Article

Differences in Macromolecular Structure Evolution during the Pyrolysis of Vitrinite and Inertinite Based on In Situ FTIR and XRD Measurements

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Abstract: An accurate understanding of molecular structure evolution during pyrolysis is essential for the clean utilization of coal. In this study, middle-rank coal was taken as the research subject, and vitrinite and inertinite samples were stripped from coal using a hand picking and sink–float separation process. In situ Fourier transform infrared (FTIR) spectroscopy and in situ X-ray diffraction (XRD) were performed to compare the macromolecular structure changes between vitrinite and inertinite during pyrolysis. The results show that the aromaticity (I), the polycondensation degree of aromatic rings (DOC), the average lateral sizes (\(L_a\)) of basic structure unit (BSU), and the stacking heights (\(L_c\)) of BSU in both vitrinite and inertinite during pyrolysis increase continuously with increasing temperature. The values of these parameters for inertinite are higher than those of vitrinite, suggesting that the aromatization degree of inertinite has always been higher than that of vitrinite. In situ FTIR spectroscopy shows that the macromolecular structure evolution of vitrinite and inertinite could be divided into three stages based on temperature: 30–200 °C, 200–300 °C, and 300–500 °C. The content of C–O–C, aromatic C=O, O–H groups, and aromatic ring C=C gradually decreases, while that of the CH\(_2\) in aliphatic hydrocarbons increases between 30 °C and 200 °C. The 200–300 °C stage is mainly filled by the synergistic effects of aliphatic and aromatic groups. The content of aliphatic groups, C–O–C groups, aromatic C=O, and aromatic ring C=C of both vitrinite and inertinite decreases greatly. The 300–500 °C stage is dominated by the aromatization and condensation of macromolecules. The substituents of the aromatic system gradually detach, leading to an increase in I and DOC. From 30 °C to 1000 °C, in situ XRD results reveal a difference in macromolecular structural evolution between vitrinite and inertinite. The arrangement of aromatic layers in vitrinite tends to be ordered during pyrolysis, whereas there are no significant changes in the inertinite. However, the aromatic layers of inertinite are always more compact than that of vitrinite. In addition, the aliphatic side chains of inertinite are more stable than that of vitrinite during the pyrolysis process.

Keywords: vitrinite and inertinite; clean utilization; pyrolysis; macromolecular structure

1. Introduction

The macromolecular structure of coal fundamentally affects its physical and chemical properties, which determines the gasification and liquefaction of coal [1]. The aromatic structure, aliphatic groups, and oxygen content of vitrinite are quite different from that of inertinite, which explains the difference in the macromolecular structure of those two macerals in different types of coal [2]. Therefore, examining the differences in the molecular structure evolution between the vitrinite and inertinite during pyrolysis can provide a theoretical basis for the clean and efficient utilization of coal.

Currently, research on the macromolecular structure of coal mainly involves taking a whole coal sample or the vitrinite as the research subject. Coal pyrolysis is divided into three stages: the activation stage, the fast pyrolysis stage, and the recombination/condensation...
stage [3,4]. Vitrinite with different degrees of thermal evolution is characterized by thermal stimulation of the molecular structure under laboratory conditions. The aliphatic carbon decreases gradually during the pyrolysis process, and the relative content of aromatic carbon continues to increase during pyrolysis [5]. Inertinite has less aliphatic carbon than vitrinite, but more aromatic carbon. Moreover, the alkane side chain length on the aromatic ring of inertinite is also shorter than that of vitrinite, and the aromatic rings of inertinite are more condensed. Coal rich in inertinite has a more ordered molecular structure and a higher content of crystalline accumulation [6–9]. The extent of the change in aromatization of inertinite during pyrolysis is less than that of vitrinite with the increase in the degree of coalification [9–12]. Therefore, the macromolecular structures between the vitrinite and inertinite are significantly different. However, most of the current studies related to conventional X-ray diffraction (XRD) and Fourier transform infrared (FTIR) spectroscopy explored the evolution characteristics of the macromolecular structure based on whole coal without the separation of macerals [13–15]. The research on a single coal maceral mostly focused on analysis of hydrocracking and depolymerization products, etc. [16]. There is a lack of research on the evolution of single-maceral macromolecular structures. A few studies have focused on the macromolecular structures of vitrinite, but less on the inertinite. This paper focuses on the difference of macromolecular structure evolution between vitrinite and inertinite in the process of pyrolysis, which can be expected to promote the understanding of evolution of macromolecular structures in coal.

For the normal pyrolysis experiment, coal samples are usually pyrolyzed under different temperatures, and then are examined by other tests [16,17], however, samples will continue to be pyrolyzed under the residual heat before samples are taken out from the experimental facility, so the experimental results may be not accurate. The experiments of in situ FTIR and in situ XRD have the advantages of in situ monitoring the variation on macromolecular structures, reducing the impact of the external environment.

A middle-rank coal sample was taken as the research subject in this study. Vitrinite and inertinite samples were separated using the methods of hand picking and the sink–float separation process. The aromatic structures, oxygen-containing functional groups, and aliphatic structures were examined by in situ FTIR and in situ XRD experiments. Then, the differences in the evolution of the macromolecular structure of the vitrinite and inertinite during pyrolysis were revealed.

