

Article

The Influence of Coal Microstructure on the Thermodynamic Behavior of Water Vapor Adsorption in Coal

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Abstract

The presence of water during coalbed methane development significantly affects gas adsorption and migration. However, the factors governing primary and secondary water vapor adsorption amounts and adsorption heats remain unclear. In this study, the chemical and pore structures of five coals with different ranks were characterized, and water vapor adsorption experiments were conducted at three temperatures. The variation patterns of water vapor adsorption and heat in coal were investigated, along with the factors influencing these parameters. More importantly, the factors affecting the primary and secondary adsorption amounts were examined, as well as the primary and secondary adsorption heats. The results indicate that the hydrophilic/hydrophobic properties of coal surfaces and the micropore fractal dimension are the primary factors influencing the amount of water vapor adsorption in coal. The oxygen-containing functional group structural parameter ‘C’ ranges from 0.22 to 0.55, and the micropore fractal dimension ranges from 2.26695 to 2.41057. The micropore fractal dimension exhibits the strongest influence on secondary adsorption ($r = 0.90$). The primary and secondary adsorption heats range from 30 to 73 kJ/mol and 34 to 47 kJ/mol, respectively. The initial adsorption heat of water vapor in coal exhibits a strong positive relationship with both the specific surface area (57.24–160.06 m²/g) and volume (0.0184–0.0515 cm³/g) of micropores, with $r > 0.90$.

Keywords: coal microstructure; water vapor adsorption; adsorption amount; adsorption heat



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1. Introduction

Amid the escalating global demand for natural gas, coalbed methane (CBM) has attracted attention worldwide for its use as an efficient and clean energy source [1,2]. China possesses abundant CBM geological resources, with 30.05×10^{12} m³ at burial depths shallower than 2000 m, ranking third globally [3,4]. Original coal reservoirs typically contain some moisture, and hydraulic measures (hydraulic fracturing, hydraulic cutting, hydraulic flushing, etc.) are commonly employed to enhance coal seam permeability and thereby improve CBM production [5,6], resulting in the long-term coexistence of CBM and water. Water in coal seams primarily exists in three forms: free water, adsorbed water, and crystal water [7]. Among these, adsorbed water in coal pores competes with CBM for adsorption sites and may lead to pore blockages, thereby influencing CBM adsorption, diffusion, and migration processes [8]. Therefore, a thorough understanding of

coal–water interactions in coal pores is essential for accurately evaluating CBM production and optimizing extraction strategies.

To characterize water vapor adsorption on coal, domestic and international scholars have conducted extensive isothermal adsorption experiments. Studies have demonstrated that water vapor adsorption isotherms on coal exhibit typical Type II characteristics, with the adsorption process comprising three phases: single-layer adsorption, then multilayer adsorption, and finally condensation in capillaries [9–11]. First, water molecules adsorb at the primary sites (mainly functional groups with oxygen) on coal surfaces. Subsequently, the adsorbed water molecules act as new sites for further adsorption and can attract more water molecules via hydrogen bonds to generate water clusters. These water clusters grow progressively until they fill the pores or undergo capillary condensation. To accurately predict the amount of water vapor adsorption, researchers have proposed various adsorption models, including the modified BET model, Dent model, Dubinin–Serpinsky model, and GAB model [12–15]. Among these, the modified BET model and the Dent model have been widely applied due to their ability to adequately describe the multilayer adsorption process.

Extensive research has demonstrated that water vapor adsorption is jointly influenced by external environmental factors (temperature and pressure) and inherent coal properties (coal rank, surface functional groups, pore structure, particle size, and mineral composition). Among external environmental factors, increasing pressure promotes water vapor adsorption, while elevated temperature inhibits it [16]. The influence of inherent coal properties on water vapor adsorption is more complex: the amount of water vapor adsorption exhibits a parabolic relationship with coal rank, initially declining and then rising as coal rank increases, which is closely connected to differences in chemical and pore structures among coals of different ranks [17]. As primary adsorption sites, functional groups containing oxygen are a key factor influencing water vapor adsorption [18]. Carboxyl, hydroxyl, carbonyl, and ether groups constitute the primary oxygen-containing functional groups found in coal [19], among which hydroxyl and carboxyl groups are the most hydrophilic [9,20]. Low-rank coals demonstrate higher water uptake due to their abundant oxygen-containing functional groups. Pore structure likewise exerts considerable influence, with moisture predominantly adsorbing in medium-sized (ranging from 2 to 50 nm) and very small pores (less than 2 nm) [21]. Parameters related to pore structure, notably pore volume and specific surface area, are strongly and positively related to how much water vapor is adsorbed [22]. In contrast, the water uptake of high-rank coals is primarily controlled by the degree of micropore development. Additionally, smaller coal particle sizes correspond to higher water uptake [23], and hydrophilic minerals in coal (such as clay minerals, including kaolinite and illite) also influence water vapor adsorption [24,25].

Adsorption thermodynamics can elucidate thermal evolution during the adsorption process and better characterize the interactions between coal and water vapor [26]. Current methods for studying water vapor adsorption thermodynamics mainly include adsorption thermodynamic models, molecular simulation, and differential scanning calorimetry (DSC). Among these, adsorption thermodynamic models typically utilize data on water vapor isothermal adsorption at different temperatures, combined with the Clausius–Clapeyron equation to calculate adsorption heat [27–29]. Molecular simulation methods involve modeling the macromolecular structure of coal and investigating the heat of water vapor adsorption at different temperatures using Monte Carlo methods [30,31]. Differential scanning calorimetry (DSC) directly obtains data on the thermal effects of water vapor adsorption by measuring real-time heat flow changes during the process [32,33]. Liu et al. processed isothermal adsorption experimental data from five coal samples at three temperatures (288 K, 298 K, and 308 K) using the modified BET model and calculated the heat of water vapor adsorption, which varied between 43 and 75 kJ/mol [34]. Liu et al. obtained

water vapor adsorption isotherms of three coal samples at 298 K, 303 K, and 308 K and proposed a water adsorption isotherm model that could quantify primary and secondary adsorption. Based on this, they derived an enhanced model to calculate the adsorption heat of water vapor on coal, with the results distributed between 45 and 77 kJ/mol [35]. Both studies revealed that the adsorption heat of water vapor tends to decrease as the adsorption amount increases.

In summary, previous research has primarily concentrated on how the chemical and pore structures of coal affect the amount of water vapor adsorption, while the influences of microstructure on primary and secondary adsorption capacities have yet to be investigated in depth. Furthermore, the variation patterns of primary and secondary adsorption heats of water vapor remain unclear, and the effects of microstructure on adsorption heat have not been elucidated. Therefore, this study systematically explored how the chemical and pore structures of coal affect the amount of water vapor adsorption and adsorption heat. In this work, five coal samples with varying metamorphic degrees were investigated. The chemical structures of the samples were characterized through Fourier transform infrared spectroscopy (FTIR) experiments, along with carbon-13 solid-state nuclear magnetic resonance (^{13}C -NMR). To characterize the pore structures of the five samples, high-pressure mercury intrusion porosimetry (MIP), low-temperature N_2 adsorption (LTN_2A), and low-temperature CO_2 adsorption (LTCO_2A) experiments were conducted, and pore fractal features across various scales were analyzed. Subsequently, water vapor adsorption experiments on coal were performed, and the adsorption data were processed using the modified BET model to investigate the adsorption and thermodynamic behaviors of water vapor on coal. This study provides new insights into the factors controlling primary and secondary water vapor adsorption amount in coal, as well as the variation patterns and influencing factors of adsorption heat, thereby contributing to a deeper understanding of coal–water interactions.

2. Materials and Methods

This section describes the experimental materials and analytical methods employed in this study. Five coal samples of different ranks were collected from various coal mines in China, and their basic properties are presented. The experimental instruments and data processing methods for chemical structure characterization (FTIR and ^{13}C -NMR) and pore structure characterization (MIP, LTN_2A , and LTCO_2A) are introduced, along with the apparatus and experimental conditions for water vapor adsorption experiments. In addition, the theoretical models for analyzing water vapor adsorption data, including the modified BET adsorption model and thermodynamic calculation methods for isosteric heat of adsorption, are also presented in this section.

2.1. Sample Collection and Preparation

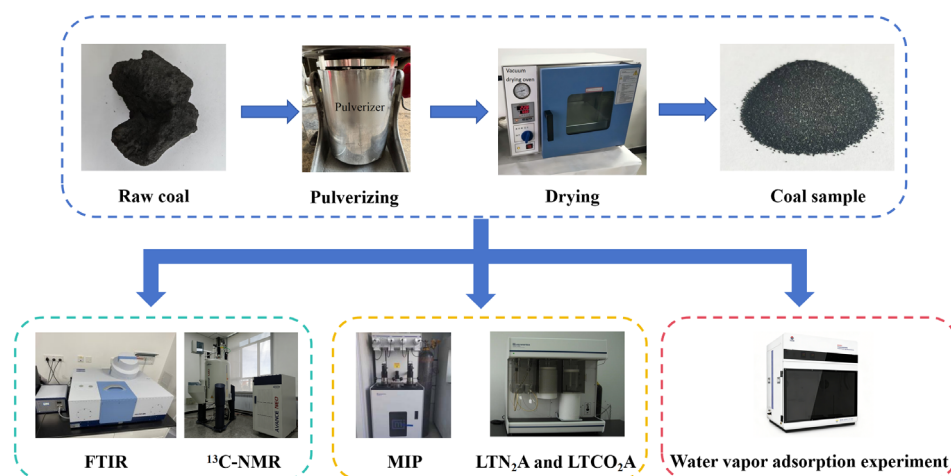
The five samples of coal of different ranks used in this study were sourced from Chengzhuang Coal Mine (CZ), Jinjia Coal Mine (JJ), Shoushan Coal Mine (SS), Daliuta Coal Mine (DLT), and Donghuai Coal Mine (DH), respectively. After they were collected from the mines, the samples were sealed in airtight containers and promptly transported to the lab. The samples were then crushed, sieved until particle sizes reached 60–80 mesh, sealed, and stored for subsequent experiments. Table 1 presents the characterization results of these five coal samples with respect to their proximate and ultimate analyses. The coal rank classification was determined according to the National Standard GB/T 5751-2009 [36].

Table 1. Proximate and ultimate analyses of the coal samples.

Coal Samples	Proximate Analysis (%)				Ultimate Analysis (%)					$R_{0,max}$ (%)	Coal Rank
	M_{ad}	A_{ad}	V_{daf}	FC_{ad}	C_{ad}	H_{ad}	O_{ad}	N_{ad}	S_{ad}		
CZ	0.72	13.88	8.83	77.86	77.59	2.84	3.48	1.21	0.28	2.37	Anthracite
JJ	0.54	15.2	10.54	75.38	76.63	3.3	2.89	1.2	0.24	2.04	Lean coal
SS	0.77	12.66	20.93	68.45	75.8	3.96	4.23	1.32	1.26	1.35	Coking coal
DLT	3.62	5.38	34.99	59.16	73.3	4.48	11.72	1.03	0.47	0.76	Fat coal
DH	3.17	42.02	51.01	26.85	39.33	3.48	9.06	1.57	1.37	0.58	Brown coal

Notes: M_{ad} , moisture on air-dried basis; A_{ad} , ash on air-dried basis; V_{daf} , volatile on dry-ash-free basis; FC_{ad} , fixed carbon, calculated as follows: $FC_{ad} = 100 - M_{ad} - A_{ad} - V_{ad}$; V_{ad} , volatile on air-dried basis; C_{ad} , carbon element on air-dried basis; H_{ad} , hydrogen element on air-dried basis; O_{ad} , oxygen element on air-dried basis; N_{ad} , nitrogen element on air-dried basis; S_{ad} , sulfur element on air-dried basis; $R_{0,max}$, maximum vitrinite reflectance.

Figure 1 illustrates the experimental workflow of this study. After pretreatment, the samples were subjected to three categories of experiments. Chemical structure characterization was performed using Fourier transform infrared spectroscopy (FTIR) and solid-state ^{13}C nuclear magnetic resonance (^{13}C -NMR). Pore structure characterization was conducted through high-pressure mercury intrusion porosimetry (MIP) for macropores, low-temperature N_2 adsorption (LTN₂A) for mesopores, and low-temperature CO_2 adsorption (LTCO₂A) for micropores. Finally, water vapor adsorption experiments were performed at three temperatures (303.15 K, 313.15 K, and 323.15 K) to investigate the adsorption behavior of coal.

**Figure 1.** Experimental workflow of this study.

2.2. Characterization of Coal Chemical Structure

The molecular structures of five coal samples with varying degrees of metamorphism were characterized using Fourier transform infrared spectroscopy (FTIR) and solid-state ^{13}C nuclear magnetic resonance (^{13}C -NMR).

2.2.1. FTIR Experiment

FTIR experiments were conducted on a VERTEX 80v infrared spectrometer manufactured by Bruker, Karlsruhe, Germany. The instrument features an evacuated optical bench with UltraScan™ interferometer, providing a spectral resolution better than 0.06 cm^{-1} and a spectral range of $50,000\text{--}5\text{ cm}^{-1}$. Prior to the experiments, samples were ground, dried, and then prepared using the KBr pellet method with a coal-to-KBr ratio of 1:100. Each sample underwent 16 scans over the wavenumber range of $400\text{--}4000\text{ cm}^{-1}$.

Fourier calculations were applied to process the infrared spectra, which helped distinguish different surface functional groups. The chemical structure parameters of the coal samples were obtained by performing peak deconvolution fitting on their infrared spectra using the PeakFit 4.12 software.

