to the development of coal pore structure and the reduction of antispontaneous combustion substances. Zhong20 analyzed the influence of water content on the low-temperature oxidation and exothermic characteristics of coal during impregnation and air drying. Zhao21 found that the crossing point temperature of coal samples with a water content of 6–13% was significantly lower than that of other coal samples with a different water content. Chen22 found that when the moisture content of coal samples ranged from 7 to 17%, the oxidation rate of coal samples reached the maximum. Deng23 found that when the moisture content of coal samples ranged from 7 to 17%, the oxidation rate of coal samples reached the maximum. Deng23 found that when the moisture content of lignite in the Mengba mine was 14.27%, the coal was most prone to spontaneous combustion. Beamish24 studied the R70 value of Australian coal samples under different water conditions. Kadiog˘lu25 studied the effect of water content on two types of lignite in Turkey. Xu26 found that there is a critical point of water content in the process of lignite oxidation that maximizes the apparent activation energy of water-immersed coal was significantly lower than that of raw coal. For the same coal sample, the production of CO in water-immersed coal is significantly higher than that in raw coal. The analysis shows that after water immersion, the content of hydroxyl and aromatic hydrocarbons in the coal increases significantly and the temperature at which fat-based and oxygen-containing functional groups participate in the reaction decreases. This indicates that the functional groups are unstable after water immersion and react violently. When the immersion time is 60 days, the activation energy is the lowest, the production of CO reaches its maximum, and the variation of each functional group is most obvious.

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the heat release. In terms of the evaluation index and standard of the moisture effect on coal spontaneous combustion, these scholars proposed that there is an optimal moisture content with which coal is prone to low-temperature oxidation; however, this was deduced with only qualitative methods, without a specific evaluation index and judgment standard.

Therefore, this study adopts the research method of combining experimental research with theoretical analysis. First, three different ranks of coal are selected, and a thermogravimetric analysis via Fourier transform infrared spectroscopy (TG-FTIR) experiment is used to analyze the weightlessness characteristics of water-immersed coal in the oxidation process. Then, the Starink method, based on multiple heating rates, is used to calculate the variation of apparent activation energy of oxidation reactions with different conversion rates. Next, the gas generated during the oxidation process of water-immersed coal samples is detected by an infrared spectrometer, and the oxidation kinetics of water-immersed coal are analyzed. Finally, diffuse reflectance infrared Fourier transform spectroscopy (DRIFTS) is used to determine the functional groups and their changes in coal samples during low-temperature oxidation. The activation energy and oxidation gas production obtained by TG-FTIR, as well as the change of functional groups obtained by DRIFTS, were used as the specific evaluation indexes to judge the influence of water on coal spontaneous combustion. There was an optimal immersion time, which made coal prone to low-temperature oxidation. It is of great significance to study the prediction and prevention of the spontaneous combustion of water-immersed coal with different coal ranks and different water immersion durations.

2. EXPERIMENTAL SECTION

To research the oxidation kinetics process of water-immersed coal, this study selects lignite from Xilinhaote Wunite (China), bitumite from Hunyuan Daciya (China), and anthracite from Anze Yuheiai (China) (i.e., three metamorphic degrees of coal samples) as the main research objects. The purpose here is to study the low-temperature oxidation kinetics and the main functional group changes against raw and water-immersed coal samples by experimental and theoretical methods.

2.1. Coal Sample Preparation. The industrial analysis of three coal samples with different degrees of metamorphism used in the experiment is shown in Table 1. The industrial analysis of coal mainly tests the four indexes of coal, moisture \( M_{ad} \) ash \( A_{ad} \), volatile \( V_{ad} \), and obtains the fixed carbon \( FC_{ad} \) through calculations. The experimental coal samples were prepared in accordance with the preparation standard of coal samples (GB/T 474-2008). First, a jaw crusher was used to crush the large coal samples. Then, the coal samples after partial crushing were taken and processed into coal samples with a smaller particle size by a grinder. After crushing, coal samples with a particle size of 2–3 mm were screened with a standard screen and then loaded into airtight bags.

