Methane Adsorption Behavior and Energy Variations of Brittle Tectonically Deformed Coal under High Temperature and High Pressure

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ABSTRACT: This paper aims to reveal the methane adsorption characteristics of brittle tectonically deformed coal (TDC) under high temperature and high equilibrium pressure and the surface free energy changes during methane adsorption. Taking the anthracite of the Yangquan mining area of China as the research object, methane adsorption tests of high temperature and high pressure were conducted to discuss the influences of coal deformation, temperature, and pressure on the gas adsorption behaviors of coal under the in situ conditions of deep coal seams. Results indicated that coal deformation and pressure had positive effects on the methane adsorption capacity of coal, whereas temperature showed negative effects. Meanwhile, the negative influences of temperature rise on gas adsorption gradually increased with the equilibrium pressure and the enhancement of coal deformation. In a given adsorption system, the adsorption potential decreased with increasing pressure while increased with temperature. In contrast, the adsorption space increased with increasing pressure and decreased with temperature rise. Meanwhile, adsorption potential decreased with the increase in adsorption space. In the process of methane adsorption, the cumulative reduction of surface free energy gradually increased, whereas the surface free energy reduction at each pressure point decreased. The cumulative and incremental reduction of surface free energy at each pressure point gradually decreased with the increase in temperature. The reduction of adsorption space and cumulative surface free energy and the changes in surface free energy at each pressure point of brittle TDCs were higher than those of primary structure coal, and the changes in the strongly deformed coal (granulitic and mortar coal) were more significant than those of the weakly deformed coal (cataclastic coal). Based on the adsorption potential theory, we drew the adsorption characteristic curves and established adsorption capacity prediction models of primary structure coal and brittle TDCs.

1. INTRODUCTION

Coal is an organic rock sensitive to stress and strain. Under tectonic compression, coal in different stress–strain environments will experience significant changes in physical and chemical structures, forming tectonically deformed coal (TDC) of different properties and intensities. Most of China’s coal-bearing basins have undergone multistage intense tectonic movements, causing coal’s primary structures to deform to varying degrees and the widely developed TDCs. Based on the differences in micro- and macrodeformation features and the stress–strain environment, previous research mostly classified TDCs into three deformation series: brittle series (primarily cataclastic, cataclastic, mortar, granulitic, platy, and flaky coal), brittle–ductile transitional series (scaly coal), and ductile series (crumpled and mylonitized coal). Pore structures, particularly nanopores, are the main spaces for adsorbing coalbed methane. Due to structural deformation, the pore structures of TDCs significantly differ from that of primary structure coal. A large number of mercury injection experiments showed that the volume and specific surface area of macro pores (with a diameter of >50 nm) of TDCs are higher than those of primary structure coal and mostly show an increasing trend with coal deformation. The mesopore structures (with a diameter of 2–50 nm) of TDCs are more developed than primary structure coal as well. Ju and Li proposed that tectonic stresses can affect coal’s nanopores by changing its macromolecular structures. Based on low-pressure N2 and CO2 adsorption tests, Fengli et al. found that the mesopore volume and specific surface area of...
brittle TDCs were higher than those of primary structure coal, while the differences in micropores (with a diameter of <2 nm) are insignificant. Cheng et al. characterized the pore structures of ductile TDCs and found that the mesopore volume and micropore surface area of ductile TDCs were higher than those of primary structure coal. Song et al. calculated the fractal dimensions of the distributions of micro- and mesopore volume and specific surface area of TDCs. The results indicated that coal deformation significantly enhanced the pore size distribution heterogeneity of micro- and mesopores in coal.

The distinct pore structures of TDCs lead to their methane adsorption properties significantly different from those of primary structure coal. Previous research demonstrated that TDCs possess higher methane adsorption capacity than primary structure coal, causing the higher coal and gas outburst risks in the distribution areas of TDCs (particularly mylonitized coal). Cheng et al. conducted methane adsorption tests on different kinds of TDCs ($R_o$ values = 1.39–1.51%) and found that with the enhancement of coal deformation, the Langmuir volume ($V_L$) of TDCs gradually increased, while the Langmuir pressure ($P_L$) gradually decreased. In the research of Meng et al., comparisons of methane adsorption characteristics of primary structure coal and TDCs at 25, 35, and 45 °C indicated that the $V_L$ values of coal showed a trend of “mylonitized coal > granulitic coal > cataclastic coal > primary structure coal”. Cheng et al. observed the significant differences of $V_L$ values between primary structure coal and TDCs and the significantly lower $P_L$ values in TDCs, which were considered to be the main reasons for the higher adsorption rate and capacity of TDCs at low adsorption pressure.