2. Samples Preparation and Methods
2.1. Samples Preparation

The reflectance (R_o) of the middle-rank coal collected in the Muli area of Qinghai Province (NW China) is 0.73%, and proximate analysis data of moisture, ash, volatile matter, and fixed carbon contents is 1.31%, 1.33%, 27.76%, and 69.6% in wt.%, respectively. The macerals were separated by hand selection and float–sink centrifugation, resulting in vitrinite and inertinite samples (Figure 1). First, the vitrinite has a brighter luster when observed with the naked eye, while the inertinite has a strong silky luster and a more obvious fibrous structure; therefore, the sample was separated into vitrinite-rich and inertinite-rich groups by the hand picking. Then, due to the density difference of the vitrinite and inertinite (the vitrinite density was 1.2–1.25 g/cm^3, and the inertinite density was 1.3–1.35 g/cm^3), the float–sink centrifugation was performed. Samples were fully mixed with ZnCl_2 heavy fluids with different density values of 1.2 g/cm^3, 1.25 g/cm^3, 1.3 g/cm^3 and 1.35 g/cm^3 in turn, and the vitrinite was floated, while the inertinite was sunk in the ZnCl_2 solution after centrifugation. As such, the vitrinite and inertinite samples were totally separated. After extraction from the ZnCl_2 heavy fluids, the separated vitrinite and inertinite samples were washed with deionized water to eliminate ZnCl_2. Then, the samples were placed in a drying oven at 60 °C and dried for 24 h for the subsequent experiments.
According to GB/T 15588–2013 and GB/T 8899–2013, the quantitative statistics of separated samples were carried out, and revealed that vitrinite and inertinite content was 90% and 95%, respectively (Table 1). The samples were crushed to 200 mesh (75 µm) and acid washed. Then, 15 g samples were placed in a plastic beaker and mixed with 80 mL of HCl (mass fraction 36%) and stirred in a water bath for 4 h at a constant temperature of 60 °C. The HCl solution was filtered off with suction, and 80 mL of HF solution (mass fraction 40%) was then added. The same water bath and acid washing operations were repeated. Finally, the residual samples were washed and filtered with ultrapure water until the filtrate showed no precipitation when AgNO₃ solution was added. The acid-washed samples were filtered through filter paper, placed in an oven at 60 °C for vacuum drying for 24 h, and deashed samples were obtained.

Table 1. Quantitative results of macerals.

| No. | Density Interval (g/cm³) | R₀,max (%) | Macerals (%) | Notes  |
|-----|------------------------|------------|--------------|--------|
|     |                        |            | Vitrinite     | Inertinite | Liptinite |
| 1   | 1.3–1.35               | 0.698      | 90           | 8        | 2        | Vitrinite |
| 2   | 1.35–1.4               | 1.526      | 5            | 95       | 0        | Inertinite |

2.2. Experimental Process

In situ FTIR spectroscopy and in situ XRD allow in situ measurements and reduce the influence of the external environment [18,19]. Physicochemical information can be obtained while the samples are being monitored. Compared to conventional FTIR spectroscopy and XRD, in situ FTIR spectroscopy and in situ XRD allow continuous heating, in situ measurements, fast speeds, and high sensitivity [20–22].

2.2.1. In Situ FTIR Spectroscopy

Experiments were performed using Bruker TENSOR II equipment (Figure 2). The prepared dry samples were mixed with KBr at a ratio of 1:100 and pressed into flakes in the sample cell. The heating coil in the bottom of the cover provided different temperatures for
samples with electricity. Atmosphere gas was transported by gas pipes. Water was conveyed through water pipes to cool the experimental device. The acquisition wavenumber range was 4000–800 cm\(^{-1}\). The number of scans, temperature range, and heating rate were 64 times, 0–500 °C, and 4 °C/min, respectively. The specific test temperature points were room temperature (30 °C), 100 °C, 200 °C, 300 °C, and 500 °C. After 2 h of heat preservation at each temperature point, the samples were purged with nitrogen, and the FTIR spectrum was obtained.

Figure 2. In situ Fourier transform infrared (FTIR) device.

A series of parameters related to the macromolecular structure in coal can be obtained from the in situ FTIR data by peak fitting. The absorption bands of the peaks in FTIR spectroscopy can be generally divided into four sections [23]: hydroxyl groups (3700–3200 cm\(^{-1}\)), aliphatic hydrocarbons (3000–2800 cm\(^{-1}\)), oxygenated groups (1800–1000 cm\(^{-1}\)), and aromatic hydrocarbons (900–700 cm\(^{-1}\)). Peak fitting analysis was performed in these four sections using a software named Peakfit, and the functional groups were assigned based on references (Table 2).