The previously prepared three ranks of coal samples were partially taken out and placed in a conical bottle and immersed in water for 60 days. In addition, some lignite samples were placed in conical bottles and immersed in water for 30 and 90 days, respectively. After immersion, the coal samples were taken out and placed in a constant-temperature drying oven with a drying temperature of 30 °C for 72 h. After drying, the raw coal and water-immersed coal samples were each crushed to a size below 0.15 mm and then stored in sealed bags to avoid light for subsequent experiments.

2.2. TG-FTIR Experiment. According to the coal thermogravimetric loss curve of different heating rates, TG-FTIR can finalize the activation energy change curve in the coal oxidation process and the kinetic mechanism function in the thermal reaction process. At the same time, the variety and quantity change of the gas produced by infrared spectroscopy may be determined. TG-FTIR provides a new way to study the microscopic reaction process of thermal oxidation and makes the research closer to the essence of chemical reactions in coal oxidation processes.

This study used an STA7200 differential thermal analyzer and a Thermo Scientific Nicolet iS50 Fourier transform infrared spectrometer to complete the experimental test. The thermogravimetric analyzer detected the mass changes of raw and water-immersed coal samples with different metamorphic degrees and different immersion times in the process of programmed heating under different fixed heating rates. The generated gas was transported to the infrared spectrometer for gas composition and content analysis.

The amounts of coal samples used in the experiment were 10 mg (±0.5 mg), the air flow was 100 mL·min\(^{-1}\), and the heating rates were 2, 5, 8, and 10 °C·min\(^{-1}\). The heating range was 30–400 °C.

2.3. DRIFTS Experiment. In this section, the Thermo Scientific Nicolet iS50 FTIR spectrometer was used to test the variation of the main functional groups with temperature for raw and water-immersed coal samples with different metamorphic degrees during the oxidation reaction process. Through a comparative analysis of the raw and water-immersed coal samples, the main functional groups in each coal sample and their change laws were determined.

The consumption of each experimental coal sample was 30 mg. The wavenumber scanning range was set to 400–4000 cm\(^{-1}\), the resolution was 4 cm\(^{-1}\), and the number of scanning was 32. The temperature increase range of the temperature control equipment was set to 30–400 °C, the temperature increase rate as 2 °C·min\(^{-1}\), the collection time as 190 min, and the air flow as 50 mL·min\(^{-1}\).

3. RESULTS AND DISCUSSION

3.1. Oxidation Kinetics of Water-Immersed Coal. The macroscopic characteristics of coal oxidation and pyrolysis are the comprehensive performance metrics of many synchronous parallel or competitive physicochemical reactions involved in coal heterogeneous structures. Therefore, the process of the
thermal oxidation of coal to spontaneous combustion is a very complex kinetic process. Obtaining the coal oxidation kinetic laws is critical to speculate on the cause and mechanism of coalfield ignition, and it is also the theoretical basis for the study of coalfield fire prevention and control.

3.1.1. Theories and Methods of Thermal Analysis Kinetics. The multiple scanning rate method, also known as the iso-conversional method, is where coal samples are subjected to the same reactions at different heating rates, and then, the dynamic analysis of the thermal analysis (TA) curves is carried out. In the absence of a kinetic mode function (also called the model-free method), a more reliable apparent activation energy, $E$, value can be obtained by this method. The apparent activation energy represents the minimum energy required to activate a coal molecule when it is transformed from an "inactive molecule" to an "active molecule". The main feature of this is that the higher the apparent activation energy required by the coal sample, the more difficult it is for the coal molecules to be activated, and the more the energy needed to be activated to participate in the chemical reaction. The Starink equation is established here for solving the apparent activation energy, $E$, as follows

$$\ln\left(\frac{\beta}{T_{1.8}}\right) = C_s - \frac{BE}{RT} = C_s - 1.0037\frac{E}{RT}$$

where $\alpha$ is the conversion rate of coal at time $t$ and refers to the percentage of the coal sample conversion mass at time $t$ and the coal sample conversion mass at the end of the reaction when the coal sample oxidation reaction occurs. Additionally, $\alpha = \frac{W_0 - W}{W_0 - W_{\infty}}$, where $W_0$ (mg) is the initial mass of coal sample before the reaction, $W_{\infty}$ (mg) is the residual coal mass at the end of the oxidation spontaneous combustion reaction, $W_t$ (mg) is the coal sample mass at time $t$, $T$ is the reaction temperature (thermodynamic temperature), $E$ is the apparent activation energy, $(kJ\cdot mol^{-1})$, $R$ is the molar gas constant, which is 8.314 J mol$^{-1}$K$^{-1}$ here, and $\beta$ is the constant heating rate (K min$^{-1}$), $B = 1.0070 - 1.2 \times 10^{-3}E$ (kJ mol$^{-1}$). $C$ is a constant, and the lower angle of $S$ of $C$ stands for the Starink method.