Aromaticity (f_a), an aromatic structural parameter of coal [37], represents the fractional content of aromatic carbon relative to total carbon. The calculation method is as follows:

$$\frac{H_{al}}{H} = \frac{H_{al}}{H_{al} + H_{ar}} = \frac{A_{2800-3000}}{A_{2800-3000} + A_{700-900}} \quad (1)$$

$$\frac{C_{al}}{C} = \left(\frac{H_{al}}{H} \times \frac{H}{C} \right) / \frac{H_{al}}{C_{al}} \quad (2)$$

$$f_{a1} = 1 - \frac{C_{al}}{C} \quad (3)$$

In these equations, H_{al}/H shows the fraction of aliphatic hydrogen to total hydrogen atoms, C_{al}/C is the ratio of aliphatic carbon to total carbon, H/C stands for the atomic ratio of hydrogen to carbon, and H_{al}/C_{al} is the hydrogen–carbon ratio in aliphatic clusters, usually taken as 1.8 [37].

$A(CH_2)/A(CH_3)$ provides a measure for assessing the aliphatic structure of coal [38]. CH_2 primarily represents the straight-chain segments of aliphatic chains, alicyclic rings, and aromatic hydrocarbon side chains, while CH_3 mainly constitutes the branched segments of aliphatic, alicyclic, and aromatic side chains. The ratio between the two indicates the aliphatic chain length and degree of branching in coal macromolecules. The calculation formula is given by:

$$\frac{A(CH_2)}{A(CH_3)} = \frac{A_{2900-2940}}{A_{2940-3000}} \quad (4)$$

‘C’ is the oxygen-containing functional group structural parameter of coal [38], indicating coal maturity. The formula is given by:

$$‘C’ = \frac{C = O}{C = O + C = C} = \frac{A_{1650-1800}}{A_{1650-1800} + A_{1600}} \quad (5)$$

2.2.2. ^{13}C -NMR Experiment

Solid-state ^{13}C nuclear magnetic resonance (^{13}C -NMR) spectra were acquired using a Bruker AVANCE III 600 MHz wide-bore NMR spectrometer (14.1 T; Bruker, Karlsruhe, Germany) equipped with a double-resonance MAS probe and 4 mm ZrO_2 rotors. The resonance frequency for ^{13}C detection was 150.9 MHz, and the sampling time was set to 4 ms with a 2 s cycle delay, a carbon–hydrogen cross-polarization contact time of 1000 μs , and a scan number of 2048. The calibration compound was adamantane.

The chemical structure parameters of coal samples were derived by performing peak fitting on the ^{13}C -NMR spectra using Origin 8.5 software. The aromaticity (f_a) represents the percentage of aromatic carbon to total carbon content [39], expressed as follows:

$$f_{a2} = \frac{C_{ar}}{C_{ar} + C_{al}} = \frac{A_{100-165ppm}}{A_{0-220ppm}} \quad (6)$$

Coal contains two types of aromatic carbons: protonated aromatic carbons f_a^H (100–129 ppm) and non-protonated aromatic carbons f_a^N . Non-protonated aromatic carbons include oxygen-bonded aromatic carbons f_a^O (148–165 ppm), substituted aromatic car-

bonds f_a^S (137–148 ppm), and bridgehead aromatic carbons f_a^B (129–137 ppm) [39]. The relationship among these parameters is:

$$f_{a2} = f_a^H + f_a^O + f_a^S + f_a^B \quad (7)$$

The ratio of bridgehead aromatic carbons to peripheral carbons is an important parameter reflecting coal structure [39], which can determine the average size of condensed aromatic rings in coal molecules, expressed as follows:

$$X_B = \frac{f_a^B}{f_a^H + f_a^O + f_a^S} \quad (8)$$

2.3. Pore Structure Characterization of Coal

Coal is a natural porous medium, with pore sizes ranging from millimeter to nanometer scales. A single experimental method can only characterize pore distribution at a certain scale and cannot thoroughly characterize the coal pore structure [40,41]. IUPAC classifies pores as macropores (>50 nm), mesopores (2–50 nm), and micropores (<2 nm). To fully analyze the pore structures in all five coal samples, three techniques were employed: high-pressure mercury intrusion porosimetry (MIP), low-temperature N₂ adsorption (LTN₂A), and low-temperature CO₂ adsorption (LTCO₂A).

2.3.1. MIP Experiments

Mercury intrusion data can effectively characterize coal macropores. The MIP measurements were conducted with an AutoPore V9620 high-pressure mercury porosimeter manufactured by Micromeritics, Norcross, GA, USA. The instrument is equipped with a high-precision capacitive detection system and an automatic mercury temperature sensor for precise mercury density calculation, with a measurable pore diameter range of 0.003–1100 µm, a maximum pressure of 60,000 psia, and a pressure resolution of 0.03 psia.

The relationship linking the pore diameter accessible to mercury to the applied pressure follows the Washburn relation [42], as shown in Equation (9), which allows the pore size to be derived.

$$r_p = -\frac{2\sigma\cos\theta}{P} \quad (9)$$

In this equation, r_p stands for pore radius, σ is mercury's surface tension, θ is the contact angle that the instrument measures, and P is the pressure.

Subsequently, using pore data for pores larger than 50 nm, combined with the thermodynamic fractal model [43], the fractal dimension of macropores was calculated according to Equation (10).

$$\ln\left(\frac{W_n}{r_n^2}\right) = D_{mac}\ln\left(\frac{V_n^{\frac{1}{3}}}{r_n}\right) + C \quad (10)$$

where W_n represents the surface energy for the n th mercury intrusion increment (J), r_n is the pore radius for the n th mercury intrusion (nm), and V_n is the pore volume for the n th mercury intrusion (cm³/g).

2.3.2. LTN₂A Experiment

The LTN₂A experiments were conducted on an ASAP2020 automatic specific surface area and porosity analyzer manufactured by Micromeritics, Norcross, USA, at 77 K. The instrument operates with a pressure range of 0–950 mmHg and a resolution up to 1×10^{-7} torr. The Barrett–Joyner–Halenda (BJH) theory was applied to calculate specific surface area, pore volume, and pore size distribution. Based on pore data for

2 nm < r < 50 nm, combined with the FHH fractal model [44], the fractal dimension of mesopores was calculated.

The FHH model is given by:

$$\ln V = A \ln \left[\ln \left(\frac{P_0}{P} \right) \right] + C \quad (11)$$

$$D_{mes} = A + 3 \quad (12)$$

where V stands for the volume of gas adsorbed at equilibrium pressure P , cm³/g; P_0 denotes the saturated vapor pressure value, MPa; A represents the linear fit slope between $\ln V$ and $\ln[\ln(P_0/P)]$; and C is a constant.

Substituting the low-temperature nitrogen desorption data into Equation (11) yields the slope, which allows us to calculate the mesopore fractal dimension (D_{mes}) through Equation (12).

2.3.3. LTCO₂A Experiment

Micropore characterization was conducted using LTCO₂A. LTCO₂A experiments were performed on an ASAP2020 automatic specific surface area and porosity analyzer, made by Micromeritics, USA, with the temperature set at 273.15 K. A density functional theory (DFT) model was used to obtain pore volume, specific surface area, and pore size distribution [45]. Based on pore data with apertures smaller than 2 nm, combined with the Sierpinski fractal model [46], the fractal dimension of microporous pores was calculated.

The Sierpinski fractal model can be expressed as follows:

$$\ln V = (3 - D_{mic}) \ln(P - P_t) \quad (13)$$

where P_t is defined as the pressure corresponding to the initial point on the CO₂ adsorption isotherm. Substituting CO₂ adsorption data at low temperature yields the micropore fractal dimension (D_{mic}).

2.4. Water Vapor Adsorption Experiment and Theoretical Models

2.4.1. Water Vapor Adsorption Experiment

Coal–water vapor adsorption isotherms were measured using a BSD-VVS multi-station gravimetric dynamic vapor sorption analyzer manufactured by BeiShiDe Instrument Technology Co., Ltd., Beijing, China. The instrument employs a microbalance with a resolution of 1 µg and a weighing capacity of 5000 mg. The relative pressure (P/P_0) control range is 0.05–98%, and the adsorption temperature range is −5 °C to 250 °C. Before adsorption, coal samples were dried in situ at 1×10^{-6} Pa and 80 °C until the weight remained constant. Subsequently, the vapor pressure was gradually raised to temperatures of 303.15 K, 313.15 K, and 323.15 K (with nitrogen as the carrier gas for water vapor). Constant vapor pressure was maintained while the weight change was continuously monitored and recorded until mass equilibrium was reached.

2.4.2. Water Vapor Adsorption Theory

The Brunauer–Emmett–Teller (BET) model was the first model commonly applied to vapor adsorption; however, it can only fit adsorption data for $P/P_0 < 0.35$ [47]. The modified BET model allows for better fitting of data across the entire relative pressure range. The form of the modified BET model is as follows [48]:

$$q = \frac{q_m K_1 \frac{P}{P_0}}{\left(1 - K_2 \frac{P}{P_0}\right) \left(1 - K_2 \frac{P}{P_0} + K_1 \frac{P}{P_0}\right)} \quad (14)$$

The adsorption isotherm data obtained from water vapor adsorption experiments were fitted using Equation (14) with the Levenberg–Marquardt algorithm in Origin 8.5 software to obtain the model parameters q_m , K_1 , and K_2 [49]. Subsequently, the obtained parameters were substituted into Equations (15) and (16) to calculate the water vapor adsorption amounts at primary sites and secondary sites.

$$q_1 = \frac{q_m K_1 \frac{P}{P_0}}{1 - K_2 \frac{P}{P_0} + K_1 \frac{P}{P_0}} \quad (15)$$

$$q_2 = \frac{q_m K_1 K_2 (\frac{P}{P_0})^2}{(1 - K_2 \frac{P}{P_0})(1 - K_2 \frac{P}{P_0} + K_1 \frac{P}{P_0})} \quad (16)$$

where P/P_0 represents the relative vapor pressure; q stands for the total adsorption amount; q_1 and q_2 refer to adsorption capacities at primary and secondary sites, respectively; q_m is the capacity for monolayer adsorption; and K_1 and K_2 are equilibrium constants for adsorption at primary and secondary sites, respectively.

2.4.3. Thermodynamic Model

The isosteric heat of adsorption (Q_{st}) can be obtained from the following equations [50]:

$$Q_{st} = RT^2 \left(\frac{\partial \ln p}{\partial T} \right)_q \quad (17)$$

$$\ln p = -\frac{Q_{st}}{RT} + W \quad (18)$$

In these equations, R stands for the gas constant, and W represents the integration constant. Based on the equilibrium pressures extracted from the fitted isotherm model at constant uptake and different temperatures, the isosteric heat of adsorption (Q_{st}) was calculated from the slope of the linear $\ln P$ versus $1/T$ plot. Specifically, a constant adsorption amount was first fixed, and then substituted into the fitted adsorption isotherm models at 303.15 K, 313.15 K, and 323.15 K to obtain the corresponding saturated vapor pressures (P) at each temperature. Subsequently, $\ln P$ was plotted against $1/T$, and the isosteric heat of adsorption (Q_{st}) was obtained by multiplying the slope of the linear fit by $-R$.

3. Results and Discussion

This section presents the results of chemical structure characterization and pore structure characterization of coal samples. Subsequently, the water vapor adsorption isotherms in coal are presented, and the effects of coal microstructure on water vapor adsorption capacity are discussed. Finally, the isosteric heat of adsorption is presented, and the effects of coal microstructure on adsorption heat of water vapor are discussed.

3.1. Chemical Structure Characteristics of Coal

3.1.1. FTIR Spectra of the Coal Samples

The infrared spectra of coal can typically be divided into four regions [51]: aromatic hydrocarbon structures ($700\text{--}900\text{ cm}^{-1}$), functional groups containing oxygen ($1000\text{--}1800\text{ cm}^{-1}$), aliphatic hydrocarbon structures ($2800\text{--}3000\text{ cm}^{-1}$), and hydroxyl groups ($3200\text{--}3600\text{ cm}^{-1}$). The assignment of infrared absorption peaks of coals is shown in Table 2. Figure 2 shows that all coal samples exhibit similar infrared spectral shapes but differ in absorption peak intensities, indicating that the five coal samples of different ranks contain similar surface functional group types but with varying amounts. All coal samples exhibit absorption peaks in the $700\text{--}900\text{ cm}^{-1}$ region, which corresponds to out-of-plane bending vibrations of substituted aromatic hydrocarbons. They also show an

absorption peak near 1600 cm^{-1} , representing aromatic ring C=C stretching. The absorption peaks at $1650\text{--}1800\text{ cm}^{-1}$ result from C=O stretching vibrations. The $2800\text{--}3000\text{ cm}^{-1}$ region corresponds to aliphatic stretching vibrations; all coal samples exhibit relatively weak absorbance peaks in this region, indicating that they contain relatively few aliphatic functional groups.

Table 2. Assignment of infrared absorption peaks of coals.

