Correlation Analysis of the Change Law of Index Gas and Active Functional Groups in the Process of High-Temperature Spontaneous Combustion of Minerals in the Fushun West Mine

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ABSTRACT: The spontaneous combustion of underground minerals causes huge property losses and ecological damage. Coal and oil shale are co-associated minerals in the Fushun West Mine, and both have the ability to undergo oxidative spontaneous combustion. To study the effect of microstructure changes on the macroscopic gas product concentration during the mineral oxidation spontaneous combustion process in the Fushun West Mine, this study used a high-temperature temperature-programmed test to obtain the change trend of gas product concentration in different oxidation stages of minerals. Using Fourier transform infrared spectroscopy technology, the changes in active functional groups of surface molecules during the process of mineral oxidation and spontaneous combustion were identified. Finally, using the gray correlation degree, correlation analysis between the concentration of gas products and the concentration of active functional groups in different oxidation stages was carried out. The key reactive functional groups affecting mineral spontaneous combustion were identified. The essential reason for the change in the gas product was revealed.

1. INTRODUCTION

Coal and oil shale are all products of coal mining. Among them, oil shale, as a coal-measure co-associated mineral, can be used as an unconventional oil and gas resource. It is a nonrenewable fossil resource such as coal. Shale oil can be extracted from oil shale by low-temperature dry distillation, which has high utilization value. In China, the coal reserves are 162.288 billion tons, and the oil shale reserves are approximately 719.9 billion tons. The average oil content of oil shale in the country is approximately 6.6%, which is converted into 47.6 billion tons of shale oil. Oil shale is often enriched above and below the coal seam to become the roof and floor of the coal seam. Taking the Fushun West Open-pit Mine as an example, its oil shale reserves are 3.2 billion tons, the average oil shale layer thickness is 145 m, and the average oil content is approximately 6.6%. The co-associated long-flame coal reserves are 1.7 billion tons, and the thickness of the coal seam is 20−210 m.

In the process of coal mining, fresh air enters the coal seam from the pores, which can easily cause the coal seam to oxidize and spontaneously combust and release gaseous products such as CO, CO₂, and CH₄. Zhang et al. believed that the exothermic process of coal oxidation is the result of the superposition of three reaction mechanisms: oxidative decomposition, gas-phase combustion, and solid-phase combustion. Hydroxyl is the most active functional group in the spontaneous combustion of coal. Xu et al. studied the reaction between free radicals and oxygen-containing functional groups and revealed...
that carbonyl radicals are important active groups for the generation of CO from coal. Mursito et al. showed through experiments that the number of oxygen-containing functional groups on the coal surface increases with increasing temperature. Zhao et al. showed that hydroxyl groups are the key functional group for the reaction of coal and oxygen to generate CH₄.

Since oil shale has a similar composition and pore characteristics to coal, it can absorb oxygen to generate adsorption heat. Therefore, the oil shale layer has a certain risk of spontaneous combustion and characteristics to coal. Mursito et al. showed that carbonyl radicals are important active groups for the reaction of coal and oxygen to generate CH₄.

In summary, there are few comparative studies on the microstructural changes of coal and oil shale in the process of high-temperature oxidation and spontaneous combustion. Therefore, this paper takes the long-flame coal, oil shale, and oil shale after dry distillation as the research object. Through a high-temperature temperature-programmed test and Fourier transform infrared (FTIR) spectroscopy technology, the change trends of CO, C₂H₄, and H₂ during the oxidation process of oil shale and divided the oxidation process into three stages: slow low-temperature oxidation, rapid heating oxidation, and stable heating. Oil shale after retorting is the solid waste residue left after oil shale is subjected to low-temperature retorting to obtain shale oil. Although the ash content is higher than that of oil shale, there is still a small amount of organic compounds remaining, and it has certain ability to absorb oxygen and release heat at low temperatures. Trikkel and Han et al. believe that oil shale can continue to be burned and utilized after dry distillation.

In summary, there are few comparative studies on the microstructural changes of coal and oil shale in the process of high-temperature oxidation and spontaneous combustion. Therefore, this paper takes the long-flame coal, oil shale, and oil shale after dry distillation as the research object. Through a high-temperature temperature-programmed test and Fourier transform infrared (FTIR) spectroscopy technology, the change trends of CO, C₂H₄, and other indicator gas concentrations that can characterize spontaneous coal combustion were compared and analyzed for mineral samples at different oxidation stages. The variation trend of the concentration of molecular functional groups on the surface of the sample was analyzed by effectively using the different oxidation stages divided according to changes in the CO concentration with temperature. Finally, the gray correlation degree was used to analyze the concentration change trend of indicator gases and active functional groups.

