Response of Molecular Structures and Methane Adsorption Behaviors in Coals Subjected to Cyclical Microwave Exposure

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ABSTRACT: To better understand the methane adsorption behavior after microwave exposure, the importance of quantitatively characterizing the effect of cyclical microwave exposure on the molecular structures of coals cannot be overemphasized, with implications for enhancing coalbed methane (CBM) extraction. Thus, cyclical microwave exposure experiments of three different metamorphic coals were conducted, and the methane adsorption capacity before and after each microwave exposure (10 in total) for 120 s was evaluated. Fourier transform infrared spectroscopy analysis and peak fitting technology were applied to quantitatively characterize the changes in the structural parameters of coal molecules. The results showed that after modification, the structural parameters like aromatic carbon fraction ($f_{ar}$), aromaticity ($I_1$ and $I_2$), degree of condensation ($DOC_1$ and $DOC_2$), and the maturity of organic matter ($^3C^*$) gradually increased with increasing exposure times, while the length of the aliphatic chain or its branching degree ($CH_2/CH_3$) and the hydrocarbon generating capacity ($^3A^*$) showed a decreasing trend. The Langmuir volume ($V_L$) of three different rank coal samples decreased from 29.2, 32.8, and 40.4 mL/g to 25.7, 29.3, and 35.7 mL/g, respectively; the Langmuir pressure ($P_L$) increased from 0.588, 0.844, and 0.942 MPa to 0.626, 1.007, and 1.139 MPa, respectively. The modification mechanism was investigated by analyzing the relationship between the methane adsorption behaviors and molecular structures in coals. The release of alkane side chains and the oxidation of oxygen-containing functional groups caused by microwave exposure decreased the number of methane adsorption sites. As a result, the methane adsorption capability decreased. In addition, the decomposition of minerals affects methane adsorption behaviors in coals. This work provides a basis for microwave modification of coal as well as in situ enhancement of CBM extraction using microwave exposure.

1. INTRODUCTION

Coalbed methane (CBM), a typical unconventional gas, provides an efficient clean energy resource and a safe mining environment for the world.1,2 The global CBM reserves are estimated at more than $2.29 \times 10^{14}$ m$^3$, which provide great development prospects.3 According to the results of the fourth round of China’s CBM resource evaluation, the total size of CBM geological resources with a depth of less than 2000 m in China is approximately $29.82 \times 10^{12}$ m$^3$, of which recoverable resources make up $12.51 \times 10^{12}$ m$^3$.4 Considering that more than 80% of CBM in China occurs in the coal matrix in an adsorbed state,5 it is of positive significance to study the adsorption behavior of methane for CBM extraction.

The coal matrix (chemical composition: carbon, hydrogen, oxygen, nitrogen, and sulfur) is composed of a large amount of heterogeneous, complex, and amorphous organic macro-

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molecules and some inorganic small molecules with different sizes embedded in the macromolecular network, and it undergoes a series of complex physicochemical changes in the process of coalification. The macromolecular structure of coal is mainly composed of aromatic rings, alkane side chains, and various functional groups connected by various chemical bridge bonds. The changes in the alkane side chains and various functional groups have significant influences on the molecular structures and reactivities of coals as well as the methane adsorption behaviors of coals. Qin et al. studied the changes in methane adsorption capacities in coals of different ranks after liquid nitrogen treatment and found that there were linear correlations between the methane adsorption capacities and coal molecular structure parameters such as aliphatic hydrocarbon, oxygen-containing, and substituted benzene functional groups. Wang et al. studied the effect of the chemical composition of coal on methane adsorption and found that nonpolar functional groups could promote CH₄ adsorption on the surface of coals; in contrast, polar oxygen-containing functional groups could weaken the CH₄ adsorption capacity. Mirzaei et al. studied the adsorption of methane in active carbons with/without surface functional groups by doping heteroatoms into the carbon framework, finding that the strong electronegative O atom in the functional groups repels the electronegative C atom in the CH₄ molecule. Yu et al., Han et al., and Kang et al. also found that the types and proportions of surface groups are closely related to the methane adsorption capabilities in coals.

Many stimulation approaches have been used by previous researchers to modify the molecular structures and methane adsorption performances of coals. One is the injection method, including steam/hot water, liquid nitrogen, and gaseous/supercritical CO₂ injection. The other is external field stimulation, including ultrasonic electric field, and electrochemical field stimulation. These approaches have achieved some positive results; however, limitations such as complex operations, construction costs, and environmental damage still exist.

Microwave exposure represents a good alternative for coal modification due to the advantages of instantaneous penetration, selective heating, feasible control, and environmental friendliness. Currently, microwave exposure has been preliminarily applied in the fields of coal dehydration, coal/oil desulfurization, hard rock fracturing, aid grinding, coal/biowaste pyrolysis, coking, oil shale exploitation, and heavy oil thermal recovery. Microwaves, as ultrahigh-frequency electromagnetic waves (3 × 10⁸ to 3 × 10¹² Hz) that consist of magnetic and electric fields perpendicular to each other, can cause high-frequency vibrations (billions for microwaves with a frequency of 2.45 × 10⁹ Hz) and friction of polar molecules or free electrons within their penetration range. The fundamental role of microwaves in the modification of materials lies in the force generated by electromagnetic waves on charged particles. Because the polarization vector produced under the action of the external electromagnetic field lags behind the electric field, the current will be in phase with the electric field, resulting in power dissipation inside the materials. In other words, the dielectric loss (the main contribution of power dissipation) is caused by the polarization of the materials (including electron polarization, dipole polarization, atomic polarization, ion polarization, and interface polarization) and the collisions of the dipoles or the collisions of the charges in the alternating electric field. The modification of coal by microwave exposure involves the interaction of the electromagnetic fields with the atoms and...
extranuclear electrons in coal molecules, leading to a change in the macromolecular structure of coal. For low-metamorphism lignite with rich branched chains, Liu et al. reported that the orderliness of the aromatic ring layer arrangement increased, the number of long chains and side chains decreased, and the proportion of C–O and –COO groups also decreased after a combination of microwave and ultrasonic treatments.49 Li et al. reported that microwave-assisted pyrolysis can decompose oxygen-containing functional groups and aliphatic hydrocarbons in the molecular structures of bituminous coal.47 Also, Tao et al. found that the vibration recovery force of the crystal lattice and the interaction force between atoms reduced in bituminous coal after microwave irradiation.48 For CBM extraction, the high-metamorphism bituminous coal and anthracite containing complex molecular structures, the response law of methane adsorption, and the molecular structures after microwave exposure still need better understanding.