Table 2. Assignment of the Fourier transform infrared (FTIR) spectral range [24].

| Wavenumber Range   | Absorption Peak Assignment                                      |
|--------------------|-----------------------------------------------------------------|
| 3600–3700          | free OH bonds                                                   |
| 3500               | OH–π–H bonds                                                    |
| 3350–3400          | self-associated OH bonds                                         |
| 3300               | OH–ether O hydrogen bonds                                       |
| 3180–3240          | cyclic OH groups                                                |
| 3200–3000          | the C–H stretching vibration of the aromatic nucleus            |
| 2940–3000          | aliphatic CH\(_2\) asymmetric stretching vibration             |
| 2940–2900          | aliphatic CH\(_2\) asymmetric stretching vibration             |
| 2863               | aliphatic CH\(_3\) symmetric stretching vibration              |
| 2848               | aliphatic CH\(_2\) symmetric stretching vibration              |
| 1700               | the stretching vibration of aromatic C=O                        |
| 1650–1520          | the stretching vibration of the aromatic ring C=C               |
| 1440–1360          | aliphatic CH\(_3\), and CH\(_2\) deformation vibration         |
| 1340–1200          | Ar–OH                                                           |
| 1100               | aryI ether                                                      |
| 1039               | alkyl ether                                                     |
| 868                | aromatic nucleus (CH), one adjacent H deformation               |
| 810                | aromatic nucleus (CH), three adjacent H deformation             |

The differences in the molecular structure of the vitrinite and inertinite during the pyrolysis process were examined. According to previous research, the following three parameters are selected to characterize the macromolecular structure [25–28]:
The aromaticity of coal (I) is expressed as a ratio of the spectrum area in 900–800 cm\(^{-1}\) (A900–800 cm\(^{-1}\)) to that in 3000–2800 cm\(^{-1}\) (A3000–2800 cm\(^{-1}\)) because the wavenumbers of this experiment start from 800 cm\(^{-1}\). The 900–800 cm\(^{-1}\) segment represents the absorption bands of aromatic structures, and the 3000–2800 cm\(^{-1}\) segment represents the C–H stretching vibrations of aliphatic structures. A higher value of I indicates a higher aromatization level.

In the degree of polycondensation of aromatic rings (DOC) (A900–800 cm\(^{-1}\)/A1600 cm\(^{-1}\)), the 1600 cm\(^{-1}\) segment represents the aromatic C=C vibration of the aromatic nucleus. A higher DOC value of coal indicates a higher condensation degree of the aromatic rings.

The length of the aliphatic side chains can be represented by CH\(_2\)/CH\(_3\) (A2900–2940 cm\(^{-1}\)/A2940–3000 cm\(^{-1}\)). The 2900–2940 cm\(^{-1}\) segment represents the asymmetric stretching vibration of alkane CH\(_2\), while 2940–3000 cm\(^{-1}\) represents the asymmetric stretching vibration of alkane CH\(_3\). A larger ratio indicates longer the aliphatic chains on the aromatic rings and worse compactness of the aromatic structure.

### 2.2.2. In Situ XRD

The experiments were carried out using a Rigaku SmartLab X-ray diffractometer (Figure 3). The samples were placed on a temperature-changing stage, and the temperature control device controlled the temperature-changing stage to heat up the samples. The X-ray tube provided X-rays which were reflected on the upper surface of samples, and received by the detector. The 200-mesh powder samples were placed in an argon test atmosphere. The test angle range was 5–80°. The scanning speed was 3°/min, and the test temperature ranged from room temperature (30 °C) to 1100 °C. The specific test temperature points were 200 °C, 400 °C, 600 °C, 800 °C, and 1000 °C. Each point was held for three minutes and tested. The heating rate was 15 °C/min, and the in situ XRD pattern was obtained.

![In situ X-ray diffraction (XRD) device.](image-url)

**Figure 3.** In situ X-ray diffraction (XRD) device.

Coal has a complex macromolecular structure, and the XRD experimental data can characterize the aggregation state of the coal macromolecular structure. According to the Bragg equation and the Scherrer equation, the crystallite structure parameters, d\(_{002}\), L\(_c\), and L\(_α\), of the coal samples can be calculated [29–32]:

\[
d_{002} = \frac{\lambda}{2 \sin \theta_{002}} \\
L_c = \frac{0.9\lambda}{\beta_{002}\cos \theta_{002}} \\
L_\alpha = \frac{1.84\lambda}{\beta_{100}\cos \theta_{100}}
\]
λ is the X-ray wavelength (λ = 0.154056 nm);
θ is the characteristic peak position;
d_{002} is the interlayer spacing (nm);
L_{c} is the average height of coal crystallites (nm);
β is the full-width half-maximum (°);
L_{a} is the average diameter of coal crystallites (nm).

3. Results and Analysis

3.1. Analysis of the In Situ FTIR Results

3.1.1. In Situ FTIR Spectrum Characteristics

Figure 4 presents the results of the in situ FTIR spectrum of the samples. The peak shape of vitrinite at 3200–3700 and 3000–2800 cm\(^{-1}\) gradually becomes flat with increasing temperature, indicating that the content of hydroxyl and aliphatic structures gradually decreased. The peak shape of the 1800–1000 cm\(^{-1}\) and 900–800 cm\(^{-1}\) segments becomes gradually sharp, indicating that the contents of oxygen-containing functional groups and aromatic structures increased gradually. The peak shape of the 3200–3700 cm\(^{-1}\) segment of inertinite has no significant change, suggesting that the hydroxyl content of the inertinite does not change significantly. The peak shape of the 3000–2800 cm\(^{-1}\) segment gradually becomes flat, indicating that the content of aliphatic structures gradually decreases. The peak shape of the 1800–1000 cm\(^{-1}\) segment does not change significantly at 30–300 °C, but becomes sharp at 300–500 °C, indicating that the content of oxygen-containing functional groups in inertinite increases significantly. The peak shape of the 900–800 cm\(^{-1}\) segment has a small sharp change at 30–300 °C and becomes sharper at 300–500 °C, suggesting that the aromatic structures increase gradually during the pyrolysis process. Therefore, in the pyrolysis process, the changes in the macromolecular structure of vitrinite and inertinite with temperature show differences.

