The Chemical and Alignment Structural Properties of Coal: Insights from Raman, Solid-State $^{13}$C NMR, XRD, and HRTEM Techniques

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ABSTRACT: The chemical and alignment structures of coal impacts coalbed methane behavior: adsorption, desorption, and diffusion. Recently, the research on accurate characterization techniques for coal structure has received widespread attention. In particular, spatial alignment is critical for the molecular modeling of coal. However, due to the great challenges of quantification, spatial alignment has often been ignored in previous studies. In this study, high-resolution transmission electron microscopy (HRTEM) was employed to quantitatively characterize the fringe length, orientation, and stacking distributions of these five coal samples with different ranks. Raman spectroscopy was utilized to investigate the overall structural disorder of the coal molecules. $^{13}$C nuclear magnetic resonance ($^{13}$C NMR) was conducted to characterize the chemical structures of coals, and XRD experiments recorded the transition of the microcrystallite structure. The results show that in the range of $\%R_o = 0.39 - 2.07\%$, the distributions of the aromatic structural units were similar: mainly composed of fringes of size equivalent to naphthalene and $2 \times 2$ and $3 \times 3$ rings. When $\%R_o > 2.07\%$, the distribution shifted to longer fringes. Moreover, all the samples showed a regional orientation, and when $\%R_o > 2.07\%$, there was significantly higher alignment. The degree of stacking of fringes were limited, most of which appeared in the form of a single layer. When $\%R_o < 2.07\%$, the stacking appeared in the form of two or three layers. However, five-layer stacking merely appeared in the sample with $\%R_o = 2.47\%$. In addition, based on the Raman data, the evolution of carbon disorder was divided into three stages: $\%R_o = 0.39 - 1.23\%$, $1.23 - 2.07\%$, and $2.07 - 2.47\%$, and aromatization caused the overall disorder to decrease. The $^{13}$C NMR data indicated that the chemical structure also transitioned in stages, with aliphatic carbon and oxygen-containing groups gradually decreasing and aromatic carbon increasing. Meanwhile, the XRD data supported increased organization (lower $d_{002}$ values) with maturities. Thus, this study provides quantitative information about the spatial alignment and the size of aromatic rings, which helps to improve a comprehensive understanding of the chemical structure of coal and coalbed methane behaviors.

1. INTRODUCTION

The complex and strongly heterogeneous nature of coal make its structural characterization very challenging.$^{1-3}$ Coal holds a considerable volume of coalbed methane, and the structural variations have a significant influence on gas storage and transport.$^{4-7}$ The micropores inside and between the macromolecules of coal are the significant gas storage locations.$^{8-11}$ The chemical and alignment structures will impact these micropores, indirectly affecting the interaction with gas. In fact, many previous studies have found that the micropore variations of coal are directly controlled by the coal chemical structure.$^{4,12-14}$ However, most studies merely focused on the influence of chemical and microcrystalline structures on micropores, and a few studies have recognized that the spatial alignment of polycyclic aromatic hydrocarbons (PHA) is also a crucial factor affecting the structure of the micropores.$^{15,16}$ It has been revealed that the micropore
structure in coal is closely related to the spatial alignment of the aromatic fringes. Therefore, quantifying the variation of the spatial alignment and structure of coal will be beneficial for improving the understanding of coal structure characterization and the interaction between gas molecules.

With software development and technological progress, numerous modern analytical techniques have been applied to investigate new information on complicated chemical structural changes in recent years, for instance, elemental analysis, Raman spectroscopy, solid-state $^{13}$C nuclear magnetic resonance(NMR)spectroscopy, high-resolution transmission electron microscopy (HRTEM), X-ray diffraction (XRD), and atomic force microscopy (AFM). It is well accepted that the fraction of aliphatic carbon is high and structural ordering is low in low-rank coals, while the well-accepted structure of higher-rank coals is less orderly than high-rank coals. In addition, Sharma et al. also investigated the chemical structure of four South African bituminous coals based on HRTEM micrographs and found that high-rank coals have higher molecular weights. In addition, this approach has been widely used in the construction of coal molecular models. For instance, Narkiewicz and Matthews established the largest Pocahontas No. 3 low-volatile bituminous coal model, and Niekerk and Matthews successfully established Permian South African coal and Illinois No. 6 Aragone Premium coal models. These constructed models determined molecular weights that compared well with the data from NMR, indicating that HRTEM micrographs analysis provides a new insight for coal model construction. Moreover, Louw et al. quantified the stacking of aromatic fringes via HRTEM micrographs analysis for coal and found that there are more stacking layers in high-rank coals.

The application of HRTEM provides a new insight into the chemical and spatial structure transitions of the coal structure during coalification. This study primarily aimed at the chemical and spatial alignment of coal structures with five different ranks. Owing to the complexity of the coal structure, it was necessary to integrate multiple advanced techniques to characterize the structure. HRTEM was applied to quantitatively examine the distribution of the fringe length, orientation, and stacking layers. Moreover, Raman spectroscopy was applied to investigate the degree of ordering and crystallinity. Specific functional groups and aromatic and aliphatic components were determined using the $^{13}$C NMR cross-polarization magic angle spinning technique. The crystalline parameters were characterized using XRD. The results of the different advanced techniques were compared to explore whether better consistency exists. Because of the limited number of five coal samples with different ranks, which not enough to determine the evolution of coal structure, the study mainly aimed to investigate the chemical and spatial alignment in the different maturation stages. These data will not only help us gain an in-depth and comprehensive understanding of the chemical and physical properties of coal but also can provide a theoretical basis for further studies, including atomistic representations of coal, coal utilization, and even more appropriately obtain coalbed gas simulations.