At present, knowledge on TDC’s methane adsorption characteristics was mostly obtained from methane adsorption experiments at room temperature, and the highest adsorption pressure is approximately 10 MPa. Besides, the Langmuir model was widely adopted, which is a monomolecular-layer adsorption model. As monomolecular-layer adsorption is based on an ideal adsorption equation and theoretically under-estimated the adsorption quantity, it is difficult to accurately measure the methane adsorption capacity. According to the adsorption potential theory proposed by Polanyi and developed by Dubinin, the surfaces of solid materials are like the gravitational field of a planet, which has a gravitational force. Under the gravitational force, the nearby adsorbate molecules will be adsorbed on the adsorbent surfaces, forming multilayer adsorption. Previous research indicated that the adsorption potential theory could accurately characterize the methane adsorption capacity of porous materials. In these years, this theory has been gradually applied to evaluate the methane adsorption capacity of coal. However, the adsorption potential theory was less used to characterize the methane adsorption behaviors of TDCs.

As the mining depth gradually increased in the last decades, predicting gas content and pressure in deep coal seams is becoming increasingly important to safely and efficiently mining coal resources and accurately evaluating the deep coalbed methane reserves. Using the typical methane adsorption experiments, we can only obtain the isothermals at fixed temperatures. Moreover, the methane adsorption behavior of TDCs at high temperature and high pressure is significantly different from that under ordinary temperature and relatively low pressure, putting forward the urgent need to characterize the methane adsorption behaviors of coal at high temperature and high pressure. According to the adsorption potential theory, the adsorption characteristic curves of any adsorption system are temperature-resistant, by which the limited isotherms at other temperatures can be obtained by processing the limited isotherms at fixed temperatures. Then, the methane adsorption quantity at any temperature and pressure can be obtained.

2. GEOLOGICAL SETTINGS

As an important anthracite production base in China, the Yangquan mining area experienced complex tectonic evolutions and developed with various TDCs (particularly brittle TDC series), bringing about high coal and gas outburst risks.
Located in the north margin of the Qinshui basin (Figure 1a), the Yangquan mining area is bounded by the Taihang mountains uplift belt to the east, the Taiyuan basin to the west and northwest, and 38° E–W-extending structural subzone.8,25,26 The basic structural pattern is a giant irregular monocline, extending in NW and dipping to SW. Secondary multiphased folds, mostly gentle and broad, developed on the monocline (Figure 1b).

Considering the geological conditions, TDC development, coal exploitation situation, and geographical position of the coal mines within the Yangquan mining area, the Xinjing, Er, and Wu mines were selected as the target mines. The tectonic framework of the Xinjing mine is a monocline inclined to SW (Figure 1c). The structural deformation of the Xinjing mine is weak in general, and the stratum dip angle ranges from 3 to 11°. The basic tectonic pattern of the Er mine is also a monocline structure extending along NW and inclined toward SW, with the dip angle of strata changing from 5 to 15° (Figure 1c). In the southern and southeastern parts, a large number of small-scale faults developed. The tectonic framework of the Wu mine is a monocline structure inclined to W (Figure 1c). The strata are generally flat dipping at 3–15°, but the formation strike is unstable. The superimposition of the secondary folds that extend in NE-NEE and NNW-NW directions is more significant in the Wu mine.

### 3. SAMPLES AND METHODS

#### 3.1. Samples and Deformation Features.

All the tested samples were collected from the newly exposed structural positions and mining faces of the Xinjing, Er, and Wu mines, following the method of sampling of coal seams (GB/T482-2008) and the method of sampling of coal petrology (GB/T19222-2003). According to micro- and macrodeformation observations (Figure 2), nine coal samples with typical deformation features were selected and classified into four deformation types: primary structure, cataclastic, mortar, and granulitic coal (with the increase in brittle deformation intensity).7,8,28,29 Table 1 lists the results of the industrial analysis [the moisture, ash, volatile matter, and fixed carbon contents and the maximum vitrinite reflectance (Ro,max)], which was conducted by following the standards of GB/T212-2008 and GB/T6948-2008. Noticeably, with the increase in coal deformation, the ash yield of TDCs generally increases. Maceral composition analysis indicates that the coal is mainly composed of vitrinite and inertinite and that the maceral compositions showed no considerable evolution rules with the enhancement of brittle deformation.