Peak Position (cm^{-1})	Standard Range (cm^{-1})	Assignment
3389	3419–3359	O-H or N-H stretching vibration (alcohols, phenols, carboxylic acids, amines)
3028	3100–3000	Aromatic C-H stretching vibration
2930	2930–2950	Aliphatic -CH ₃ asymmetric stretching vibration
2920	2915–2920	-CH ₂ asymmetric stretching vibration
2860	2961–2855	-CH ₂ symmetric stretching vibration
2515	2510–1520	Free -SH stretching vibration
1730	1730–1740	Aliphatic C=O stretching vibration
1705	1700–1710	Aromatic C=O stretching vibration (esters, acids, aldehydes, ketones)
1600	1589–1593	Aromatic ring C=C stretching vibration
1435	1380–1460	CH ₂ and CH ₃ deformation vibration in alkyl chains
1157	1300–1100	C-O stretching vibration (phenols, alcohols, ethers, esters)
1000	1040–910	Mineral matter (kaolinite, etc.)
872	900–860	Aromatic C-H out-of-plane bending (1 adjacent H, pentasubstituted benzene)
814	860–800	Aromatic C-H out-of-plane bending (2 adjacent H, tetrasubstituted benzene)
790	810–750	Aromatic C-H out-of-plane bending (3 adjacent H, trisubstituted benzene)
750	770–735	Aromatic C-H out-of-plane bending (4 adjacent H, disubstituted benzene)

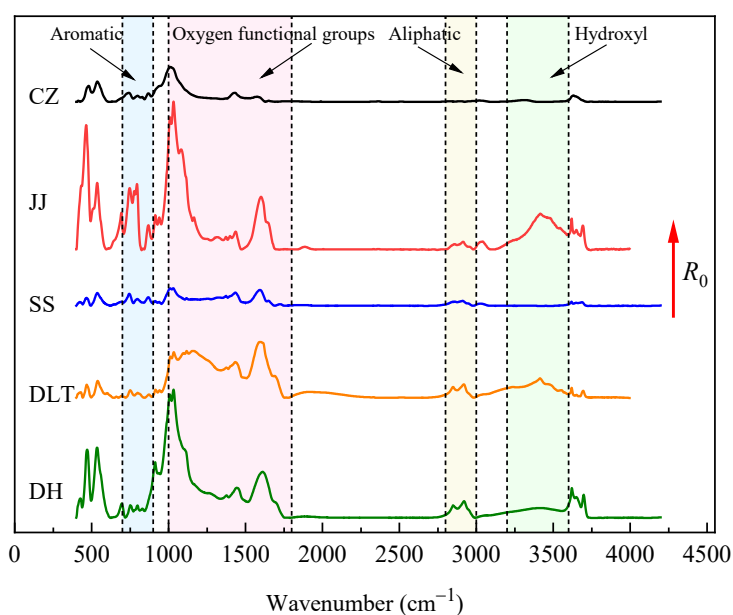
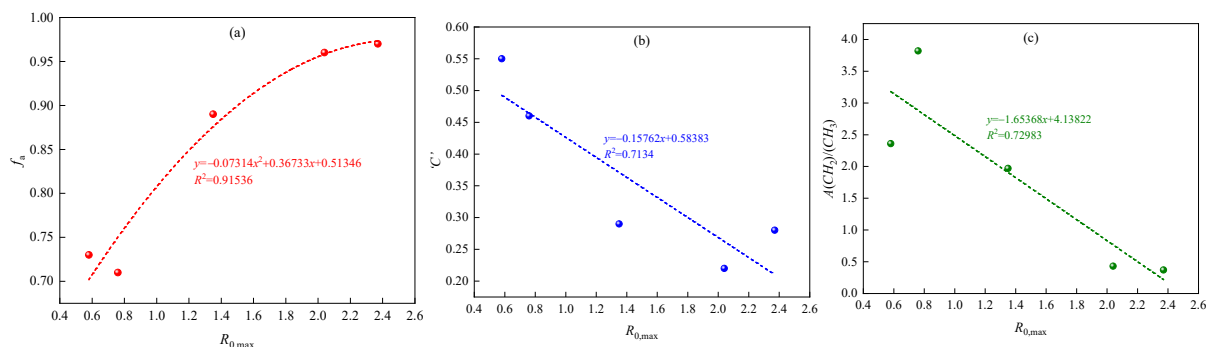


Figure 2. Infrared spectra of five coal samples.

The chemical structure parameters derived from peak deconvolution fitting are presented in Table 3. The relationships between these three parameters and $R_{0,\max}$ are shown in Figure 3. The data show that f_a increases with increasing $R_{0,\max}$, while 'C' and $A(\text{CH}_2)/A(\text{CH}_3)$ gradually decrease with increasing $R_{0,\max}$. This indicates that during the coalification process, aromatic structures gradually increase, while aliphatic structures and oxygen-containing functional groups gradually decrease, which is consistent with previous studies [52].

Table 3. FTIR structure parameter of the coal samples.

Coal Samples	$R_{0,max}$	f_{a1}	'C'	$A(CH_2)/A(CH_3)$
CZ	2.37	0.97	0.28	0.37
JJ	2.04	0.96	0.22	0.43
SS	1.35	0.89	0.29	1.97
DLT	0.76	0.71	0.46	3.82
DH	0.58	0.73	0.55	2.36

**Figure 3.** Relations between $R_{0,max}$ and FTIR structure parameters: (a) f_{a1} , (b) 'C', (c) $A(CH_2)/A(CH_3)$.

3.1.2. ^{13}C -NMR Spectra of the Coal Samples

The ^{13}C -NMR spectra of all five coal samples, shown in Figure 4, mainly consist of an aliphatic carbon region (chemical shifts ranging from 0 to 90 ppm) and an aromatic carbon region (chemical shifts between 100 and 165 ppm). Higher-rank coals exhibit flattened peak shapes in the aliphatic region, which indicates that aliphatic carbon content decreases as metamorphism progresses.

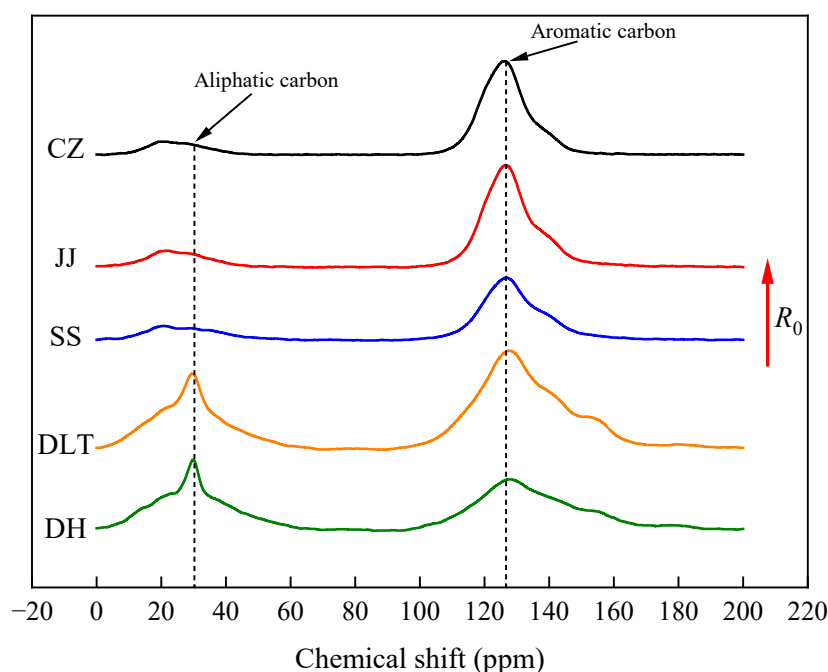
**Figure 4.** ^{13}C -NMR images of coal samples.

Table 4 presents structural parameters derived from the spectral analysis. The relationships between each parameter and $R_{0,max}$ are shown in Figure 5. Here, f_a and f_a^H increase with increasing $R_{0,max}$. Although f_a^B shows a slight decrease at higher $R_{0,max}$ values, it still exhibits an overall increasing trend with increasing $R_{0,max}$. These results indicate that

the number of aromatic hydrocarbons gradually increases with increasing metamorphic degree. However, f_a^O decreases with increasing $R_{0,max}$, suggesting that oxygen-containing functional groups gradually decompose with increasing metamorphic degree, which is consistent with the view that deoxygenation occurs during the coalification process [53].

Table 4. ^{13}C -NMR structure parameters of the coal samples.

Coal Samples	f_{a2}	f_a^H	f_a^B	f_a^S	f_a^O	X_B
CZ	0.8631	0.5556	0.1982	0.1001	0.0092	0.2296
JJ	0.849	0.4587	0.2726	0.0929	0.0226	0.3211
SS	0.7828	0.394	0.2423	0.1087	0.0339	0.3095
DLT	0.662	0.2946	0.1315	0.1268	0.0943	0.1987
DH	0.4851	0.2221	0.0985	0.0713	0.0677	0.2031

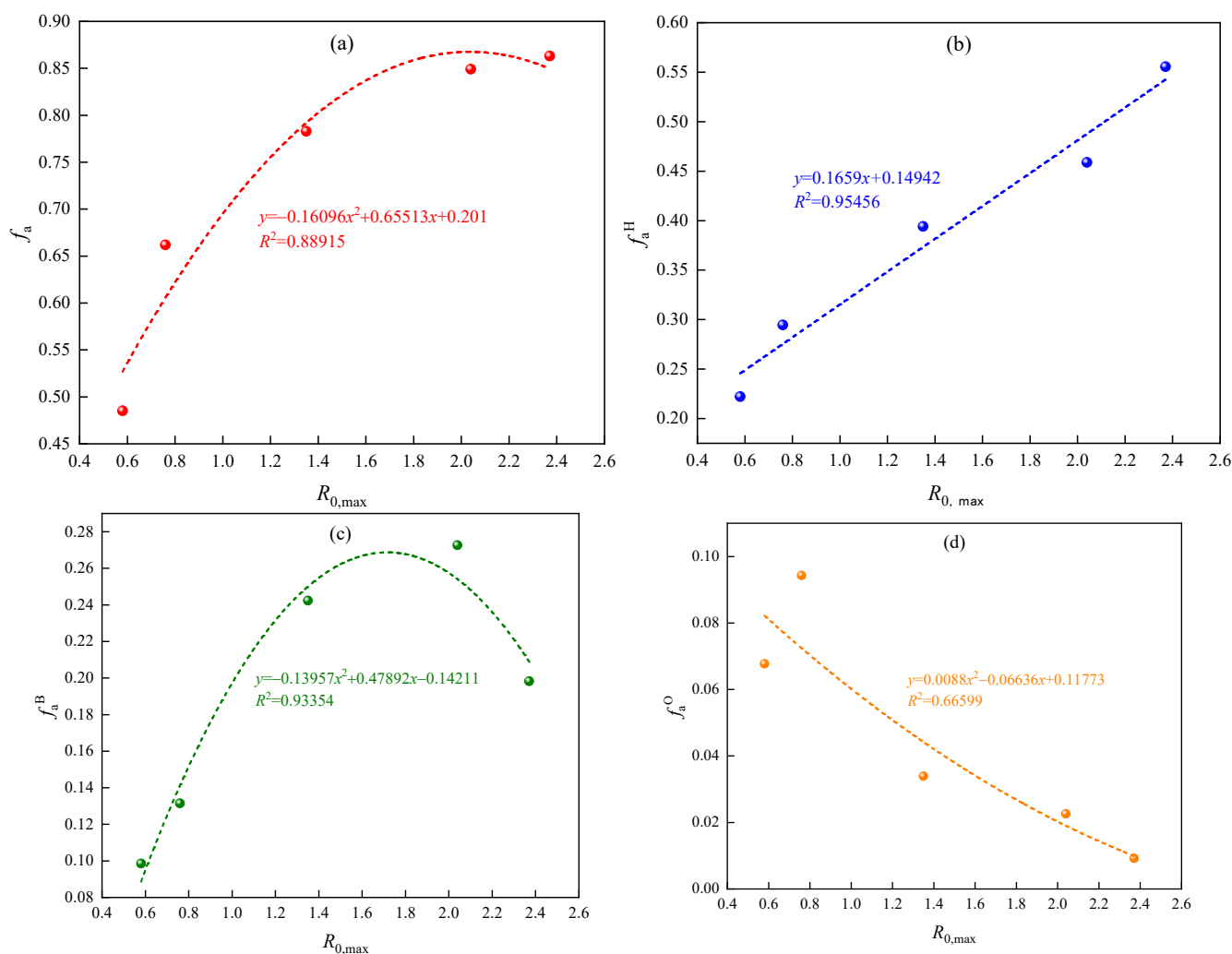


Figure 5. Relations between $R_{0,max}$ and FTIR structure parameters: (a) f_{a2} , (b) f_a^H , (c) f_a^B , (d) f_a^O .

3.2. Characterization of Coal Pore Structure

3.2.1. Pore Structure Characterization by MIP

Figure 6 shows the mercury intrusion–extrusion curves for all coal samples, all of which feature hysteresis loops. For CZ and DLT coal samples, the intrusion and extrusion curves do not overlap, indicating a pore morphology dominated by well-connected open pores. Above 100 MPa, the intrusion and extrusion curves of CZ and JJ coal samples nearly overlap, suggesting that the micropores and small pores in these two coal samples are predominantly semi-closed. Additionally, below 100 MPa, the mercury intrusion

volume of all five coal samples increases slowly; above 100 MPa, the intrusion volume rises rapidly, indicating well-developed micropores in the coal. Table 5 summarizes the pore structure parameters derived from mercury intrusion porosimetry. The specific surface area varies between 8.472 and 33.371 m²/g, while the pore volume varies between 0.02 and 0.076 cm³/g. The largest specific surface area and pore volume are found in the DLT sample, and the smallest in the JJ sample. Mesopore surface areas and volume exceed those of macropores across all coal samples, indicating that mesopores are more developed than macropores.

