Relationship between the Geological Origins of Pore-Fracture and Methane Adsorption Behaviors in High-Rank Coal

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ABSTRACT: Coal is characterized by a complex pore-fracture network and functional groups, which are derived from various geological origins and which further affect methane adsorption. To explore the relationship between the geological origins of pore-fractures and methane adsorption behaviors, we conducted pore structure tests and adsorption isotherms on six Qinshui high-rank coals. The pores and fractures were observed using an optical microscope (OM), a field emission scanning electron microscope (FESEM), and a high-resolution transmission electron microscope (HRTEM), and the pore structure parameters were determined using mercury intrusion and low-pressure N₂ and CO₂ adsorption. High-pressure CH₄ adsorption isotherms were obtained at 30 °C using the manometric method. Results show that the Qinshui high-rank coals develop five stages of pore size distribution, consisting of the smaller micropore stage (0.3−1 nm), the larger micropore and smaller mesopore stage (1−10 nm), the mesopore and smaller macropore stage (10−110 nm), the microfracture stage (0.11−40 µm), and the larger macropore stage (>40 µm). The micropores dominate the total pore volume (PV) and specific surface area (SSA). Pores and fractures of various morphologies and sizes have different geological origins, which are related to coalification and stress field evolution. Methane adsorption on coals mainly occurs in the micropores as a form of volume filling. The maximum pore size for complete gas filling (MPSCGF) ranges from 0.60 to 0.88 nm in Qinshui high-rank coals. The coal-forming geological processes, such as coalification and stress field evolution, contribute to various pores and fractures, which show different pore sizes and functional groups. The geological origins of pores and fractures control the methane adsorption behaviors in coals by way of the pore size and functional groups. Surface coverage-related methane adsorption behavior occurs in fractures, primary pores, and large-scale secondary pores, while micropore filling is the methane adsorption behavior in macromolecular pores and small-scale secondary pores. The aim of this study is to provide a new insight into the methane adsorption on coals from the geological process of the formation and modification of pores and fractures.

1. INTRODUCTION

Coal, which is affected by multistage coalification and tectonic activities, is characterized by a complex pore-fracture structure and a strong surface chemical heterogeneity.¹ Gas storage in coals correlates with the pore-fracture structure and functional group distribution.²,³ Storage by methane adsorption on coal is considered to be a physical process resulting from intermolecular interactions between methane and pore walls.⁴,⁵ This affinity is not only related to a higher specific surface area (SSA) of micropores⁶ but also determined by the volume filling of methane in micropores.⁷ Several theoretical, experimental, and numerical simulation studies have been carried out on the relationship between pore size and methane adsorption capacity, and a series of advances have been made.⁸−¹¹ Pore size not only determines the methane adsorption amount but also affects the methane adsorption behavior on coals.¹²,¹³ Various methane adsorption behaviors on coal exist together, and the volume filling only appears in pores smaller than 2 nm (micropore), while monolayer and multilayer adsorptions are more common in meso- and macropores.¹⁴ In addition, the interaction between functional groups and methane is also quite different, especially the influence of oxygen-containing functional groups on methane adsorption is controversial.¹⁵,¹⁶ Yu et al.¹⁷ found that aromatic nuclei have the highest methane adsorption capacity and the adsorption capacity of the oxygen-containing functional groups on methane is stronger than that of the methyl group. More and more scholars believe that the methane adsorption behavior on coals is jointly controlled by pore size and functional groups, with pore size showing an increasing effect as the coal rank increases.¹⁸ It is a fact that pore size and functional groups

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In this study, mercury intrusion and gas adsorption were conducted on Qinshui high-rank coals to evaluate the pore-fracture structure and the methane adsorption capacity. First, a full-scale pore size distribution on the Qinshui high-rank coals was established and the formation and modification of different genetic types of pores and fractures with methane adsorption behaviors on coals.

In this study, mercury intrusion and gas adsorption were conducted on Qinshui high-rank coals to evaluate the pore-fracture structure and the methane adsorption capacity. First, a full-scale pore size distribution on the Qinshui high-rank coals was established and the formation and modification of different genetic types of pores and fractures in high-rank coal were expatiated. Then, we analyzed the relationship between pore size and methane adsorption. Third, the maximum pore size for complete gas filling (MPSCGF) was calculated to establish methane adsorption models in pores and fractures of different sizes using crushing and sieving. Our group had different scale pores and fractures in the Qinshui high-rank coal varies during the geological history, resulting from the evolution of the pore and fracture. However, there is a lack of understanding of the relationship between the geological origins and formation of pores and fractures with methane adsorption on coals.