**Table 1. Basic Information of Coal Samples**

| sample no. | mine   | coal structure    | Ro,max (%) | proximate analysis (%) | maceral composition (%) |
|------------|--------|-------------------|------------|------------------------|-------------------------|
|            |        |                   |            | M<sub>ad</sub> | A<sub>d</sub> | V<sub>daf</sub> | FC<sub>d</sub> | vitrinite | inertinite | exinite | minerals |
| XJ1<sup>b</sup> | Xinjing | primary structure | 2.30       | 1.38 | 7.84 | 7.39 | 85.35 | 78.29 | 19.72 | 1.99 |
| E1<sup>c</sup> | Er     | cataclastic       | 2.45       | 2.63 | 8.11 | 7.48 | 85.02 | 86.76 | 12.38 | 0.95 |
| E2<sup>c</sup> | Er     | cataclastic       | 2.72       | 3.03 | 6.05 | 7.22 | 87.16 | 74.64 | 24.55 | 0.82 |
| XJ4<sup>c</sup> | Xinjing | mortar            | 2.14       | 1.34 | 18.79 | 9.89 | 73.18 | 81.41 | 11.31 | 7.27 |
| E3<sup>c</sup> | Er     | mortar            | 2.18       | 3.06 | 10.08 | 8.83 | 81.98 | 85.35 | 12.67 | 0.40 | 0.59 |
| W5<sup>c</sup> | Wu     | granulitic        | 2.25       | 2.54 | 15.78 | 13.34 | 78.50 | 77.92 | 21.18 | 0.90 |
| W3<sup>c</sup> | Wu     | granulitic        | 2.68       | 2.42 | 19.72 | 9.06 | 73.01 | 78.73 | 20.55 | 0.36 | 0.36 |
| W4<sup>c</sup> | Wu     | granulitic        | 2.21       | 2.04 | 42.08 | 15.21 | 49.11 | 90.22 | 3.79 | 5.99 |
| XJ3<sup>b</sup> | Xinjing | primary structure | 2.23       | 1.66 | 10.44 | 10.13 | 80.49 | 76.38 | 22.14 | 0.18 | 1.29 |

*Notes: Ro,max: maximum oil-immersed reflectance of vitrinite; M<sub>ad</sub>: moisture content on an air-dried basis; A<sub>d</sub>: ash yield on a dry basis; V<sub>daf</sub>: volatile matter yield on a dry and ash-free basis; and FC<sub>d</sub>: fixed carbon content on a dry basis. The data were collected from the literature Fengli et al. Adapted with permission from ref 8. Copyright (2019) Elsevier. The data were collected from the literature Li et al. Adapted with permission from ref 30. Copyright (2021) American Chemical Society.*

**Figure 2.** Macro- and microdeformation features of primary structure coal (a,a’), and brittle TDCs (b,b’,c,c’,d,d’). Notes (a,a’), were taken from the sample E1, primary structure coal; (b,b’), were taken from the sample XJ4, cataclastic coal; (c,c’), were taken from the sample E3, mortar coal; and (d,d’), were taken from the sample W4, granulitic coal. Adapted with permission from ref 8, Copyright (2019) Elsevier, ref 30, Copyright (2021) American Chemical Society.
3.2. Methane Adsorption Experiments at High Temperature and High Pressure. The methane adsorption tests were conducted using a high-pressure isothermal adsorption instrument (GAI-100), following the standard experimental method of high-pressure isothermal adsorption of coal (GB/T 19560-2008). First, the primary structure coal and brittle TDCs were ground into 60–80 mesh particles (approximately 0.18–0.25 mm in diameter), from which 400 g of coal particles was taken out and divided into three sections (each section weighs 125–150 g). The three sections from the same sample were then used to conduct methane adsorption tests at 30, 50, and 70 °C, respectively. Before methane adsorption tests, the moisture-equilibrium treatment was conducted using a sealed container with a supersaturated solution of potassium sulfate. Then, the moisture-saturated coal particles were moved into sample rooms for methane adsorption experiments. The adsorption equilibrium pressures were set at 1, 4, 7, 10, 13, 16, 19, and 23 MPa.

3.3. Calculation of Adsorption Potential and Adsorption Space Volume. Proposed by Polanyi in 1914, the adsorption potential theory is a thermodynamic theory suitable for physical adsorption. It reflects the changes in Gibb's free energy of adsorbent adsorbing unit molar mass of the adsorbate. According to adsorption potential theory, there is a gravitational field in the space near adsorbent surfaces, and the adsorbate molecules falling into the spaces will be adsorbed. The spaces affected by the gravitational field were referred to as the adsorption spaces. \(^{21,31}\) When describing the gas adsorption processes on the adsorbent, Polanyi proposed that the dispersion force dominates the interactions between the gas adsorbent and the solid adsorbate, and for a given adsorption system, the relationship curve between adsorption potential and adsorption space (referred to as adsorption characteristics curves) is unique and independent of temperature. \(^{24,31}\) Therefore, based on adsorption potential theory, adsorption isotherms at any temperature and pressure can be calculated with an obtained adsorption isotherm at a given temperature.

The adsorption potential and adsorption pressure can be correlated using eq 1. \(^{32,33}\)

\[
\epsilon = \int P_0 \frac{R T}{P} dP = RT \ln \frac{P_0}{P_i}
\]

where \(\epsilon\) means adsorption potential, J/mol; \(P_i\) means the equilibrium pressure of ideal gas at a given temperature, MPa; \(P_0\) means the saturated vapor pressure at the temperature \(T\), MPa; \(R\) means the universal gas constant and takes the value of 8.3144 J/(mol·K); and \(T\) means the adsorption temperature, K.