![Figure 4. In situ FTIR spectra of vitrinite and inertinite.](image-url)
Aromatic Structure Absorption Bands

The wavenumber range of the aromatic structure is 800–900 cm\(^{-1}\), which is assigned to the out-of-plane deformation vibration region of the H atom adjacent to the aromatic ring [33]. The peak at 810 cm\(^{-1}\) represents the aromatic nucleus (C–H), and three adjacent H deformations, of which the hydrogen atom is called a type III hydrogen atom on the aromatic nucleus. The type III hydrogen atom on the aromatic nucleus represents the direction of the polycondensation process of middle-high rank bituminous coal. Hence, it can indicate the degree of aromatic ring polycondensation [34]. The peak of 868 cm\(^{-1}\) is assigned to the aromatic nucleus (C–H), and one adjacent H deformation. This hydrogen atom is called a type I hydrogen atom on the aromatic nucleus, with two adjacent and more than two adjacent hydrogen atomic states [34]. The peak at 3000–3200 cm\(^{-1}\) represents the C–H stretching vibration of the aromatic nucleus [35].

At 30 °C, the content of each group in vitrinite is smaller than that in inertinite. When heated to 200°C, the aromatic nucleus (C–H) with three adjacent H deformations, the aromatic nucleus (C–H) with five adjacent H deformations, and the aromatic nucleus C–H do not change significantly in vitrinite and inertinite. At 200–300 °C, both vitrinite and inertinite show an increase in the content of aromatic nuclei (C–H), one adjacent H deformation, and aromatic nucleus C–H. At the 300–500 °C stage, many aromatic nuclei (C–H) and three adjacent H deformations come into being in vitrinite and inertinite. The number of aromatic nuclei (C–H), one adjacent H deformation, and the aromatic nucleus C–H is reduced (Figures 5 and 6). Hence, the aromatic structure content of vitrinite is less than that in inertinite. With increasing temperature during pyrolysis, coalification continues, and the degree of aromatization of both vitrinite and inertinite increases gradually. However, the degree of aromatization in inertinite is still much higher than that in vitrinite.

![Figure 5](image-url)

**Figure 5.** In situ FTIR peak fitting diagram of the aromatic structure of samples.

Oxygen-Containing Functional Groups Absorption Band

The wavenumber range, 1000–1800 cm\(^{-1}\), characterizes the absorption band of oxygen-containing functional groups, and the assignment of this segment is complicated. Ether oxygen C–O–C includes alkyl and aryl ethers. The peak near 1039 cm\(^{-1}\) is assigned to the stretching vibration of alkyl ether [36]. The peak near 1100 cm\(^{-1}\) represents the stretching vibration of aryl ether [37]. The peak at 1200–1340 cm\(^{-1}\) is assigned to the Ar–OH stretching vibration [38]. The characteristic peaks around 1360–1440 cm\(^{-1}\) represent the aliphatic CH\(_2\) and CH\(_3\) vibrations, respectively [13,24]. The peak at 1600 cm\(^{-1}\) represents the stretching vibration of the aromatic ring C=C [24]. The peak near 1700 cm\(^{-1}\) characterizes the stretching vibration of aromatic C=O [39].
At 200–300 °C, the content of C–O–C groups, aromatic C=O, and aromatic ring C=C of vitrinite does not change significantly, but that of inertinite decreases. The total amount of oxygen-containing functional groups greatly increases. At 300–500 °C, the content of C–O–C groups and aromatic ring C=C of vitrinite and inertinite increase significantly; however, the content of aromatic C=O of vitrinite does not change significantly, but that of inertinite decreases. The total amount of oxygen-containing functional groups decreases significantly (Figures 7 and 8). Coalification is enhanced continuously with increasing temperature, and the oxygen-containing functional groups of vitrinite and inertinite detach.

![Figure 6](image1.jpg)

**Figure 6.** Fitting results of the aromatic structure of samples.

At 30 °C, the total contents of oxygen-containing functional groups in both vitrinite and inertinite are similar; however, there are slightly more aliphatic CH$_2$ and CH$_3$ and fewer Ar–OH groups, C–O–C groups, aromatic ring C=C, and aromatic C=O in vitrinite. During pyrolysis up to 200 °C, both vitrinite and inertinite show a slight decrease in the content of C–O–C groups, aromatic C=O, and aromatic ring C=C. The content of aliphatic CH$_2$ and CH$_3$ decrease significantly, the content of Ar–OH groups increases significantly, and the total amount of oxygen-containing functional groups shows a decreasing trend. At 200–300 °C, the content of C–O–C groups, aromatic C=O, and aromatic ring C=C of vitrinite and inertinite are reduced greatly. However, the content of aliphatic CH$_2$ and CH$_3$ and Ar–OH groups increases considerably, and the total amount of oxygen-containing functional groups greatly increases. At 300–500 °C, the content of C–O–C groups and aromatic ring C=C of vitrinite and inertinite increase significantly; however, the content of aliphatic CH$_2$ and CH$_3$ and Ar–OH groups decreases significantly. The content of aromatic C=O of vitrinite does not change significantly, but that of inertinite decreases. The total amount of oxygen-containing functional groups decreases significantly (Figures 7 and 8). Coalification is enhanced continuously with increasing temperature, and the oxygen-containing functional groups of vitrinite and inertinite detach.