Fourier transform infrared (FTIR) spectroscopy analysis, a nondestructive analysis method, can identify the type and relative content of surface groups such as –CH3, –CH2, C==C, C==O, –O–, and –OH groups through the vibrations of specific chemical bonds, especially some polar chemical bonds.50 Many characteristic parameters (fl, I1, I2, DOC1, DOC2, CH2/CH3, “A”, and “C”) in the coal molecular structures can be obtained by the deconvolution of FTIR spectra.51 Lin et al. semiquantitatively analyzed the changes in the functional groups and structural parameters of coal dust before and after explosion using the deconvolution of FTIR spectra.52 Chen et al. quantitatively studied the chemical functional groups in the macerals of coals of various ranks combined with reflectance micro-FTIR and KBr-FTIR spectroscopy analyses.53 In addition, Meng et al.,54 Liu et al.,55 Jiang et al.,56 and Xin et al.57 studied the change/evolution characteristics of the coal structural parameters by FTIR analysis in different experimental environments.

Therefore, research on the structural evolution characteristics of coal molecules modified by cyclical microwave exposure has become an important basic work for revealing the mechanism of methane adsorption in coal. In this study, methane adsorption measurements in coals of various metamorphic degrees before and after modification were carried out, and the adsorption parameters were obtained by Langmuir fitting. FTIR spectroscopy and peak fitting technology were utilized to characterize the changes in the structural parameters of coal molecules. Finally, the modification mechanism of methane adsorption in coal by cyclical microwave exposure was discussed.

2. RESULTS AND DISCUSSION

2.1. Influence of Cyclical Microwave Exposure on Methane Adsorption Behaviors in Coals. Figure 1 shows the methane adsorption capacity of three coals of different metamorphic degrees at pressures of 1, 2, 3, and 4 MPa. The methane adsorption amount of all coal samples before and after modification gradually increased, and the increment decreased with increasing gas pressure. After microwave exposure modification, the methane adsorption capacity of all the three coal samples showed a decreasing trend. Taking the 4 MPa pressure condition as an example, the isothermal adsorption capacity of methane in the SCG, SQ, and SH samples decreased from 25.9, 24.6, and 31.9 mL/g to 23.8, 22.7, and 28.7 mL/g after five microwave exposures, respectively, decreasing by 7.9, 7.6, and 10.1%. Then, the value decreased to 22.6, 22.0, and 26.7 mL/g after 10 microwave exposures, a decrease of 12.5, 10.6, and 16.4%, respectively. The results showed that microwave exposure can reduce the adsorption of methane in coal, and the cyclical modification effect decreased with increasing modification times. The main reason was that the structural parameters of coal molecules were changed within the microwave electromagnetic field. As a result, the positions and quantity of methane adsorption sites in coals were changed by microwave exposure.

The Langmuir equation was introduced to quantitatively characterize the adsorption behavior of methane in coal as follows

\[ V = \frac{V_L P}{P + P_L} \]

where \( P \) is the pressure of methane, MPa; \( V \) is the methane adsorption amount at pressure \( P \) mL/g; \( V_L \) is the Langmuir volume, which is the maximum amount of methane adsorbed in coal at a certain temperature, mL/g; and \( P_L \) is the Langmuir pressure, which is the pressure at half of the maximum adsorption amount, MPa.

Table 1 shows the Langmuir fitting parameters before and after cyclical microwave exposure. The methane saturated adsorption \( (V_L) \) of raw coal samples SCG, SQ, and SH was 29.2, 32.8, and 40.4 mL/g, respectively. Then, this value decreased to 26.9, 31.0, and 37.6 mL/g, respectively, after five cycles of microwave exposure and decreased to 25.7, 29.3, and 35.7 mL/g after 10 cycles. The Langmuir pressure \( (P_L) \) increased from 0.588, 0.844, and 0.942 MPa to 0.596, 0.959, and 1.032 MPa, respectively, after five cycles and increased to 0.626, 1.007, and 1.139 MPa after 10 cycles. Both the decrease in \( V_L \) and increase in \( P_L \) indicated a decline in the methane adsorption capacity in coal after cyclical microwave exposure. Fu et al. also observed this phenomenon.57 In contrast to that of samples SCG and SQ, the methane adsorption curve variation of sample SH was larger after 10 microwave exposures. This is because anthracite has a higher degree of metamorphism and graphitization, resulting in better electrical properties, which made the SH sample more sensitive to microwave exposure. The results were also found by Hong that the dielectric constant increased with the coal rank without considering the effects of moisture and minerals.58

Table 1. Methane Adsorption Data of Raw and Modified Coals

| Samples   | Modification Scheme | \( V_L \) (mL/g) | \( P_L \) (MPa) | Correlation Coefficient \( R^2 \) |
|-----------|---------------------|-----------------|----------------|----------------------------------|
| SCG       | Unmodified          | 29.2            | 0.588          | 0.9998                           |
|           | After 5 cycles      | 26.9            | 0.596          | 0.9992                           |
|           | After 10 cycles     | 25.7            | 0.626          | 0.9999                           |
| SQ        | Unmodified          | 32.8            | 0.844          | 0.9976                           |
|           | After 5 cycles      | 31.0            | 0.959          | 0.9998                           |
|           | After 10 cycles     | 29.3            | 1.007          | 0.9999                           |
| SH        | Unmodified          | 40.4            | 0.942          | 0.9988                           |
|           | After 5 cycles      | 37.6            | 1.032          | 0.9991                           |
|           | After 10 cycles     | 35.7            | 1.139          | 0.9981                           |

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three different rank coal raw samples and samples modified by microwave irradiation for 10 exposure cycles. After 10 cycles of microwave exposure, the absorption peaks near 3400, 2920, 2850, and 1030 cm\(^{-1}\) notably decreased in intensity. This is because under microwave exposure, the self-associating hydrogen bonds were broken, some alkane side chains such as methyl and methylene groups were released as gas, and some silicate minerals were decomposed. The peaks near 1700 cm\(^{-1}\) slightly increased in intensity, indicating an increase in the number of carboxyl groups. The peak intensities near 865, 800, and 745 cm\(^{-1}\) of SCG and SH all increased, which was due to the appearance of penta-, tri-, and disubstituted aromatic benzene rings, respectively, while the change in SQ was not obvious. The peak intensity near 1430 cm\(^{-1}\) of SH decreased remarkably due to the decomposition of carbonate, while the other two coals showed little change. In addition, the peaks near 540 and 460 cm\(^{-1}\) decreased in intensity, indicating the decomposition of sulfur-containing minerals.