2. SAMPLES AND METHODS

2.1. Samples. The high-rank coals were collected from six coal mines in Qinshui Basin (Yw, Lc, Xj, Bf, Cz, and Sh coal mines). Each sample was aliquot into four sets (2–3 cm for mercury intrusion, 35–60 mesh for determining vitrinite reflectance and maceral observation, 60–80 mesh for gas adsorption, >100 mesh for proximate and ultimate analyses) with different sizes using crushing and sieving. Our group had conducted the proximate and ultimate analyses in our previous studies, and the basic parameters of these coals are shown in Table 1. The proximate and ultimate analyses and petrographic properties of Qinshui high-rank coals are as follows:

Table 1. Proximate and Ultimate Analyses and Petrographic Properties of Qinshui High-Rank Coals

| Sample no. | Rv/% | Vitrinite | Inertinite | Mineral | Mdaf | Aad | VMdaf | FCdaf | Hdaf | Cdaf | Ndaf | Odaf |
|------------|------|-----------|------------|---------|------|-----|-------|-------|------|------|------|------|
| Lc         | 2.19 | 72.60     | 21.40      | 6.00    | 1.10 | 11.98 | 13.44 | 76.19 | 4.12  | 91.73 | 1.12  | 2.44  |
| Yw         | 2.38 | 73.16     | 23.66      | 3.18    | 1.96 | 5.72  | 11.59 | 83.36 | 3.90  | 91.17 | 1.09  | 2.84  |
| Xj         | 2.64 | 68.86     | 28.54      | 2.59    | 1.66 | 10.02 | 10.10 | 80.89 | 3.96  | 91.52 | 1.06  | 3.05  |
| Bf         | 2.83 | 69.74     | 27.50      | 2.75    | 2.05 | 9.40  | 9.86  | 81.67 | 3.85  | 91.82 | 1.06  | 2.42  |
| Cz         | 2.96 | 75.80     | 21.40      | 2.80    | 2.71 | 12.18 | 6.94  | 81.72 | 3.21  | 92.84 | 1.01  | 3.27  |
| Sh         | 3.33 | 79.84     | 18.36      | 1.80    | 1.48 | 13.12 | 6.32  | 81.39 | 2.15  | 93.45 | 1.00  | 2.98  |

2.2. Pore Characterization. 2.2.1. Visual Observation. The different scale pores and fractures in the Qinshui high-rank coals were observed using an optical microscope (OM), a field emission scanning electron microscope (FESEM), and high-resolution transmission electron microscopy (HRTEM). The OM observation was carried out under reflected light using a Leitz MPVIII microphotometer. The coals were at the size of 2 cm x 2 cm x 4 cm with one polished and burnished surface. The FESEM analysis was conducted using a ZEISS Sigma300 high-performance FESEM. Bulk coals were crushed and polished into little lumps approximately 8 mm across and 7 mm high using a polishing and burnishing machine. The HRTEM observations were performed on a 200 kV transmission electron microscope (FEI Tecnai G2 F20). The pulverous coals were diluted with ethanol and homogenized to disperse the particles.

2.2.2. Mercury Intrusion Porosimetry (MIP). The MIP analyses were carried out in the Key Laboratory of Coalbed Methane Resources and Reservoir Formation Process of the Ministry of Education, China University of Mining and Technology. Samples with sizes of 2–3 cm were vacuum-dried at a temperature of 110 °C for 4 h and then placed in an AutoPore IV 9510, Micrometrics Instrument, which could automatically control the experiments via a software that was embedded in the instrument. After evacuation, the samples were pressurized from 3.52 kPa to 414 MPa and the mercury contact angle and surface tension during intrusion were set to 130° and 0.48 N/m, respectively. Due to the compressibility of coal pores at high pressures, especially low mesopores at pressures above 20 MPa, the results from mercury intrusion were corrected for coal compressibility. The experimental procedure and data calculation followed the standard method (ISO 15901-1:2005).

2.2.3. Low-Pressure Nitrogen Adsorption (LPNA) and Low-Pressure Carbon Dioxide Adsorption (LPCA). The LPNA and LPCA analyses were conducted on 60–80-mesh coals. The coals (about 20 g each) were degassed under a vacuum at 120 °C for 12 h prior to adsorption analysis. The adsorption measurements were carried out at 0 °C in an ice bath for CO2 and at −196 °C in liquid nitrogen for N2 using the Autosorb IQ series Micropore physisorption/chemisorption analyzer from Quantachrome. The instruments were employed according to the determination methods of pore distribution and porosity in solid porous materials (ISO 15901-2:2006 and ISO 15901-3:2007). The pore structure parameters were calculated automatically using Autosorb computer software at relative pressures (P/P0) in the range of 0.01 < P/P0 < 0.995 for N2 adsorption and 0 < P/P0 < 0.032 for CO2 adsorption. The pore volume (PV), SSA, pore size, and the average pore diameter from N2 adsorption were evaluated from density functional theory (DFT). The micropore SSAs, micropore volume, and the average micropore diameter were determined from CO2 adsorption data also using the DFT method.