![Figure 7](image2.jpg)

**Figure 7.** Fitting diagram of in situ FTIR spectra of oxygen-containing functional groups in samples.
with the continuous increase in temperature. However, the aliphatic hydrocarbon content process, the content of aliphatic side chains in vitrinite and inertinite decreases gradually. Vitrinite is still higher than that of inertinite (Figures 9 and 10). Hence, during the pyrolysis process, the CH$_2$ content of vitrinite is always higher than that of inertinite. At 200–300 $^\circ$C, the CH$_2$ and CH$_3$ contents of vitrinite and inertinite are reduced greatly. However, the content of aliphatic CH$_2$ and CH$_3$ decrease. In vitrinite, the change rate of the CH$_2$ content is lower than that of the CH$_3$ content; however, inertinite shows an opposite trend. At 300–500 $^\circ$C, the CH$_2$ and CH$_3$ content of vitrinite and inertinite are reduced greatly. The reduction rate of the vitrinite is higher than that of the inertinite, but the content of each group in vitrinite is still higher than that of inertinite (Figures 9 and 10). Hence, during the pyrolysis process, the content of aliphatic side chains in vitrinite and inertinite decreases gradually with the continuous increase in temperature. However, the aliphatic hydrocarbon content of vitrinite is always higher than that of inertinite. In both vitrinite and inertinite, the CH$_2$ content is always higher than CH$_3$ content. Aliphatic hydrocarbons in coal exist mostly in the form of long chains with few branches. At this stage, the coal structure is loose, which is more conducive to coal pyrolysis to form colloids [13,40].

**Aliphatic Structure Absorption Bands**

The peak at 3000–2800 cm$^{-1}$ represents the aliphatic structure, which belongs to the C–H stretching vibration region of aliphatic hydrocarbons [24]. There are obvious peaks near 2850 cm$^{-1}$ and 2920 cm$^{-1}$, which are respectively assigned to the stretching vibrations of symmetrical CH$_2$ and asymmetric CH$_2$ [40]. The characteristic peaks near 2870 cm$^{-1}$ and 2950 cm$^{-1}$ are assigned to the stretching vibrations of symmetrical CH$_3$ and asymmetric CH$_3$, respectively [40].

At 30 $^\circ$C, the CH$_2$ content in both vitrinite and inertinite is higher than the CH$_3$ content; vitrinite has more CH$_2$ and CH$_3$ than inertinite. When heating to 200 $^\circ$C, the CH$_2$ content of vitrinite and inertinite and the CH$_3$ content of vitrinite increases slightly, while the CH$_3$ content of inertinite shows no significant change. The content of each group in vitrinite is always higher than that of inertinite. At 200–300$^\circ$C, the CH$_2$ and CH$_3$ contents of vitrinite and inertinite decrease. In vitrinite, the change rate of the CH$_2$ content is lower than that of the CH$_3$ content; however, inertinite shows an opposite trend. At 300–500 $^\circ$C, the CH$_2$ and CH$_3$ content of vitrinite and inertinite are reduced greatly. The reduction rate of the vitrinite is higher than that of the inertinite, but the content of each group in vitrinite is still higher than that of inertinite (Figures 9 and 10). Hence, during the pyrolysis process, the content of aliphatic side chains in vitrinite and inertinite decreases gradually with the continuous increase in temperature. However, the aliphatic hydrocarbon content of vitrinite is always higher than that of inertinite. In both vitrinite and inertinite, the CH$_2$ content is always higher than CH$_3$ content. Aliphatic hydrocarbons in coal exist mostly in the form of long chains with few branches. At this stage, the coal structure is loose, which is more conducive to coal pyrolysis to form colloids [13,40].

**Figure 8.** Peak fitting results of oxygen-containing functional groups in samples.

**Figure 9.** In situ FTIR peak fitting diagram of the aliphatic structure of samples.

**Figure 10.** Peak fitting results of the aliphatic structures of samples.
The peak at 3200–3700 cm$^{-1}$ characterizes the hydroxyl absorption band, and there are strong hydroxyl absorption peaks in this segment, which mainly includes three types: cyclic OH groups, O–H–π-H bonds, and free OH groups. The peak at 3180–3240 cm$^{-1}$ characterizes the cyclic OH groups [41]. The peak around 3300 cm$^{-1}$ represents the OH–ether O hydrogen bonds [35,41], and the peaks around 3350–3400 cm$^{-1}$ represent self-associated OH bonds [40]. The peak at 3500 cm$^{-1}$ characterizes the O–H–π-H bonds formed with π electrons on the aromatic rings [42], and the peak at 3600–3700 cm$^{-1}$ is assigned to free OH groups [33].