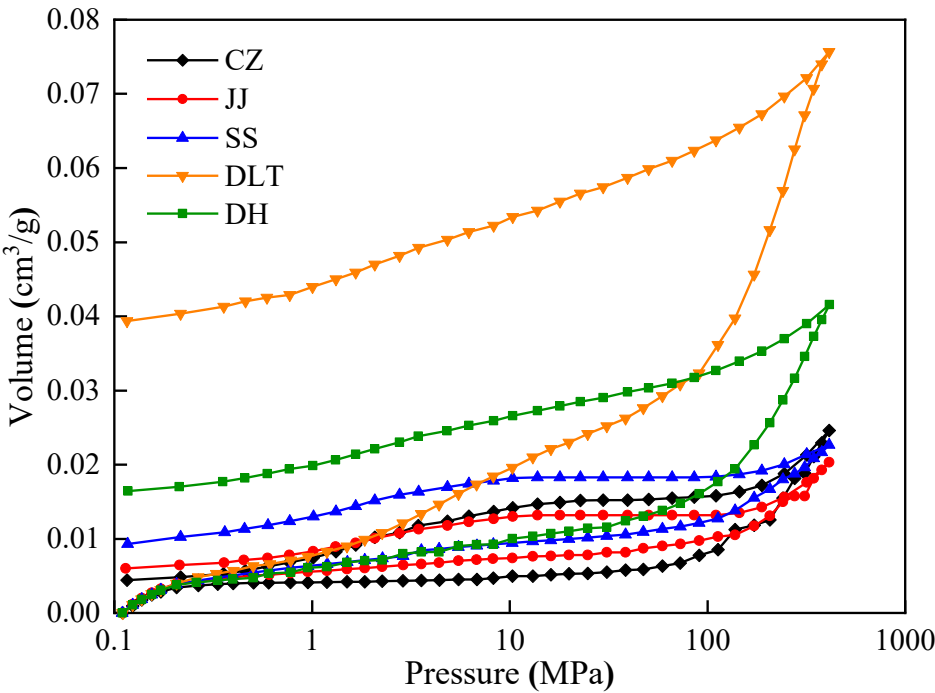


Figure 6. Advance and retreat mercury curves for five coal samples.

Table 5. Pore structure parameters of the five coal samples measured via MIP.

Coal Samples	S_t (m ² /g)	V_t (cm ³ /g)	Specific Surface Area (m ² /g)		Pore Volume (cm ³ /g)	
			2–50 nm	>50 nm	2–50 nm	>50 nm
CZ	14.15	0.025	14.1119	0.0381	0.0197	0.0053
JJ	9.154	0.02	9.1085	0.0455	0.0122	0.0078
SS	8.472	0.023	8.3937	0.0783	0.0128	0.0102
DLT	33.371	0.076	32.9642	0.4068	0.0518	0.0242
DH	20.973	0.042	20.8378	0.1352	0.0306	0.0114

Notes: S_t , total specific surface area; V_t , total pore volume.

The thermodynamic model was used to calculate the fractal dimensions of macropores. Figure 7a–e presents the fractal dimension fitting curves, which show a strong linear relationship between $\ln(W_n/r_n^2)$ and $\ln(V_n^{1/3}/r_n)$. The fitting coefficients R^2 all exceed 0.99, which shows that the macropore systems in these five coal specimens have clear fractal features. Table 6 presents the macropore fractal dimension values (D_{mac}). For all coal specimens, the fractal dimension ranges from 2.52345 to 2.78738, with the SS sample exhibiting the highest D_{mac} , indicating that this coal sample has the most complex macropore structure.

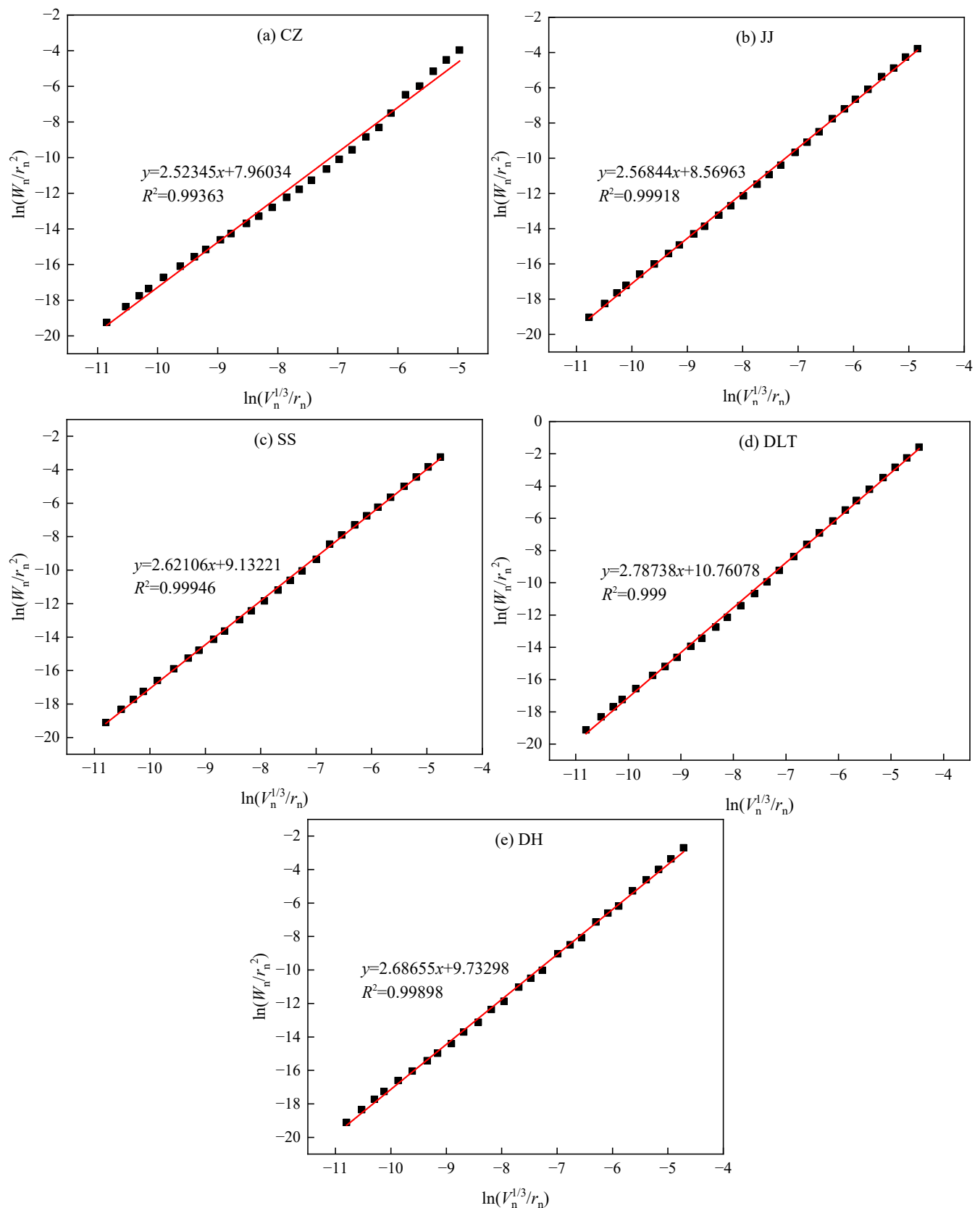


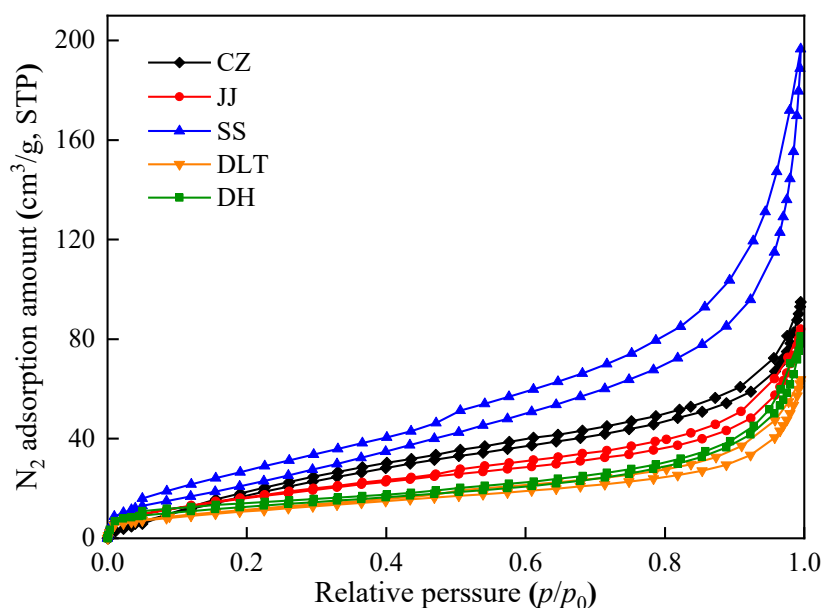
Figure 7. Relationship between $\ln(W_n/r_n^2)$ and $\ln(V_n^{1/3}/r_n)$ based on MIP: (a) CZ coal sample, (b) JJ coal sample, (c) SS coal sample, (d) DLT coal sample, (e) DH coal sample.

Table 6. Fractal dimension calculation results based on MIP.

Coal Samples	Fitting Equation	R^2	Slope of Equation	Fractal Dimension (D_{mac})
CZ	$y = 2.52345x + 7.96034$	0.99363	2.52345	2.52345
JJ	$y = 2.56844x + 8.56963$	0.99918	2.56844	2.56844
SS	$y = 2.62106x + 9.13221$	0.99946	2.62106	2.62106
DLT	$y = 2.78738x + 10.76078$	0.99900	2.78738	2.78738
DH	$y = 2.68655x + 9.73298$	0.99898	2.68655	2.68655

3.2.2. Pore Structure Characterization by LPN₂A

Figure 8 displays the N₂ adsorption data obtained at low temperature for every coal specimen. According to IUPAC classification criteria, all five specimens yield Type II isotherm profiles. The adsorption capacities differ between coal samples. The largest value is observed for the SS coal sample, followed by the CZ, JJ, DH, and DLT samples. Except for the DH sample, the coal samples exhibit adsorption hysteresis phenomena. The hysteresis loops of the four coal specimens fall into the H3 category based on IUPAC standards [45], marked by slowly changing adsorption and desorption branches at medium–low relative pressures, along with a quick rise in adsorption amounts at high relative pressures. The relatively sharp apex of the curve indicates parallel-plate and slit-shaped pore morphologies [54]. Table 7 presents the pore structure parameters derived from low-temperature N₂ adsorption experiments. The mesopores (2–50 nm) with the largest specific surface area and pore volume are found in the SS coal sample, suggesting that it has the most developed mesopores.

**Figure 8.** N₂ adsorption–desorption curves at 77 K.**Table 7.** Pore structure parameters of the five coal samples measured by LTN₂A.

Coal Samples	S_t (m ² /g)	V_t (cm ³ /g)	Specific Surface Area (m ² /g)		Pore Volume (cm ³ /g)	
			0.38–2 nm	2–50 nm	0.38–2 nm	2–50 nm
CZ	70.34	0.0849	15.92	54.42	0.0072	0.0777
JJ	53.85	0.0757	9.87	43.98	0.0045	0.0712
SS	113.53	0.1655	14.63	98.90	0.0066	0.1589
DLT	35.45	0.0545	2.79	32.66	0.0013	0.0532
DH	39.82	0.0688	5.46	34.36	0.0025	0.0663

The mesopore fractal dimensions were calculated using the FHH model. The relationship of $\ln V$ versus $\ln(\ln(P/P_0))$ is shown in Figure 9. All coal samples have high fitting degrees ($R^2 > 0.9$), suggesting that their mesopores possess obvious fractal characteristics. The mesopore fractal dimension results are presented in Table 8. The CZ coal sample has the largest D_{mes} , indicating that this coal sample has the most complex mesopore structure.