## 2. MATERIALS AND METHODS

### 2.1. Samples Preparation and Pyrolysis Experiment

The five different maturity samples from well-known coalfields in China were collected: Dananhu coal sample from Xinjiang Autonomous Region (XJ-1), Carboniferous Permian Coal Seam from Guizhou province (GZ-2), Xining and Xinyuan Coalfield samples from Shanxi Province (SX-3 and SX-4), and Laochang Coalfield sample from Yunnan Province (LC-5). To avoid experimental differences caused by microscopic components in the coal, in this study, we carefully selected vitrain parts from the raw coal by hand before all the experiments. After separation, the vitrinite content was greater than 95% in the five samples.
Pyrolysis experiments have been considered as an effective method to investigate the coalification process and determine the coal ranks. In this study, we used this experiment to determine the coal ranks and obtain the elemental C and O contents. Before each experiment, the vitrinite samples were crushed with an agate mortar to less than 80 mesh, resulting in approximately 30 g. All the pyrolysis experiments were performed at the Jiangsu Geology and Mineral Design and Research Institute in China. The results for the five coal vitrinite samples are shown in Table 1.

### 2.2. Raman Spectroscopy Analysis

Previous studies have shown that Raman spectroscopy can not only provide information on the maturity of organic matter but also reflect the degree of ordering and crystallinity. The Raman experiments in this work were acquired using a Senterra Raman spectrometers produced by Bruker (Germany). Monochromatic excitation was performed with a 532 nm laser with a data acquisition time of 2 s. The spectral resolution of the recorded Stokes Raman spectra was set to 9–18 cm⁻¹ at the Raman shift of 45–4500 cm⁻¹. Extended scans shifting from 1000 to 1800 cm⁻¹ for the first-order and from 2400 to 3000 cm⁻¹ for the second-order were performed on each sample. Here, we focus on the latter. In order to determine the precise band position, width, and relative intensity, the built-in curve fitting analysis tool of the Origin software was used to deconvolute and fit the obtained Raman spectra. For all spectra, a baseline correction was applied to the spectra in the shift range of 1000–2000 cm⁻¹. Finally, the Raman spectrum was divided into five Gaussian band combinations D1, D2, D3, D4, and G, in which the shift of the D1 peak was fixed at approximately 1350 cm⁻¹, and the position of the D2-D5 bands was adjusted to obtain the best fitting effect. Furthermore, various Raman parameters were determined: the band position difference of the G and D1 bands (G-D1) and the peak area ratio of the D1 and G bands (A_D1/A_G).

### 2.3. Solid-State Cross-Polarization Magic-Angle Spinning (CP/MAS) ¹³C NMR

After more than three decades of the development of the NMR theory, ¹³C solid-state NMR technology is considered to be the most advantageous tool for the structural characterization of natural organic matter. The ¹³C NMR spectra of the five coal samples were measured using a Bruker Advance III 600 spectrometer produced by Bruker Company (Germany) at the Institute of Coal Chemistry (Chinese Academy of Sciences). The samples were characterized at a contact time condition of 3 ms and a pulse repetition delay of 3 s under a rotation frequency of 4 kHz. Moreover, we combined the total sideband suppression technology to obtain the semi-quantitative compositional information. To better quantitatively understand the relative content of the different carbon types, we deconvoluted the ¹³C NMR spectra and calculated the NMR parameters (Table 3).

### 2.4. X-ray Diffraction Analysis

The XRD analysis involving the determination of the carbonaceous material crystallite properties in the different ranks of coal was carried out in the Advanced Analysis and Computation Center of the China University of Mining & Technology using the D8 ADVANCE, produced by Bruker Company (Germany). The operating conditions of the X-ray tube were \( U = 40 \text{ kV} \) and \( I = 30 \text{ mA} \), and the XRD scans were conducted on a Cu target diffractometer using K radiation. The XRD curve consists of 002 and 100 peaks, in which the 002 peak is closely related to the aromatic layer stacking at approximately 15–30°. Information regarding the significant crystallite structure of the interlayer spacing (\( d_{002} \)), average crystallite diameter (\( L_c \)), and crystallite height (\( L_h \)) was obtained through curve fitting using the Origin7.5 software and then could be determined using the Bragg’s and Scherrer equations (eqs 1–3).

\[
d_{002}(\text{Å}) = \lambda / 2 \sin \theta_{002} \tag{1}
\]

\[
L_c(\text{Å}) = 0.9 \lambda / (\beta_{002} \cos \theta_{002}) \tag{2}
\]

\[
L_h(\text{Å}) = 1.84 \lambda / (\beta_{100} \cos \theta_{100}) \tag{3}
\]

where \( \lambda \) is the wavelength of the X-ray (Å), \( \theta_{002} \) and \( \theta_{100} \) are the peak positions of the 002 and 100 bands (°), and \( \beta_{002} \) and \( \beta_{100} \) are the peak widths at half height of 002 and 100 bands, respectively.