At 30 °C, vitrinite has a higher content of O–H–π-H bonds than inertinite, and the content of free O–H groups of vitrinite is much smaller than that of inertinite. When heating to 300 °C, in both vitrinite and inertinite, the content of O–H–π-H bonds gradually increases, and the content of free O–H groups decreases gradually. The change rate of each group content in vitrinite is higher than that in inertinite. The O–H–π-H bond content of vitrinite is much more than that of inertinite, and the content of free O–H groups is much less than that of inertinite. At the stage of 300–500 °C, the O–H–π-H bond content of the vitrinite decreases to a certain extent, but that of the inertinite increases; additionally, the content of free O–H groups in both vitrinite and inertinite increases gradually, and the content of self-associated OH bonds arises gradually (Figures 11 and 12).

**Figure 10.** Peak fitting results of the aliphatic structures of samples.

**Figure 11.** Fitting diagram of in situ FTIR spectrum of the hydroxyl absorption band of samples.
As shown in Figure 13a, the I of both vitrinite and inertinite shows an exponential growth trend during the pyrolysis process, in which I is relatively stable from 30 °C to 200 °C, and increases gradually from 200 °C to 500 °C, suggesting that during pyrolysis, the proportion of aromatic structures of coal increases gradually, and the degree of aromatization of coal increases continuously. At 30–300 °C, there is no significant difference in I between vitrinite and inertinite. At 300–500 °C, the I of inertinite is higher than that of vitrinite.

As shown in Figure 13b, the DOC of both vitrinite and inertinite has a linear positive correlation with temperature. The DOC of inertinite is slightly higher than that of vitrinite. In the pyrolysis process, the DOC of vitrinite and inertinite increases gradually. Combining Figures 4 and 13a, at the stage of 30–300 °C, the I shows a slow growth trend, and the DOC increases gradually. At the stage of 30–300 °C, the aromatic substitution reaction and condensation reaction of aromatic rings are not obvious, but at 300–500 °C, with increasing temperature, the condensation reaction of aromatic rings gradually intensifies, and the
aromatic substitution reaction occurs violently, leading to an increase in the degree of condensed cyclization.

**Aliphatic Structure**

As shown in Figure 14, there are some differences in the changes of CH$_2$/CH$_3$ in the vitrinite and inertinite during the pyrolysis process. With increasing temperature, the CH$_2$/CH$_3$ value of vitrinite shows a parabolic trend and reaches the lowest value at 200 °C. This suggests that the CH$_2$ content of vitrinite decreases continuously during the pyrolysis process and reaches the minimum at 200 °C. After 200 °C, the space between the aromatic rings decreases gradually, and the structure of coal becomes more compact. The CH$_2$/CH$_3$ value of inertinite does not show a clear correlation, indicating that temperatures below 500 °C have no apparent catalytic effect on the detachment of aliphatic side chains in the inertinite.

![Figure 14. Aliphatic structure parameters of samples.](image)

### 3.2. Analysis of In Situ XRD Results

#### 3.2.1. In Situ XRD Pattern Characteristics

Figure 15 shows the spectrum obtained by in situ XRD. Two XRD peaks are observed near 26° and 43°, which correspond to the 002 and 100 peaks, respectively, representing the structural characteristics of aromatic rings [43]. The 002 diffraction band is generated by the local parallel stacking of curved layers [44]. With the continuous increase in temperature, the two XRD peaks are gradually sharpened to a certain extent. Compared to that of the vitrinite, the peak shape of the inertinite is sharper, and the peak value is higher. Table 3 lists the calculated results of the spectra in the two intervals of 10–35° and 35–50°, respectively.

**Table 3.** In situ X-ray diffraction (XRD) structural parameters.

| Maceral Category | Temperature (°C) | 2θ$_{002}$ (°) | d$_{002}$ (nm) | FWHM | L$_c$ (nm) | 2θ$_{100}$ (°) | L$_a$ (nm) |
|------------------|-----------------|----------------|--------------|------|------------|----------------|------------|
| **Inertinite**   |                 |                |              |      |            |                |            |
| 30               |                 | 25.579         | 0.34796      | 6.841| 1.191      | 43.104         | 1.093      |
| 200              |                 | 26.052         | 0.34175      | 6.596| 1.236      | 42.998         | 1.074      |
| 400              |                 | 25.594         | 0.34776      | 5.804| 1.404      | 43.401         | 1.595      |
| 600              |                 | 25.354         | 0.35099      | 5.342| 1.524      | 44.299         | 1.738      |
| 800              |                 | 25.573         | 0.34804      | 4.717| 1.727      | 42.848         | 1.912      |
| 1000             |                 | 25.491         | 0.34915      | 3.552| 2.293      | 42.955         | 2.720      |
| **Vitrinite**    |                 |                |              |      |            |                |            |
| 30               |                 | 24.320         | 0.36567      | 8.014| 1.014      | 42.959         | 1.094      |
| 200              |                 | 24.805         | 0.35864      | 6.204| 1.311      | 44.388         | 1.301      |
| 400              |                 | 24.919         | 0.35703      | 5.233| 1.555      | 44.251         | 1.350      |
| 600              |                 | 24.983         | 0.35613      | 5.619| 1.448      | 43.511         | 1.503      |
| 800              |                 | 25.104         | 0.35444      | 5.138| 1.584      | 42.764         | 1.742      |
| 1000             |                 | 25.229         | 0.35271      | 4.338| 1.877      | 44.968         | 2.757      |
Table 3. In situ X-ray diffraction (XRD) structural parameters.