3.1.2. Calculation of Thermal Analysis Kinetics. Based on the above thermogravimetric experiments, this study investigated the kinetic characteristics of the raw coal and water-immersed coal samples of lignite, bituminous, and anthracite, as well as water-immersed lignite with 30, 60, and 90 days, respectively. Using the Starink method, based on various heating rates, the low-temperature oxidation process of coal was divided into two stages, namely, water evaporation and desorption and oxygen gain. The change law of the apparent activation energy of the oxidation reaction with the conversion rate in the two stages was calculated, respectively.

3.1.2.1. Characteristic Temperature. The TG/DTG curve obtained by thermogravimetric analysis of raw lignite samples is shown in Figure 1.

Critical temperature ($T_i$) refers to the temperature corresponding to the first minimum value point on the DTG curve from room temperature ($30\, ^\circ C$). As the temperature increases, the moisture and adsorbed gas in the coal begin to evaporate and desorb from coal. During this period, coal also has an adsorption effect on oxygen. However, since the evaporation and desorption rates are gradually accelerated and much higher than the adsorption rates, when the difference between them reaches the maximum, the maximum weight loss rate point of the coal sample will be reached, which is the critical temperature ($T_i$).

Dry temperature ($T_2$) refers to the temperature corresponding to the first minimum value point on the TG curve from room temperature ($30\, ^\circ C$). It is also the temperature at which the coal sample mass is reduced to the minimum value before the actual coal spontaneous combustion. Dry temperature ($T_2$) is the end temperature point of water evaporation and desorption stage in the process of coal sample oxidation and heating. It is also the transition temperature point when the coal sample enters the stage of oxygen gain.

Active temperature ($T_3$) is the corresponding temperature point when the TG curve begins to increase after the dry temperature ($T_2$). In the range of dry temperature ($T_2$) to active temperature ($T_3$), the adsorption and consumption of oxygen by coal body are in a dynamic balance state.

Speed-up temperature ($T_4$) is the temperature corresponding to the maximum point on the DTG curve before the ignition temperature. Before the speed-up temperature point ($T_4$), the oxygen adsorption rate of the coal sample is greater than the consumption rate, and the quality of the coal sample increases rapidly.

Thermal decomposition temperature ($T_5$) is the temperature corresponding to the maximum point in the TG curve. The mass of the coal sample reaches the maximum through the adsorption of oxygen.

3.1.2.2. Water Evaporation and Desorption Stage. First, the water evaporation and desorption stage ($30\, ^\circ C$ to dry temperature, $T_2$) in the low-temperature oxidation reaction process of each coal sample was taken as the whole reaction process; then, the Starink method was used to calculate the variation of the apparent activation energy, $E$, with the conversion rate $\alpha$ in the water evaporation and desorption stage of different coal samples during low-temperature oxidation.

The variations of the activation energy with the conversion of coal samples at the water evaporation and desorption stages are shown in Figures 2 and 3.

In Figure 2, lignite ($0$) represents raw lignite. Lignite ($60$), bituminous coal ($60$), and anthracite coal ($60$), respectively, represent lignite, bituminous coal, and anthracite coal with water immersion time of 60 days. It can be seen from Figure 1 that the activation energies of the raw coal and water-immersed coal samples with different metamorphic degrees decrease with an increase of conversion. This indicates that water evaporation and gas desorption reactions are increasingly easy in this stage, and the weight loss reaction of the coal sample is easier. The degree of the coal—oxygen compounding reaction is relatively low, and the weight loss of the coal sample
reaches its lowest point at the dry temperature point ($T_2$). For coal with the same metamorphic degree, the apparent activation energy of the water-immersed coal sample is obviously lower than that of the raw coal sample. That indicates that the energy required for the evaporation and desorption of water-immersed coal samples is less, and that the reaction is easier. For coal samples with different metamorphic degrees, the apparent activation energy of the raw coal and water-immersed coal sample increases with the increase of metamorphic degree.