### 2.5. High-Resolution Transmission Electron Microscopy (HRTEM)

High-resolution transmission electron microscopy (HTREM) has been considered an analytical method that was employed to quantitatively characterize the multiscale spatial and structural organization of the coal. HRTEM images were obtained in the State Laboratory for Coal Conversion (Chinese Academy of Sciences) using an FEI F20 Field Emission Electron Microscope produced in the USA. The acceleration voltage was 200 kV, and the point resolution and crystal lattice resolution were 0.23 and 0.14 nm, respectively. Before the experiment, the samples were pulverized to less than 200 mesh (0.074–0.2 mm) using a mortar. Then, these finely ground samples were in full contact with ethanol for 10–30 min using ultrasonic vibration. Next, approximately 2–3 drops of the translucent suspension were placed on a TEM copper grid with holey amorphous carbon, and the sample particles adhered to the hole edges for observation. The samples were first examined at moderate magnification to find the sharp thin layer at the edge of the coal particles under TEM. Several images of the black and white lattice fringes were taken from different spots to obtain a fine view and analyzed using Adobe Photoshop and Auto CAD software.

| sample name | \( R \) % | \( M_{ad} \) | \( A \) % | \( S_{ad} \) % | \( O_{ad} \) % | \( C_{ad} \) % | \( H_{ad} \) % | \( N_{ad} \) % |
|-------------|---------|---------|---------|-------------|-------------|-------------|-------------|-------------|
| XJ-1        | 0.39    | 9.54    | 7.03    | 0.72        | 20.56       | 72.60       | 4.80        | 1.26        |
| GZ-2        | 1.23    | 1.02    | 30.39   | 0.91        | 6.94        | 85.30       | 5.05        | 1.41        |
| SX-3        | 2.07    | 0.92    | 22.00   | 0.32        | 6.87        | 87.37       | 4.11        | 1.23        |
| SX-4        | 2.43    | 1.14    | 6.98    | 0.47        | 4.71        | 89.70       | 3.78        | 1.30        |
| LC-5        | 2.47    | 1.92    | 6.25    | 1.05        | 4.22        | 90.60       | 2.96        | 1.10        |

- \( R \) : vitrinite reflectance; \( M_{ad} \) : moisture, air dry; \( A \) : ash, dry; \( S_{ad} \) : total sulfur; \( O_{ad} \) : oxygen, dry and ash free; \( C_{ad} \) : carbon, dry and ash free; \( H_{ad} \) : hydrogen, dry and ash free; \( N_{ad} \) : nitrogen, dry and ash free.

\( ^{a} \text{R}_{\text{f}} \) is the obtained Raman peak positions, width, and relative intensity of the 002 and 100 peaks, in which the 002 peak is closely related to the aromatic layer stacking at approximately 15–30°. Information regarding the significant crystallite structure of the interlayer spacing (\( d_{002} \)), average crystallite diameter (\( L_c \)), and crystallite height (\( L_h \)) was obtained through curve fitting using the Origin7.5 software and then could be determined using the Bragg’s and Scherrer equations (eqs 1–3).

\[ d_{002}(\text{Å}) = \lambda / 2 \sin \theta_{002} \]

\[ L_c(\text{Å}) = 0.9 \lambda / (\beta_{002} \cos \theta_{002}) \]

\[ L_h(\text{Å}) = 1.84 \lambda / (\beta_{100} \cos \theta_{100}) \]
The data determined through HRTEM image analysis were the fringe length distribution, the orientation, and relative position. According to the principle of the parallelogram-shaped aromatic rings introduced by Mathews et al., the fringe length was converted into the molecular size. In addition, the orientation and stacking degree determined the spatial position of the aromatic fringes. Therefore, we quantified the angular distribution of the fringes by counting the coordinates of the endpoints of the fringes and recorded the angular distribution in the form of eight 15° angle bins. Each angle statistical chart was rotated so that the fringe angles were roughly concentrated in the same direction. Moreover, based on the method of stacking of aromatic fringes determined by Louw et al. and Sharma et al., the stacking was primarily determined by the parallel aromatic fringes and the vertical distance between the midpoints of the aromatic fringes. Here, the direct distance between the midpoints and the fringe angle difference was <5 Å and <20°, respectively.

3. RESULTS

3.1. Raman Spectroscopy. It is generally accepted that the complex structure of coal is closely related to coal maturity. Figure 1 displays the measured Raman spectra of the five coal samples, stacked in order of their vitrinite reflectance. All five samples produced clean Raman spectra with two clearly identifiable bands at approximately 1580 and 1350 cm⁻¹, which are assigned to the G and D bands, respectively. The D band is caused by Raman-active A_g symmetry associated with lattice defects and discontinuities of the sp² carbon network, and the G band is caused by the breathing of aromatic rings. The intensity of the G band is clearly larger than that of the D1 band. The curve-fitting procedure for the five samples is shown in Figure 2. The detailed Raman spectra derived from the curve-fitted are listed in Table 2. From Table 2, the center shift position of the G band is obtained from 1578 to 1591 cm⁻¹ and from 1365 to 1346 cm⁻¹ for the D band. With the increase in maturity, the bands of G and D become narrower, and the band spacing increases. In addition to the D1 and G bands, the D3 band is the third largest area and intensity of amorphous carbon. As the maturity increases, the proportion of the shoulder band of the G and D2 components gradually decreases. The gradual increase in the dominance of the D1 band over the G band is consistent with the generation of defects in the aromatic plane, but the latter does not increase significantly, which indicates that graphitization has not yet occurred.