2.2.2. Change in Aliphatic Structures. Figure 3a shows the change in \(f_\text{CH}\) of three different rank coals after microwave treatment cycles. The \(f_\text{CH}\) values of the three kinds of coal samples with different metamorphic degrees increased with increasing exposure times. The \(f_\text{CH}\) value of samples SCG, SQ, and SH all increased, which was consistent with the degree of coalification. After 10 exposure modifications, the \(f_\text{CH}\) value of SCG, SQ, and SH increased to 0.698, 0.791, and 0.974, respectively, corresponding to the increases of 5.4, 3.3, and 2.0%, respectively.

Figure 3b,c shows the changes in \(I_1\) and \(I_2\), representing the ratio of the relevant peak area of the stretching vibrations and out-of-plane deformation vibrations of aromatic \(-\text{CH}\) groups to that of the stretching vibrations of aromatic \(\text{C} \equiv \text{C}\) groups. After modification, \(\text{DOC}_1\) increased from 0.013, 0.063, and 0.172 to 0.021, 0.075, and 0.200, respectively, increasing by 59.0, 19.4, and 16.2%; \(\text{DOC}_2\) increased from 0.088, 0.275, and 0.932 to 0.137, 0.400, and 1.166, respectively, increasing by 55.6, 45.3, and 25.0%. The continued increase suggests that the degree of polycrystalline of the aromatic structure increased with increasing microwave exposure time, as shown in Figure 4.

2.2.3. Change in Aliphatic Structures. Figure 5a,b shows the change in the length of aliphatic side chains and the capacity of hydrocarbon generation. The \(CH_2/CH_3\) value of unmodified samples was in the order SCG > SH > SQ, while the total amount of \(-\text{CH}_2\) and \(-\text{CH}_3\) groups was in the order SCG > SQ > SH (as shown in Figure 2). The reason for this phenomenon was that several jumps occurred in the process of coalification with the increase in \(R_{\text{O,max}}\). The SCG sample was a type of bituminous coal with the lowest coalification degree and a large number of aliphatic side chains. Therefore, the \(CH_2/CH_3\) value of the raw SCG samples was the largest. Then, the first jump of coalification (\(R_{\text{O,max}}\) approximately greater than 0.6%) occurred, and the aliphatic functional groups and alkane side chains connected to the aromatic core condensed rings began to release as volatiles composed of \(\text{CH}_4\), \(\text{CO}_2\), and \(\text{H}_2\text{O}\). Meanwhile, bituminization began to take place, and asphaltens were produced. During the second coalification jump (\(R_{\text{O,max}}\) approximately equal to 1.3–1.7%), a large number of hydrogen-rich aliphatic side chains were broken and shortened, and a large number of small molecular alkanes were released, resulting in a sharp decrease in the \(CH_2/CH_3\) value. Therefore, the \(CH_2/CH_3\) value of raw SQ samples was minimal. After the third coalification jump (\(R_{\text{O,max}}\) approximately equal to 2.5%) in SH, the breaking of alicyclic bonds increased the relative methylene content and thus increased the \(CH_2/CH_3\) value.

After microwave modification, the \(CH_2/CH_1\) and “A” values of coal samples of various ranks all showed a declining trend, indicating a reduction in the length of alkane side chains. The reason was that the chemical bonds with weak energy were broken under the microwave exposure treatment. The exfoliated methyl, ethyl, and propyl groups were released in the form of small molecular alkanes, as shown in Figure 6. The \(CH_2/CH_1\) and “A” values of SH coal appeared to have changed the most because the total number of side chains of SH was much less than that of SCG and SQ, resulting in a more significant change in the ratio of methylene to methyl groups.

2.2.4. Change in Oxygen-Containing Functional Groups. Figure 7 shows the changes in the maturities of organic matter in coals before and after modification. After modification, “C” of all the three coals increased. The reason is that the oxidation of carboxyl, aliphatic, hydroxyl, and aldehyde groups increased the content of carboxyl groups, even though a small number of carboxyl groups decomposed at the higher temperatures induced by microwave exposure. The \(\text{C} \equiv \text{C}\) group abundance of the SCG samples decreased slightly, while the changes in SQ and SH were not obvious. As a result, it can be calculated from eq 12 that the maturity of organic matter in modified coals increased after microwave exposure.

2.2.5. Change in Hydroxyl Groups. The abundance of hydroxyl groups in the SCG, SQ, and SH samples all decreased after cyclical microwave exposure due to the decrease in free \(-\text{OH}\), self-associated \(-\text{OH}\), and phenol/alcohol \(-\text{OH}\) groups. The free \(-\text{OH}\) group evaporated as steam due to the heating...
The effect of microwaves, and the hydrogen bond in self-associated $\text{−OH}$ was broken by microwave exposure.

Complex chemical reactions take place between phenolic hydroxyl groups and alcoholic hydroxyl groups or between them and their surrounding groups under microwave catalysis. A schematic diagram of the microwave catalytic reactions is shown in Figure 8.

2.3. Relationship between the Adsorption Capacity Variation and Molecular Structure Variation. The modification mechanism of microwave exposure on coal lies in the resulting changes in coal molecular structures. Figure 9 shows the relationship between the methane saturated adsorption capacity and the molecular structure parameters of coals. During the process of cyclical modification, the

Figure 3. Quantitative characterization of the aromatic structure parameters of three different rank coal samples before and after cyclical microwave exposure. (a–e) Changes in $f_e$, $I_1$, $I_2$, $\text{DOC}_1$, and $\text{DOC}_2$.

Figure 4. Schematic diagram of aromatic polycondensation. C: dark gray; H: light gray.