Figure 2 shows that the activation energy of lignite samples with different immersion times decreases gradually with the increase of conversion in the water evaporation and desorption stage. The activation energy of the water-immersed coal samples is lower than that of the raw coal samples. Before 60 days of water immersion, the activation energy gradually decreases with the increase of immersion time. The activation energy of lignite (60) is the smallest when compared with lignite (0), lignite (30) and lignite (90), and the low-temperature oxidation reaction of coal was very easy. However, when the immersion time was 90 days, the activation energy of the coal samples increased significantly.

3.1.2.3. Oxygen Gain Stage. Firstly, the oxygen gain stage (dry temperature, $T_3$, to thermal decomposition temperature, $T_5$) in the oxidation reaction process of each experimental coal sample was taken as the overall reaction process. Then, the change of apparent activation energy, $E$, with the conversion $\alpha$ was calculated in the oxygen gain stage of coal samples during the low-temperature oxidation process.

By calculation, the variation of the activation energy of coal samples with the conversion rate in the oxygen gain stage is shown in Figures 4 and 5.

Figure 3 shows that the activation energy of lignite samples with different immersion times decreases gradually with the increase of conversion in the water evaporation and desorption stage. The activation energy of the water-immersed coal samples is lower than that of the raw coal samples. Before 60 days of water immersion, the activation energy gradually decreases with the increase of immersion time. The activation energy of lignite (60) is the smallest when compared with lignite (0), lignite (30) and lignite (90), and the low-temperature oxidation reaction of coal was very easy. However, when the immersion time was 90 days, the activation energy of the coal samples increased significantly.

3.1.2.3. Oxygen Gain Stage. Firstly, the oxygen gain stage (dry temperature, $T_3$, to thermal decomposition temperature, $T_5$) in the oxidation reaction process of each experimental coal sample was taken as the overall reaction process. Then, the change of apparent activation energy, $E$, with the conversion $\alpha$ was calculated in the oxygen gain stage of coal samples during the low-temperature oxidation process.

By calculation, the variation of the activation energy of coal samples with the conversion rate in the oxygen gain stage is shown in Figures 4 and 5.

It can be seen from Figure 4 that for different metamorphic degrees, the variations of the activation energy with the conversion of the raw coal and the water-immersed coal sample are consistent. The activation energy increases with the increase of conversion. In the oxygen gain stage, the adsorption capacity of the coal samples for oxygen is greater than that of the consumption. The apparent activation energy mainly reflects the difficult degree of coal–oxygen adsorption. The activation energy of the three different ranks of coal has the tendency to decrease after immersion, which makes the activation energy of the coal sample smaller in the stage of coal–oxygen adsorption. This is due to the change of the surface and internal structure of the coal sample after immersion and the enhancement of connectivity, which
promotes the diffusion of oxygen in pores and makes the contact surface of oxygen and hence the coal sample to increase. The coal−oxygen compounding reaction is easier, resulting in the low-temperature oxidation process of the water-immersed coal sample being more likely to occur.

As can be seen from Figure 5, the activation energy of lignite samples with different immersion times increases gradually with an increase of conversion in the oxygen gain stage. The activation energy of the water-immersed coal sample is lower than that of the raw coal sample, which is the same as the stage of water evaporation and desorption. Before 60 days of water immersion, the activation energy gradually decreases with an increase of immersion time. When the immersion time was 90 days, the activation energy of coal samples increased significantly, indicating that when the immersion time was 60 days, the coal samples were more prone to spontaneous combustion.

3.2. Gas Production Law during the Oxidation of Water-Immersed Coal. In the process of the thermogravimetric analysis experiment, the gas of each experimental coal sample was produced in the process of low-temperature oxidation. Then, the gas was transported to the Fourier infrared spectrometer for analysis of the composition and content. The more the gas produced, the stronger the signal in the detector, and the more obvious the generated spectral peak. The vibration peak with a spectral range of 2200−2050 cm⁻¹ is the absorption spectrum of CO, the main symbol gas of coal spontaneous combustion. Figure 6 shows the three-dimensional (3D) diagram of gas generated during the combustion process of the coal samples.