3.2. 13C NMR Spectroscopy. 13C NMR experiments were performed on five coal samples to characterize the chemical structures of the coals. Figure 3 displays the 13C NMR spectra of coals with different ranks. Also, these 13C NMR spectra clearly consist of three distinct bands: aliphatic carbon (shift: 0–90 ppm), aromatic carbon (shift: 100–156 ppm), and carbonyl carbon (shift: 165–220 ppm). In these five coal samples, only the XJ-1 sample had an aliphatic carbon peak area greater than that in the aromatic carbon peak, indicating that there are more aliphatic carbon structures within the coal structure in the sample. However, in the other four samples (GZ-2, SX-3, SX-4, and LC-5), the peak area of aliphatic carbon is significantly smaller than that of aromatic carbon. Overall, the aliphatic carbon showed a decreasing trend with increasing maturity, while the aromatic carbon exhibited an increasing trend. However, during the early stage of coalification, especially from the sample of XJ-1 (%R_o = 0.39%) to GZ-2 (%R_o = 1.23%), the aliphatic peak intensity decreased significantly. In contrast, the intensity of the aromatic peak increased significantly with %R_o ranging from GZ-2 (%R_o = 2.07%) to LC-5 (%R_o = 2.47%). In addition, the peak area of carbonyl carbon showed a downward trend. 13C NMR parameters were also calculated using the curve-fitting method, and the results are shown in Table 3. It is obvious that the value of f_a (proportion of aromatic carbon bonded to hydroxyl or ether oxygen) and f_c (proportion of carbonyl) show a decreasing trend as the maturity increases, indicating that the oxygen-containing functional groups was tailored down from the chemical structure of coal during the process of coalification. f_H (proportion of protonated and aromatic carbon) and f_B (proportion of aromatic bridgehead) are attributed to aromatic carbons, which tend to increase gradually during coalification, and the proportion of f_H in the LC-5 sample is nearly half of the total, suggesting an increase of protonated aromatic carbons. However, the other aromatic parameter of f_A (proportion of alkylation aromatic) increases first and then decreases, reaching the maximum (0.12) in the SX-2 sample. In contrast, the aliphatic carbon parameter of f_c (proportion of CH or CH2) and f_B (proportion of aromatic bridgehead) decreased significantly with an increase in maturation, suggesting that the aliphatic structure fell off during the coalification process.

3.3. XRD Structural Parameters. The XRD spectra for different ranks of coal samples are depicted in Figure 4, where two distinct peaks of 002 and 100 can be seen. The peak of 002 (2θ = 15°–30°) is obvious and corresponds to the stacking structure of the aromatic layers. The peak of 100 in the high-angle region (2θ = 40°–50°) is relatively poorly defined. Small spikes on the peaks are also observed for the samples of SX-3, SX-4, and especially for GZ-2, which demonstrates the residual minerals in the coal samples. However, the spikes did not interfere with the intensities of the 100 and 002 peaks of the three coal samples. As the maturity increases, the background intensity of 002 increases and the shape of the 002 peak becomes sharper and shifts to larger angles. Although the change is not significant, the peak of 100 tends to increase slightly, suggesting a higher order for high-rank samples. Furthermore, the peaks move to larger

Figure 1. Raman spectra of coal samples.

Figure 3. 13C NMR spectra of coal samples.
angles as the carbon content increases. The calculated crystallite structural parameters are presented in Table 4. The $d_{002}$ is an important indicator of the perfection in the stacking structure periodicity. All five coals demonstrate a $d_{002}$ in close proximity to graphite ($d_{002}$ for graphite is 3.36–3.37 Å). During the process of coalification, $d_{002}$ exhibits a gradual

Figure 2. Curve-fitting Raman spectra of the five coal samples (red dotted line experimental Raman spectra; green line fitting peaks; purple shaded area final results of generated curve-fitting).
3.4. HRTEM Micrographs. Figure 5 shows the HRTEM micrographs of the five coal samples. By comparing the HRTEM micrographs of coal samples with different ranks, it can be clearly seen that the fringes of the first three samples (%R_\text{o} values of 0.39–2.07%) were short and aligned to a certain extent. However, for the high-rank coal samples, the lattice fringes were longer with better alignment. The false-colored fringes of the five coal samples were processed to intuitively observe, as shown in Figure 5. In order to quantitatively investigate the characteristics of the lattice fringes, based on the method proposed by the Mathews group, the aromatic fringes are assigned to different-sized aromatic rings. From Figure 5, the different rank coal samples are all composed of 1×1 to 8×8 aromatic rings. In addition, the distribution, orientation, and stacking of the lattice fringes of different sizes for the different rank samples exist. These differences are quantified in the following sections.

4. DISCUSSION

4.1. Raman Characterization. Figure 6a demonstrates that the band position difference of the G and D1 bands is positively related to %R_\text{o}. The growth of the difference (G-D1) is remarkable, up to approximately 25 cm⁻¹. However, the peak area ratio (A_{D1}/A_G) was negatively correlated with %R_\text{o} (Figure 6b). Therefore, the variation of Raman parameters during the coalification process is not linear, and it is composed of three stages at %R_\text{o} = 0.39–1.23%, %R_\text{o} = 1.23–2.07%, and %R_\text{o} = 2.07–2.47%, respectively. This reflects the complex coalification mechanisms. As shown in Figure 6,

Table 2. Raman Structural Parameters Determined from the Spectrum³

| sample | 2ϑ_{D1} (°) | 2ϑ_{G} (°) | β_{D1} (rad) | β_{G} (rad) | d_{D1} (Å) | Lc (Å) | La (Å) |
|--------|-------------|-------------|--------------|--------------|------------|--------|--------|
| XJ-1   | 23.71       | 41.23       | 0.24         | 15.83        | 3.75       | 5.81   | 10.96  |
| GZ-2   | 24.29       | 42.90       | 0.12         | 16.04        | 3.66       | 11.40  | 10.88  |
| SX-3   | 25.56       | 44.16       | 0.07         | 14.21        | 3.48       | 20.90  | 12.34  |
| SX-4   | 25.70       | 43.69       | 0.08         | 12.35        | 3.46       | 18.18  | 14.17  |
| LC-5   | 25.38       | 42.18       | 0.08         | 8.85         | 3.50       | 17.09  | 19.67  |