Figure 8. A schematic diagram of the microwave catalytic reactions.
adsorption capacity changed linearly or exponentially with the change in structural parameters. The polycondensation of aromatic rings, the breaking and shedding of methyl/methylene groups, the oxidation of oxygen-containing functional groups, and the removal of hydroxyl groups all affect the changes in the number of methane adsorption sites. In particular, the decrease in the number of alkane side chains (Figure 9f) and the oxidation of carboxyl groups (Figure 9h) made the largest contributions to the reduced methane adsorption performance in coal. Zhang et al. found that a decrease in alkane side chain abundance reduced the methane adsorption capacity.59 Meng et al. and Hao et al. found that pore entrances may be blocked and that the dispersed interactions of methane with small pore walls may be reduced by oxygen-containing functional groups; that is, a higher oxygen content would weaken the methane adsorption performance in coals. In addition, the decomposition of some sulfur-containing minerals such as pyrite weakens the methane adsorption capacity in coal.

3. IMPLICATIONS AND SIGNIFICANCE
The coal matrix, water, and minerals within the microwave penetration distance can all be rapidly heated by microwaves. Coal seams beyond the microwave penetration distance need to be heated by heat conduction. Previous studies have shown that temperature increases in reservoirs can improve the extraction efficiency of CBM.62,63 By the COMSOL numerical simulation, Huang et al.,64,65 Li et al.,66 and Hong et al. found that microwave irradiation can increase the temperature of coal seams rapidly and has great application prospects in enhancing CBM extraction. Wang et al. found through real-time microwave loading experiments that microwave irradiation can effectively accelerate the methane desorption rate in coal.68,69 The symbol $D_p$ is introduced to quantitatively characterize the penetration depth of microwaves in the coal stratum. It is defined as the distance where the microwave power decays to $e^{-1}$ of its surface power and can be obtained by eq 2.65,70

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Figure 5. Quantitative characterization of aromatic structure parameters of three different rank coal samples before and after cyclical microwave exposure. (a,b) Changes in $CH_2/CH_3$ and “A”.

Figure 6. Schematic diagram of alkane side chain scission under microwave exposure.

Figure 7. Quantitative characterization of the maturity of organic matter in three different rank coal samples before and after cyclical microwave exposure.

Figure 8. Schematic diagram of microwave catalytic reactions.
where $\lambda_0$ represents the microwave wavelength in vacuum, m; $\varepsilon_r'$ represents the real part of the relative permittivity of coal, dimensionless; and $\varepsilon_r''$ represents the imaginary part of the relative permittivity of coal, dimensionless.

Considering that the influence range (irradiation zone and conduction zone) of a single microwave launcher is not wide enough to stimulate the reservoir, it is necessary to arrange multiple sets of microwave excitation devices. Coal is relatively transparent to microwaves; thus, the penetration depth is approximately on the scale of meters.\textsuperscript{71,72} In addition, eq 2 shows that the wavelength is proportional to the penetration distance of the microwaves. In engineering applications, a
lower microwave frequency could be chosen to achieve a better effect.

4. CONCLUSIONS

(1) The variations in methane saturated adsorption capacity and molecular structure parameters with microwave exposure times were characterized by CH₄ adsorption and FTIR tests. After exposure, the methane saturated adsorption capacity showed a continuously decreasing trend. The molecular structural parameters \( f_{\text{ar}}, I_1, I_2, DOC_1, DOC_2, \) and “C” increased, while \( CH_2/CH_3 \) and “A” decreased.

(2) The polycondensation of aromatic rings, the release of alkane side chains, and the oxidation of oxygen-containing functional groups caused by microwave exposure are the reasons for the changes in coal molecular structure parameters. The last two aspects have a dominant effect on the adsorption of methane by reducing the adsorption sites of methane.

(3) Bituminous coal with two metamorphic degrees and anthracite were analyzed and discussed by FTIR and CH₄ adsorption tests after microwave exposure, and more kinds of different metamorphic degree coals (lignite, more bituminous coal with different metamorphic degrees, and anthracite with higher metamorphic degree) via more convincing means of characterization (X-ray diffraction, high-resolution transmission electron microscopy, pore structure, and chemical compositions) will be tested and analyzed in our further research.

5. METHODS

5.1. Sample Preparation. The samples of long-flame coal (SCG), coking coal (SQ), and anthracite (SH) prepared for the experiments were obtained from the working faces of 6up115, 15201, and 15303, which belong to the Suancigou coal mine (Ordos Basin, Inner Mongolia, China), Shaqu no. 2 coal mine (Linxing block, Ordos Basin, Shanxi, China), and Sihe no. 2 well (Qinshui Basin, Shanxi, China), respectively, which are located in no. 6 coal seam (upper part of the second rock section of the Carboniferous Taiyuan Formation), no. 5 coal seam (lower part of the Shanxi Formation), and no. 15 coal seam (the top of the first section of the Taiyuan Formation), respectively. All the manually selected coal samples retained the primary sedimentary structure with complete and clear primary bedding, and only a small number of endogenous and exogenous fractures were developed. The samples were sealed carefully with plastic film while underground and sent to the laboratory as soon as possible to avoid changes in their chemical composition caused by oxidation. Before the experiments, the coal samples were ground and sieved to obtain sizes of 60–80 mesh and <200 mesh, respectively.

The mean maximum vitrinite reflectance \( (R_0,\text{max}) \), proximate analysis, and ultimate analysis followed the standards of GB/T 6948-2008, GB/T 212-2008, and GB/T 476-2001, respectively. The analysis results are shown in Table 2. The metamorphic degree of sample SH is stronger than that of sample SQ, and sample SCG has the smallest metamorphic degree.

Table 3. Positions and Assignments of the Absorption Peaks Corresponding to the Hydroxyl Groups in Coal

| Wavenumber (cm\(^{-1}\)) | Assignment of the Absorption Peak |
|---------------------------|----------------------------------|
| 2800–3100                 | OH—N                            |
| 3200                      | ring OH                         |
| 3300                      | OH—ether O                      |
| 3516                      | self-associated OH              |
| 3516                      | OH—\( \pi \) bond               |
| 3611                      | free OH                         |
5.2. Experimental Process and Apparatus. The experimental procedure for cyclical microwave exposure is shown in Figure 10. The SCG samples were exposed for 120 s in the resonant cavity of the microwave oven and then they were removed and cooled naturally in air for 300 s. With this treatment process, the modification procedure of coal samples was completed after 10 cycles. The appropriate amounts of raw coal samples and modified samples after each cycle were taken for the methane adsorption test and FTIR test. Before the test, the samples were dried to a constant weight in a vacuum drying oven at 373.15−378.15 K to remove free water from the coal samples. The cyclical modification experiments, methane adsorption tests, and FTIR tests of the SQ and SH coal samples were carried out with the same method.