From Figure 6, it can be seen that the gas produced by the coal sample in the process of oxidation and heating changes significantly with changes in temperature. According to the experimental results, the spectral changes at wavenumber 2185 cm⁻¹ were selected to study the variation of CO generated by each experimental coal sample with the temperature, as shown in Figure 7.

As can be seen from Figure 7a−c, the CO production of the three ranks of coal samples all showed an increasing trend with increasing temperature. Among them, for the same coal sample, the amount of CO released by the water-immersed coal sample is obviously greater than that of the raw coal sample. In the water evaporation and desorption stage, due to the adsorption of oxygen by coal molecules, the oxygen molecules on the surface of coal sample inhibit the escape of gas generated by the reaction of the coal sample. So, less CO is released, and the water-immersed lignite shows a decrease in the production of CO. Due to the high degree of metamorphism of water-immersed bituminous coal and anthracite, the production of CO still shows an increasing trend, with only slight changes. Water-immersed bituminous coal shows slight fluctuations in the curve, while water-immersed anthracite...
shows a slowing trend in the curve, but the production of CO is still larger than the raw coal sample. During the thermal decomposition stage, the adsorption of oxygen by the coal samples is gradually weakened and the consumption of oxygen by the coal–oxygen reaction is gradually enhanced. The active structure in the coal molecules is heavily activated to participate in the reaction. The change amount of CO produced by the raw and water-immersed lignite sample is

Figure 6. Three-dimensional (3D) diagram of gas generated by the low-temperature oxidation reaction of each experimental coal sample.
the most obvious, followed by the anthracitic coal and finally bituminous coal.

As can be seen from Figure 7d, the overall change trend of CO produced by coal samples with different immersion times is the same. In the water evaporation and desorption stage, the CO production of coal samples increases with the increase of temperature for different immersion times. In the oxygen gain stage, the CO production of the water-immersed coal sample for 60 days decreases first and then increases with the temperature. Because in this stage the coal molecules adsorb oxygen and the oxygen molecules on the surface of the coal sample inhibit the escape of CO generated by the reaction, the CO released is less and presents a decreasing trend temporarily. The CO productions of the water-immersed coal samples were all larger than those of the raw coal samples. The coal samples, after immersion, have developed a larger surface pore structure, where oxygen intake increases, which provides favorable conditions for the rapid increase of the production amount and rate of CO. Among them, before 60 days of water immersion, with the increase of immersion time, the amount of CO production gradually increased. When the immersion time was 90 days, the amount of CO production decreased obviously but was still higher than that of raw coal, indicating that when the immersion time was 60 days, the amount of CO production was the largest.

### 3.3. Micromorphology of Water-Immersed Coal

Through the above studies, it can be found that the apparent activation energy and CO release amount of water-immersed coal are significantly different from those of raw coal. Therefore, this study carries on the scanning electronic microscopy (SEM) experiment, providing the proof for our research intuitively. The SEM results of the experimental coal samples are shown in Figure 8.

Figure 8 shows the SEM images of the raw coal samples and the water-immersed coal samples with different metamorphic degrees and of water-immersed lignite with different immersion times (30, 60, and 90 days). It can be seen from Figure 8 that there are some folds and pore structures on the surface of the raw coal and water-immersed coal samples, and there are some differences between the coal samples. There are some pores on the surface of the raw coal sample, but when the raw coal sample is immersed in water, the number of pores on the surface of the coal sample increases obviously. Also, with the increase of immersion time, the changes of pore quantity and pore size of the coal sample surface are more obvious. The surface of the coal sample is rougher after immersion. This indicates that the water immersion process has a certain pore-reaming effect on the coal sample, and the pore structure swelling in the raw coal strengthens the connectivity between the pores, and the material on the coal sample surface also falls off. After the coal sample is immersed in water, the surface folds and enlarged pores will increase the contact area with oxygen, increasing the possibility of oxygen adsorption by the coal sample and thus increasing the risk of spontaneous combustion of water-immersed coal.