2. EXPERIMENTAL SECTION

2.1. Sample Preparation. The mineral samples required for the test are from the Fushun West Mine: raw coal (long-flame coal, low-metamorphic coal), oil shale, and oil shale after dry distillation. Each sample was crushed in air and sieved to remove five different particle sizes of 0–0.9, 0.9–3, 3–5, 5–7, and 7–10 mm. One kilogram of each particle size was mixed evenly to prepare raw coal samples, oil shale, and oil shale after dry distillation. Five kilograms of each of the three prepared mixed particle size samples was used for the temperature-programmed test. Ten grams of each sample was crushed to 80–120 mesh for the infrared test.

2.2. High-Temperature Test Equipment and Conditions. The high-temperature temperature-programmed test adopted the XKGW-1 high-temperature temperature-programmed experimental system. Its structural composition is shown in Figure 1. The experimental system includes the following: gas source, high-temperature reaction furnace, sample tank, and gas chromatograph.

To ensure smooth airflow and reduce ventilation resistance, the air path was supplied by a combination of φ8 copper pipe, SPB-3 automatic air pump, and high-pressure gas cylinder and was connected to the rotameter through a tee. The air supply to the experimental tank could be adjusted by a rotameter. The furnace chamber size of the high-temperature reaction furnace (Figure 2) was 65 × 45 × 40 cm³, and the shape was box type. The inner-layer furnace chamber material was ceramic fiber, and the outer layer was carbon steel material. The high-temperature experimental system.
reaction furnace can simultaneously accommodate six sample tanks with a maximum diameter of 10 cm or a single sample tank with a diameter of 30 cm for high-temperature temperature-programmed experiments. The sample tank used in this experiment was made of high-temperature resistant carbon-silicon material, with a size of 30 cm in diameter and 20 cm in height. There was a lid on the top of the tank body, the lid and the tank body were fixed by flange connection, and a graphite gasket was sandwiched in the middle to improve the airtightness of the experimental sample tank. The sample tank was placed vertically in the middle of the furnace, and a-10 cm-high support placed under the sample box to support the tank. Manual sampling was used for gas collection. According to the specific requirements of the experiment, when the temperature of the sample increased by 15 °C, a disposable syringe was used to connect the air outlet reserved on the gas outlet pipe, and the gas in the reaction sample tank was collected slowly and evenly. Gas composition analysis was then performed using a gas chromatograph.

The high-temperature program temperature test conditions were as follows: the sample tank was filled with 1 kg of mixed-particle-size-samples, the air flow rate of the air pump was set to 120 mL·min⁻¹, and the temperature rise range was set to 30–600 °C.

2.3. Infrared Experimental Equipment and Conditions. The test adopted the INVENIO FTIR spectrometer manufactured by the Bruker company in Germany. 1 mg of the prepared sample was weighed and dried. Then, it was placed in the sample chamber of the FTIR spectrometer for testing. The test range was set as 400–4000 cm⁻¹, heating rate was 5 °C·min⁻¹, air flow was 120 mL·min⁻¹, and cumulative number of scans was 770.

2.4. Correlation Analysis Method. The relative correlation analysis method was used in the experiment to calculate and analyze the correlation between the macroscopic gas concentration and the active groups in different oxidation stages of the mineral spontaneous combustion process and obtain the key active groups that affect the oxidation reaction of each stage.

The specific calculation steps of the relative correlation analysis are as follows:

a. Determine the analysis index system according to the analysis purpose and collect analysis data.

Let m data sequences form the following matrix

\[
\begin{pmatrix}
X'_1(1) & X'_1(2) & \cdots & X'_1(m) \\
X'_2(1) & X'_2(2) & \cdots & X'_2(m) \\
\vdots & \vdots & \ddots & \vdots \\
X'_n(1) & X'_n(2) & \cdots & X'_n(m)
\end{pmatrix}
\]

\[m\text{ is the number of indicators, and }\]

\[X'_i = (X'_i(1), X'_i(2), \ldots, X'_i(m))^T, i = 1, 2, \ldots, n.\]

b. Determine the reference data column

The reference data column is written as

\[X'_0 = (X'_0(1), X'_0(2), \ldots, X'_0(m))\]

c. Perform nondimensionalization on the indicator data.

The dimensionless calculation formula is

\[X_i(k) = \frac{X'_i(k)}{\sum_{k=1}^{m} X'_i(k)}\quad i = 1, 2, \ldots, n; k = 1, 2, \ldots, m\]

The dimensionless data sequence forms the following matrix

\[
\begin{pmatrix}
X'_0(1) & X'_1(1) & X'_1(2) & \cdots & X'_1(m) \\
X'_0(2) & X'_2(1) & X'_2(2) & \cdots & X'_2(m) \\
\vdots & \vdots & \vdots & \ddots & \vdots \\
X'_0(m) & X'_n(1) & X'_n(2) & \cdots & X'_n(m)
\end{pmatrix}
\]

d. Calculate the absolute difference between each evaluated object index sequence (comparison sequence) and the corresponding element of the reference sequence one by one.

\[|X'_0(k) - X_i(k)|, (i = 1, 2, \ldots, n; k = 1, 2, \ldots, m),\]

where \(n\) is the number of evaluated objects.

e. Confirm according to the correlation sequence of each observation object, obtain the analysis result.