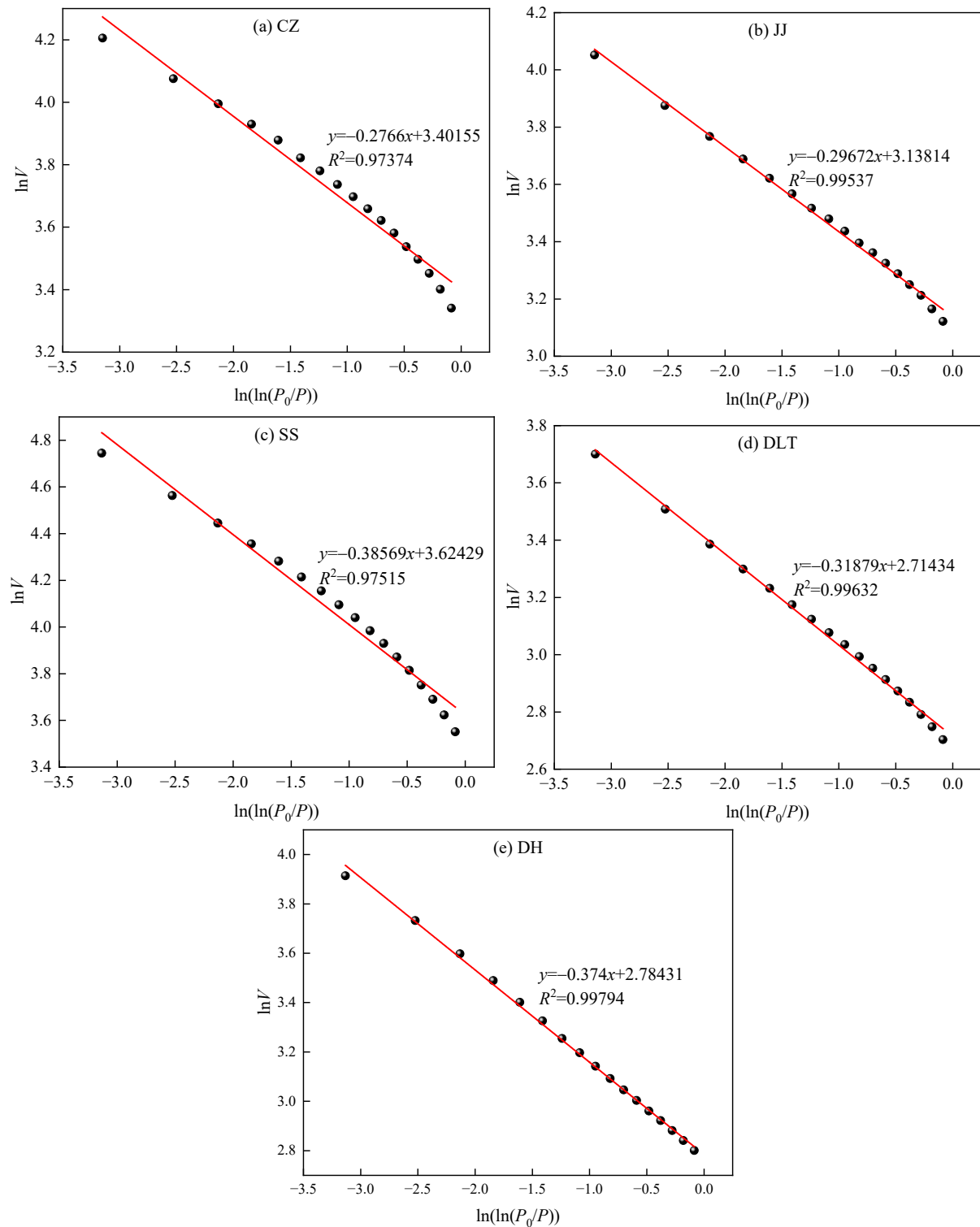


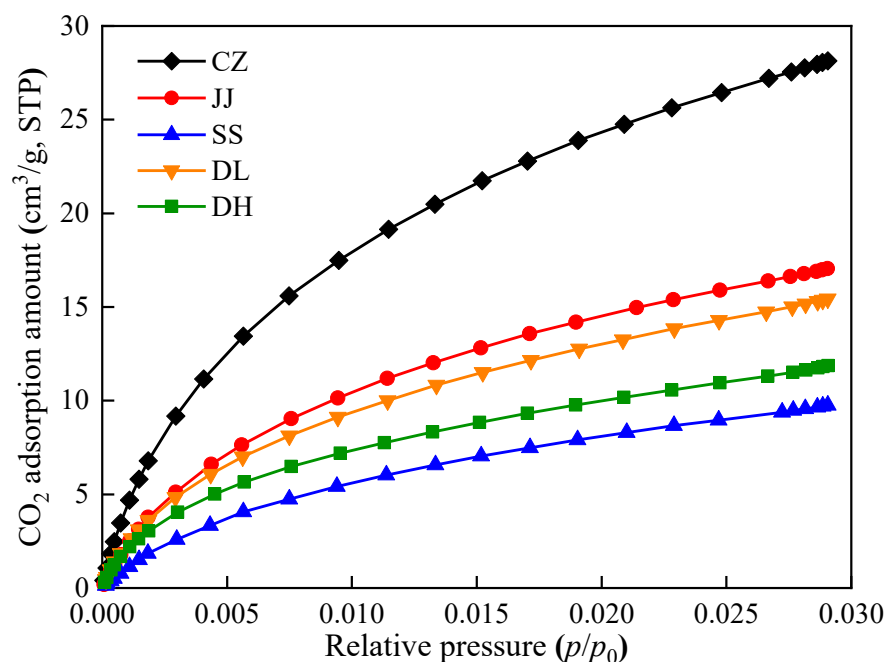
Figure 9. Relationship between $\ln V$ and $\ln(\ln(P_0/P))$ based on LTN₂A: (a) CZ coal sample, (b) JJ coal sample, (c) SS coal sample, (d) DLT coal sample, (e) DH coal sample.

Table 8. Fractal dimension calculation results based on LTN₂A.

Coal Samples	Fitting Equation	R^2	Slope of Equation	Fractal Dimension (D_{mes})
CZ	$y = -0.27660x + 3.40155$	0.97374	−0.27660	2.72340
JJ	$y = -0.29672x + 3.13814$	0.99537	−0.29672	2.70328
SS	$y = -0.38569x + 3.62429$	0.97515	−0.38569	2.61431
DLT	$y = -0.31879x + 2.71434$	0.99632	−0.31879	2.68121
DH	$y = -0.3740x + 2.78431$	0.99794	−0.3740	2.6260

3.2.3. Pore Structure Characterization by L_TCO₂A

Figure 10 presents the CO₂ adsorption profiles for coal specimens. The adsorption capacity across all five specimens rises with increasing relative pressure. According to IUPAC criteria, coal CO₂ adsorption data follow Type I isotherm patterns, reflecting the characteristics of CO₂ adsorption in pores smaller than 2 nm. The CO₂ adsorption in coal is dominated by physisorption, which is driven by weak interactions such as van der Waals forces [55,56]. Figure 10 shows that the high-rank coal CZ has significantly higher CO₂ adsorption capacity than the medium- and low-rank coal samples, indicating greater micropore development in higher-rank coals. The pore structure parameters derived from CO₂ adsorption tests are listed in Table 9. The CZ specimen exhibits the highest micropore surface area and volume, 160.06 m²/g and 0.0515 cm³/g, indicating superior micropore development.

**Figure 10.** CO₂ adsorption curves at 273.15 K.**Table 9.** Pore structure parameters of the five coal samples measured by L_TCO₂A.

Coal Samples	S_t (m ² /g)	V_t (cm ³ /g)
CZ	160.06	0.0515
JJ	94.51	0.031
SS	57.24	0.0204
DLT	74.49	0.0229
DH	59.99	0.0184

The fractal dimensions of micropores ($d < 2$ nm) were calculated using the Sierpinski model. Figure 11 illustrates the relationship between $\ln(P - P_t)$ and $\ln V$. The fitting degrees of all coal samples are above 0.98, indicating that the micropores of all coal samples possess fractal characteristics. Table 10 shows the micropore fractal dimension (D_{mic}) calculation results. The DLT coal sample has the largest D_{mic} , suggesting that it has the most complex micropore structure.

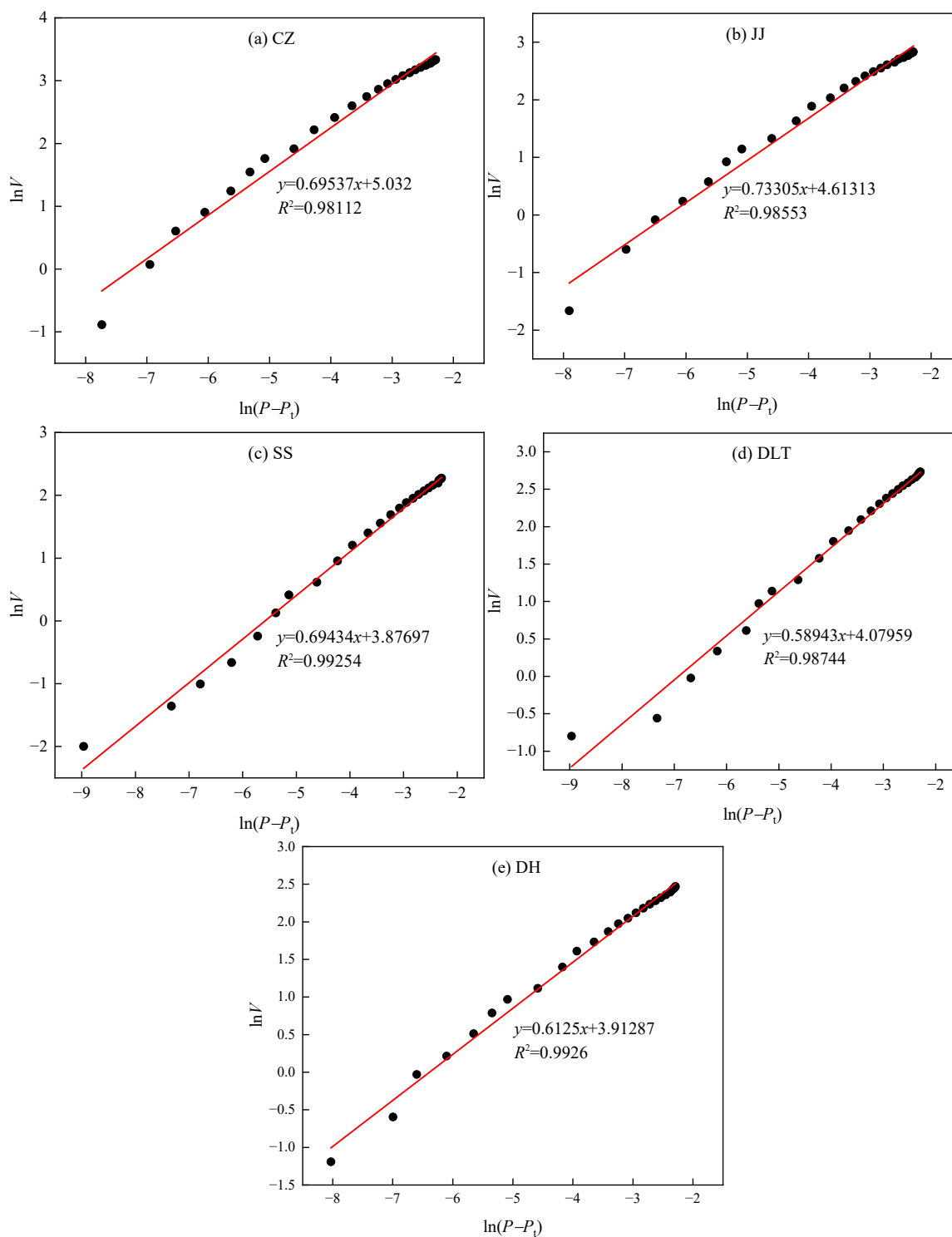


Figure 11. Relationship between $\ln V$ and $\ln(P - P_t)$ based on LTCO₂A: (a) CZ coal sample, (b) JJ coal sample, (c) SS coal sample, (d) DLT coal sample, (e) DH coal sample.

Table 10. Fractal dimension calculation results based on LTCO₂A.

Coal Samples	Fitting Equation	R^2	Slope of Equation	Fractal Dimension (D_{mic})
CZ	$y = 0.69537x + 5.03200$	0.98112	0.69537	2.30463
JJ	$y = 0.73305x + 4.61313$	0.98553	0.73305	2.26695
SS	$y = 0.69434x + 3.87697$	0.99254	0.69434	2.30566
DLT	$y = 0.58943x + 4.07959$	0.98744	0.58943	2.41057
DH	$y = 0.6125x + 3.91287$	0.99260	0.61250	2.38750

3.2.4. Combined Pore Structure Characterization

The micropore, mesopore, and macropore characteristics of all five specimens were analyzed using LTCO₂A, LTN₂A, and MIP, respectively. Distributions of specific surface area and volume of macropores, mesopores, and micropores in every specimen are shown in Tables 11 and 12. Table 11 shows that in the SS specimen, the mesopores account for the largest share, 63.32%, of the total specific surface area, while in the other four coal samples, the micropores contribute the most to the total specific surface area. Table 12 shows that mesopores account for the majority of the pore volume in all coal samples, with proportions exceeding 50%. Among these, the mesopore contribution to the total pore volume is most pronounced in SS coal—as high as 83.85%.

Table 11. Characteristics of pore surface area distribution in the full pore diameter section of coal samples.

Coal Samples	S_t (m ² /g)	Pore Surface Area (m ² /g)			Proportion of Pore Surface Area (%)		
		S_{mic}	S_{mes}	S_{mac}	S_{mic}/S	S_{mes}/S	S_{mac}/S
CZ	214.51	160.06	54.42	0.0381	74.62	25.37	0.02
JJ	138.54	94.51	43.98	0.0455	68.22	31.75	0.03
SS	156.22	57.24	98.90	0.0783	36.64	63.31	0.05
DLT	107.56	74.49	32.66	0.4068	69.25	30.36	0.38
DH	94.49	59.99	34.36	0.1352	63.49	36.36	0.14

Notes: S_{mic} , micropore surface area; S_{mes} , mesopore surface area; S_{mac} , macropore surface area.

Table 12. Characteristics of pore volume distribution in the full pore diameter section of coal samples.

Coal Samples	V_t (cm ³ /g)	Pore Volume (cm ³ /g)			Proportion of Pore Volume (%)		
		V_{mic}	V_{mes}	V_{mac}	V_{mic}/V	V_{mes}/V	V_{mac}/V
CZ	0.1345	0.0515	0.0777	0.0053	38.29	57.77	3.94
JJ	0.110	0.0310	0.0712	0.0078	28.18	64.73	7.09
SS	0.1895	0.0204	0.1589	0.0102	10.77	83.85	5.38
DLT	0.1003	0.0229	0.0532	0.0242	22.83	53.04	24.13
DH	0.0961	0.0184	0.0663	0.0114	19.15	68.99	11.86

Notes: V_{mic} , micropore volume; V_{mes} , mesopore volume; V_{mac} , macropore volume.

Furthermore, to assess pore structure complexity, the volume proportions of pores in different size ranges were used as weights to determine the overall fractal dimension of the specimens' pores [57,58]. The formula is given below:

$$D_t = \sum_{i=1}^n \frac{V_i}{V_t} D_i \quad (19)$$

where D_t represents the comprehensive fractal dimension (dimensionless), V_t represents the total pore volume (cm³/g), V_i represents the volume of pores in different

size ranges (cm^3/g), and D_i represents the fractal dimension of pores in different size ranges (dimensionless).

Table 13 presents the comprehensive fractal dimension values of the coal pores. Based on these comprehensive fractal dimensions, the coal samples are ranked as follows (from highest to lowest): DLT > DH > SS > JJ > CZ. This ranking reflects the degree of pore structure heterogeneity and complexity: the DLT sample exhibits the most complex and heterogeneous pores, whereas the CZ sample possesses a relatively simple structure.