2.3. CH4 Adsorption Isotherm Experiments. To measure the adsorption isotherms, coal samples were sieved with a 60–80 mesh and dried for 2 h at 105 °C. Next, moisture equilibration of six coals was conducted according to the ASTM Standard D 1412-93. To restore the coals to bed
Table 2. Physical—Structural Properties of Samples from MIP, LPNA, and LPCA

| methods    | properties                  | Lc  | Yw  | Xj  | Bf  | Cz  | Sh  |
|------------|------------------------------|-----|-----|-----|-----|-----|-----|
| MIP        | total intrusion volume (10⁻¹ cm³/g) | 0.35 | 0.39 | 0.35 | 0.35 | 0.38 | 0.33 |
|            | total pore area (m²/g)          | 17.87 | 22.03 | 18.50 | 19.73 | 21.17 | 18.49 |
|            | average pore diameter (4V/A) (nm) | 7.80 | 7.10 | 7.50 | 7.00 | 7.30 | 7.00 |
|            | porosity (%)                   | 4.44 | 4.79 | 4.30 | 4.33 | 4.84 | 4.22 |
| LPNA       | DFT surface area (10⁻¹ m²/g)    | 2.98 | 7.27 | 1.82 | 1.18 | 11.95 | 2.47 |
|            | DFT pore volume (10⁻⁴ cm³/g)    | 17.64 | 5.41 | 5.63 | 8.59 | 37.8 | 10.00 |
|            | DFT pore diameter (nm)          | 10.13 | 29.40 | 2.58 | 12.55 | 6.79 | 6.79 |
| LPCA       | DFT pore volume (cm³/g)        | 0.05 | 0.06 | 0.05 | 0.05 | 0.08 | 0.07 |
|            | DFT surface area (m²/g)        | 160.67 | 192.00 | 164.62 | 177.13 | 251.72 | 226.46 |
|            | DFT average pore width (nm)    | 0.50 | 0.50 | 0.52 | 0.50 | 0.50 | 0.50 |

Figure 1. High-pressure CH₄ adsorption isotherms using pressure (a) and density (b) at 30 °C.

3. RESULTS

3.1. Pore Structure Properties. The results of MIP, LPNA, and LPCA methods are presented in Table 2. The results show that the ranges of the PV, SSA, and average pore diameter of the Qinshui high-rank coals determined by MIP are 0.033–0.039 cm³/g, 17.87–22.03 m²/g and 7.0–7.8 nm, respectively. These pore structure parameters determined by LPNA are 5.41 × 10⁻⁴–37.8 × 10⁻⁴ cm³/g, 0.118–1.195 m²/g, and 2.58–29.4 nm, respectively, and they are 0.05–0.08 cm³/g, 160.67–251.72 m²/g, and 0.5–0.52 nm, respectively, according to LPCA. In general, the development of micropores and macropores is relatively uniform, but the pore structure parameters of mesopores vary. Significantly, the PV and SSA measured by LPNA are much lower than those measured by MIP and LPCA, and the latter account for more than 99% of the total PV and SSA in the Qinshui high-rank coals. The significantly low PV and SSA determined by LPNA may have resulted from (1) the fact that mesopores weakly developed in these Qinshui high-rank coals (2) the mobility of liquid nitrogen is too low to enter the pore with a nanoscale pore throat, resulting in a significant decline of the detectable pore. Therefore, the PV and SSA determined by LPNA can be ignored when methane adsorption behaviors in pores of various sizes are discussed.

3.2. CH₄ Adsorption Isotherms and Fitting Data. The equilibrium excess adsorption isotherms for CH₄ at 30 °C and up to 12 MPa are displayed in Figure 1a. For the fitting of supercritical gas adsorption, pressure is replaced by gas density, as shown in Figure 1b. The adsorption curves in these two diagrams show a similar Langmuir-like tendency. All of the excess adsorption amounts have a rapid increase at low pressures.
(0–4 MPa) but a slow increase at high pressures (4–12 MPa). The increase rates are 0.28 and 0.04 mmol/g·MPa, respectively. The highest adsorption amount (1.83 mmol/g) at the pressure of 12 MPa was recorded for the Sh coal and the lowest amount (1.22 mmol/g) for Lc coal. The adsorption curves of Yw, Xj, and Bf coals present significant repetitions and crossovers. These similar adsorption curves at the entire range of pressures probably result from the similar coal properties of these above coals. The adsorption fitting parameters obtained from the MDR model are summarized in Table 3.

4. DISCUSSION

4.1. Full-Scale Pore Size Distribution (PSD) and Pore-Fracture Development. LPCA can probe micropores in the range of 0.3 nm ≤ d ≤ 1.5 nm, determined using the DFT method. Effective PSD analyzed using LPNA is in the range of 2 nm ≤ d ≤ 0.3 μm. However, the LPNA data indicated that mesopores of size between 2 nm and 0.3 μm could be ignored in the total mesopore volume because of their extremely low PV and SSA values. MIP can detect most of the mesopores and macropores with pore sizes ≥3 nm. According to Table 2, the MIP and gas adsorption results indicated that the development order of pores in the Qinshui high-rank coals is micropore > macropore > mesopore. The mesopore and its contribution on gas adsorption can be neglected in Qinshui high-rank coals. Therefore, a combination of PSD determined by MIP and LPCA is presented here to show the complete PSD of the high-rank coal (Figure 2a,b). Although pores ranging from 1.5 to 3 nm are missing using LPCA and MIP, a high connectivity can be discerned in the PSD, implying that the development of these pores has a similar distribution to their neighbors. Hence, it can be suggested that the PSD determined by MIP and LPCA can indicate the complete PSD of the Qinshui high-rank coals in this study. In addition, these coals have low mineral contents, and statistical results indicate that inorganic minerals account for 1.8–6.0% of the total coal maceral. The pores and fractures in macerals can represent the whole pore-fracture system of Qinshui high-rank coals in terms of both quantity and genetic types. Also, the micropores are mainly distributed in the organic matters, especially vitrinite, and hence, the major fraction of methane is stored in organic-related pores and fractures. Based on these reasons, the pores and fractures in this study focus on the voids in and around the macerals.