As the in situ temperature of coal seams is much higher than the critical temperature of methane, the methane gas cannot be liquefied under the in situ environment, and consequently, the saturated vapor pressure of methane loses its physical meaning. \(^{21,34}\) Therefore, we used the calculation formula of saturated vapor pressure under supercritical conditions established by Amankwah in this paper (eq 2) \(^{35}\)

\[
P_0 = P_c \left( \frac{T}{T_c} \right)^k
\]

where \(P_c\) means the critical pressure of methane and takes the value of 4.62 MPa; \(T_c\) means the critical temperature of methane and takes the value of 190.3 K; and \(k\) is a coefficient related to the studied adsorption system.

The \(k\) values were determined by adopting the evaluation method used in the literature Cui et al., Yawen and Pan, and Xiong et al., which mainly considered the two aspects: (a) the calculated adsorption potential values being positive and (b) the fitting degree of the \(e = -\alpha (T - T_c)\) logarithmic equations. \(^{36-38}\) Based on the equilibrium pressure and temperature conditions of this work, the calculated \(k\) value equals 3.5.

The adsorption space refers to the spaces in coal where methane can be adsorbed under given temperature and pressure, which is calculated using eq 3.

\[
\omega = V_{ad} \frac{M}{\rho_{ad}}
\]

where \(\omega\) means the adsorption space, cm\(^3\)/g; \(V_{ad}\) means the absolute adsorption quantity, mol/g; \(M\) is the molecular mass of methane, g/mol; and \(\rho_{ad}\) means the density of adsorbed methane (g/cm\(^3\)) and is calculated using eq 4.

\[
\rho_{ad} = \rho_k \exp \left[ -\alpha (T - T_b) \right]
\]

where \(\rho_k\) means the density of methane at the boiling point, 0.424 g/cm\(^3\); and \(T_b\) means the boiling temperature of methane and takes the value of 111.5 K. \(\alpha\) means the thermal expansion coefficient of methane. According to Dubinin and Astakhov, the theoretical value of the \(\alpha\) value of methane equals 0.001515, which was adopted in this work. \(^{40}\)

The methane adsorption quantity values obtained during methane adsorption tests are mostly Gibbs adsorption quantity, whereas the theoretical adsorption models require the absolute adsorption quantity. \(^{41}\) As the in situ fluid pressure and temperature of coal seams are mostly higher than the critical pressure (4.59 MPa) and critical temperature (–82.6 °C) of methane, methane in coal seams mostly exists in the above-critical state. In this case, the Gibbs adsorption quantity will be less than the absolute adsorption quantity, and the differences gradually increase with equilibrium pressure. \(^{39,44}\) As a result, in the above-critical state, the Gibbs adsorption quantity cannot represent the true adsorption quantity nor accurately describe the true methane adsorption capacity of coal. \(^{12,45}\)

Therefore, before characterizing the methane adsorption behaviors and mechanisms of coal under above-critical conditions, it is needed to transform the originally obtained Gibbs adsorption quantity into the absolute adsorption quantity (eq 5). \(^{24,45}\)

\[
V_{ad} = \frac{V_{ap}}{1 - \rho_k / \rho_{ad}}
\]

where \(V_{ap}\) means apparent adsorption quantity, mol/g, and \(\rho_k\) means the density of adsorbate gas under the tested temperature and pressure, g/cm\(^3\).

The density of methane gas under given temperature and pressure conditions can be calculated using eq 6.

\[
\rho_k = \frac{m_k}{V_k} = \frac{M \cdot n_k}{Z \cdot R \cdot T}
\]

where \(m_k\) (g) and \(V_k\) (cm\(^3\)) mean the mass and volume of \(n_k\) mol methane gas under temperature \(T\) (K) and pressure \(P\) (MPa), respectively. \(Z\) means the compression factor of methane under temperature \(T\) and pressure \(P\) (MPa) and was determined with the help of the reference fluid thermodynamic and transport properties (REFPROP) software. \(^{46}\)
3.4. Calculation of Surface Free Energy. Coal has a macromolecular structure comprising different basic structural units and various bridged bonds. The cores of basic structural units are mostly composed of 2−5 condensed aromatic rings and/or hydrogenated aromatic rings, whereas the side chains are mostly alkyl and various functional groups. The carbon atoms that construct the coal macromolecular skeleton attract each other and are in a state of force equilibrium under ideal conditions. When pore surfaces are formed, the vacancy on one side of the carbon atoms on pore surfaces causes a stress imbalance, and there will be gravitational stress near pore surfaces that promotes the adsorbate to move inside the coal interior. Under this trend, the carbon atoms will possess energies which are referred to as the surface free energy.