The P70F20CL-DG(B0) microwave oven produced by Guangdong Galanz Company was used to perform cyclical irradiation modification experiments of coal samples. The dimensions of the resonator cavity were 180 mm × 315 mm × 329 mm. The frequency of the microwave generator was 2450 M ± 50 Hz, and its power was set to 700 W.

A 3H-2000PHD high-pressure gas adsorption and desorption velocity analyzer produced by Beishide Instrument Technology Co., Ltd. was applied to perform the methane adsorption tests. During the tests, the coal samples were first degassed for 300 min in a vacuum environment at a temperature of 378.15 K and then maintained in the environment for 120 min. Next, methane adsorption was started. The maximum adsorption pressure was set to 4 MPa, with an adsorption temperature of 298.15 K, an adsorption equilibrium time of 1800 s, and an equilibrium standard deviation of 0.008 MPa. Samples with sizes of 60−80 mesh were used, and the operations met the requirements of the tests.3,23

A Nicolet iS5 FTIR instrument produced by Thermo Fisher was used to carry out the FTIR tests. The detection wavenumber range of the device was 400−4000 cm⁻¹ with a resolution of 4 cm⁻¹. Before the test, 1 mg coal samples with a size of <200 mesh and 150 mg spectral pure KBr were dried and then they were combined in an agate mortar. The sample mixtures were ground to a size of <2 μm and turned gray to avoid errors caused by scattered light. Next, the samples were placed into a pressing die and pressed on a hydraulic press at 8000 kPa/cm² for 30 s, becoming transparent tablets with a diameter of 13 mm. In each scan, a pure KBr tablet in the same experimental environment was used as a reference for background scanning.

5.3. Experimental Data Processing. 5.3.1. Peak Fitting of the FTIR Spectrum. The peaks displayed in the FTIR spectrum are usually the superposition of multiple peaks, which makes it difficult to quantitatively analyze the changes of each group directly with the original FTIR spectrum. The method of peak fitting can feasibly identify each subpeak and quantitatively analyze its parameters, including peak position, peak height, peak half-width, and peak area.

The peak analyzer module in Origin 2017 software was used for peak fitting. The peak type was set as Gaussian. The approximate position and number of subpeaks were preliminarily determined by the second derivative of a spectral line. In the process of fitting, parameters such as peak position, peak height, and peak half-width were adjusted by fitting the control option, and the least-squares method was used for iterative calculation until the sum of squares of residual error was minimal. The fitting data need to be normalized to calculate the structural parameters.

Figure 11 shows the fitting results of the FTIR spectrum of raw SH samples. The regions of 900−700, 1800−1000, 3000−2800, and 3600−3000 cm⁻¹ correspond to the aromatic structures, oxygen-containing functional groups, aliphatic structures, and hydroxyl groups of coal surface groups, respectively.

5.3.2. Quantitative Characterization of the Molecular Structure Parameters. The molecular structure parameters of 3f₁, f₁, f₂, f₃, DOCl, DOCh, CH₃/CH₂ “A”, and “C” can be calculated by eqs 3−12, which were obtained from previous studies.3,77

\[ f_{\lambda} = 1 - \frac{C_{\lambda}}{C_{\lambda0}} \]  

\[ C_{\lambda0} = \frac{(H_{\lambda0}/H_{\lambda})/(H_{\lambda0}/C_{\lambda})}{H_{\lambda}/C_{\lambda0}} \]  

\[ H_{\lambda} = \frac{A_{3000−2800}}{A_{3000−2800} + A_{900−700}} \]  

\[ I_1 = \frac{A_{3100−3000}}{A_{3000−2800}} \]  

\[ I_2 = \frac{A_{900−700}}{A_{3000−2800}} \]  

\[ DOCl = \frac{A_{3100−3000}}{A_{1600}} \]  

\[ DOC_1 = \frac{A_{900−700}}{A_{1600}} \]  

\[ CH_2 = \frac{A_{2940−2900}}{A_{3000−2940}} \]  

\[ CH_3 = \frac{A_{2940−2900}}{A_{3000−2940}} \]  

\[ “A” = \frac{A_{3000−2800}}{A_{3000−2800} + A_{1600}} \]  

\[ “C” = \frac{A_{1800−1650}}{A_{1800−1650} + A_{1600}} \]  

where \( C_{\lambda0}/C_{\lambda} \) is the percentage of aliphatic carbon to total carbon; \( H_{\lambda0}/H_{\lambda} \) is the percentage of aliphatic hydrogen to total hydrogen; \( H_{\lambda0}/C_{\lambda0} \) is the ratio between total hydrogen atoms and total carbon atoms, which can be calculated by ultimate analysis; \( H_{\lambda}/C_{\lambda} \) is the amount ratio between aliphatic hydrogen atoms and aliphatic carbon atoms, which is approximately 1.8; \( A_{3100−3000} \) is the region of peaks attributed to the stretching vibrations of aromatic C–H groups; \( A_{3000−2800} \) and \( A_{900−700} \) are the regions of absorption peaks corresponding to the aliphatic structures and aromatic structures, respectively; and \( A_{2940−2900} \) and \( A_{3000−2940} \) denote the regions of absorption peaks of −CH₂ and −CH₃ groups, respectively. Among these, −CH₂ groups mainly constitute the straight part of aromatic side chains and aliphatic chains, while −CH₃ groups constitute the branched part. \( A_{1800−1650} \) represents the region of peaks corresponding to the vibrations of C=O groups. \( A_{1600} \) is the region from the absorption peak attributed to the C=C vibrations of aromatic structures.
5.3.3. Hydroxyl Groups. According to the different association modes of hydrogen bonds, the hydroxyl groups in coal can be classified into six types, as shown in Table 3.78,79

DATA AVAILABILITY STATEMENT
The data used to support the findings of this study are available from the corresponding author upon request.