According to the PSD of PV and SSA, the development of pores and fractures in Qinshui high-rank coals can be divided into five stages. They include the smaller micropores (stage I, 0.3–1.0 nm), the larger micropores and smaller mesopores (stage II, 1.0–10 nm), the mesopores and smaller macropores (stage III, 10–110 nm), microfractures (stage IV, 0.11–40 μm), and the larger macropores (stage V, >40 μm). From Figure 2, it can be discerned that there are obvious changes in PV in stage I, and the peak occurs near 0.5 nm. There is a stable distribution of PV in stage II, but a decrease occurs in stage III. The poor development of PV can be observed in stage IV, but some increases appear in stage V, and the maximum value is similar to that in stage III, suggesting a development of macrofractures. Comparatively, the distribution of SSA is characterized by a monotone decrease with the increase in pore size. The maximum SSA occurs near 0.5 nm, similar to the PV distribution. Subsequent to the peak, the SSA falls into a continuous reduction and it is almost zero during stages IV and V. These results suggest that no matter what the shapes of pores and fractures are after the pore size is larger than 1 nm, there is no effect on the total SSA.

4.2. Formation and Modification of Various Pores and Fractures in High-Rank Coals. The pores in coal can be divided into primary pores and secondary pores according to their genesis, and their morphology and quantity are quite different.27 During the coalification and tectonic movement, the pores in coals show the deformation, reduction, and even extinction of primary pores but the formation, expansion, and deformation of secondary pores. The formation of fractures in coals is due to the mechanics-driven failure of the original structure. According to the formation mechanism, the fractures consist of structurally unstable fractures and stress-induced fractures.27 The structurally unstable fractures are due to the matrix shrinkage during gas emission from coal macromolecules.

### Table 3. Adsorption Parameters Fitted by the MDR Model

| sample no. | equilibrium moisture content/% | \(n_0\) mmol/g | D | \(R^2\) | \(E/\) kJ·mol⁻¹ |
|------------|-------------------------------|--------------|---|---------|-----------------|
| Lc         | 3.42                          | 1.79         | 0.068 | 0.97    | 9.74            |
| Yw         | 3.01                          | 2.02         | 0.070 | 0.97    | 9.60            |
| Xj         | 3.27                          | 2.14         | 0.080 | 0.99    | 8.91            |
| Bf         | 3.36                          | 2.07         | 0.075 | 0.95    | 9.21            |
| Cz         | 2.89                          | 2.27         | 0.066 | 0.94    | 9.81            |
| Sh         | 2.45                          | 2.55         | 0.070 | 0.92    | 10.29           |

"Annotation: \(n_0\) maximum adsorption capacity; D, a constant related to the affinity of coal for the methane; \(R^2\), goodness of fit; \(E\), adsorption heat.

![Figure 2. Pore size distribution of PV and SSA at the full scale of Qinshui high-rank coals. (a) PSD vs PV; (b) PSD vs SSA.](https://doi.org/10.1021/acsomega.1c07402)
Therefore, they are commonly characterized by extension attributes. However, the stress-induced fractures are derived from tectonic stress and overburden stress, and hence, they have various mechanical origins. These fractures occur in groups because of the regional distribution of the stress field, and their direction is highly determined by the tectonic stress field.
4.2.1. Primary Pores. Primary pores, formed in peat accumulation, mainly include plant tissue pores and intergran pores of organic matter. Their pore size is generally in the micron scale, belonging to mesopores and macropores. Because the plant debris suffered from strong gelation, compaction, and multistage tectonic activities, plant tissue pores, derived from cell cavities, presented an irregular, sharp, and scattered distribution. The quantity and size of plant tissue pores have a negative relationship with coal rank, and their development is controlled by maceral.28 The occurrence of these pores is infrequent in Qinshui high-rank coals, which can only be observed in fusinite and semifusinite, and their shapes demonstrate a strong deformation. During deposition and coal formation, the increasing vertical stress and multistage tectonic stress in different directions cause the original plant tissue pores to undergo various deformations and compressions (Figure 3a).

The intergran pores result from the stacking of macerals in different shapes. The shapes are irregular, semiregular, and round, and the size is similar to that of plant tissue pores. These pores are generated from the accumulation of organic matter particles, which are derived from the humification and mechanical damage during early coalification, but these may also be the result of tectonic-induced damage during tectonic uplift and subsidence.29 The characteristics of these pores are similar to the clastic rock reservoir, and the deformation of these pores also occurs under various tectonic stress fields. The compaction among the clastics plays a significant role in the decrease in intergran pores (Figure 3b). Overall, during the coalification and tectonic activities, deformation and modification are the major evolution of the primary pores.