Table 3. ¹³C NMR Parameters of Coal Samples and Carbon Assignment³

| sample | f_1 | f_2 | f_3 | f_4 | f_5 | f_6 | f_7 | f_8 | f_9 | f_10 | f_11 | f_12 | f_13 | f_14 | f_15 | f_16 | f_17 |
|--------|-----|-----|-----|-----|-----|-----|-----|-----|-----|-----|-----|-----|-----|-----|-----|-----|-----|
| XJ-1   | 0.50| 0.15| 0.35| 0.23| 0.13| 0.12| 0.05| 0.06| 0.49| 0.13| 0.36| 0.11|     |     |     |     |     |
| GZ-2   | 0.69| 0.11| 0.58| 0.34| 0.24| 0.10| 0.10| 0.14| 0.31| 0.10| 0.21| 0.08|     |     |     |     |     |
| SX-3   | 0.74| 0.07| 0.67| 0.29| 0.38| 0.04| 0.09| 0.16| 0.26| 0.08| 0.18| 0.07|     |     |     |     |     |
| SX-4   | 0.75| 0.06| 0.69| 0.26| 0.43| 0.02| 0.05| 0.19| 0.25| 0.11| 0.14| 0.06|     |     |     |     |     |
| LC-5   | 0.78| 0.04| 0.74| 0.25| 0.49| 0.01| 0.03| 0.21| 0.22| 0.12| 0.10| 0.07|     |     |     |     |     |

³f_1: total aromatic carbon; f_2: carbonyl; f_3: aromatic ring; f_4: non-protonated and aromatic; f_5: protonated and aromatic; f_6: hydroxyl or ether oxygen; f_7: alkylation aromatic; f_8: aromatic bridgehead; f_9: total aliphatic carbon; f_10: CH₃ or non-protonated; f_11: CH; or CH₂; f_12: bonded to oxygen.
when \( R_o = 0.39 - 1.23\%), there is a sharp linear increase and reduction in G-D1 and \( A_D1/A_G \) respectively. When \( R_o = 1.23 - 2.07\% \), the value of G-D1 slightly decreases but is still linearly reduced for \( A_D1/A_G \). In addition, when \( R_o = 2.07 - 2.47\% \), the value of G-D1 increases, but the value of \( A_D1/A_G \) tends to remain steady. In the early stage of coali

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cation (% \( R_o = 0.39 - 1.23\% \)), the sharp linear changes of both \( A_D1/A_G \) and G-D1 are observed in Figure 6. This illustrates the proceeding of aromatization. However, when \( R_o = 1.23 - 2.07\% \), \( A_D1/A_G \) continues to show a clear downward trend in Figure 6b, indicating a further increase in aromatization. However, this change in aromatization is a relatively gradual process compared with that the stage of \( R_o = 0.39 - 1.23\% \), which also can be proven by the slight decrease in the value of G-D1 as shown in Figure 6a. Meanwhile, the aromatic rings and degree of graphitization are significantly enhanced. When \( R_o = 2.07 - 2.47\% \), as \( R_o \) rises, the band position difference of G-D1 continues to increase, while \( A_D1/A_G \) tends to be relatively stable, which proves the enhancement of condensation of aromatic rings, and confirming that the amorphous carbon structures have disappeared to a large extent and kept in a relatively stable stage. A similar finding was also obtained by He et al.28 during the coalification process, there is a tendency for defects and disorder in the coal structure to decrease.

4.2. Chemical Structures Characteristics. Figure 7 shows that the \( ^{13}C \) NMR parameters all change as the vitrinite reflectance changes. Consistent with the Raman parameters, the evolution of the chemical structure is also divided into three stages. Overall, the aromatic ring (\( f'_a \)), aromatic carbon (\( f_a \)), protonated aromatic carbon (\( f_a^{H+} \)), and aromatic bridgehead (\( f_a^H \)) increase with \( R_o \), ranging from 0.39 to 2.47\%. In contrast, the total aliphatic carbon (\( f_a^{CH} \), CH or CH2 (\( f_a^{H2} \)), hydroxyl or ether oxygen (\( f_a^O \)), and carbonyl (\( f_a^C \)) tend to decrease. At the stage of \( R_o = 0.39 - 1.23\% \), the growth rate of aromatic carbon (\( f_a \)) and aromatic ring (\( f'_a \)) are fast (Figure 7a,d). Similarly, in this stage, the total aliphatic carbon (\( f_a^{CH} \)) and CH or CH2 (\( f_a^{H2} \)) decrease at a fast rate.

Figure 5. HRTEM micrographs and false-colored fringes of five coal samples: (a1) XJ-1 HRTEM image; (b1) GZ-2 HRTEM image; (c1) SX-3 HRTEM image; (d1) SX-4 HRTEM image; (e1) LC-5 HRTEM image; (a2) XJ-1 false-colored fringes; (b2) GZ-2 false-colored fringes; (c2) SX-3 false colored; (d2) SX-4 false-colored fringes; (e2) LC-5 false-colored fringes; the blue box is the selected thinner edge area.