Table 13. Composite fractal dimensions of the coal samples.

Coal Samples	D_t	Macropore		Mesopore		Micropore	
		V_{mac}/V_t	D_{mac}	V_{mes}/V_t	D_{mes}	V_{mic}/V_t	D_{mic}
CZ	2.55517	0.039405	2.52345	0.577695	2.7234	0.3829	2.30463
JJ	2.57075	0.070909	2.56844	0.647273	2.70328	0.281818	2.26695
SS	2.58144	0.053826	2.62106	0.838522	2.61431	0.107652	2.30566
DLT	2.64504	0.241276	2.78738	0.530409	2.68121	0.228315	2.41057
DH	2.58751	0.118626	2.68655	0.689906	2.6260	0.191467	2.38750

Notes: D_t , total pore fractal dimension; D_{mic} , micropore fractal dimension; D_{mes} , mesopore fractal dimension; D_{mac} , macropore fractal dimension.

3.3. Water Vapor Adsorption Behavior and Influencing Factors

3.3.1. Water Vapor Adsorption Isotherms at Different Temperatures

Figure 12 illustrates the water vapor adsorption isotherms for all five coal samples at 303.15 K, 313.15 K, and 323.15 K. The results show that the amount of water vapor adsorption of each coal sample increases with increasing relative pressure/absolute pressure. The relationship between water vapor adsorption isotherms and relative pressure and temperature is not obvious; however, the water vapor adsorption isotherms are clearly negatively correlated with absolute pressure and temperature—i.e., water vapor adsorption decreases with increasing temperature. This stems from the substantial elevation in saturation vapor pressure at higher temperatures. For example, the saturated vapor pressure of water is 4.2455 kPa at 303.15 K, while it rises to 12.344 kPa at 323.15 K. Therefore, isotherms under relative pressure are insensitive to temperature, showing only slight differences, while under absolute pressure conditions, the adverse effect of increased temperature on adsorption can be clearly demonstrated. This pattern is consistent with previous research results [35]. The modified BET model was applied to fit the adsorption isotherms for all five coal samples at the three temperatures. Table 14 shows the fitting parameters, with all RMSE values less than 0.12829 and all R^2 values greater than 0.98, indicating good fitting results.

The primary and secondary adsorption isotherms at different temperatures calculated using the modified BET model are shown in Figure 13. Both primary and secondary adsorption capacities increase with increasing relative pressure; however, the primary adsorption rate gradually decreases, while the secondary adsorption rate gradually increases. Beyond a specific relative pressure, the amount of secondary adsorption begins to exceed that of primary adsorption, and secondary adsorption begins to dominate the adsorption process. Additionally, in all coal samples, the primary adsorption amount is smaller at 323.15 K than at the two lower temperatures, while secondary adsorption shows the opposite trend.

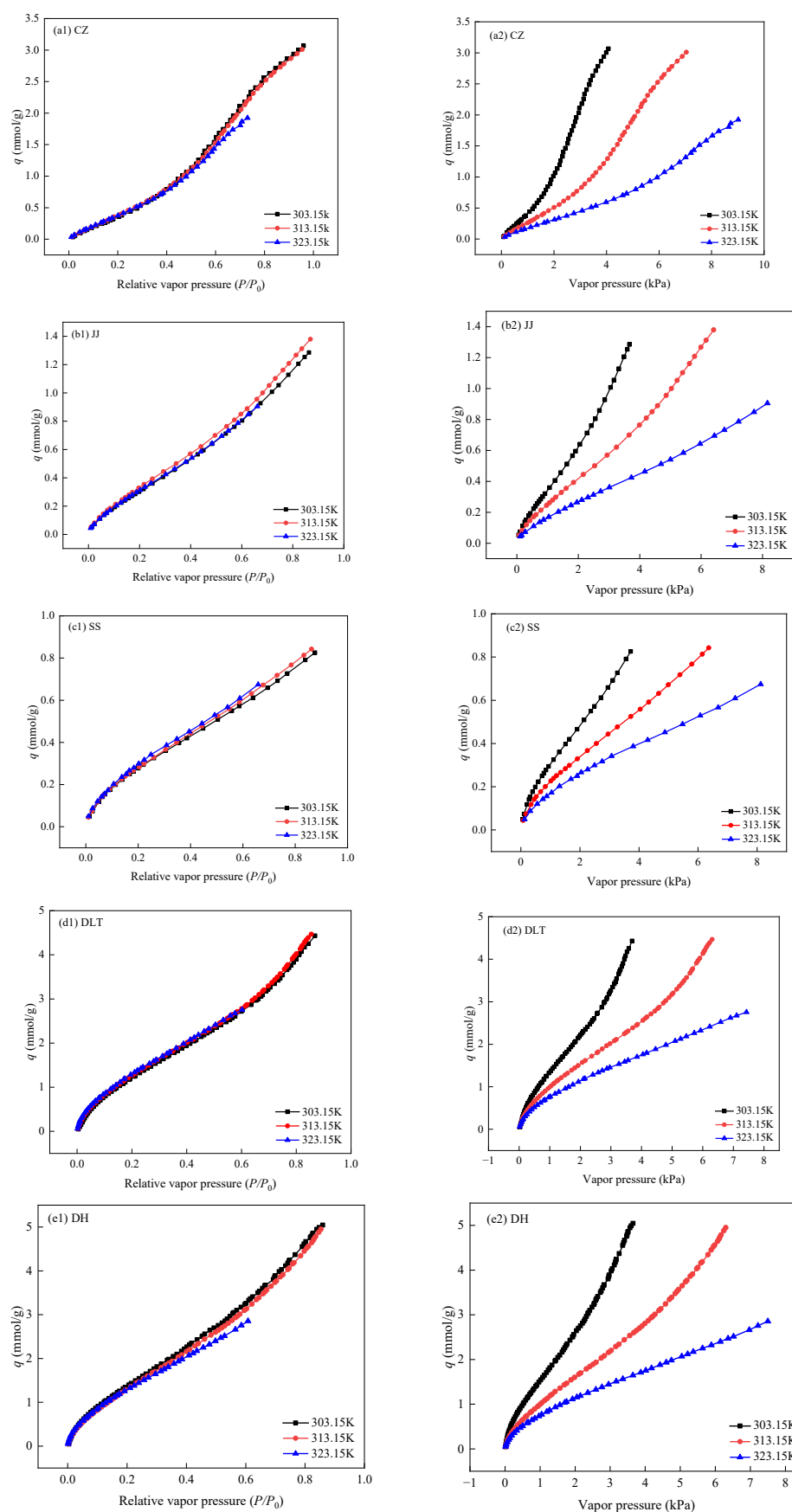
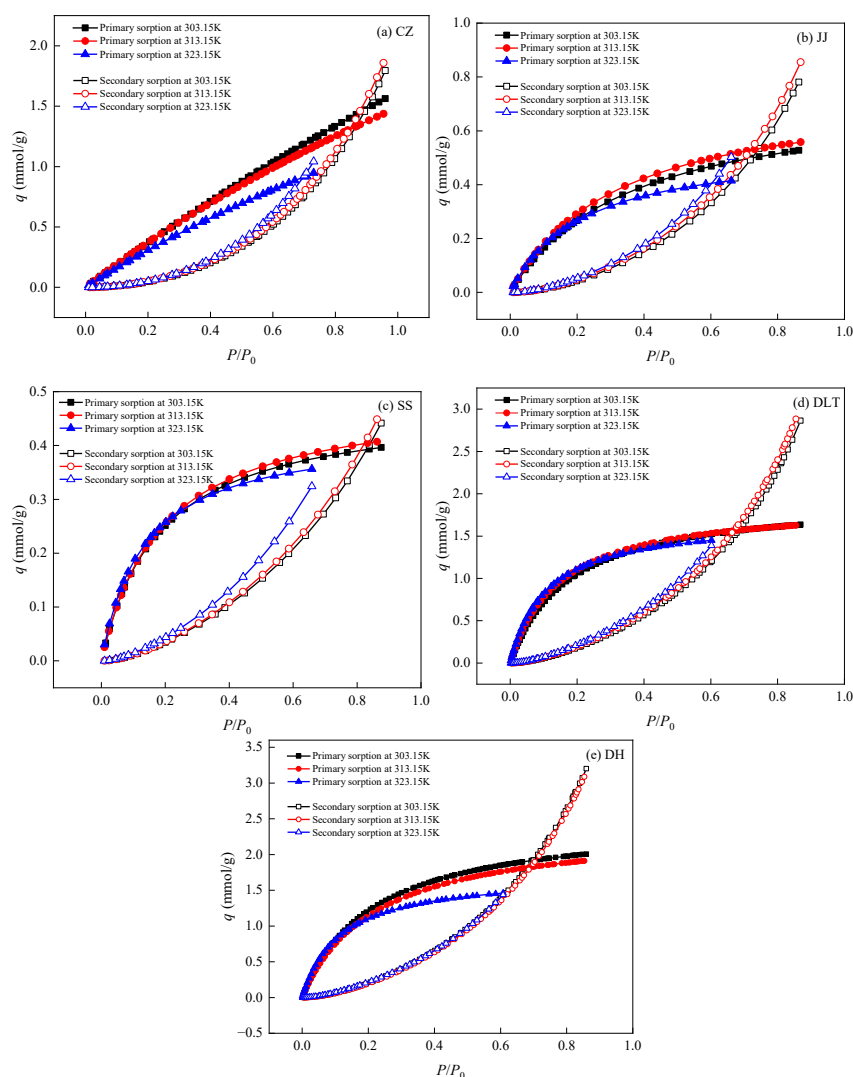


Figure 12. Relationship between water vapor adsorption and relative vapor pressure or vapor pressure: (a1,a2) CZ coal sample, (b1,b2) JJ coal sample, (c1,c2) SS coal sample, (d1,d2) DLT coal sample, (e1,e2) DH coal sample.

Table 14. Fitting parameters of modified BET model for water vapor adsorption isotherms of coal samples.

Coal Samples	Temperature (K)	q_m (mmol/g)	K_1	K_2	RMSE	R^2
CZ	303.15	1.682	1.27686	0.6487	0.12829	0.98153
	313.15	1.6359	1.32128	0.65299	0.11162	0.98562
	323.15	1.51213	1.08954	0.71693	0.03315	0.99682
JJ	303.15	0.59771	3.51014	0.69093	0.01473	0.99852
	313.15	0.62489	3.79377	0.69619	0.01645	0.99844
	323.15	0.46674	5.50073	0.8279	0.00991	0.9985
SS	303.15	0.43111	6.13038	0.60181	0.0085	0.99865
	313.15	0.44467	5.9443	0.60776	0.01068	0.99798
	323.15	0.39084	8.20815	0.72355	0.00738	0.99825
DLT	303.15	1.74071	6.49856	0.73263	0.01769	0.99979
	313.15	1.71619	7.62058	0.748	0.02525	0.99962
	323.15	1.57272	10.00139	0.81206	0.04217	0.99705
DH	303.15	2.17227	5.41288	0.71495	0.053	0.99867
	313.15	2.07483	5.23612	0.72339	0.04374	0.9991
	323.15	1.58791	9.5313	0.81639	0.04066	0.99751

**Figure 13.** Adsorption quantity of water vapor on primary and secondary sites: (a) CZ coal sample, (b) JJ coal sample, (c) SS coal sample, (d) DLT coal sample, (e) DH coal sample.

3.3.2. Effects of Coal Microstructure on Water Vapor Adsorption Amount

This study first employed Pearson correlation analysis to analyze the correlations between the chemical structure and pore structure parameters of coal and the total water vapor adsorption, primary adsorption, and secondary adsorption amounts ($T = 303.15\text{ K}$, $P/P_0 = 0.85$), thereby identifying the factors that significantly influence the amount of each adsorption type [59]. The Pearson correlation coefficient (r) quantifies the linear association linking two variables, bounded between -1 and 1 , where larger absolute values indicate stronger correlations [60]. According to statistical principles, when the sample size $n = 5$ and the significance level $\alpha = 0.05$, the critical value of the Pearson correlation coefficient is 0.878 , meaning that when $|r| > 0.878$, a linear correlation between two variables can be considered significant. Based on this, linear regression analysis was performed on the screened significantly correlated parameters to verify their correlations. Figure 14 presents the correlation analysis between the microstructural parameters and adsorption capacities of the coal samples.

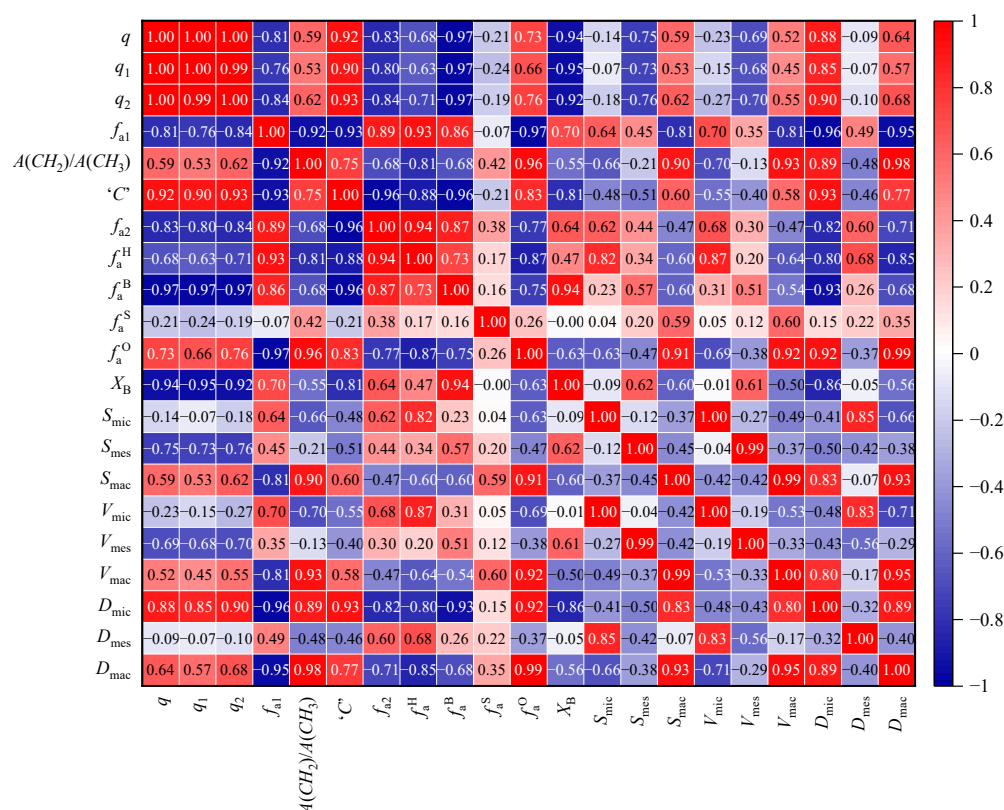


Figure 14. Pearson's correlation coefficients between water vapor adsorption amount and coal structure parameters.