### 3.4. Change Analysis of the Main Functional Groups in the Water-Immersed Coal Samples

#### 3.4.1. Test Results of the Functional Group Changes in the Water-Immersed Coal Samples

With an increase of temperature, the determination of coal samples by an infrared spectrometer may deviate and the position of peaks may shift, resulting in inaccurate analysis of the variation of the absorption peak strength of the functional groups. Therefore, the 3D images of each experimental coal sample were decomposed. The infrared spectra at temperatures of 30, 50, 70, 90, 110, 150, 170, 190, 210, 230, 250, 270, 290, 310, 330, and 350 °C were taken, respectively, to smooth the curve and correct the baseline, as shown in Figures 9−11.

It can be seen from Figures 9−11 that although the absorption peak intensity of the infrared spectroscopy is different at different temperatures, the position of the absorption peak is basically unchanged, with only a slight
deviation. This indicates that the functional group types of each experimental coal sample have not changed significantly during the low-temperature oxidation process, but their contents have changed. Peakfit software was used to separate the peaks from the infrared spectra of the experimental coal samples at various temperature points. Finally, the ratio of the peak area to the total area of different functional groups was used as the relative content of functional groups for
comparative analysis. The changes of the peak area percentage of the hydroxyl, aliphatic, aromatic hydrocarbon, and oxygen functional groups with temperature were analyzed.

3.4.2. Analysis of Hydroxyl Change. Spectral peaks in the range of 3550−3200 cm$^{-1}$ with hydroxyl (−OH) in all three ranks of the coal samples were selected for analysis. In Figure 12, $ΔS$ is the difference between the peak area of the hydroxyl (−OH) group at the beginning and the end of low-temperature oxidation of each coal sample. As can be seen from Figure 12a−c, within the range of 30−350 °C, the hydroxyls (−OH) in raw and water-immersed coal samples of lignite and anthracitic coal show a trend of first decreasing and then increasing. This indicates that hydroxyl (−OH) in coal samples is a very active group. In the water evaporation and desorption stage, the hydroxyl group (−OH) participates in the oxidation reaction from the beginning of the reaction, gradually reduces, and gives off heat. During the oxygen gain stages, the hydroxyl group (−OH) begins to increase. Because

![Infrared spectra of temperature changes of raw lignite and water-immersed coal samples.](https://dx.doi.org/10.1021/acsomega.0c01513)
The hydroxyl ($\text{−OH}$) is constantly consumed during the coal oxidation reaction. However, at the same time, the hydroxyl ($\text{−OH}$) is constantly formed by the reaction, and the formation amount of hydroxyl ($\text{−OH}$) is higher than the consumption of hydroxyl ($\text{−OH}$). The hydroxyl ($\text{−OH}$) in bituminous coal shows a tendency of first decreasing, then increasing and then decreasing, indicating that the hydroxyl ($\text{−OH}$) in bituminous coal participates in the reaction at the initial stage of the oxidation reaction. In the water evaporation and desorption stage, the trend is decreasing. In the oxygen gain stage, the first increase is because the initial content of hydroxyl ($\text{−OH}$) in bituminous coal is relatively small, but the aliphatic group greatly participates in the reaction, and then the aliphatic hydrocarbon and oxygen react to form the hydroxyl ($\text{−OH}$). It can also be clearly seen by the change in the content of the aliphatic groups of bituminous coal in Figure 13b that the aliphatic groups in bituminous coal samples continue to decrease. It indicates that oxidation produces

Figure 10. Infrared spectra of the temperature changes of raw bituminous coal and water-immersed coal samples.

Figure 11. Infrared spectra of the temperature changes of raw anthracitic coal and water-immersed coal samples.
hydroxyl (−OH) and then the hydroxyl (−OH) groups are further oxidized with the increase of oxidation temperature or the action of chemical bonds. So, when the oxidation temperature increases, the hydroxyl (−OH) begins to decrease, and in the process of continuous formation and reduction, the total content changes depend on the difference in the amount of formation and consumption.

For the same coal sample, the total variation of hydroxyl in the water-immersed coal samples of lignite and bituminous coal was greater than that of the raw coal samples, decreasing by 3.35 and 2.59% respectively. It indicates that the reaction of hydroxyl in the coal samples after water immersion was more intense, while the total variation of hydroxyl in anthracitic coal after water immersion was increased by only 0.18%.