4.2.2. Secondary Pores. Secondary pores form during a series of physicochemical reactions in coalification and mainly consist of gas pores after volatile emission and macromolecule pores after polycondensation of the benzene ring. The different macerals have various hydrocarbon-generation widows and potentials, resulting in secondary gas pores usually occurring independently. Generally, secondary gas pores are the most developed in vitrinite. Secondary gas pores are the product of the detachment of the volatile side chain and functional groups from coal macromolecules. The initial pore size ranges from subnanoscale to nanoscale, and the shape of these nanopores is basically round or oval. However, with the increase in gas generation amount, gas pores expand and merge with each other and eventually approach the micron scale (Figure 4a).

Significantly, pores of a larger size tend to have a more complex shape. This is because (1) larger pores are formed by the amalgamation of several smaller pores during thermal evolution; (2) the larger pores have a lower curvature of the pore wall and therefore present a stronger deformation. Another type of micropore with a smaller size exists inside the macromolecule structure of coals. As the coal rank increases, the aliphatic chain in the coal macromolecule cuts down and the aromatic nucleus occurs in polycondensation. These micropores decrease during the early thermal evolution because of the reduction of the aliphatic chain and then exhibit a significant increase.30 A previous study suggested that the macromolecule pores are composed of the aliphatic chain in low-rank coals, but these pores occur between the aromatic structure layers in high-rank coals.31 The coalification prompts the polycondensation of the micromolecule aromatic nucleus and the direction arrangement of the aromatic structure, resulting in increases in the micropore volume between the aromatic structure layers (Figure 4b). The pore size of the macromolecule pores is determined by the extension and accumulation of the aromatic nucleus and commonly ranges from the subnanoscale to the nanoscale.

4.2.3. Structurally Unstable Fractures. Structurally unstable fractures are relatively small and independent and have no specific direction. Their formation sites appear near the suture between macerals and minerals or different macerals. The shape of fractures is constrained by the edge of the matrix and therefore shows a high curvature. The formation of this fracture results from the different physical and chemical properties of the macerals. During coalification, different macerals experience various deformations and hydrocarbon expulsions, resulting in a shrinkage of the matrix. Hence, a gap appeared between the macerals, and it further extended along the original contact face. Therefore, it is clear that these fractures are characterized by the extensional attribute. The difference in compositions and origins among the macerals in contact with each other results in the mechanical structure of these macerals being unstable during coalification and various stress fields. Therefore, the fractures preferentially generate along the edge of macerals. Also, structurally unstable fractures can form between the organic matter and minerals. However, these fractures are more likely to be open at the organic matter side because of the stability of minerals during the changes in temperature and pressure. The formation mechanism of this fracture had been reported by our group, and this fracture is also referred to as differential deformation fracture.32 These fractures enlarge the SSA of organic matter and produce a fresh face of the unsaturated
function groups and therefore provide new sites associated with unbalanced charges. On the one hand, with the process of coalification and the change in physical–chemical conditions, the dehydration of the coal matrix and the detachment of the side chain on coal macromolecules cause a matrix shrinkage. On the other hand, the accumulation of gas produces a locally high pressure, resulting in a breakthrough toward the extensional face caused by the matrix shrinkage. Therefore, this fracture presents a considerable extension in the macerals (Figure 5).

4.2.4. Stress-Induced Fracture. The role of external force on coal also directly facilitates the formation of fractures; these fractures show complex shapes, and their arrangement, size, and direction show a significant affinity with the stress field. Generally, the ground stress is divided into compression, tension, and shear, and each stress can produce various fractures during the whole coalification process. The most representative fractures in coals are cleat systems, including face cleat and bull cleat. The width of these fractures commonly ranges from a few microns to tens of microns but approaches several millimeters in some tensional structural positions. The formation of cleats is affected by macerals, coalification, ground stress, and so on, resulting in significant variation in their extension, aperture, and density. Generally, cleat systems, characterized by a stable geometry and open structure, comprise two sets of fractures, which are mutually perpendicular and also perpendicular to the bedding. The origins of cleats are controversial. However, because of the uniformity and directivity of the cleat system in coal seams, as well as maceral-related selective development of the cleats, most scholars tended to consider a mixed origin combined with coalification and stress effect. In addition, tectonic stress can easily result in the formation of various fractures by means of the physical damage of the coal matrix. Although the properties of tectonic stress fields are different, all of these fractures are characterized by a rough surface and a weak...
maceral selection. For example, after the formation of Carboniferous-Permian coals, the Qinshui Basin experienced multiple tectonic activities and conversions of stress fields, and therefore, many tectonogenetic fractures were produced. This is why the Qinshui high-rank coals show an increase in macropore distribution. These fractures widely distribute in various macerals, and the fracture aperture has a wide range from the micron scale to millimeters, and the multistage tectonic activities result in multistage fracture systems and their connection (Figure 6). The compression-induced fractures have a straight shape and present a weak maceral selection. Different groups of these fractures cut the coals into rhombic nubs. However, tension-induced fractures show curvelike and steplike shapes and have a rough or serrated surface. When they cross different macerals, their trend and width significantly change. These results are associated with the mechanical strength of different macerals. Because the stress-induced fracture is the result of physical damage, coal macromolecule units on the fracture surface break, producing unsaturated side chains and heterocycles. Therefore, a higher roughness and charge unsaturation occur on the fracture surface.