As shown in Figure 14, the total water vapor adsorption, primary adsorption, and secondary adsorption amounts are closely related to some chemical structure parameters of coal, including $'C'$, f_a^B , and X_B . The relationships between various adsorption capacities and $'C'$, f_a^B , and X_B are presented in Figure 15. The results demonstrate that various water vapor adsorption capacities are highly positively correlated with $'C'$, while highly negatively correlated with f_a^B and X_B . This indicates that the surface hydrophilicity/hydrophobicity properties of coal play key roles in water uptake: oxygen-containing functional groups such as carboxyl and hydroxyl groups can directly adsorb water molecules through hydrogen bonding, thereby increasing water uptake, while an increase in aromatic structures implies weaker coal hydrophilicity, leading to a decrease in the amount of water vapor adsorption [22]. Additionally, Figure 14 also demonstrates that

various water vapor adsorption capacities are related to pore structure, with the correlation with D_{mic} being especially significant. Figure 15d illustrates the relationships between D_{mic} and various adsorption capacities. As shown, all adsorption amounts are linearly and positively correlated with D_{mic} . A high fractal dimension of micropore structure represents a high degree of complexity of the pore structure surface, which can provide more adsorption sites and is therefore positively correlated with the adsorption amount. Notably, D_{mic} is significantly positively correlated with the total ($r = 0.88$) and secondary adsorption amounts ($r = 0.90$), but its correlation with the primary adsorption amount does not reach the significance level ($r = 0.85 < 0.878$). This means that D_{mic} has a weaker influence on the primary adsorption amount than on the secondary adsorption amount. This is because primary adsorption mainly depends on polar adsorption sites, with relatively low requirements for pore geometry, while secondary adsorption involves the growth of water clusters, which requires suitable pore structures. A complex pore surface represented by a high fractal dimension provides more nucleation sites and favorable spaces for the growth of water clusters. Therefore, its promoting effect is more pronounced during the secondary adsorption stage.

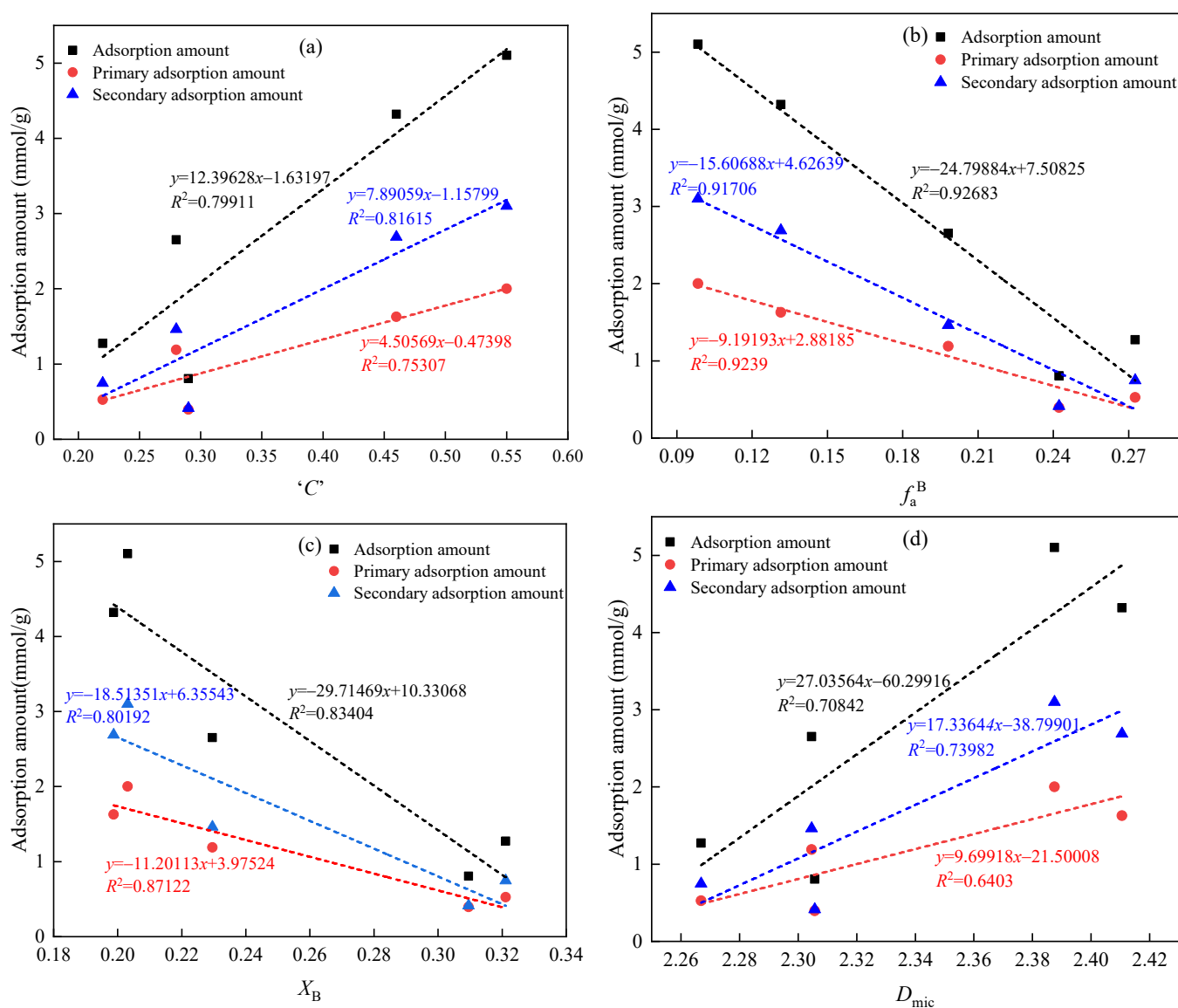


Figure 15. Relationships between water vapor adsorption amount and structure parameters: (a) 'C', (b) f_a^B , (c) X_B , (d) D_{mic} .

In addition, to further elucidate the relationship between coal rank and water vapor adsorption amount, the correlations of total water vapor adsorption amount, primary adsorption amount and secondary adsorption amount ($T = 303.15\text{ K}$, $P/P_0 = 0.85$) with the maximum vitrinite reflectance of coal ($R_{0,\max}$) are plotted in Figure 16. The results show that the total water vapor adsorption amount exhibits a U-shaped parabolic trend with the increase in coal rank: all adsorption amounts decrease first and then increase with the rise in coal rank. This trend is consistent with previous studies reporting a parabolic-shaped relationship between water uptake and coal rank [61,62]. In addition, the primary and secondary adsorption amounts show a similar variation trend with coal rank. This variation trend stems from the combined effects of chemical properties and pore structure during coalification. Low-rank coal contains abundant oxygen-containing functional groups, thus exhibiting stronger hydrophilicity [63]. For example, the low-rank coal DH has the highest water vapor adsorption amount. With the progress of coalification, the content of oxygen-containing functional groups decreases and the aromatic structure increases gradually, leading to the enhancement in hydrophobicity. Meanwhile, the microporous structure of coal sample SS is not well developed, with a microporous specific surface area of only $57.24\text{ m}^2/\text{g}$, which results in its minimum water vapor adsorption amount. With the further progress of coalification, although the content of oxygen-containing functional groups is relatively low, the microporous structure develops gradually. In particular, the high-rank coal CZ has the largest microporous specific surface area ($160.06\text{ m}^2/\text{g}$) and microporous volume ($0.0515\text{ cm}^3/\text{g}$), which provide more adsorption sites for water molecules. Therefore, the water vapor adsorption amount of coal sample CZ is significantly higher than that of coal samples SS and JJ.

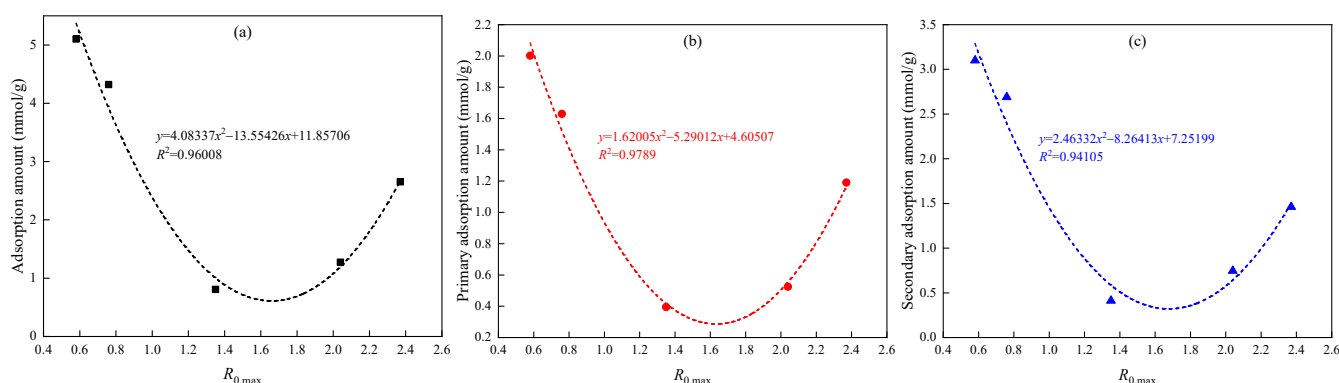


Figure 16. Relationships between water vapor adsorption amount and $R_{0,\max}$: (a) adsorption amount, (b) primary adsorption amount, (c) secondary adsorption.

In summary, the water vapor adsorption behavior of coal is jointly controlled by surface chemical properties and pore structure, with their relative contributions varying with coal rank. For low-rank coal, abundant oxygen-containing functional groups dominate water uptake through hydrogen bonding, while for high-rank coal such as anthracite, the microporous structure becomes the dominant factor. This finding is consistent with the conclusion of Chen et al., who reported that low-rank coals such as long-flame coal contain large amounts of oxygen-containing functional groups, which have a more significant contribution to water-holding capacity than the development of micropores; whereas for highly mature coals such as anthracite, few oxygen-containing functional groups are observed, and the water-holding capacity is closely related to the development of micropores [17].

3.4. Heat of Water Vapor Adsorption and Influencing Factors

3.4.1. Isosteric Heat of Adsorption

The isosteric adsorption heat serves as an important thermodynamic parameter, revealing interactions between gases or vapors and porous systems [26]. In this study, the total, primary, and secondary heats of water vapor adsorption on coal were calculated using the modified BET model. As Figure 17 shows, the heat of adsorption (Q_{st}) of water vapor on the five coal samples ranged from 30 to 54 kJ/mol, exhibiting two distinct trends. For CZ anthracite, the heat of adsorption showed a gradual decrease with increasing adsorption capacity, whereas for the other four coal samples, it exhibited an initial increase followed by a decrease. This difference is primarily attributed to variations in surface chemical properties and pore structures among coals of different metamorphic degrees. Regarding primary adsorption, except for the CZ coal sample, whose adsorption heat declined with increasing uptake, the heats of adsorption rose as the adsorption amount increased. The heat of primary adsorption varied over a wide range across different adsorption capacities, with values from 30 to 73 kJ/mol. For secondary adsorption, the heat of adsorption of the CZ coal sample still decreased with increasing adsorption amount, while for the others, it gradually increased to a peak and then tended to stabilize. The values varied within a relatively narrow range, mainly within 34–47 kJ/mol. This also demonstrates that the water molecules interact more strongly with primary sites than with secondary sites.

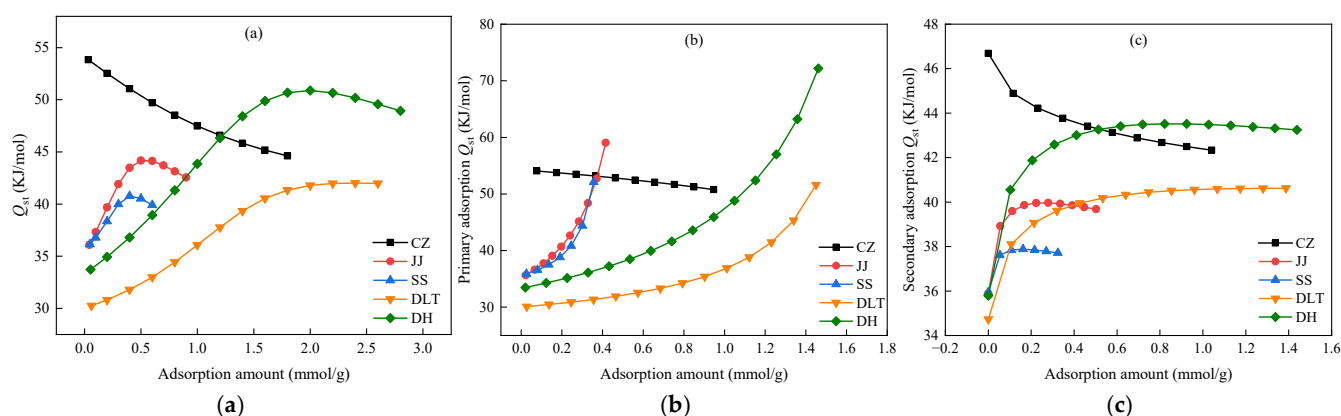


Figure 17. Relationships between (a) adsorption amount and heat of adsorption; (b) primary adsorption amount and heat of adsorption; (c) secondary adsorption amount and heat of adsorption.