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Notes
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REFERENCES
(1) Yan, F.; Lin, B.; Zhu, C.; Zhou, Y.; Liu, X.; Guo, C.; Zou, Q. Experimental investigation on anthracite coal fragmentation by high-voltage electrical pulses in the air condition: Effect of breakdown voltage. Fuel 2016, 183, 583–592.
(2) Yuan, L. Strategic thinking of simultaneous exploitation of coal and gas in deep mining. J. China Coal Soc. 2016, 41, 1–6.
(3) Pan, Z.; Wood, D. A. Coalbed methane (CBM) exploration, reservoir characterisation, production, and modelling: A collection of published research (2009-2015). J. Nat. Gas. Sci. Eng. 2015, 26, 1472–1484.
(4) Geng, M.; Chen, H.; Chen, Y.; Zeng, L.; Chen, S.; Jiang, X. Methods and results of the fourth round national CBM resources evaluation. Coal Sci. Technol. 2018, 46, 64–68.
(5) Gao, C.; Liu, D.; Li, Z.; Cai, Y.; Fang, Y. Fluid performance in coal reservoirs: A comprehensive review. Geofluids 2021, 2021, 6611075.
(6) Li, S.; Ni, G.; Nie, B.; Lu, S.; Li, X.; Wang, G. Microstructure characteristics of lignite under the synergistic effect of oxidizing acid and ionic liquid [Bmim][Cl]. Fuel 2021, 289, 119940.
(7) Ji, Y.; Zhang, Y.; Huang, Z.; Shao, Z.; Gao, Y.; Xiao, S. Variation characteristics of molecular structure unit during low-temperature oxidation of lignite coal. J. Cent. South Univ. 2020, SI, 2614–2623.
(8) Qin, L.; Wang, P.; Li, S.; Lin, H.; Wang, R.; Wang, P.; Ma, C. Gas adsorption capacity changes in coals of different ranks after liquid nitrogen freezing. Fuel 2021, 292, 120404.
(9) Wang, Z.; Zhang, S.; Zhang, X.; Li, P.; Li, J. Effect of microstructure and chemical composition of coal on methane adsorption. J. Nat. Gas. Sci. Eng. 2020, 82, 103507.
(10) Mirzaei, S.; Ahmadpour, A.; Shahsavand, A.; Nakhai Pour, A.; LotfiKatooli, L.; Garmroodi Asil, A.; Poulabi, B.; Arami-Niya, A. Experimental and simulation study of the effect of surface functional groups decoration on CH4 and H2 storage capacity of microporous carbons. Appl. Surf. Sci. 2020, 533, 147487.
(11) Yu, S.; Zhu, Y.; Li, W. Macromolecule simulation and CH4 adsorption mechanism of coal vitrinite. Appl. Surf. Sci. 2017, 396, 291–302.
(12) Han, J.; Bogomolov, A. K.; Makarova, E. Y.; Yang, Z.; Lu, Y.; Li, X. Molecular simulations on adsorption and diffusion of CO2 and CH4 in moisture coals. Energy Fuels 2017, 31, 13528–13535.
(13) Kang, G.; Kang, T.; Guo, J.; Kang, J.; Zhang, R.; Zhang, X.; Zhao, G.; Zhang, B.; Li, L.; Zhang, L. Effect of electric potential gradient on methane adsorption and desorption behaviors in lean coal by electrochemical modification: Implications for coalbed methane development of Donggu mining. China. ACS Omega 2020, 5, 24073–24080.
(14) Liang, W.; Yan, J.; Zhang, B.; Hou, D. Review on coal bed methane recovery theory and technology: Recent progress and perspectives. Energy Fuels 2021, 35, 4633–4643.
(15) Liu, S.; Li, X.; Wang, D.; Zhang, D. Experimental study on temperature response of different ranks of coal to liquid nitrogen soaking. Nat. Resour. Res. 2021, 30, 1467–1480.
(16) Qin, L.; Wang, P.; Li, S.; Lin, H.; Zhao, P.; Ma, C.; Yang, E. Gas adsorption capacity of coal frozen with liquid nitrogen and variations in the proportions of the organic functional groups on the coal after freezing. Energy Fuels 2021, 35, 1404–1413.
(17) Wang, K.; Pan, J.; Wang, E.; Hou, Q.; Yang, Y.; Wang, X. Potential impact of CO2 injection into coal matrix in molecular terms. Chem. Eng. J. 2020, 401, 120671.
(18) Cheng, Y.; Zeng, M.; Lu, Z.; Du, X.; Yin, H.; Yang, L. Effects of supercritical CO2 treatment temperatures on mineral composition, pore structure and functional groups of shale: implications for CO2 sequestration. Sustainability 2020, 12, 3927.
(19) Ge, Z.; Zeng, M.; Cheng, Y.; Wang, H.; Liu, X. Effects of supercritical CO2 treatment temperature on functional groups and pore structure of coals. Sustainability 2019, 11, 7180.
(20) Sun, Y.; Zhai, C.; Ma, H.; Xu, J.; Yu, X.; Wang, Y. Changes of coal molecular and pore structure under ultrasonic stimulation. Energy Fuels 2021, 35, 9847–9859.
(21) Li, Y.; Guo, Y.; Wang, D. Coal surface structure and gas adsorption under direct current electric field treatment. J. China Coal Soc. 2016, 41, 786–792.
(22) Yan, F.; Xu, J.; Lin, B.; Peng, S.; Zou, Q.; Zhang, X. Effect of moisture content on structural evolution characteristics of bituminous coal subjected to high-voltage electrical pulses. Fuel 2019, 241, 571–578.
(23) Zhang, X.; Zhang, R.; Kang, T.; Hu, Y.; Li, C. Experimental and mechanistic research on methane adsorption in anthracite modified by electrochemical treatment using selected electrode materials. Sci. Rep. 2019, 9, 17163.
(24) Zhang, X.; Kang, T.; Hou, M.; Kang, J.; Guo, J.; Li, L.; Zhang, R.; Hu, Y. Experimental research on the effects of electrode materials on methane adsorption and desorption in anthracite modified by electrochemical treatment. Chin. J. Geophys. 2020, 63, 2466–2477.
(25) Wang, Z.; Wang, X. Promotion effects of microwave heating on coalbed methane desorption compared with conductive heating. Sci. Rep. 2021, 11, 9618.

(26) Ge, L.; Zhang, Y.; Wang, Z.; Zhou, J.; Cen, K. Effects of microwave irradiation treatment on physiochemical characteristics of Chinese low-rank coals. Energy Convers. Manage. 2013, 71, 84−91.

(27) Ge, L.; Liu, X.; Feng, H.; Chu, H.; Xu, C.; Zhang, Y.; Wang, Z. The Influence of Anionic Additives on the Microwave Dehydration Process of Lignite. Energy Fuels 2020, 34, 9401−9410.

(28) Li, C.; Liao, J.-J.; Yin, Y.; Mo, Q.; Chang, L.-P.; Bao, W.-R. Kinetic analysis on the microwave drying of different forms of water in lignite. Fuel Process. Technol. 2018, 176, 174−181.