According to the theory of surface chemistry, the surface tension reduction caused by the adsorption of methane on coal can be described using the Gibbs formula (eq 7)\(^\text{\textsuperscript{32,50}}\)

\[
-\sigma = RT\Gamma\ln P
\]  

(7)

where \(\sigma\) means surface tension, J/m\(^2\), and \(\Gamma\) means surface excess (mol/m\(^2\)) and can be calculated using eq 8, which refers to the methane concentration difference between coal surfaces and interiors.\(^\text{\textsuperscript{18}}\)

\[
\Gamma = \frac{V}{SV_0}
\]  

(8)

where \(V\) means methane adsorption quantity, L; \(V_0\) means the molar volume of gas under the standard condition and takes the value of 22.4 L/mol; and \(S\) means the specific surface area of coal, m\(^2\)/g.

Figure 3. Gibbs methane adsorption isotherms on equilibrium moisture basis of primary structure coal (a), brittle TDCs (b–d), and coal samples collected from the Xinjing mine (e) and Er mine (f).
Substituting eq 9 in eq 8 and integrating the obtained equation, we can get eq 9.

\[ \Delta \gamma = \frac{RTV}{SV_0} \ln(P) \] (9)

where \( \Delta \gamma \) means the reduction of surface free energy, J/m², representing the difference of surface free energy of coal surfaces before and after adsorbing adsorbate gases.

Differentiating \( P \) of eq 9, we can get eq 10 to quantify the changes in surface free energy at each pressure point.

\[ \Delta \gamma_P = \frac{RTV}{SV_0 P} \] (10)

4. RESULTS AND DISCUSSION

4.1. Methane Adsorption Behaviors at High Pressure and Different Temperatures. The CH₄ adsorption isotherms of the primary structure coal and brittle TDCs are shown in Figure 3. In general, the methane adsorption quantity gradually increased with the equilibrium pressure. Differences also existed in different pressure ranges of adsorption isotherms. In the low equilibrium pressure stage (0−5 MPa), the methane adsorption quantity increased rapidly with equilibrium pressure, and the adsorption isotherms at different temperatures were relatively close to each other, which indicates that the influence of temperature on methane adsorption is insignificant under low equilibrium pressure. In the high equilibrium pressure range (5−25 MPa), the

![Figures](a) primary structure coal (b) cataclastic coal (c) mortar coal (d) granulitic coal (e) Coal from the Xinjing mine (f) Coal from the Er mine)
increasing rate of methane adsorption quantity gradually decreased with the increase in pressure.

In the high-pressure sections, the adsorption isotherms largely reached their maximum and remained, but considerable differences in increasing rate existed in the adsorption isotherms of different TDCs. We take the methane adsorption isotherms of different TDCs and primary structure coal at 30 °C as an example, which is close to the current temperature of the target coal seam. The adsorption quantity of the primary structure coal mostly reached the maximum value at 22.5 MPa (Figure 3a). Although the cataclastic coal showed a certain increase at 22.5 MPa, the increasing rate was very limited (Figure 3b), indicating that the methane adsorption quantity generally reached the maximum adsorption capacity. However, in the adsorption isotherms of the mortar and granulitic coal, there were still noticeable increases in the adsorption quantity (Figure 3c,d), indicating that these samples exhibit a higher methane adsorption capacity. In summary, the methane adsorption capacity of brittle TDCs is mostly higher than that of primary structure coal, and the granulitic and mortar coal generally showed a higher methane adsorption capacity than the cataclastic coal (Figure 3e,f).

At an equilibrium pressure of 5–25 MPa, the difference of adsorption quantity between different temperatures gradually increased, indicating that the negative effect of temperature rise on methane adsorption increased. To sum up, in the low-pressure stage, the equilibrium pressure is the dominant factor affecting methane adsorption quantity, whereas in the high-pressure stage, the positive effects of increasing pressure on methane adsorption gradually decreased, and the negative effects of temperature rise increased. As a result, the differences in the methane adsorption quantity between primary structure coal and different TDCs gradually decreased with the increasing temperature (Figures 3e,f and 4e,f).

Figure 4 shows the methane adsorption isotherms drawn using absolute adsorption quantity values. In an equilibrium pressure of <5 MPa, there were little differences between the Gibbs and absolute adsorption quantity. When the equilibrium pressure exceeded 5 MPa, the absolute adsorption quantity deviated from the Gibbs adsorption quantity, and the differences gradually increased with equilibrium pressure. These variation features have been demonstrated in the previous research.