The relational order formula is

\[r_{bh} = \frac{1}{m} \sum_{k=1}^{m} \rho f(k)\]

3. RESULTS AND DISCUSSION

3.1. Mineral Functional Group Analysis. It can be seen from the infrared spectra of each sample that the functional groups contained in the experimental samples are basically the same, but the numbers of all functional groups are different, which shows that there are differences in the absorption peak intensities of different samples. The peak intensity of the four characteristic absorption peaks of the sample is analyzed as follows:

Hydroxyl is one of the more active functional groups in the oxidation process and is the main functional group that releases water vapor, carbon dioxide, and other products during the oxidation reaction. The peaks in the 3550–3200 cm⁻¹ range are ascribed to intermolecular associative hydroxyl hydrogen bonds, those in the 3624–3613 cm⁻¹ region to intramolecular hydroxyl hydrogen bonds, and those in the 3697–3652 cm⁻¹ range to free hydroxyl groups. There are differences in the three types of hydroxyl groups contained in different coal samples. Oil shale after dry distillation contains the most free hydrogen bonds,
intramolecular hydrogen bonds, and intermolecular associative hydrogen bonds. The raw coal samples contains the fewest free hydroxyl groups and intramolecular hydrogen bonds. Oil shale contains the least amount of intermolecular hydrogen bonds.

Aliphatic hydrocarbons have the fastest reaction rates of all functional groups. The peaks in the range 2875−2845 cm\(^{-1}\) are attributed to the symmetrical stretching vibration of the methylene group. The peaks at 2940−2920 cm\(^{-1}\) are due to the asymmetric stretching vibration of the methylene group. The peaks in the 2975−2950 cm\(^{-1}\) region are attributed to the asymmetric stretching vibration of the methyl group. The peaks in the ranges 1470−1430 °C and 1380−1370 cm\(^{-1}\) are attributed to methyl deformation vibrations. The presence of methyl and methylene groups was detected in all experimental samples, and the methyl group had a higher deformation shock absorption intensity. The content of methylene -CH\(_2\) is slightly higher than that of methyl. Among them, the methylene absorption intensity of oil shale after dry distillation is higher than that of other samples, and the methyl absorption intensity of raw coal samples is higher than that of other samples.

Oxygen-containing functional groups are the main active groups in the oxidation process of samples, and they have a great influence on the chemical properties of samples. They are mainly distributed in the wavenumber range between 1800and 1000 cm\(^{-1}\), including carbonyl C=O, carboxyl -COOH, ether oxygen R−O−R, and other functional groups, of which 1300−1015 cm\(^{-1}\) represents the stretching vibration of aliphatic ether C−O−C. Coal also contains C−O stretching vibrations of phenol, alcohol, and ether at a peak position of 1250−1050 cm\(^{-1}\). Figure 3 shows that the C−O−C absorption intensity of the sample is generally high, the C−O−C functional group in the oil shale after dry distillation has the highest absorbance, and the C−O−C oxygen-containing functional group content in the raw coal sample is low.

The spectral bands of aromatic hydrocarbons are mainly distributed in two regions: the first region is 1625−1575 cm\(^{-1}\), which belongs to the in-plane bending vibration of C−C in the aromatic ring. The C=C double shoulder absorption peak intensity of the raw coal sample is strong, which is mainly because the C=C double bond is the main structure of the aromatic ring. The original sample is not oxidized, the double bond structure is stable, and the content is large, which indicates that the peak intensity is large. The 900−700 cm\(^{-1}\) spectral peaks are attributed to the deformation vibrations of various substituted aromatic hydrocarbons Ar−CH. The functional groups mainly belong to the substituted benzene hydrocarbons containing three hydrogen atoms, and the oil shale after dry distillation has a high absorption wave intensity, while the raw coal sample has a low wave absorption.

3.1.1. Transfer Rule of Hydroxyl Functional Groups during Different Oxidation Stages. It can be observed from Figures 4−6 that the number of hydroxyl groups in the three samples is always changing, and the overall trend of coal and rock samples is similar, with the strength decreasing. Among the three samples, the absorbance of intermolecular associative hydroxyl hydrogen bonds in the wavenumber range 3550−3200 cm\(^{-1}\) was the lowest, and it decreased obviously at low temperatures. After 100 °C, the absorbance decreased to 0 and became stable. For other hydroxyl functional groups, in the initial stage of oxidation, hydroxyl groups react with oxygen to generate CO and H\(_2\)O. At the same time, some unsaturated hydrocarbons are oxidized to generate hydroxyl groups, but the generation rate is faster than the consumption rate, so the initial stage shows an increasing trend. As the temperature increases, the oxidation rate increases, and the aliphatic hydrocarbon side chain of the sample reacts with oxygen to generate new hydroxyl groups, thus causing the absorbance of the sample to increase. However, after dry distillation, the absorbance of the overall hydroxyl functional group of oil shale began to decrease due to the effect of dry distillation. After the temperature exceeds 400 °C, the hydroxyl functional group content decreases rapidly, and the decrease is the largest. This is due to the intensified reaction of the late reaction, and the free hydroxyl groups and intramolecular hydrogen bonds continue to react, eventually generating oxygen-containing functional groups and water.