(29) Zhang, Z.; Yan, G.; Zhu, G.; Zhao, P.; Ma, Z.; Zhang, B. Using microwave pretreatment to improve the high-gradient magnetic-separation desulfurization of pulverized coal before combustion. Fuel 2020, 274, 117826.

(30) Vishnu Priya, M. L. S. N.; Arunraj, B.; Rajesh, N. Twin-fold new methodology arising from microwave induced carbonization of newspaper waste for the adsorptive desulfurization of model oil. Fuel 2021, 299, 120873.

(31) Zheng, Y. L.; Ma, Z. J.; Yang, S. Q.; Zhao, X. B.; He, L.; Li, J. C. A microwave thermal irreversibility index (MFI) of hard igneous rocks. Int. J. Rock Mech. Min. Sci. 2021, 138, 104566.

(32) Dekay, S. M.; Rafezi, H.; Hassanii, F.; Kermani, M.; Sasmoto, A. P. Experimental investigation on the effects of microwave irradiation on kimberlite and granite rocks. J. Rock Mech. Geotech. Eng. 2021, 13, 267−274.

(33) Singh, V.; Dixit, P.; Venugopal, R.; Venkatesh, K. B. Ore pretreatment methods for grinding: Journey and prospects. Miner. Process. Extr. Metall. Rev. 2019, 40, 1−15.

(34) Meng, Y.; Yan, Y.; Jiang, P.; Zhang, M.; Oladejo, J.; Wu, T.; Pang, C. H. Investigation on breakage behaviour of oil shale with high grinding resistance: A comparison between microwave and conventional thermal processing. Chem. Eng. Process. 2020, 151, 107909.

(35) Reddy, B. R.; Vinu, R. Evidence of interactions in microwave-assisted co-pyrolysis of different varieties of coals. J. Energy Inst. 2021, 95, 18−29.

(36) Lin, Y.-L.; Zheng, N.-Y. Biowaste-to-biochar through micro-FTIR spectroscopy. Energy 2021, 225, 120213.

(37) Binner, E.; Mediero-Munoyerro, M.; Huddle, T.; Kingman, S.; Dodds, C.; Dimitrakis, G.; Robinson, J.; Lester, E. Factors affecting the microwave cooking of coals and the implications on microwave cavity design. Fuel Process. Technol. 2014, 125, 8−17.

(38) Binner, E.; Lester, E.; Kingman, S.; Dodds, C.; Robinson, J.; Wu, T.; Wardle, P.; Mathews, J. P. A review of microwave coal processing. J. Microwave Power Electromagn. Energy 2014, 48, 35−60.

(39) Zhu, J.; Li, Y.; Yang, Z.; Duan, M. Three-dimensional numerical simulation on the thermal response of oil shale subjected to microwave heating. Chem. Eng. J. 2021, 407, 127197.

(40) He, L.; Ma, Y.; Yue, C.; Wu, J.; Li, S.; Wang, Q.; Wang, B. Transformation mechanisms of organic S/N/O compounds during microwave pyrolysis of oil shale: A comparative research with conventional pyrolysis. Fuel Process. Technol. 2021, 212, 106065.

(41) Adam, M.; Anbari, H.; Hart, A.; Wood, J.; Robinson, J. P.; Rigby, S. P. In-situ microwave-assisted catalytic upgrading of heavy oil: Experimental validation and effect of catalyst pore structure on activity. Chem. Eng. J. 2021, 413, 127420.

(42) Shang, H.; Yue, Y.; Zhang, J.; Wang, J.; Shi, Q.; Zhang, W.; Liu, L.; Omar, S. Effect of microwave irradiation on the viscosity of crude oil: A view at the molecular level. Fuel Process. Technol. 2018, 170, 44−52.

(43) Ximing, Z. H. H.; Hu, X.; Lai, S. The research into kinetic principle of microwave effect on chemical reaction. J. South China Univ. Technol. (Nat. Sci.) 1997, 9, 46−50.

(44) Amini, A.; Latifi, M.; Chaouki, J. Electrification of materials processing via microwave irradiation: A review of mechanism and applications. Appl. Therm. Eng. 2021, 193, 117003.

(45) Mishra, R. R.; Sharma, A. K. Microwave—material interaction phenomena: Heating mechanisms, challenges and opportunities in material processing. Composites, Part A 2016, 81, 78−97.

(46) Liu, J.; Qu, S.; He, Z.; Yu, Y. Experiments and 3D Molecular Model Construction of Lignite under Different Modification Treatment. Processes 2020, 8, 399.

(47) Li, H.; Shi, S.; Lin, B.; Lu, J.; Ye, Q.; Lu, Y.; Wang, Z.; Hong, Y.; Zhu, X. Effects of microwave-assisted pyrolysis on the micro-structure of bituminous coals. Energy 2019, 187, 115866.

(48) Tao, G.; Cai, C.-c.; Chen, P.; Min, F.; Zhang, M. The characterization on organic sulfur occurrence in coking coal and mechanism of microwave action on thiophene. Spectros. Spectral Anal. 2020, 40, 1321−1327.

(49) Wu, M.; Hu, X.; Zhang, Q.; Xue, D.; Zhao, Y. Growth environment optimization for inducing bacterial mineralization and its application in concrete degradation. Constr. Build. Mater. 2019, 209, 631−643.

(50) Zhou, H.; Wu, C.; Pan, J.; Wang, Z.; Niu, Q.; Du, M. Research on molecular structure characteristics of vitrinite and inertinite from bituminous coal with FTIR, micro-raman, and XRD spectroscopy. Energy Fuels 2021, 35, 1322−1335.

(51) Lin, S.; Liu, Z.; Zhao, E.; Qian, J.; Li, X.; Zhang, Q.; Ali, M. A study on the FTIR spectra of pre- and post-explosion coal dust to evaluate the effect of functional groups on dust explosion. Process Saf. Environ. Prot. 2019, 130, 48−56.

(52) Chen, Y.; Mastalerz, M.; Schimmelmann, A. Characterization of chemical functional groups in macerals across different coal ranks via micro-FTIR spectroscopy. Int. J. Coal Geol. 2012, 104, 22−33.

(53) Meng, D.; Yue, C.; Wang, T.; Chen, X. Evolution of carbon structure and functional group during Shenmu lump coal pyrolysis. Fuel 2021, 287, 119538.