Figure 6. Raman parameters and \( R_o \) correlation: (a) the relationship between \( R_o \) and (G-D1) band positions; (b) the relationship between \( R_o \) and \( A_D1/A_G \).
suggesting that this stage is in the proceeding of aromatization. In addition, the rapid decline in aliphatic side chains \( (f_{al}) \) is the main characteristic. However, at the stage of \( \%R_o = 1.23 - 2.07\% \), the growth rate of aromatic carbon \( (f_a) \) and aromatic ring \( (f_a') \) slow down compared with the stage of \( \%R_o = 0.39 - 1.23\% \). In the meantime, the decline rate of the total aliphatic carbon \( (f_{al}) \) and CH or CH\(_2\) \( (f_{al}H) \) become low. However, the decline rate of the hydroxyl or ether oxygen \( (f_{al}P) \) and carbonyl \( (f_{al}C) \) becomes high (Figure 7g,h) and enables the increase in the atomic ratio of aromatic carbon. The degree of aromatization is enhanced at this stage, and its main feature is the rapid decline of oxygen. When \( \%R_o = 2.07 - 2.47\% \), the aromatic ring \( (f_a) \) and aromatic carbon \( (f_a') \) continue to increase. In contrast, CH or CH\(_2\) \( (f_{al}H) \) still decreases, and protonated aromatic carbon \( (f_{al}H') \) (Figure 7 b) and aromatic bridgehead \( (f_{al}B) \) (Figure 7 c) still increase,
indicating the enhancement of condensation of aromatic rings. This is consistent with the results of Raman spectroscopy that the aliphatic structure has largely tailored off from the coal structure at this stage.

4.3. Crystallite Structural Characteristics. The parameter \( d_{002} \) is an important indicator for the evolution of degree of the coal BSUs. Figure 8 shows the values of \( d_{002} \), \( I_c \) and \( L_c \) of the coal crystallite structures as a function of the vitrinite reflectivity (\( \% R_o \)). The trend of the \( d_{002} \) values with increasing \( \% R_o \) was divided into three distinct stages (Figure 8a). The first stage occurs in the range of \( \% R_o = 0.39–1.23 \%). The \( d_{002} \) value decreased significantly in this stage. A similar decrease was observed in the pyrolysis coal samples.\(^{40} \) In the second stage of \( \% R_o = 1.23–2.07 \%), the downward trend of the \( d_{002} \) value was more significant than in the previous stage, which is consistent with the decreasing trend of the \( A_{D1}/A_{G} \) in the Raman parameter during this stage. It has been proven that aromatization can increase the degree of stacking of the coal crystallite structure. However, in the third stage \(( \% R_o = 2.07–2.47 \%)\), the \( d_{002} \) value decreased slightly for SX-4 coal and remained stable.

As seen in Figure 8b, with an increase of \( \% R_o \), the variation of \( L_c \) for all the coal samples is also characterized by three stages. In the stage of \( \% R_o = 0.39–1.23 \%), the \( L_c \) value decreased slightly. On the contrary, in the second stage of \( \% R_o = 1.23–2.07 \%), the \( L_c \) value of the five coal samples increased gradually. In the third stage, \( \% R_o = 2.07–2.47 \%), the value of \( L_c \) increased significantly.

Figure 8c shows the variation of the \( L_c \) values of coals with different ranks. The \( L_c \) value of \( \% R_o = 0.39–1.23 \%) significantly increased. When \( \% R_o \) ranged from 1.23 to 2.07%, the growth of the \( L_c \) value was more significant. However, when \( \% R_o = 2.07\%–2.47\% \), \( L_c \) showed a slight downward trend, with a maximum value of 20.90 obtained at \( \% R_o = 2.07\% \). Similar findings can also be found in other papers.\(^{19,25,44} \)

In the stage of \( \% R_o = 0.39–1.23 \%), the \( d_{002} \) value decreases, \( L_c \) slightly decreases, and the increase of \( L_c \) may be due to the small molecules swelling in the layer spacing and the hydrogen bonds breaking.\(^{23} \) Significant changes in the XRD parameters in the second stage demonstrated the development of a graphitized structure.\(^{25} \) During the last stage, small changes in \( d_{002} \), \( L_o \) and \( L_c \) reflect the crystallite structure stability. Overall, during the coalification process, the crystallite structures vary with decreasing layer spacing and increasing crystal diameter and height.\(^{25} \)

It is known that graphite-like structures are more likely to occur in high-rank coals.\(^{35} \) The lowest distance between two adjacent crystal layers was found to be 3.46 Å for the high-rank coal sample of SX-4 \(( \% R_o = 2.07\%)\) in this work, which is closer to a perfect graphite single crystal with \( d_{002} \) in the range of 3.36–3.37 Å than other samples. Therefore, it can be found that graphite-like parameters also have significant effects on the crystallite structure. The disorder parameter of the \( D_1 \) band area to the \( G \) band area was found in the different ranks of coal depending on \( d_{002} \) and \( L_c \) distinctly. Figure 9 illustrates the relationship between the Raman parameters \( A_{D1}/A_{G} \) and the crystallite structure parameters \((d_{002}, L_c)\). Generally, the \( A_{D1}/A_{G} \) parameter is proportional to \( d_{002} \) in Figure 9a \( (R^2 = 0.95) \), indicating that as the coal rank increases, the degree of disorder decreases, and the interlayer spacing also decreases. On the contrary, the \( A_{D1}/A_{G} \) parameter is inversely proportional to \( L_c \) in Figure 9b \( (R^2 = 0.95) \). This means that the decrease in disorder is the result of the increase in crystallite height. Furthermore, it also demonstrates that as the coal rank increases, the degree of disorder decreases, the crystal height increases, and the interlayer spacing decreases, indicating more aromatic layers in the stacking structure.