3.1.2. Transfer Law of Aliphatic Hydrocarbon Functional Groups at Different Oxidation Stages. The activity of methyl and methylene is greater during the reaction process, and the overall trend is decreasing. The variation trends of the symmetric stretching vibration of methylene and the asymmetric stretching vibration of methane in the three samples are similar, and the absorbance slowly decreases from the low-temperature stage to 0 and then fluctuates stably. Among them, the raw coal decreases to 0 at 350 °C, and the remaining samples decrease to 0 at 500 °C, indicating that it has completely participated in the oxidation reaction. The methyl deformation vibrations at 1470−1430 cm\(^{-1}\) are different among the samples. In raw coal, the vibration absorbance of methyl deformation is the highest, and it starts to decrease slowly at low temperatures, accelerates at 300 °C, and tends to stabilize after 430 °C, fluctuating up and down. In oil shale, the absorbance of methyl deformation vibration has a trend of first rising and then decreasing with increasing temperature. The absorbance of the methyl deformation vibration between 100 and 400 °C increases by more than 2 times and then decreases rapidly. After dry distillation, the absorbance of the methyl deformation vibration in oil shale decreases slowly with temperature at first and then turns at 450 °C, and the decreasing speed is accelerated. In the early stage of oxidation, aliphatic hydrocarbons are attacked by...
oxygen and is broken into more aliphatic hydrocarbons, while methyl groups are oxidized to generate CO, CO$_2$, and hydrocarbon gases. As the temperature increases, the sample oxidizes rapidly, and the side chains and oxygen recombine to generate more CO and water vapor precipitation, resulting in a continuous reduction of aliphatic hydrocarbon side chains and a decrease in the light absorption intensity. At high temperatures, the absorbance of methyl and methylene functional groups decreased close to 0, indicating that aliphatic hydrocarbons at the stretching vibration peak are mainly consumed during the oxidation process. The consumption of methylene is greater than that of methyl, indicating that methylene is more active in the oxidation process.

3.1.3. Transfer Rule of Oxygen-Containing Functional Groups at Different Oxidation Stages. In raw coal and oil shale, the absorbance of aliphatic ether C−O−C stretching vibration showed a slow increase at low temperature before the temperature reached 300 °C, which is due to the formation of secondary groups containing C−O−C during the oxidation process, resulting in an increase in absorbance. With increasing temperature, the oxidation reaction accelerated and then showed a rapid downward trend; in the oil shale and mixed samples after dry distillation, the absorbance showed a similar change trend, which first decreased slowly and then decreased rapidly after exceeding 400 °C. The characteristic absorption peaks of phenol, alcohol, and ether C−O with a wavenumber of approximately 1263 cm$^{-1}$ are unique in raw coal. The absorbance is generally lower than that of the aliphatic ether C−O−C stretching vibration, but the change trend is similar, and they all increase before 400 °C and then decrease rapidly.

3.1.4. Transfer Rule of Aromatic Functional Groups at Different Oxidation Stages. The main functional groups of
aromatic hydrocarbons are characterized by the deformation vibration of various substituted aromatic hydrocarbons with a wavenumber of approximately 794 cm\(^{-1}\) and the C–C in-plane vibration of aromatic ring compounds with a wavenumber of approximately 1605 cm\(^{-1}\). The C–C in-plane vibration of unsaturated aromatic compounds is one of the important signs to identify the presence or absence of a benzene ring. Combined with the vibration intensity of aromatic hydrocarbons, the stability of the nuclear structure of the substance can be determined. The C–C in-plane vibration absorbance of aromatic compounds in raw coal is greater than that of other samples, and the change range is large. When the temperature is low, it decreases slowly. As the temperature increases, the absorbance of the vibration in the C–C plane rises slightly due to the intensified oxidation reaction between the C–C bond and the side chain of aliphatic hydrocarbons. The reason is that the aliphatic hydrocarbon side chain participates in the oxidation reaction, resulting in a decrease in its content and a relative increase in the aromatic ring structure. In other samples, the absorbance of the C–C in-plane vibration of aromatic ring compounds decreased to the lowest point at approximately 200 °C. The absorbance of various substituted aromatic hydrocarbons with a wavenumber of approximately 794 cm\(^{-1}\) is low in raw coal, decreases slowly, and has a slight upward trend after approaching the lowest point at 300 °C. The reason is also that the content of the aliphatic hydrocarbon side chain is reduced due to the participation of the oxidation reaction, and the aromatic ring structure is relatively increased. However, the deformation shock absorbance of various substituted aromatic

![Graphs showing absorbance vs. temperature for different samples](https://doi.org/10.1021/acsomega.2c03562)
hydrocarbons in the other samples maintained a uniform decreasing trend throughout the oxidation process (Figure 7).