| Maceral Category | Temperature (°C) | $\theta_{002}$ (°) | $d_{002}$ (nm) | FWHM | $L_{c}$ (nm) | $\theta_{100}$ (°) | $L_{a}$ (nm) |
|------------------|------------------|--------------------|----------------|-------|--------------|--------------------|-------------|
| Inertinite       | 30               | 25.579             | 0.34796        | 6.841 | 1.191        | 43.104             | 1.093       |
|                  | 200              | 26.052             | 0.34175        | 6.596 | 1.236        | 42.998             | 1.074       |
|                  | 400              | 25.594             | 0.34776        | 5.804 | 1.404        | 43.401             | 1.595       |
|                  | 600              | 25.354             | 0.35099        | 5.342 | 1.524        | 44.299             | 1.738       |
|                  | 800              | 25.573             | 0.34804        | 4.717 | 1.727        | 42.848             | 1.912       |
|                  | 1000             | 25.491             | 0.34915        | 3.552 | 2.293        | 42.955             | 2.720       |
| Vitrinite        | 30               | 24.320             | 0.36567        | 8.014 | 1.014        | 42.959             | 1.094       |
|                  | 200              | 24.805             | 0.35864        | 6.204 | 1.311        | 44.388             | 1.301       |
|                  | 400              | 24.919             | 0.35703        | 5.233 | 1.555        | 44.251             | 1.350       |
|                  | 600              | 24.983             | 0.35613        | 5.619 | 1.448        | 43.511             | 1.503       |
|                  | 800              | 25.104             | 0.35444        | 5.138 | 1.584        | 42.764             | 1.742       |
|                  | 1000             | 25.229             | 0.35271        | 4.338 | 1.877        | 44.968             | 2.757       |

3.2.2. In Situ XRD Structural Parameters

As shown in Figure 16a, the $d_{002}$ value of the vitrinite is much higher than that of the inertinite. With increasing temperature, the $d_{002}$ of the vitrinite shows a downward trend. According to this experiment, the $d_{002}$ of vitrinite decreases by approximately 0.013 nm, while that of inertinite shows no obvious change. The arrangement of aromatic layers in vitrinite gradually becomes regular during the pyrolysis process, while there is no significant change in inertinite. However, the aromatic interlayer spacing of inertinite is much smaller than that of vitrinite, suggesting that the aromatic layers of the inertinite are more regular and compact. The $L_{c}$ of vitrinite and inertinite shows an obvious upward trend with increasing temperature, and the $L_{c}$ of the inertinite is larger than that of the vitrinite (Figure 16b). The average stacking thickness of the microcrystalline layers of the inertinite increases gradually, but the layer-stacking thickness of vitrinite is still smaller than that of inertinite. The $L_{a}$ values of both vitrinite and inertinite increase with increasing temperature, and the increase of the $L_{a}$ of vitrinite is slightly larger than that of inertinite. In this experiment, the $L_{a}$ values of inertinite and vitrinite increase by approximately 1.6 and 1.7 nm, respectively. However, the $L_{a}$ value of inertinite is still higher than that of vitrinite (Figure 16c). Hence, the plane extensibility of the basic structural unit (BSU) of both vitrinite and inertinite increases significantly during the pyrolysis process. At the 600–1000 °C stage,
the increase rate of the plane extensibility of BSU of vitrinite is higher than that of inertinite. However, the plane extensibility of vitrinite is still smaller than that of inertinite.

![Figure 16. In situ XRD microcrystalline structure parameters.](image)

4. Discussion

The macromolecular structure evolution characteristics of vitrinite and inertinite during pyrolysis include the following.

(1) During pyrolysis, the macromolecular structures of vitrinite and inertinite change with increasing temperature. The DOC of vitrinite and inertinite increases, and the plane extensibility and the $L_c$ increase continuously, indicating that both the vitrinite and inertinite of low–middle rank coals have an evolution trend of increasing degree of aromatization in the early stages of pyrolysis. The increase in aromatization is reflected mainly in the continuous expansion of the aromatic structural units. The differences in the structural evolution of vitrinite and inertinite are reflected mainly by the continuous decrease in the $d_{002}$ peak of vitrinite with increasing temperature, in which the reduced value is 0.013 nm, but there is no obvious change in inertinite.

Second, the I, DOC, $L_a$, and $L_c$ of inertinite are always higher than those of vitrinite, indicating that the degree of inertinite aromatization is always higher than that of vitrinite.

(2) The pyrolysis process of vitrinite and inertinite can be divided into three stages. Between 30 °C and 200 °C, the content of aromatic groups in vitrinite and inertinite shows no obvious change, while that of aliphatic groups increases slightly. The total amount of oxygen-containing functional groups decreases gradually. The content of C–O–C groups, aromatic C=O, and aromatic ring C=C has a small decrease in a relatively stable situation. The content of aliphatic CH$_2$ and CH$_3$ decreases significantly, and that of Ar–OH groups increases significantly (Figure 17). The content of O–H–π–H bonds increases greatly, and that of free O–H groups decreases greatly. There is no significant change in the I and DOC (Figure 13), which suggests that aliphatic and aromatic structures are enriched slightly at this stage. The enlargement of the aromatic structural system is not obvious in this stage, and the detachment of oxygen-containing functional groups and the enrichment of aliphatic hydrocarbons are the dominating chemical reactions [45].