Furthermore, at temperatures of 303.15–323.15 K, the heat of water vapor adsorption ranges from 30 to 54 kJ/mol, while for methane on coal of the same rank, the heat of adsorption ranges from 20 to 24 kJ/mol [64]. The difference between the two indicates that hydrogen bonding between water molecules leads to stronger interactions between coal and water vapor. Therefore, if water is present, methane molecules can only adsorb on low-energy sites, reducing the amount of methane adsorption in coal. This is consistent with existing research results [65,66].

3.4.2. Effects of Coal Microstructure on Isosteric Heat of Adsorption

The heat of water vapor adsorption on coal is governed by both surface chemical properties and pore structure [35]. As discussed in Section 3.4.1, the adsorption heat of the CZ coal sample decreased with increasing adsorption amount, whereas for all other coal samples, the adsorption heat initially increased with the adsorption amount, peaked, and then gradually stabilized. Therefore, to investigate the effects of coal microstructure on adsorption heat, the initial values of total adsorption heat ($Q_{st,0}$), primary adsorption heat ($Q_{st1,0}$), and secondary adsorption heat ($Q_{st2,0}$) were extracted for each coal sample.

The correlations between these parameters and the chemical structure and pore structure parameters of coal were then analyzed. The methodology for analysis was consistent with the description in Section 3.3.2.

The correlation analysis results between the initial values of total, primary, and secondary heats of adsorption and the chemical structure and pore structure parameters of coal are displayed in Figure 18. The initial values of various heats of adsorption are strongly correlated with the micropore structure parameters of coal, with especially significant correlations with micropore specific surface area (S_{mic}) and micropore volume (V_{mic}). Figure 19 illustrates the relationships between the initial adsorption heats and the S_{mic}/V_{mic} parameters of coal. The results indicate that the initial values of various heats of adsorption are all highly positively correlated with S_{mic} and V_{mic} , indicating that micropore structure is the key factor determining the initial heat of adsorption. This is because when water molecules enter micropores, the adsorption potentials of adjacent pore walls superimpose, and a single water molecule is simultaneously affected by multiple pore walls. The binding energy is much higher than that of planar adsorption, which leads to an increase in the heat of adsorption [67]. Moreover, a larger micropore specific surface area and pore volume provide more adsorption sites [22]. This enhances water vapor adsorption in the low-pressure region, yielding higher initial heats of adsorption. Furthermore, Figure 18 reveals that the Pearson correlation coefficients between the initial values of various heats of water vapor adsorption and S_{mic} and V_{mic} are very similar. Notably, the Pearson correlation coefficients between the initial values of total and primary heats of adsorption and S_{mic} and V_{mic} are equal. Combined with the phenomenon in Figure 17, where the initial value of primary heat of adsorption is very close to that of total heat of adsorption, this indirectly confirms that primary adsorption dominates during the initial stage of water vapor adsorption.

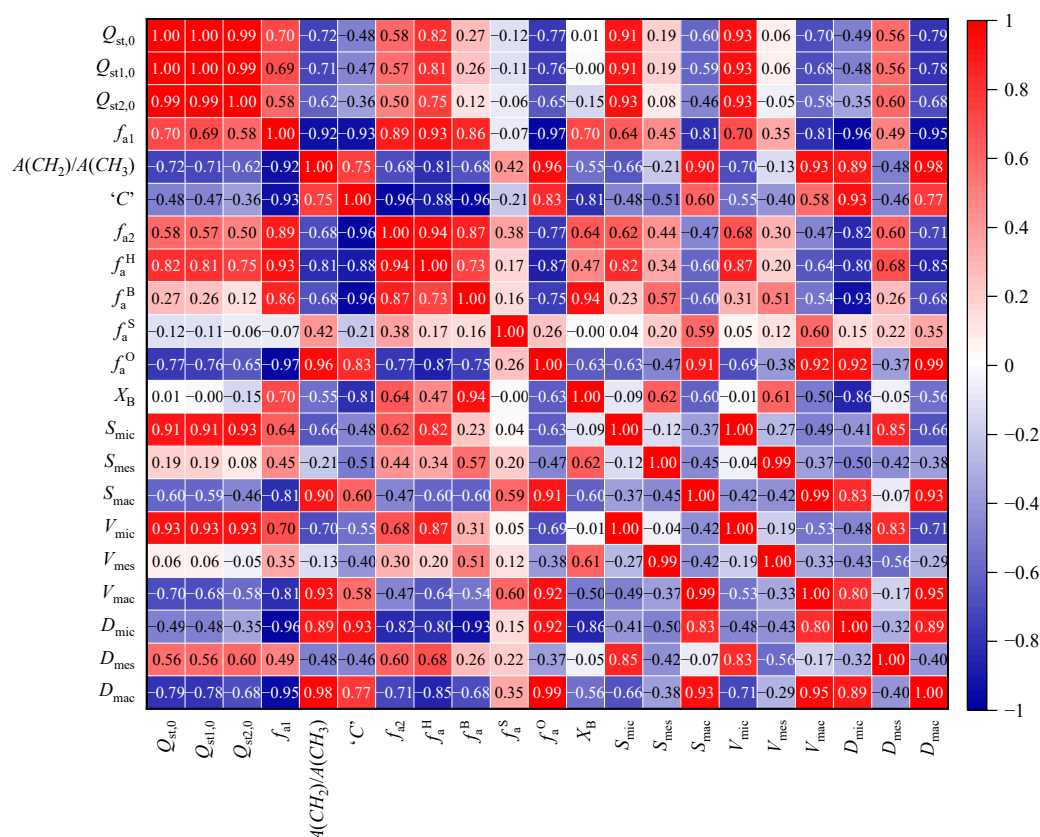


Figure 18. Pearson's correlation coefficients between initial value of adsorption heat and coal structure parameters.

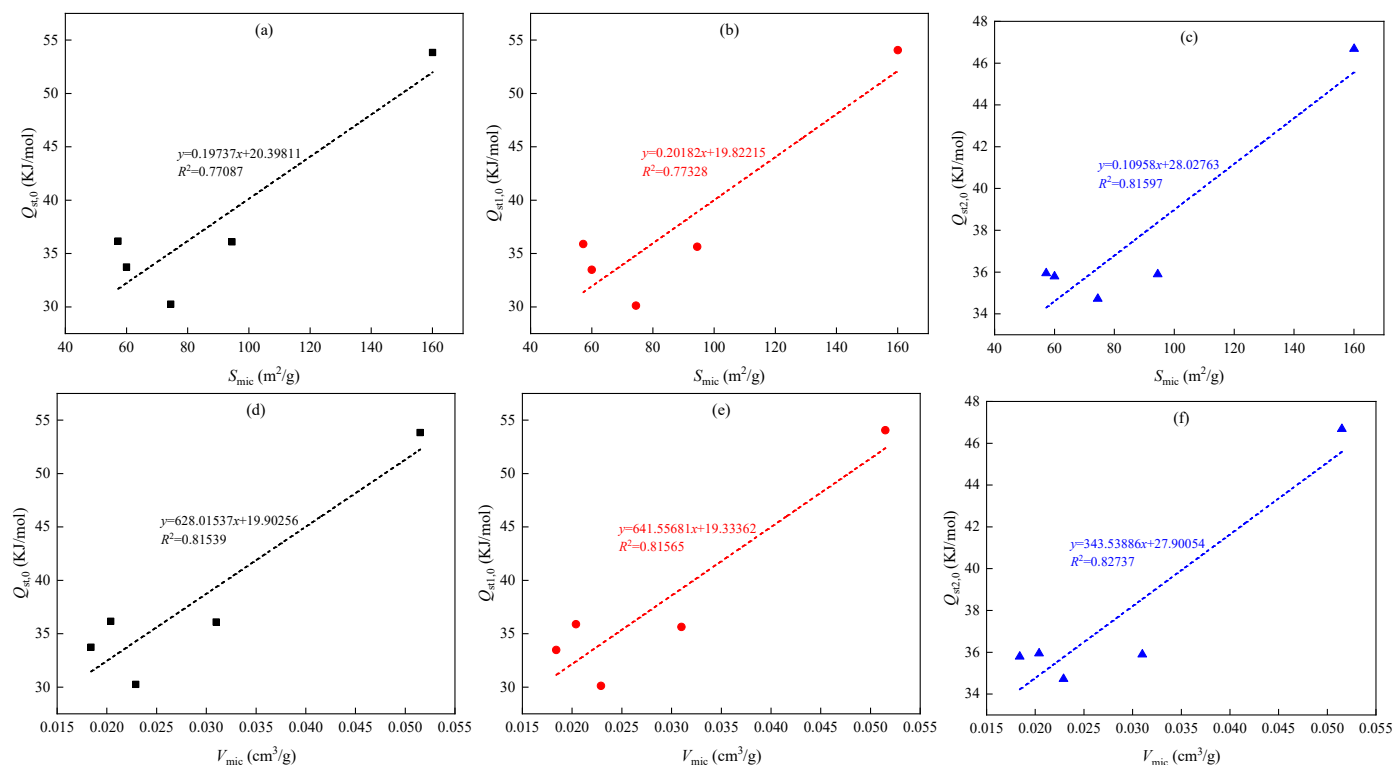


Figure 19. Relationships between initial value of adsorption heat and pore structure parameters: (a) $Q_{st,0}$ and S_{mic} , (b) $Q_{st,0}$ and S_{mic} , (c) $Q_{st,0}$ and S_{mic} , (d) $Q_{st,0}$ and S_{mic} , (e) $Q_{st,0}$ and S_{mic} , (f) $Q_{st,0}$ and S_{mic} .

4. Conclusions

In this study, the chemical structures of coal were analyzed using FTIR and ^{13}C -NMR. Pore structures were characterized using MIP, LTN₂A, and LTCO₂A. Subsequently, water vapor adsorption isotherms of coal samples were measured at 303.15 K, 313.15 K, and 323.15 K to obtain water vapor adsorption capacities and adsorption heat values. The influences of the chemical and pore structures on the amount of water vapor adsorption and adsorption heat were systematically investigated. The key findings are summarized below:

1. For the high-rank CZ coal, the total, primary, and secondary adsorption heats all decreased with increasing water vapor adsorption amount. For the other four coal samples, the total adsorption heat gradually increased to a peak and then decreased, the primary adsorption heat increased with increasing adsorption amount, and the secondary adsorption heat increased initially and then stabilized. The total adsorption heat ranges from 30 to 54 kJ/mol, the primary adsorption heat from 30 to 73 kJ/mol, and the secondary adsorption heat from 34 to 47 kJ/mol.
2. The surface hydrophilicity/hydrophobicity of coal is a critical factor governing the amount of water vapor adsorption. The related parameters ' C ', f_a^B , and X_B range from 0.22 to 0.55, 0.0985 to 0.2726, and 0.1987 to 0.3211, respectively. The water vapor adsorption capacity is highly positively correlated with ' C ' ($r > 0.9$), while it is significantly negatively correlated with f_a^B and X_B ($|r| > 0.9$).
3. The micropore fractal dimension varies between 2.26695 and 2.41057. An increase in micropore fractal dimension promotes water vapor adsorption, with its most pronounced effect observed on the amount of secondary adsorption, where the correlation coefficient between secondary adsorption amount and micropore fractal dimension reaches 0.90.

4. Micropore structure is the dominant factor determining the initial values of adsorption heat. The correlation coefficients between the initial values of water vapor adsorption heat and both micropore specific surface area (57.24–160.06 m²/g) and micropore volume (0.0184–0.0515 cm³/g) all exceed 0.9. The initial values of both total and primary adsorption heats vary within 30–55 kJ/mol, showing high consistency, which corroborates primary adsorption's predominance during the initial stage of the adsorption process.
5. This study primarily examined the influence of the surface chemical properties and pore structure of coal on the thermodynamic behavior of water vapor adsorption. However, the types and amounts of mineral constituents in coal (e.g., clay minerals) may also play significant roles in the adsorption process. Accordingly, future research will systematically elucidate the mechanisms by which mineral composition and content influence coal–water vapor adsorption characteristics and thermodynamic behavior.

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Abbreviations

The following abbreviations are used in this manuscript:

M_{ad}	Moisture
A_{ad}	Ash
V_{ad}	Volatile
F_{cad}	Fixed carbon
C_{ad}	Carbon element
H_{ad}	Hydrogen element
O_{ad}	Oxygen element
N_{ad}	Nitrogen element
$R_{0,max}$	Maximum vitrinite reflectance
S_t	Total pore surface area
S_{mic}	Micropore surface area
S_{mes}	Mesopore surface area
S_{mac}	Macropore surface area
V_t	Total pore volume
V_{mic}	Micropore volume
V_{mes}	Mesopore volume

V_{mac}	Macropore volume
D_t	Total pore fractal dimension
D_{mic}	Micropore fractal dimension
D_{mes}	Mesopore fractal dimension
D_{mac}	Macropore fractal dimension

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