3.2. Gas Product Analysis. The variation law of gas products of mineral samples is shown in Figures 8−12. The trends of CO concentration of the three samples with temperature are shown in Figure 8. CO was precipitated during the low-temperature stage. Then, the concentration increased rapidly at 200 °C, and the CO concentration of oil shale and oil shale after dry distillation peaked at 300 °C and then began to decline, while the CO concentration of fresh coal was produced in large quantities and continued to increase. The reaction of the three samples after 300 °C indicates that a strong oxidation reaction had occurred and began to enter the spontaneous combustion stage; therefore, the spontaneous combustion of coal can be predicted. The CO₂ and CH₄ in the three samples showed a fluctuating trend in the early stage due to the desorption of coal-occurring gas, and they should not be used as coal spontaneous combustion indicator gases. The concentrations of C₂H₆ and C₂H₄ were extremely low when the temperature was lower than 100 °C, and the gas concentration increased slowly with increasing temperature. When the temperature exceeded 300 °C, the gas concentrations of the three samples all increased rapidly, indicating that the spontaneous combustion of coal has reached the violent reaction stage. The change trend of C₂H₄ with temperature curve was obvious, and CO and C₂H₄ were selected as coal spontaneous combustion and ignition index gas for separate analysis.

3.2.1. Analysis of CO Gas Concentration Change. Figures 13−15 show that a small amount of CO can be detected in each sample at the beginning of the experiment, and the CO concentration increases in a parabolic form with increasing
When the temperature was low, although the oxygen supply was sufficient, the CO concentration increased slowly. The sample mainly reacted with water and oxygen to form water–oxygen complexes, and some complexes were converted into CO and precipitated. After exceeding 100 °C, the output of CO began to increase, and the concentration increased significantly after 200 °C. The increasing trend of the CO concentration of each sample was slightly different. The CO concentration of raw coal generally increased with increasing temperature, showed a downward trend between 350 and 400 °C, and then began to increase again, reaching a peak of 60,760 ppm at 555 °C. After that, it began to decline until the end of the experiment. The variation trend of the CO concentration in oil shale after dry distillation was in the form of an obvious parabola. The growth rate was slow before 165 °C and increased rapidly after 165 °C. There was a slight downward trend between 300 and 315 °C, which then began to rise again, reaching a peak of 40,720 ppm at 330 °C. After that, it began to decrease until the end of the experiment, and the CO concentration was basically maintained at 15,000 ppm. Oil shale was slightly different from dry distillation. The CO concentration in the oil shale increased rapidly after 210 °C, reaching a peak of 32,150 ppm at 300 °C. Then, it rapidly decreased to 13,060 ppm at 45 °C, increased to 24,740 ppm at 360 °C, and then gradually began to decrease.

**Figure 7.** Relationship between the absorbance of aromatic hydrocarbon functional groups and the temperature of each sample: (a) fresh coal, (b) retorted oil shale, and (c) oil shale.
until the end of the experiment, where it was basically maintained between 5000 and 10,000 ppm. It can be seen from the above analysis that the CO concentration of each sample is, raw coal, retorted oil shale, and oil shale.

3.2.2. \( \text{C}_2\text{H}_4 \) Concentration. Figures 16–18 show that the change trends of the \( \text{C}_2\text{H}_4 \) concentration in the five samples were similar, and all were parabolic. \( \text{C}_2\text{H}_4 \) could be detected between 100 and 150 °C, indicating that \( \text{C}_2\text{H}_4 \) was a high-temperature reaction product rather than occurring in the sample, and it can be used as an indicator gas to characterize the degree of spontaneous combustion of the sample. After 300 °C, \( \text{C}_2\text{H}_4 \) began to precipitate in large quantities and then reached a peak at approximately 450 °C. Among them, the peak concentration of \( \text{C}_2\text{H}_4 \) gas in fresh coal was the highest, which was 10,083 ppm, which is one-sixth of the concentration of CO at the same temperature. The peak concentration of \( \text{C}_2\text{H}_4 \) from large to small was fresh coal, oil shale, and oil shale after dry distillation. The oil shale after dry distillation was the lowest, at only 2037 ppm.

3.2.3. Oxidation Stage Division. As shown in Table 1, by analyzing the changes in the CO concentration of each sample by growth rate analysis, the characteristic temperature point of each sample can be obtained. By observing the data in Table 1, the critical temperature, dry cracking temperature, and active temperature of each sample all occurred in a low-temperature environment. During the heating process, both raw coal and oil shale first reached the critical point of reaction at 75 °C, the fresh coal reached the dry cracking temperature at 120 °C, and when the temperature reached 315 °C, the raw coal first begins to burn. After dry distillation, the temperature of oil shale reaching each characteristic point lagged behind that of other samples. Therefore, during the heating process of the three experimental
samples, the fresh coal was the most likely to react, and the oil shale after dry distillation was the most difficult to react.