As can be seen from Figure 12d, the content of hydroxyl (−OH) in coal samples all shows a trend of decreasing first and then increasing, but the total variation of hydroxyl (−OH) is different. With the increase of immersion time, the total variation of hydroxyl (−OH) shows an increasing trend, indicating that the reaction of hydroxyl (−OH) is more intense. Between 30 and 60 days of immersion, the change of total hydroxyl (−OH) is the largest.

3.4.3. Analysis of Aliphatic Group Change. The spectral peaks of 2975−2915 and 2882−2840 cm−1 with aliphatic groups (−CH3, −CH2) in all three ranks of coal samples were selected for analysis, as shown in Figure 13.

In Figure 13, ΔS is the difference between the peak area of aliphatic groups (−CH3, −CH2) at the beginning and the end of low-temperature oxidation of each experimental coal sample. As can be seen from Figure 13a−c, which are within the range of 30−350 °C, the aliphatic groups (−CH3, −CH2) in the raw coal samples and the water-immersed coal samples of lignite...
Figure 13. continued
and anthracite coal show a trend of first increasing and then decreasing. The aliphatic groups (−CH3, −CH2) in the raw coal samples of bituminous coal and the water-immersed coal samples show a trend of decreasing. This shows that in the process of the oxidation reaction, the methyl and methylene (−CH3, −CH2) groups of the raw coal and water-immersed coal samples of the three ranks of the coal samples participate in the oxidation reaction. At the beginning of the oxidation reaction, the production of methyl and methylene (−CH3, −CH2) of the raw coal and water-immersed coal samples of lignite and anthracite coal are the most obvious here, and this is because the low-temperature oxidation stage of coal is mainly the activation stage. After low-temperature activation, the activation stage. After low-temperature activation, the aromatic ring (C=C) content is due to the lower degrees of lignite and bituminous coal. The structure of aromatic hydrocarbons also contains a certain amount of heterocyclic and alicyclic rings. As the temperature increases, the structure of the aromatic rings is damaged to a certain extent due to the interaction of unstable cyclic hydrocarbons with oxygen. The variation of the raw coal samples was 2.25 and 1.78%, respectively. Anthracite coal has a high degree of coalification. There are a few heterocyclic and alicyclic rings in the structure of aromatic hydrocarbons. Anthracite coal has more stable chemical properties, and a small amount of change, which is only 0.21%. For the same coal sample, compared with

![Figure 13. Variation of aliphatic group peak area of each experimental coal sample.](https://dx.doi.org/10.1021/acsomega.0c05113)

3.4.4. Analysis of Aromatic Hydrocarbon Change. The spectral peaks in the range of 1635–1595 cm⁻¹ with aromatic hydrocarbon (C=C) in all three ranks of coal samples were selected for analysis, as shown in Figure 14.

In Figure 14, ΔS is the difference between the peak area of the aromatic ring (C=C) at the beginning and the end of low-temperature oxidation of each experimental coal sample. As can be seen from Figure 13a–c, during the whole oxidation and temperature increase stage of the coal sample, the aromatic ring (C=C) content in the raw and water-immersed coal samples of lignite and bituminous coal increases first and then decreases. The raw and water-immersed coal samples of anthracite coal show an increasing trend. However, the increasing trend of the aromatic ring (C=C) content is related to the reaction of the active aliphatic hydrocarbon side chain with oxygen. The shedding of the fatty side chain makes the aromatic ring structure of coal relatively to develop, and the decrease of the aromatic ring (C=C) is due to the lower degrees of lignite and bituminous coal. The structure of aromatic hydrocarbons also contains a certain amount of heterocyclic and alicyclic rings. As the temperature increases, the structure of the aromatic rings is damaged to a certain extent due to the interaction of unstable cyclic hydrocarbons with oxygen. The variation of the raw coal samples was 2.25 and 1.78%, respectively. Anthracite coal has a high degree of coalification. There are a few heterocyclic and alicyclic rings in the structure of aromatic hydrocarbons. Anthracite coal has more stable chemical properties, and a small amount of change, which is only 0.21%. For the same coal sample, compared with
the raw coal sample, the content of the aromatic ring (C=C) in the water-immersed coal sample shows a significant increase, indicating that after water immersion, the aromatic ring (C=C) becomes relatively unstable, with a larger range of change.