As illustrated in Figure 4, at each temperature, the methane adsorption quantity of all samples increased with the equilibrium pressure, and three stages can be identified in the methane adsorption isotherms: the methane adsorption quantity increased rapidly (Stage 1, with an equilibrium pressure of <5 MPa); the increasing rate of adsorption quantity gradually decreased (Stage 2, 5–10 MPa); and the methane adsorption quantity increased stably (Stage 3, 10–25 MPa). In Stage 1, the adsorption quantity of primary structure coal and brittle TDCs increased at a largely same rate with increasing pressure. In Stage 3, however, the increasing rate of brittle TDCs was notably higher than that of primary structure coal, and the strongly deformed coal (the mortar and granulitic coal) showed a higher increasing rate than the weakly deformed coal (the cataclastic coal), which is in accordance with the change rules of Gibbs adsorption isotherms. These features indicate that in the low-pressure stage, the positive effects of equilibrium pressure on the adsorption quantity of primary structure coal and brittle TDCs is largely the same, whereas in the high-pressure stage, the positive effects of

### Table 2. Methane Adsorption Constants of the Primary Structure Coal and TDCs at 30 °C

| sample no. | coal structure | \( V_{\text{L, e}} \) (cm\(^3\)/g) mean | \( P_{\text{L, e}} \) (MPa) mean | \( V_{\text{L, daf}} \) (cm\(^3\)/g) mean | \( P_{\text{L, daf}} \) (MPa) mean | moisture content on equilibrium moisture base (wt %) |
|-----------|----------------|-----------------|-----------------|-----------------|-----------------|-----------------|
| XJ1       | primary structure | 48.31 | 50.61 | 4.81 | 4.80 | 53.48 | 57.23 | 4.78 | 4.79 | 2.35 |
| E1        | cataclastic | 52.91 | 4.80 | 60.98 | 4.80 | 5.32 |
| E2        | cataclastic | 82.64 | 77.29 | 10.83 | 11.98 | 92.59 | 91.34 | 10.76 | 10.76 | 11.91 | 5.50 |
| XJ4       | mortar | 71.94 | 13.12 | 90.09 | 13.05 | 1.84 |
| E3        | mortar | 91.74 | 86.86 | 10.42 | 9.71 | 111.11 | 107.64 | 10.50 | 9.77 | 7.10 |
| W5        | granulitic | 81.9 | 9.00 | 104.17 | 9.03 | 5.83 |
| W3        | granulitic | 87.72 | 81.53 | 13.96 | 11.07 | 114.94 | 116.24 | 13.95 | 11.06 | 4.49 |
| W4        | granulitic | 77.52 | 9.73 | 142.86 | 9.79 | 4.25 |
| XJ3       | granulitic | 79.37 | 9.52 | 90.91 | 9.45 | 2.96 |

### Table 3. Methane Adsorption Constants of the Primary Structure Coal and TDCs at 50 °C

| sample no. | coal structure | \( V_{\text{L, e}} \) (cm\(^3\)/g) mean | \( P_{\text{L, e}} \) (MPa) mean | \( V_{\text{L, daf}} \) (cm\(^3\)/g) mean | \( P_{\text{L, daf}} \) (MPa) mean | moisture content on equilibrium moisture base (wt %) |
|-----------|----------------|-----------------|-----------------|-----------------|-----------------|-----------------|
| XJ1       | primary structure | 33.90 | 43.40 | 3.08 | 3.39 | 37.74 | 41.91 | 3.09 | 3.39 | 2.37 |
| E1        | cataclastic | 52.91 | 3.70 | 60.98 | 3.70 | 5.34 |
| E2        | cataclastic | 61.73 | 54.12 | 10.75 | 10.09 | 69.93 | 64.38 | 10.78 | 10.12 | 5.56 |
| XJ4       | mortar | 46.51 | 9.43 | 58.82 | 9.46 | 2.07 |
| E3        | mortar | 49.50 | 52.38 | 4.74 | 5.44 | 59.17 | 64.55 | 4.76 | 5.44 | 6.26 |
| W5        | granulitic | 55.25 | 6.14 | 69.93 | 6.12 | 6.07 |
| W3        | granulitic | 60.24 | 54.68 | 11.50 | 8.59 | 78.74 | 77.38 | 11.46 | 8.57 | 4.47 |
| W4        | granulitic | 49.75 | 6.85 | 90.91 | 6.85 | 4.13 |
| XJ3       | granulitic | 54.05 | 7.41 | 62.50 | 7.40 | 3.25 |
Increasing pressure were higher in brittle TDCs and increased with the enhancement of coal deformation. Moreover, the negative effects of temperature rise on the adsorption quantity varied in different pressure stages. In Stage 1, the methane adsorption isotherms of different temperatures were close or even coincide, indicating that the temperature influences were insignificant under low equilibrium pressure. In Stages 2 and 3, the adsorption quantity differences between different temperatures gradually increased with the equilibrium pressure, indicating that the negative effects of temperature rise gradually increased. The methane adsorption isotherms at different temperatures showed that the negative effects of temperature rise on adsorption quantity are more significant in brittle TDCs than those in primary structure coal and gradually increase with the enhancement of brittle deformation. As a result, at 50 and 70 °C, the methane adsorption capacity of the cataclastic coal was close or even higher than that of the mortar and granulitic coal.