4.3. Pore Size Effect on Methane Adsorption. Our data indicated that there is no relationship between methane adsorption capacity with the PV and SSA of mesopores and macropores (Figure 7a−d), but a high positive correlation (0.73 and 0.75) occurs in the micropores (Figure 7e,f). However, this result does not deny that methane adsorption occurs in mesopores and macropores. Previous studies suggested that the methane adsorption capacity showed some positive relationship with SSA of mesopores and macropores in coals or shales.36,37 This observation did not occur in this study, which may result from the fact that our coals extremely develop micropores, and mesopores and macropores can be neglected during methane adsorption.

The high negative correlation between adsorption heat and micropore size also suggests that pore size plays a significant role in methane adsorption (Figure 8a). The high adsorption heat that occurred in micropores is attributed to the overlap of adsorption potentials in narrow pores.12 A smaller pore size contributed to a higher overlap of the adsorption potential between the opposite pore walls, and therefore, more methane molecules were attracted, which resulted in a micropore filling and a high adsorption heat.7 Interestingly, according to our data, when the pore size is smaller than 1.14 nm, the adsorption capacity is negatively correlated with pore size, while when the pore size is larger than 1.14 nm, the adsorption capacity remains unchanged (Figure 8b). This observation is also supported by previous studies.12,39 The strong adsorption potential allows volume filling in the narrow micropores. However, the increase in pore size causes the decrease in adsorption potential in the center of pores and the pore center loses its attraction to methane. When the pore size reaches a certain value, the adsorption potential between pore walls has no overlap, and adsorption only occurs on the pore wall. At this time, the increase in pore size does not affect the adsorption capacity anymore. In this study, this value is approximately three times the methane molecular dynamic diameter (0.38 nm), suggesting that the maximum pore size for methane completely filling is less than the height of three layers of adsorbed methane in Qinshui high-rank coals. Therefore, according to the relationship between the methane adsorption capacity and micropore size, it can be speculated that there is an upper limit of the pore size, namely, MPSCGF, above which the adsorption potential of the pore wall cannot attract methane in the pore center, and the volume filling cannot occur anymore. The MPSCGF of Qinshui high-rank coals will be evaluated considering the number of adsorbed methane layers later.

4.4. Methane Adsorption in Various Pores and Fractures and Its Control Mechanism. 4.4.1. MPSCF and Various Adsorption Behaviors in Coals. A previous study demonstrated that coals with different pore size distributions and chemical structures (i.e., oxygen-containing functional group) contribute to various methane adsorption behaviors.38 Although our fitting results indicated extremely high R² values (Table 4) and previous studies also demonstrated that the MDR

![Figure 8. Relationship between the micropore diameter evaluated from the DR method with adsorption heat (a) and adsorption capacity (b).](https://doi.org/10.1021/acsomega.1c07402)

| Sample | Lc | Yw | Xj | Bf | Cz | Sh |
|--------|----|----|----|----|----|----|
| A/cm²·g⁻¹ | 178.54 | 214.03 | 183.12 | 196.86 | 272.89 | 244.95 |
| λ | 0.95 | 0.90 | 1.14 | 1.00 | 0.79 | 1.00 |
| d/nm | 0.72 | 0.68 | 0.88 | 0.77 | 0.60 | 0.76 |
number of molecule layers in the adsorbed phase. It will be clear how large a pore can be completely filled using adsorbed molecule layers. The equation is given by

\[ V_a = A \left[ \frac{1}{10^{-3} \rho_a A v} \right]^{1/3} \lambda \]  

where \( V_a \) is the maximum volume of the adsorbed phase that can be calculated from the maximum absolute adsorption capacity and \( A \) is the SSA of the adsorbent, which is the sum of SSAs determined by MIP and LPCA. \( \rho_a \) is the density of the adsorbed phase (0.42 g/cm\(^3\)), \( A v \) is Avogadro’s number (6.022 \times 10^{23}), and \( \lambda \) is the average number of adsorbate layers.

When the oppositely adsorbed methane molecules are just in contact at infinite pressure, the pore size is equal to the height of the adsorbed phase. This pore size is considered to be MPSCGF. The calculation method is as follows

\[ D = 2 \times d_{\text{gas}} \times \lambda \]  

where \( D \) is the pore size, which is the upper limit for the gas molecule completely filling, \( d_{\text{gas}} \) is the kinetic diameter of the gas molecule (0.38 nm for CH\(_4\)), and \( \lambda \) is the average number of adsorbate layers.