As can be seen from Figure 14d, the aromatic hydrocarbons in both raw and water-immersed coal samples show a trend of a small increase and then decrease. As the immersion time increases, the change amount of the aromatic ring (C=C) shows a trend of first decreasing, then increasing, and then decreasing. When the lignite sample was immersed in water for 60 days, the change amount of the aromatic ring (C=C) is the largest, which was 2.62%, indicating that the aromatic ring (C=C) is extremely unstable and has a large fluctuation range.

3.4.5. Analysis of Oxygen Functional Group Change. Spectral peaks in the range of 1330−1160 cm⁻¹, where the oxygen-containing functional groups, phenol, alcohol, ether, and ester bonds (C−O) exist in all three ranks of coal samples, were selected for analysis, as shown in Figure 15.

In Figure 15, ΔS is the difference between the peak area of phenol, alcohol, ether, and ester bonds (C−O) at the beginning and the end of low-temperature oxidation of each experimental coal sample. The C−O bonds in the oxygen functional groups are mainly the primary methoxy C−O in the alcohol, phenol, ether, and ester in the raw coal, and the secondary C−O is formed by the contact between the −CH₃ and oxygen molecules in the side chains of aliphatic hydrocarbons after the break. As can be seen from Figure 14a−c that the C−O bonds in the molecular structure of lignite and water-immersed lignite samples increased gradually with the increase of temperature. This indicates that phenol, alcohol, ether, esters, and other carbon oxides (C−O) are produced continuously during the coal oxidation process. The
variation of water-immersed coal is more than 9.84\%, indicating that the number of functional groups involved in the reaction is more. The content of C=O in bituminous coal samples always fluctuates near the fitting line, but the variation is not large, which is only 0.61\% here. The anthracritic coal samples show an upward trend as a whole, and the variation of the functional groups is 3.37\% here. The water-immersed coal samples of the bituminous and anthracitic coal have a tendency of increasing first and then decreasing with the increase of temperature. This indicates that carbon oxides such as phenol, alcohol, ether, and ester in coal will also participate in the reaction in large quantities, resulting in a decrease of their content.

As can be seen from Figure 15d, the C=O bonds in the raw and water-immersed coal samples show an increasing trend with the increase of temperature. This indicates that during the coal oxidation process, carbon oxides (C=O) such as phenol, alcohol, ether, and ester are continuously produced in the lignite sample before and after water immersion. With an increase of immersion time, the changes of phenol, alcohol, ether, and ester bonds (C=O) increase first and then decrease. When lignite is immersed in water for 60 days, the increase of phenol, alcohol, ether, and ester bonds (C=O) is the largest, at 9.82\%. Although the changes decrease slightly at 90 days of immersion, they are all larger than the increase in raw lignite.

4. CONCLUSIONS
In this paper, TG-FTIR and DRIFTS were used to study the oxidation reaction process of raw coal and water-immersed coal, and the following conclusions are drawn:

(1) In the stage of water evaporation and desorption, the activation energy of each experimental coal sample decreases with an increase of conversion. This indicates
that the evaporation and desorption of water and gas in the coal sample become easier and easier, and the apparent activation energy of the coal sample increases with an increase of the degree of metamorphism. When the immersion time is 60 days, the activation energy required for lignite coal—oxygen recombination by water immersion is the lowest, and the reaction easily occurs.

(2) The CO produced in coal samples during low-temperature oxidation tends to increase with an increase of temperature. For the same coal sample, the production of CO in the water-immersed coal sample is larger than that in raw coal sample, and the oxidation reactivity is enhanced in the whole stage of oxidation reaction. When the immersion time is 60 days, the gas production of water-immersed lignite is the largest.

(3) Under the same metamorphic degree, the change of functional groups with temperature before and after water immersion is almost the same, but the change amount is different. After water immersion, the change of hydroxyl and aromatic hydrocarbon content is obviously increased, and the temperature of fatty and oxygen-containing functional groups participating in the reaction decreases. This indicates that the functional groups are unstable and easily participate in the reaction and that the reaction is intense after water immersion.

(4) For lignite coal samples, with an increase of water immersion time, the variation of functional groups in water immersion coal samples is the same with the change of temperature. The variation of functional groups in water-immersed coal samples is lower than that in the raw coal samples. When the immersion time is 60 days, the variation of functional groups is the most obvious.

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**Notes**

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