Table 2–4 list the methane adsorption parameters (the Langmuir volume and Langmuir pressure) of primary structure coal and brittle TDCs at different temperatures. At 30 °C, the Langmuir volume and the Langmuir pressure of primary structure coal on equilibrium moisture basis ($V_{L,e}$ and $P_{L,e}$) were noticeably lower than those of brittle TDCs, and the mortar coal exhibited the highest $V_{L,e}$ (86.86 cm$^3$/g on average). For the same sample, the Langmuir volume on dry and ash-free basis ($V_{L,da}$) was higher than the $V_{L,e}$, indicating that the moisture and mineral contents in coal inhibit methane adsorption on coal. The $V_{L,e}$ of brittle TDCs was much higher than that of primary structure coal, and the $V_{L,e}$ mostly increased with the enhancement of coal deformation, indicating that the brittle deformation has a positive effect on the methane adsorption capacity of coal.

For the same sample, the Langmuir volume ($V_{L,e}$ and $V_{L,da}$) at 50 and 70 °C was lower than that at 30 °C, indicating the negative effects of temperature rise on the methane adsorption capacity of coal. However, changes in $P_{L,e}$ were not obvious with temperature changes. At 50 and 70 °C, the $V_{L,e}$ of brittle TDCs was higher than that of primary structure coal. As for different types of TDCs, the $V_{L,e}$ of cataclastic coal at 50 °C was higher than that of the mortar coal and granulitic coal, while the $V_{L,da}$ of cataclastic coal at 50 °C was higher than that of mortar coal but lower than granulitic coal. At 70 °C, the $V_{L,e}$ and $V_{L,da}$ of cataclastic coal were higher than those of mortar and granulitic coal. Moreover, at 50 and 70 °C, the $V_{L,e}$ of mortar coal was largely the same as that of granulitic coal, whereas the $V_{L,da}$ of mortar coal was noticeably lower than that of granulitic coal.

To sum up, both the $V_{L,e}$ and $V_{L,da}$ of primary structure coal and brittle TDCs decreased with the increase in temperature (Figure 5), and the decreasing rate generally decreased with the increasing temperature, indicating that the negative effects of temperature rise on the methane adsorption capacity of coal gradually decreased with the increasing temperature. Moreover, the mortar and granulitic coal showed a higher sensitivity to temperature rise than the cataclastic coal. Under normal temperature, the methane adsorption capacity of the strongly deformed coal (mortar and granulitic coal) was higher than that of the weakly deformed coal (cataclastic coal). Therefore, with shallow burial depth and the same geological conditions, the distribution areas of the strongly deformed coal exhibit higher risks of coal and gas outburst than that of the weakly deformed coal and primary structure coal. At high temperature conditions, the negative effects of temperature rise on the methane adsorption capacity of coal gradually decreased with the increasing temperature. Moreover, the mortal and granulitic coal showed a higher sensitivity to temperature rise than the cataclastic coal.

Figure 5. $V_{L,e}$ (a) and $V_{L,da}$ (b) of the primary structure coal and TDCs at different temperatures.
temperatures, the methane adsorption capacity of the weakly deformed coal was higher than that of the strongly deformed coal and primary structure coal. Consequently, in deep coal seams, the distribution areas of the weakly deformed coal exhibit a higher CBM content than that of the strongly deformed coal and primary structure coal. Therefore, the distribution areas of the weakly deformed coal should be favorable areas for CBM exploration and development in the deep coal reservoirs.

4.2. Adsorption Potential and Adsorption Space. The adsorption potential of the primary structure coal and brittle TDCs at different temperatures and pressure conditions was calculated using eq 1. Figure 6 illustrates that the adsorption potential of coal was largely independent of the coal structure and was significantly influenced by temperature and pressure. At the same temperature, the adsorption potential of coal decreased with the equilibrium pressure, and the decreasing rate gradually slowed down with the increase in pressure. In the low equilibrium pressure stage, the adsorption potential—pressure curves decreased steeply, whereas the adsorption potential decreased slowly in the high-pressure stage. At a pressure of approximately 23 MPa, the adsorption potential largely remained. The higher the equilibrium pressure is, the less is the adsorption potential required for coal to adsorb methane and the easier for the coal to adsorb methane. Under the same equilibrium pressure, the adsorption potential of coal gradually increased with temperature. Therefore, the higher the temperature is, the easier the adsorbate molecules to break away from van der Waals force and the more is the adsorption potential required for coal to adsorb methane.