(54) Liu, X.; Song, D.; He, X.; Nie, B.; Wang, L. Insight into the macromolecular structural differences between hard coal and deformed soft coal. Fuel 2019, 245, 188−197.

(55) Jiang, J.; Zhang, S.; Longhurst, P.; Yang, W.; Zheng, S. Molecular structure characterization of bituminous coal in Northern China via XRD, Raman and FTIR spectroscopy. Spectrochim. Acta, Part A 2021, 255, 119724.

(56) Xin, H.-h.; Wang, D.-m.; Qi, X.-y.; Qi, G.-s.; Dou, G.-l. Structural characteristics of coal functional groups using quantum chemistry for quantification of infrared spectra. Fuel Process. Technol. 2014, 118, 287−295.

(57) Fu, X.; Lun, Z.; Zhao, C.; Zhou, X.; Wang, H.; Zhou, X.; Xu, Y.; Zhang, H.; Zhang, D. Influences of controlled microwave field irradiation on physicochemical property and methane adsorption and desorption capability of coals: Implications for coalbed methane (CBM) production. Fuel 2021, 301, 121022.

(58) Hong, Y. D. Ph.D. Thesis, China Univ. Min. Technol, 2017.

(59) Zhang, L.; Kang, T.; Kang, J.; Zhang, X.; Zhang, B.; Chai, Z.; Zhang, R.; Wang, Y.; Kang, G.; Zhao, G. Effect of cyclical microwave modification on the apparent permeability of anthracite: A case study of methane extraction in Sihe mine, China. ACS Omega 2021, 6, 15001−15011.

(60) Meng, J.; Zhong, R.; Li, S.; Yin, F.; Nie, B. Molecular model construction and study of gas adsorption of Zhaohuazhuang coal. Energy Fuels 2018, 32, 9727−9737.

(61) Hao, S.; Wen, J.; Yu, X.; Chu, W. Effect of the surface oxygen groups on methane adsorption on coals. Appl. Surf. Sci. 2013, 264, 433−442.

(62) Wang, Z.; Wang, X.; Zuo, W.; Ma, X.; Li, N. The influence of temperature on methane adsorption in coal: A review and statistical analysis. Adsorp. Sci. Technol. 2019, 37, 745−763.

(63) Guo, P.; Cheng, Y. Permeability prediction in deep coal seam: Heating mechanisms, challenges and opportunities in material processing. Composites, Part A 2016, 81, 78−97.

(64) Huang, J.; Xu, G.; Chen, Y.; Chen, Z. Simulation of microwave’s heating effect on coal seam permeability enhancement. Int. J. Min. Sci. Technol. 2019, 29, 785−789.
(65) Huang, J.; Xu, G.; Hu, G.; Kizil, M.; Chen, Z. A coupled electromagnetic irradiation, heat and mass transfer model for microwave heating and its numerical simulation on coal. *Fuel Process. Technol.* 2018, 177, 237–245.

(66) Li, H.; Shi, S.; Lin, B.; Lu, J.; Lu, Y.; Ye, Q.; Wang, Z.; Hong, Y.; Zhu, X. A fully coupled electromagnetic, heat transfer and multiphase porous media model for microwave heating of coal. *Fuel Process. Technol.* 2019, 189, 49–61.

(67) Hong, Y.-d.; Lin, B.-q.; Li, H.; Dai, H.-m.; Zhu, C.-j.; Yao, H. Three-dimensional simulation of microwave heating coal sample with varying parameters. *Appl. Therm. Eng.* 2016, 93, 1145–1154.

(68) Wang, Z.; Wang, X.; Ma, X.; Li, X.; Zhu, Z. Laboratory measurements of methane desorption behavior on coal under different modes of real-time microwave loading. *Adsorption* 2020, 26, 61–73.

(69) Wang, Z.; Ma, X.; Wei, J.; Li, N. Microwave irradiation’s effect on promoting coalbed methane desorption and analysis of desorption kinetics. *Fuel* 2018, 222, 56–63.

(70) Peng, Z.; Lin, X.; Li, Z.; Hwang, J.-Y.; Kim, B.-G.; Zhang, Y.; Li, G.; Jiang, T. Dielectric characterization of Indonesian low-rank coal for microwave processing. *Fuel Process. Technol.* 2017, 156, 171–177.

(71) Lester, E.; Kingman, S.; Dodds, C. Increased coal grindability as a result of microwave pretreatment at economic energy inputs. *Fuel* 2005, 84, 423–427.

(72) Kumar, H.; Lester, E.; Kingman, S.; Bourne, R.; Avila, C.; Jones, A.; Robinson, J.; Halleck, P. M.; Mathews, J. P. Inducing fractures and increasing cleat apertures in a bituminous coal under isotropic stress via application of microwave energy. *Int. J. Coal Geol.* 2011, 88, 75–82.

(73) Zhang, J.; Wei, C.; Zhao, C.; Zhang, T.; Lu, G.; Zou, M. Effects of nano-pore and macromolecule structure of coal samples on energy parameters variation during methane adsorption under different temperature and pressure. *Fuel* 2021, 289, 119804.

(74) He, X.; Liu, X.; Nie, B.; Song, D. FTIR and Raman spectroscopy characterization of functional groups in various rank coals. *Fuel* 2017, 206, 555–563.

(75) Jiang, J.; Yang, W.; Cheng, Y.; Liu, Z.; Zhang, Q.; Zhao, K. Molecular structure characterization of middle-high rank coal via XRD, Raman and FTIR spectroscopy: Implications for coalification. *Fuel* 2019, 239, 559–572.

(76) Li, X.; Zeng, F.; Wang, W.; Dong, K.; Cheng, L. FTIR characterization of structural evolution in low-middle rank coals. *J. China Coal Soc.* 2015, 40, 2900–2908.

(77) Guo, Y.; Bustin, R. M. Micro-FTIR spectroscopy of liptinite macerals in coal. *Int. J. Coal Geol.* 1998, 36, 259–275.

(78) Hao, P.-y.; Meng, Y.; Zeng, F.; Yan, T.; Xu, G. Quantitative study of chemical structures of different rank coals based on infrared spectroscopy. *Spectrosc. Spectral Anal.* 2020, 40, 787–792.

(79) Painter, P. C.; Sobkowiak, M.; Youtcheff, J. FT-i.r. study of hydrogen bonding in coal. *Fuel* 1987, 66, 973–978.