The differences in the structural evolution of vitrinite and inertinite at 30–200 °C are mainly described in three aspects (Figure 14): oxygen-containing functional groups, aliphatic structures, and hydroxyl structures. Compared with inertinite, the aromatic C=O content of vitrinite does not change significantly. With the increasing temperature, the aliphatic structure content of vitrinite and inertinite increases, and the CH$_2$/CH$_3$ value gradually decreases in vitrinite; however, there is no obvious change in inertinite, suggesting that the degree of branching of vitrinite increases or the alicyclic hydrocarbon is observed at this stage [46].
At 200–300 °C, both vitrinite and inertinite have a slight increase in the aromatic nucleus (CH), one adjacent H deformation, and an increase in the content of CH in the aromatic nucleus. The CH2 and CH3 content in the aliphatic structure of the vitrinite and inertinite decreases. On the other hand, the total amount of oxygen-containing functional groups increases. There is a decrease in C–O–C groups, aromatic C=O, and aromatic ring C=C in both vitrinite and inertinite, while the contents of aliphatic CH2 and CH3 and Ar–O–H groups increases greatly (Figure 17), and the I and DOC also increase (Figure 13). This stage is filled mainly by the synergistic effects of aliphatic and aromatic groups. The continuous detachment of aliphatic substances leads to a continuous increase in the aromatic structure system. The ether bonds in the oxygen-containing functional groups are broken and detached, and the conversion to phenolic hydroxyl groups and aliphatic CH2 and CH3 causes their increases.

The differences in structure evolution between vitrinite and inertinite at 200–300 °C are shown mainly in the aliphatic structure. The reduction of CH2 content in the aliphatic structure of vitrinite is much smaller than that of inertinite, and the decrease in CH3 content is much larger than that of inertinite. The change rate of the CH2 content in vitrinite is lower than that of the CH3 content, but the opposite is true for inertinite. The CH2/CH3 value of vitrinite increases gradually, and that of inertinite remains basically unchanged (Figure 14). This suggests that the length of aliphatic hydrocarbons and their branched chains of the vitrinite continue to increase at this stage, and the alicyclic hydrocarbons in the aromatic structure system continue to detach.

At 300–500 °C, many aromatic nuclei (C–H) and three adjacent H deformations in vitrinite and inertinite come into being. The content of aromatic nuclei (C–H) and one adjacent H deformation reduces with the increasing temperature. The total amount of oxygen-containing functional groups is reduced significantly, and the content of ether bonds and aromatic ring C=C increase significantly, while aliphatic CH2 and CH3 and
Ar–O–H groups decrease significantly. The CH\textsubscript{2} and CH\textsubscript{3} content in the aliphatic structure decreases significantly (Figure 17), and the I and DOC increase significantly (Figure 13). Hence, this stage is dominated by the aromatization and condensation of macromolecules, and the substituents of the aromatic system gradually detach.

The structural evolution differences between vitrinite and inertinite at 300–500 °C are shown mainly in the fact that the aromatic C=O content of vitrinite has no obvious change. With increasing temperature, the content of CH\textsubscript{2} and CH\textsubscript{3} decreases, suggesting that the CH\textsubscript{2}/CH\textsubscript{3} value of vitrinite increases gradually (Figure 14), caused by the detachment of alicyclic hydrocarbons in the aromatic system [47]. At this stage, many alicyclic hydrocarbons are detached, resulting in an increase in the content of active sites and the expansion of the aromatic structure system. The content of aromatic C=O of the inertinite decreases, but that of C–O–C groups increases, and the CH\textsubscript{2}/CH\textsubscript{3} value remains basically unchanged (Figure 14), suggesting that the aromatic structure system of the inertinite continues to expand at this stage, which is influenced by the detachment of alicyclic hydrocarbons and the aromatic C=O breaking and splicing.

5. Conclusions

(1) During the pyrolysis process, both the inertinite and vitrinite show an increasing degree of aromatization. With increasing pyrolysis temperature, aromaticity (I), poly-condensation degree of aromatic rings (DOC), average lateral sizes (L\textsubscript{a}) of BSU, and stacking heights (L\textsubscript{c}) of BSU in vitrinite and inertinite increase, but the aromatization level of inertinite has always been higher than that of vitrinite.

(2) In the temperature range of 30–500 °C for the in situ FTIR spectroscopy, the macromolecular structure evolution of vitrinite and inertinite is divided into three stages: 30–200 °C, 200–300 °C, and 300–500 °C. At 30–200 °C, the detachment of oxygen-containing functional groups and the enrichment of alicyclic hydrocarbons occurs. The 200–300 °C stage is filled mainly by the synergistic effects of alicyclic and aromatic groups. The stage of 300–500 °C is dominated by the aromatization and condensation of macromolecules. The substituents of the aromatic system gradually detach, leading to an increase in I and DOC.

(3) In the temperature range of 30–1000 °C by in situ XRD, the difference in macromolecular structure evolution between vitrinite and inertinite is manifested mainly by the arrangement of aromatic layers, which tends to be more and more ordered in vitrinite regular during the pyrolysis process, while there is no significant change in inertinite. However, the aromatic layers of inertinite are always more compact than that of vitrinite. In addition, the alicyclic side chains of inertinite are more stable than that of vitrinite during pyrolysis.

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