At the same time, by observing the change trend of CO concentration in each sample, it can be found that the CO concentration of the three samples increased slowly before the active temperature, and the CO precipitated in large quantities after the active temperature. After the ignition point, the increase in the CO concentration gradually slowed down and showed a downward trend. Therefore, we divided each sample into the low-temperature oxidation stage from the start of the experiment to the activation temperature, the rapid heating stage between the activation temperature and the ignition temperature, and the high-temperature combustion stage after the ignition point, as shown in Figures 13–15.

3.3. Analysis of Main Active Groups Affecting Spontaneous Combustion of Minerals. 3.3.1. Correlation Analysis between CO and Main Functional Groups of Minerals.

(1) Low-temperature oxidation stage

In the low-temperature oxidation stage, the main sources of gas were release, oxidation, and cracking of the adsorbed gas in the sample itself. Correlation analysis mainly calculates the correlation between the gas concentration and the change in functional groups during the oxidation and cracking process. At this stage, the growth of gaseous products was slow. At this time, the activity of the functional groups was low, the temperature was low, the rate of the oxidation reaction was low, and the heat generated was also low.
Table 2 shows that the CO concentration of the three samples was relatively small in correlation with each functional group. At this stage, the concentration of CO was relatively low, mainly from the decomposition and release of water–oxygen complexes generated by the reaction of the sample with water and oxygen. In addition, because the heat of oxidation of coal cannot be accumulated at low temperatures, the temperature was low, the activity of functional groups was not high, and the oxidation reaction was weak, resulting in no greater correlation between the CO concentration and the active functional groups. In particular, oil shale and oil shale after dry distillation had low correlations with various active functional groups at this stage, indicating that the energy required for the oxidation reaction of the rock sample was relatively high, and it was difficult to have a redox reaction with oxygen at low temperatures.

Figure 12. Relationship between C$_2$H$_4$ concentration and temperature.

Figure 13. Relationship between CO concentration and temperature of fresh coal.

(2) Rapid heating stage

The rapid heating stage was a process in which the gas generated by the oxidation of the sample increased from a slow increase to a rapid increase, and the CO began to increase rapidly near the active temperature. Table 3 shows that the correlation between the three samples and various functional groups began to increase gradually at this stage, indicating that with increasing temperature, the activity of functional groups began to increase.

The correlation between CO and various functional groups in the post-distillation oil shale at this stage was greater than that of other samples, indicating that the molecules in the retorted oil shale at this stage were more active, resulting in an accelerated gas production rate. Among the influences of various functional
groups in the molecule, the asymmetric stretching motion of methylene had the greatest correlation, followed by the symmetric stretching motion of methylene. The symmetrical and asymmetric stretching motions of methylene in this stage dominate the production of CO in oil shale after dry distillation. Compared with fresh coal, the correlation of methylene asymmetric expansion and contraction movement in oil shale also showed a higher degree of correlation. In Figure 5, the absorbance corresponding to the methylene functional group had a gentle trend at both ends and a steep trend in the middle, indicating that the asymmetric methylene group had the greatest activity at this temperature stage. In comparison, in the raw coal molecule, the activities of methyl groups, methylene groups, and −CH bonds connected with aromatic hydrocarbon were greater than those of other functional groups. In particular, the −CH group connected to the aromatic ring still maintained a high correlation, indicating that it continued to react in the rapid heating stage to promote the production of CO.

(3) High-temperature combustion stage

After the ignition point, the sample changed from oxidation to combustion and entered the high-temperature stage. The CO concentration decreased in the early stage of this temperature stage and then increased again. During the combustion stage, the internal functional groups of the sample molecules changed greatly. As the temperature increased, the active functional groups that previously participated in the reaction were consumed in large quantities, and the stable benzene ring also began to break and participate in the reaction. The correlation
between each functional group and CO concentration was significantly increased in the lower temperature oxidation stage and the rapid heating stage, and the active functional groups that dominated CO production also changed.

Table 4 shows that the CO generation of the three samples has a high correlation with each functional group. The correlation between the ether bond $\text{C} = \text{O} = \text{C}$ and CO in raw coal was the highest, up to 0.9549, and its absorbance showed a rapid decreasing trend at high temperatures and became smooth after exceeding 550 °C. This result was consistent with the change trend that the CO concentration maintains a certain growth rate after entering the high-temperature stage and reaches a peak value at 550 °C. The $\text{C} = \text{O} = \text{C}$ in the raw coal was broken by O$_2$ molecules in the high-temperature stage, which dominates the output of CO in the high-temperature stage of the raw coal. The methylene symmetry and asymmetric stretching motions of oil shale and oil shale after dry distillation were the main functional groups with the highest correlation to CO production. Its absorbance decreased rapidly at high temperatures, and the CO concentrations of oil shale and oil shale reached their peak values after dry distillation. This proves that the aliphatic hydrocarbon activity of the two was further increased at this stage, and with the end of the reaction, the functional group content gradually decreased.