The calculation results of the average number of adsorbed layers and MPSCGF are listed in Table 4. At the temperature of 30 °C, the average number of the adsorbed methane molecule layer ranges from 0.79 to 1.14, indicating a monolayer adsorption on Qinshui high-rank coals. These results suggested that methane could not form two or more adsorbed layers on the single pore surface of Qinshui high-rank coals. Comparison of the MPSCGF and the micropore size distribution of Qinshui high-rank coals indicates that the range of the dominant micropore size is less than that of MPSCGF (Figure 9a). Above the MPSCGF, due to the decrease in attraction to methane in the pore center, volume filling becomes impossible in these pores, but coverage-like adsorption can still be formed on the surface of the pores. Molecule modeling results also demonstrated that as the pore size increased, the adsorbed methane only occurred on the surface of the pore and the value of the adsorbed density remained unchanged in those larger pores, and its pore size for volume filling is similar to our calculation. Accordingly, methane adsorption behaviors in pores of different sizes can be established. (1) In the micropores below MPSCGF, methane shows a volume filling adsorption (Figure 9b). (2) In the micropores above MPSCGF, methane shows a monolayer surface coverage adsorption, and a multilayer adsorption occurs only on a few high-energy adsorption sites. A low accumulation of methane may occur in the center of pores because of the interaction of adsorbed layers on the pore walls (Figure 9c). (3) In the mesopores and macropores, only the monolayer adsorption and a few multilayer adsorptions occur (Figure 9d).

**4.4.2. Functional Groups of High-Rank Coals and Their Effects on Methane Adsorption.** Although the methane adsorption capacity on different functional groups of coals is controversial, it has been widely accepted that there are significant differences in the adsorption capacity in different functional groups.\(^{15,16}\) Therefore, the difference in chemical structures on pores with the same size can also contribute to various methane adsorption behaviors. Pores and fractures, generated from different geological origins, are characterized by various surface chemical structures. Force-induced fracture is a product of the cracking of the coal macromolecule and the aliphatic chain, and even polymerized aromatic nuclei have been split. Hence, a high heterogeneity and roughness appeared on the surface of these fractures at the macromolecule level, producing many high-energy charge underbalance-related adsorption sites. However, after the cracking of the aliphatic side chain and polycondensation, species of functional groups and heterogeneity on the macromolecule pore and the secondary pore decrease. The aromatic structures constitute the surface of these pores, resulting in a uniform adsorption capacity. Recent numerical modeling results suggested that the pore wall consisting of oxygen-containing functional groups is more attractive to methane than that of benzene rings.\(^{31}\) Basically, primary pores, large secondary pores, and early-generated fractures had experienced a complex coalification and in fact led to the homogenization and ordering of the functional
groups on the surface of pores and fractures. As a result, the aromatic rings became the main chemical structures on the surface of these pores and fractures. In contrast, many high-energy charge underbalance-related adsorption sites were produced on the surface of the newly generated fractures, resulting from the cracking of the functional groups. Therefore, the adsorption potential of primary pores, large secondary pores, and fracture after deformation and coalification may be lower than that of new fractures with a rough surface.

Our group’s study on Sh and Yw coals using FT-IR reported that these two coals presented a similar content of oxygen-functional groups, but C–H side chains on the aromatic ring of Yw coal were significantly higher than that of Sh coal. This result indicated that as the coal rank increases, polycondensation and ordering of the aromatic structure occur. It should be noted that the C=C absorption peak intensity of SH coal is obviously lower than that of Yw coal. This is because Sh coal has a higher rank and the polycondensation and ordering of the aromatic structure hamper the benzene skeleton vibration, hence considerably reducing the C=C absorption peak intensity. The lower absorption peak of Sh coal distributed from 700 to 900 cm⁻¹ also indicated that the C–H side chain on the benzene ring shows a significant decrease and the benzene ring condenses to form a large-scale aromatic structure. Coalification reduces the heterogeneity of functional groups on the surface of high rank coal, so the effect of the difference of functional groups on methane adsorption decreases as coal rank increases. However, the generation of macromolecule pores and smaller primary pores of the subnanoscale in high-rank coals results in a dominant control on methane adsorption. The results of adsorption isotherm Sh and Yw coals also indicated that coal, characterized by a higher SSA of the micropore, shows a higher methane adsorption and micropores of smaller sizes have a stronger attraction to methane. Therefore, in high-rank coals, the functional groups present a weaker effect on adsorption and the wide distribution of oxygen-functional groups and under-saturated functional groups may only occur in the newly generated fracture (e.g., cracking of coal macromolecules).

4.4.3. Control Mechanism Related to the Geological Origins of Pores and Fractures on Methane Adsorption on High-Rank Coals. The methane adsorption behaviors on coals are controlled by the pore size and chemical structure on the pore wall, which are the products of deposition, coalification, and tectonic activities. Therefore, the geological origins of pores and fractures are closely related to the methane adsorption behavior. In fact, the geological origins of pores and fractures are the basic control mechanisms of methane adsorption. This is because various functional groups, pores, and fractures indicate different geological evolutions, and the types of functional groups and the sizes of pores and fractures are determined by the specific geological process. For example, the coalification contributed to the formation of micropores and the separation of the oxygen-containing functional group. The in situ stress not only causes the deformation of the existing pores and fractures but also induces the formation of new fractures. Previous studies of molecular simulation had demonstrated that the methane adsorption behaviors on various functional groups and in pores of various sizes in coals were relatively fixed. Therefore, as long as the sizes of pores and fractures and functional groups are taken as the bridge, the corresponding relationship between the geological origins of pores and fractures with the methane adsorption behavior can be established. Furthermore, the controlling mechanism of geological origins of pores and fractures on methane adsorption behavior can also be clarified.