4.4. Spatial Alignment of Coal Samples Based on HRTEM. 4.4.1. Lattice Fringe Distribution. The length of aromatic fringe was converted to the corresponding molecular size after the approach of Mathews et al.\(^{22} \) using the central hypothesis that the fringe was as deep as it was wide assuming a parallelogram–ring catenation. Thus, lattice fringes could be attributed to aromatic parallelograms according to their length. And the fringe length is counted according to the assignment of the aromatic fringe length by the Mathews group.\(^{44} \)

The lattice fringe length distributions are shown in Figure 10. For the samples with the \( \% R_o \) range \((0.39–2.07\%) \), the aromatic structural unit distributions are similar: mainly composed of naphthalene \((30–47\%)\), 2 × 2 rings \((15–35\%)\), and 3 × 3 rings \((7–33\%)\). The frequency of naphthalene decreases distinctly as the maturity increases. The frequency of the 2 × 2 rings increases in the range of \( \% R_o \) \((0.39–2.07\%) \) and then decreases slightly in the range of \( \% R_o \) \((2.07–2.47\%) \). A positive correlation between the 3 × 3 rings and \( \% R_o \) is observed in Figure 10 \((R^2 = 0.91)\). In addition, 4 × 4 rings and 5 × 5 rings are partly distributed in the high rank samples of SX-4 and LC-5 but are less distributed in the other low-rank samples. In the low-rank coal sample of XJ-1, naphthalene contributes to nearly half of the total aromatic.
Figure 10. Distributions of the lattice fringe length of five coal samples (there is a positive correlation between the frequency of 3 × 3 rings and \( R^2 = 0.91 \)).

rings. Moreover, all the aromatic fringes are smaller than the 5 × 5 rings. Compared with the XJ-1 sample, 8 × 8 rings appear in the samples of SX-4 and LC-5. When \( \% R_o > 2.07 \% \), there is a shift toward the size of 3 × 3 rings. Therefore, as the maturity increases, the size of the aromatic ring increases, which is similar to the maturity-responsive kerogen and other coal types. Moreover, this result agrees with the results from the XRD experiment parameter \( L_s \). Compared with other coal samples, the five coal samples in this work had a higher frequency of 3 × 3 rings. It may be due to the differences in organic matter or the deposition environment.

PHA mainly exists in the form of aromatic layers in the macromolecular structure of the coal. The aromatic layers are mainly controlled by the temperature and pressure of the deposition environment. The value of \( \% R_o \) is a direct indicator of temperature and pressure. Therefore, the increase in temperature and pressure promotes the growth of aromatic rings.

4.4.2. Fringe Orientation. The orientation bar charts and rose diagrams of the lattice fringe micrographs for the five different rank coal samples are shown in Figure 11. For a clear demonstration, all the statistical rose diagrams have been rotated, and all the fringes are concentrated in the vertical direction. It can be observed from the rose diagrams (in Figure 11) that there is regional heterogeneity in the orientation distribution. The aromatic fringes of the coal samples all have their own preferential alignment. When \( \% R_o < 2.07 \% \), the fringe distribution is scattered, and the degree of orientation is weak. However, at \( \% R_o > 2.07 \% \), as the length of the aromatic fringes increases, the degree of orientation increases (similar to a rank series of kerogen). As shown in the rose diagrams, the trend of fringe angle distribution increases as the \( \% R_o \) increases but with a significant increase at \( \% R_o = 2.07 \% \) (sample SX-3). Here, the orientation is quantified by the proportion of aromatic fringes in the primary direction (75–120°) of the total fringes. In the low-rank sample of XJ-1, aromatic fringes have the lowest orientation, contributing only to 35%. A previous work has concluded that the fringes are oriented randomly in low-rank coal. Compared with the previous study, this study found that even at the stage of lignite, aromatic fringes have partial orientation. The orientation degree increases slightly with \( \% R_o \) in the range of 0.39–2.07% (35–45%), but when \( \% R_o > 2.07 \% \), the orientation degree changes significantly, especially in the sample of LC-5, reaching 81% of the total fringe. Based on the above Raman results, it can be assumed that in the low-rank coal samples, there are more heterocyclic compounds or amorphous carbon structures on the chain side of aromatic clusters, leading to a weak degree of orientation. However, according to the Raman data at this stage, the aromatization and rearrangement are enhanced. A majority of heterocyclic compounds and amorphous carbon have tapered down, resulting in a significant increase in the size of the single aromatic fringe. Moreover, the alignment and orientation of the aromatic fringes become strong. Liu et al. also established the relationship between the H/C ratio and fringe orientation and concluded that aliphatic structures have a negative impact on the fringe orientation alignment. Overall, the aromatization promotes the orientation of the aromatic fringes.