3.3.2. Correlation Analysis between C$_2$H$_4$ and Main Functional Groups in Sample.

(1) Low-temperature oxidation stage

![Figure 16. Relationship between C$_2$H$_4$ concentration and temperature of fresh coal.](#)

![Figure 17. Relationship between C$_2$H$_4$ concentration and temperature in retorted oil shale.](#)
The correlation results between \( \text{C}_2\text{H}_4 \) and active functional groups in the low-temperature oxidation stage are shown in Table 5. The correlation between \( \text{C}_2\text{H}_4 \) and each functional group in the low-temperature oxidation stage of the three samples was low. The reason was similar to the low correlation between the CO concentration and active functional groups; because the \( \text{C}_2\text{H}_4 \) concentration was small, the overall correlation was low. At this stage, a small amount of \( \text{C}_2\text{H}_4 \) was precipitated, the activity of the functional group was low, the oxidation reaction was weak, and the gas concentration did not show a high degree of correlation with the active functional group. In contrast, the hydrogen bonds associated with intermolecular and aromatic hydrocarbons in fresh coal were the main functional groups that generated \( \text{C}_2\text{H}_4 \).

(2) Rapid heating stage

In the rapid heating stage, the \( \text{C}_2\text{H}_4 \) concentration was at the beginning of the rising trend, the molecular active groups on the surface of the sample gradually began to participate in the reaction, and the absorbance of each functional group showed a downward trend. As shown in Table 6, because \( \text{C}_2\text{H}_4 \) was an incomplete reaction product and had not been precipitated in large quantities at this time, there was no high correlation between \( \text{C}_2\text{H}_4 \) and active functional groups in other samples except for oil shale after dry distillation. Relatively speaking, the
relationship between the symmetry and asymmetric expansion and contraction of methylene groups in oil shale and oil shale after dry distillation was the greatest. The absorbance of its functional groups decreased slowly but had an accelerating trend. As the corresponding C$_2$H$_4$ concentration began to increase, the rate of increase began to accelerate. At this stage, the methylene functional group in the oil shale after dry distillation started to react to generate C$_2$H$_4$ under the influence of the temperature increase. In general, the correlation between functional groups in rock samples and C$_2$H$_4$ was greater than that in coal samples, indicating that in the rapid heating stage, the activity of functional groups in rock samples was greater than that in coal samples, which promoted the development of oxidative spontaneous combustion reactions and produces hydrocarbons.

(3) High-temperature combustion stage

In the high-temperature combustion stage, the C$_2$H$_4$ concentrations of the three samples all reached the peak concentration and then the content gradually decreased. Table 7 shows that both raw coal and oil shale show a high correlation with the symmetric and asymmetric expansion and contraction of methylene. The absorbance of the methylene functional group in the three samples all showed a rapid declining trend when entering the high-temperature combustion stage and then tended to be flat at approximately 500 °C, corresponding to the change in the C$_2$H$_4$ concentration that peaked at 450 °C and then slowly decreased to 500 °C and stabilized. The reaction of C$_2$H$_4$ production in the high-temperature stage of these three samples was dominated by methylene functional groups.

In addition, the production of C$_2$H$_4$ from raw coal and dry distillation oil shale was closely related to C−O−C. The decreasing trend of C−O−C absorbance had a significantly accelerated change in the high-temperature stage, and the reaction stopped until the end of 600 °C, which was consistent with the change trend of the C$_2$H$_4$ concentration in the two samples. The correlation between the C=C structure and the C$_2$H$_4$ concentration increased at this stage, indicating that its activity increased in the combustion stage, and the bond broke and began to participate in the reaction. In particular, the correlation degree of oil shale after dry distillation was the highest, indicating that dry distillation affects the structural stability of double bonds, making it easier to participate in the reaction than C=C in oil shale.

### 4. CONCLUSIONS

(1) The CO produced by the spontaneous combustion of minerals was, in the descending order, raw coal, oil shale after dry distillation, and oil shale. The CO of each sample increased parabolically with increasing temperature. The

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Table 4. Correlation between CO and Active Functional Groups in the High-Temperature Combustion Stage

| functional group                           | fresh coal | oil shale after dry distillation | oil shale |
|-------------------------------------------|------------|---------------------------------|-----------|
| free hydroxyl −OH                         | 0.7093     | 0.8224                          | 0.6885    |
| intramolecular hydrogen bonding −OH       | 0.6870     | 0.8030                          | 0.6338    |
| intermolecular associative hydrogen bond −OH | 0.7064     | 0.7558                          | 0.6164    |
| symmetric stretching of methylene         | 0.7198     | 0.9752                          | 0.9785    |
| methyl asymmetric stretching motion        | 0.7431     | 0.9671                          | 0.9630    |
| methyl deformation vibration              | 0.8933     | 0.6491                          | 0.5555    |
| C=C                                       | 0.7751     | 0.6202                          | 0.8011    |
| C−O                                       | 0.8335     |                                 |           |
| C−O−C                                     | 0.9549     | 0.6132                          | 0.5869    |
| aromatic hydrocarbons Ar−CH               | 0.8465     | 0.6766                          | 0.5644    |