Pore-fracture and functional groups in high-rank coals, originating from different geological processes, such as coalification and tectonic deformation, and the possible methane adsorption behaviors in these pores and fractures are summarized in Table 5. Generally, the methane adsorption behavior in fractures is a coexistence of monolayer and multilayer adsorption. The formation of fractures is charac-

| Table 5. Characterizations and Origins of Pore-Fractures in High-Rank Coals and the Possible Methane Adsorption Behaviors in These Pores and Fractures |
|---|---|---|---|
| pore size | main functional groups | geological origins | possible adsorption behavior |
| 0.3–1 nm | aromatic structure | coalification | (1) polycondensation of benzene ring | volume filling |
| | (1) aromatic structure | | (2) coalification related side chain off | |
| | (2) side chain on benzene ring | | (1) coalification related side chain off | monolayer + multilayer surface coverage |
| | (C–H) | | (2) expansion of gas pore | |
| | (3) aliphatic side chains | | | |
| 1–10 nm | aromatic structure | coalification and deformation | (1) compression and deformation | monolayer + multilayer surface coverage |
| | (1) aromatic structure | | | |
| | (2) side chain on benzene ring | | | |
| | (C–H) | | (1) coalification related side chain off | |
| | | | (2) expansion of gas pore | |
| | (3) oxygen-containing groups | | | |
| 0.11–40 μm | aromatic structure | coalification and deformation | (1) compression and deformation | monolayer + multilayer surface coverage |
| | (1) side chain on benzene ring | | | |
| | (C–H) | | (2) coalification related expansion of gas pore | |
| | (2) aromatic structure | | | |
| | (3) oxygen-containing groups | | | |
| 10–110 nm | aliphatic side chains | cracking and deformation | matrix shrinkage induced fracture | monolayer + multilayer surface coverage |
| | (1) methyl and methylene | | | |
| | (2) oxygen-containing groups | | | |
| | (3) aromatic structure | | | |
| 110 nm | | | | |
| >110 nm | | | | |
| | (1) aliphatic side chains | | | |
| | (2) oxygen-containing groups | | | |
| | (3) aromatic structure | | | |
| | (4) aliphatic side chains | | | |
| | | | | |
terized by a mechanical origin, and fractures have a relatively large size varying from tens of nanometers to millimeters. Therefore, the attraction of the fracture wall to methane in the center of the fracture is negligible, and methane presents a monolayer adsorption on the fracture. In addition, the surface of the physical damage-induced fracture has many new side chains and unsaturated groups. The high-energy adsorption sites of fractures, primary pores, and large-scale secondary pores have a large size ranging from the nanoscale to the millimeter scale, and monolayer surface coverage-related methane adsorption mechanism occurs in these spaces. However, multilayer adsorption may appear in some new fractures, resulting from their rough surfaces and new high-energy functional groups. Micropore filling involves the methane adsorption mechanism in the macromolecular pore and the small-scale secondary gas pore because of the overlap of the adsorption potential from their narrow pore size.

### 5. CONCLUSIONS

1. Micropore is the major constituent of the pore-fracture system in Qinshui high-rank coals and accounts for the majority of the total PV and SSA. Qinshui high-rank coals develop five stages of pore-fracture, including the smaller micropore stage (0.3−1 nm), the larger micropore and smaller mesopore stage (1−10 nm), the mesopore and smaller macropore stage (10−110 nm), the microfracture stage (0.11−40 μm), and the larger macropore stage (>40 μm). The peak value of pore size distribution was in the micropore stage (0.5 nm), while the second peak occurs in the larger macropore stage.

2. The primary pores are mostly in the millimeter scale, and they are deformed during coalification and tectonic activities. The secondary pores have a widespread size ranging from the subnanoscale to the micron scale. They are the result of the reconstruction of coal macromolecules and the detachment of the micromolecule side chain. Fractures in coals are due to the change in the mechanical environment. Structurally unstable fractures, controlled by coalification, have a small pore size and are located near the maceral suture. The force-induced fracture is the complete product of the change in the stress field. This fracture width ranges from microns to the millimeter scale, and its surface is commonly rough and charge-unsaturated.

3. Methane adsorption capacity and adsorption heat have a high correlation with the PV and SSA of micropores, but no relationship with the PV and SSA of the mesopores and macropores, suggesting that methane adsorption on coals mainly occurs in the micropores. Due to the overlap of the adsorption potential in the narrow pore, a smaller pore size contributes to higher heat. The MPSCGF ranges from 0.60 to 0.88 nm in Qinshui high-rank coals. Volume filling only occurs in micropores of sizes below MPSCGF. Above the MPSCGF, methane is adsorbed on the pore wall as a monolayer with a minor multilayer surface coverage.

4. The geological origin of pores and fractures primarily controls methane adsorption behaviors on coals. Fractures, primary pores, and large-scale secondary pores have a large size ranging from the nanoscale to the millimeter scale, and monolayer surface coverage-related methane adsorption mechanism occurs in these spaces. However, multilayer adsorption may appear in some new fractures, resulting from their rough surfaces and new high-energy functional groups. Micropore filling involves the methane adsorption mechanism in the macromolecular pore and the small-scale secondary gas pore because of the overlap of the adsorption potential from their narrow pore size.

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**Notes**

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