4.4.3. Fringe Stacking. The stacking of aromatic fringes has been widely investigated. There are mainly face-to-face, stepped stacking, herringbone, and T-shaped stacking aromatic fringe stacking styles based on the aromatic ring sizes. Different stacking styles occur in certain aromatic structures, such as face-to-face stacking, which occurs in pure crystals of larger polyaromatic structures. Aliphatics, heteroatoms and polyaromatic aromatic structures will affect the interlayer stacking. Here, all the samples are present in the form of face-to-face. The stacking ratio, as measured by the ratio of layers in a stack, is much more extensive for the high-rank coals. Also, according to the method proposed by Louw al., it was suitable for stacking recognition. Here, we define the stacking ratio to be calculated by the ratio of the number of stacked fringes to the counted number of the false color fringes. As shown in Figure 12, it can be seen clearly that all five coal samples have a low stacking ratio (3.15–14.38%). Most of the fringes (85.62–96.85%) exist as a single layer, similar to previous research. For samples from XJ-1 to SX-3 (\( R_o = 0.39–2.07 \% \)), the fringe stacking ratio is between 3.15 and 7.16% and significantly increases in samples from SX-4 to LC-5, between 9.15 and 14.38%. The fringe stacking change trend increases as the fringe length increases with \( \% R_o \) and both have a significant transition at \( \% R_o = 2.07 \% \). Figure 13 illustrates the frequency distribution of the aromatic fringe stacking layers. Clearly, there are only two layer stacks in sample XJ-1, which are close to the SHE and PLQ. The GZ-2 and SX-3 samples had contributions from two or three layers. However, only five layers were found in sample LC-5. These results are in good agreement with those obtained from the XRD technique.

PHA stacking units refer to the fact that the aromatic fringes form stiff linkages in the form of short aliphatic side chains and cycloalkanes under the \( \pi \)-\( \pi \) interaction, which prevent the folding of aromatic fringes to a certain extent and form a parallel or quasi-parallel structure. It is well-known that the vitrinite reflectivity \( (\% R_o) \) jumps at 0.5–0.6, 1.1–1.2, 1.2–1.5, 2.2–2.3, 2.8–2.9, and 3.7–3.9% during the coalification process. Sample SX-3 (\( R_o = 2.07 \% \)) approaches the fourth coalification jumping point. At this stage, as the aromatization and ring condensation increase, resulting in the rearrangement of the crystallite structure and increasing the number of stacked layers. Moreover, there is another view that the degree of crystallinity in low-rank samples is low, and part of the low-crystalline carbon disappears or is converted to...
high-crystalline carbon during the coalification process, resulting in increased stacking layers.

5. CONCLUSIONS

Here, the spatial alignment and structural characteristics of coal samples were investigated using HRTEM micrograph quantitative analysis. Raman spectroscopy was utilized to analyze the overall structural disorder of the structure. In addition, $^{13}$C NMR spectroscopy was employed to study the chemical structure, and the XRD spectrum also recorded the microcrystalline structure of different rank coal samples. Also, these following conclusions can be drawn from this study:

(i) The variation of ordering during the coalification process is nonlinear, and the overall evolutionary paths have stage characteristics with three stages at $\% R_o = 0.39 - 1.23\%$, $\% R_o = 1.23 - 2.07\%$, and $\% R_o = 2.07 - 2.47\%$. Aromatization occurs in the stage of $\% R_o = 0.39 - 1.23\%$. As $\% R_o$ increases, the growth rate of aromatization at the stage of $\% R_o = 1.23 - 2.07\%$ is a relatively gradual process compared with that the stage of $\% R_o = 0.39 - 1.23\%$. For $\% R_o = 2.07 - 2.47\%$, the amorphous carbon structures disappeared substantially and the coal structure disorder decreased.

(ii) When $\% R_o = 0.39 - 1.23\%$, the rapid decline in aliphatic side chains ($f_l(H)$) is the main characteristic. However, at the stage of $\% R_o = 1.23 - 2.07\%$, the oxygen-containing groups that fall off from the coal molecular structure are more significant. In addition, at the stage of $\% R_o = 2.07 - 2.47\%$, the aliphatic structure largely tailored and condensation of aromatic rings enhanced.

(iii) The variation of the crystallite structure was also divided into three stages. In the first stage, the $d_{002}$ value decreases, $L_a$ slightly decreases, and $L_c$ increases. When $\% R_o = 1.23\% - 2.07\%$, significant changes occurred in the XRD parameters, suggesting the rapid development toward the graphitized crystallite structure. In the last stage, the crystallite parameters remain stable. Meanwhile, there was a good linear relationship

Figure 11. Angle distribution of the aromatic fringe from the HRTEM micrographs.
between the Raman disorder parameter \((A_{D1}/A_G)\) and XRD crystallite structure parameters \((d_{002}, L_c)\).

(iv) Through HRTEM micrographs, quantitative analysis concluded that the aromatic fringes were similar in distribution for different rank coal samples and mainly composed by naphthalene (30–47%), \(2 \times 2\) rings (15–35%), and \(3 \times 3\) rings (7–33%). The \(3 \times 3\) rings have a good positive correlation with \(\%R_o\). When \(\%R_o > 2.07\%\), there was a shift toward longer fringes. For all samples, the aromatic fringes showed regional orientation, and the quantitative orientation was characterized by fringes contributing to the major direction (75–120°). The lowest orientation degree was only 35% in sample XJ-1, and a higher orientation degree occurred when \(\%R_o > 2.07\%\) (35–81%). Moreover, there was a limited degree of stacking for all samples (3.15–14.38%). When \(\%R_o < 2.07\%\), most stacks are in the form of only two or three layers. However, when \(\%R_o > 2.07\%\), the stacking layers increase, and even five-layer stacking appears in the sample of LC-5.

![Figure 12. Distribution of lattice fringe stacking.](image)

![Figure 13. Frequency distribution of stacked layers for samples of lattice fringe.](image)

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Notes
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