Table 5. Degree of Correlation between C$_2$H$_4$ and Active Functional Groups in the Low-Temperature Oxidation Stage

| functional group                           | fresh coal | oil shale after dry distillation | oil shale |
|-------------------------------------------|------------|---------------------------------|-----------|
| free hydroxyl −OH                         | 0.5099     | 0.5003                          | 0.5001    |
| intramolecular hydrogen bonding −OH       | 0.5057     | 0.5002                          | 0.5001    |
| intermolecular associative hydrogen bond −OH | 0.5168     | 0.5010                          | 0.5015    |
| symmetric stretching of methylene         | 0.5017     | 0.5002                          | 0.5003    |
| methyl asymmetric stretching motion        | 0.5031     | 0.5004                          | 0.5002    |
| methyl deformation vibration              | 0.5031     | 0.5004                          | 0.5004    |
| C=C                                       | 0.5061     | 0.5001                          | 0.5013    |
| C−O                                       | 0.5041     |                                 |           |
| C−O−C                                     | 0.5035     | 0.5014                          | 0.5001    |
| aromatic hydrocarbons Ar−CH               | 0.5218     | 0.5003                          | 0.5004    |

Table 6. Degree of Correlation between C$_2$H$_4$ and Active Functional Groups in the Rapid Heating Stage

| functional group                           | fresh coal | oil shale after dry distillation | oil shale |
|-------------------------------------------|------------|---------------------------------|-----------|
| free hydroxyl −OH                         | 0.5001     | 0.5645                          | 0.5035    |
| intramolecular hydrogen bonding −OH       | 0.5001     | 0.5378                          | 0.5021    |
| intermolecular associative hydrogen bond −OH | 0.5002     | 0.5609                          | 0.5077    |
| symmetric stretching of methylene         | 0.5007     | 0.5697                          | 0.5078    |
| methylene asymmetric stretching motion     | 0.5007     | 0.5862                          | 0.5053    |
| methyl deformation vibration              | 0.5002     | 0.5354                          | 0.5022    |
| C=C                                       | 0.5004     | 0.5309                          | 0.5047    |
| C−O                                       | 0.5003     |                                 |           |
| C−O−C                                     | 0.5003     | 0.5484                          | 0.5020    |
| aromatic hydrocarbons Ar−CH               | 0.5008     | 0.5539                          | 0.5054    |
Corresponding Authors

ACS Omega generates ether bonds, resulting in a large amount of CO in the reaction of other functional groups (such as carboxyl groups) continues to react to promote gas production during the rapid fresh coal still maintains a high correlation, indicating that it the reaction in large quantities. In addition, the oxidation fresh coal was attacked by oxygen molecules and participated in the reaction in large quantities. In addition, the oxidation reaction of other functional groups (such as carboxyl groups) generates ether bonds, resulting in a large amount of CO in the high-temperature stage of fresh coal. The methylene functional group determines the output of C2H4. The methylene functional group in oil shale was the main functional group with the highest correlation with CO and C2H4. The CO production in the oil shale after dry distillation had the highest correlation with the methylene functional group, and C2H4 had the highest correlation with the C–O–C functional group. The aliphatic hydrocarbon activity of oil shale and oil shale after dry distillation further increased at this stage and completely participated in the spontaneous combustion reaction.

(2) In the low-temperature oxidation stage, CO and C2H4 were less precipitated, the activity of functional groups was low, and the correlation between the concentration of mineral-produced indicator gases and various functional groups was small. However, it could still be found that −CH linked to aromatic hydrocarbons was the main functional group for CO production from raw coal.

During the rapid heating stage, the aliphatic functional groups in the two rock samples dominated the production of CO and C2H4. The −CH group connected to the aromatic ring in the fresh coal still maintains a high correlation, indicating that it continues to react to promote gas production during the rapid heating stage.

In the high-temperature combustion stage, C–O–C in the fresh coal was attacked by oxygen molecules and participated in the reaction in large quantities. In addition, the oxidation reaction of other functional groups (such as carboxyl groups) generates ether bonds, resulting in a large amount of CO in the high-temperature stage of fresh coal. The methylene functional group determines the output of C2H4. The methylene functional group in oil shale was the main functional group with the highest correlation with CO and C2H4. The CO production in the oil shale after dry distillation had the highest correlation with the methylene functional group, and C2H4 had the highest correlation with the C–O–C functional group. The aliphatic hydrocarbon activity of oil shale and oil shale after dry distillation further increased at this stage and completely participated in the spontaneous combustion reaction.

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Notes

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