The variations of adsorption space of the primary structure coal and brittle TDCs with equilibrium pressure and temperature are illustrated in Figure 7. At the same temperature, the adsorption space of coal increased with the equilibrium pressure, and the increasing rate gradually increased with the increase in pressure. Under the same equilibrium pressure, the adsorption space of coal decreased with temperature. In the low equilibrium pressure stage, the adsorption space of primary structure coal and brittle TDCs was largely the same under the same temperature and pressure. In the high-pressure stage, however, the brittle TDCs exhibited a higher adsorption space than the primary structure coal, and the differences increased with the increase in equilibrium pressure. Moreover, the methane adsorption space of the
mortar and granulitic coal was significantly higher than that of the cataclastic coal. Moreover, based on the adsorption potential and adsorption space data, the relationships between them can be obtained, which are referred to as the adsorption characteristic curves.51 Figure 8 illustrates that for each TDC type, the relationships between the adsorption potential and adsorption space at any temperature and pressure can be unified into a constant adsorption characteristic curve. In other words, the adsorption characteristic curve of an adsorption system is independent of the equilibrium pressure and temperature. In the coal–methane adsorption system, the adsorption potential has a logarithmic relationship with the adsorption space (eq 11).

$$\varepsilon = a \ln \omega + b$$  \hspace{1cm} (11)
With the same adsorption space, the adsorption potential of the mortar and granulitic coal was the highest, followed by cataclastic coal, and the primary structure coal was the lowest. The greater the adsorption potential is, the lower is the equilibrium pressure required for coal to adsorb the same amount of methane, and consequently, the coal with greater adsorption potential exhibits a higher methane adsorption capacity. Therefore, the methane adsorption capacity of brittle TDCs is higher than that of primary structure coal and increases with the enhancement of coal deformation.

Furthermore, a prediction model of the adsorption quantity can be constructed by combining eqs 1−6 and 11, shown in eq 12.

$$V_{ad} = \frac{\rho_{ad-exp}}{M} \left[ \frac{RT \ln(P/P_0) - b}{a} \right]$$  

(12)

where $V_{ad}$ means absolute adsorption quantity, cm$^3$/g, and $a$ and $b$ are adsorption parameters related to methane adsorption capacity, determined from the adsorption characteristic curves.

Based on the obtained prediction model, we can calculate the methane adsorption quantity of coal at different temperatures and equilibrium pressure and then the gas content and saturation of coal seams under in situ conditions. To verify the accuracy of the obtained prediction models, we calculated the predicted values of methane adsorption quantity (expressed as $V_{ad,cal}$) at the tested pressure and temperature points by substituting the equilibrium pressure values to the prediction models. Then, the average relative deviation (ARD; eq 13) and the standard deviation (SD; eq 14) of relative deviation were calculated to evaluate the deviation degrees of $V_{ad,cal}$ from the experimentally measured adsorption quantity (expressed as $V_{ad,exp}$) (Table 5 and Figure 9).

The ARD mainly varied between 5 and 12%, and the SD mainly ranged from 0.05 to 0.15 cm$^3$/g. In general, the predicted methane adsorption isotherms have a high fitting degree, considering the wide temperature range (30−70 °C), temperature range (0−22.5 MPa), and the fact that the prediction models were not obtained from the methane adsorption isotherms of the single sample but from different samples of the same TDC type. Moreover, the deviations of the calculated methane adsorption isotherms at 50 °C were significantly lower than that at 30 and 70 °C, with the smallest ARD and SD values. As for the different pressure sections, the excellent accuracy was mostly observed in the three pressure−temperature ranges (Figure 9): the low−medium-pressure sections at 30 °C (0−15 MPa), the medium-pressure sections (5−20 MPa) at 50 °C, and the medium−high-pressure sections (10−22.5 MPa) at 70 °C. The segmentation phenomenon can be well-explained by analyzing the characteristic curves. The abovementioned three $P−T$ ranges correspond to the middle sections of the characteristic curves, where the $\varepsilon−\omega$ points are the most concentrated, and then, the obtained $\varepsilon−\omega$ logarithmic equations best reflected the adsorption curve of the middle sections. It can be predicted that increasing the number of the tested samples of the same TDC type and adding the temperature points within the target temperature range should be effective ways to increase the number of points located at the ends of characteristics curves and then obtain prediction models with higher predictable accuracy and being applicable to wider temperature and pressure ranges.

Figure 9. Experimental and calculated methane adsorption isotherms on primary structure coal (a) and TDCs (b−d).
\[
\sum = | - | \times \frac{N}{V}
\]

\[
\frac{i}{N}
\]

\[
\text{data, exp, data, cal, data}
\]

\[
(13)
\]

\[
\sum = | - | \times \frac{N}{V}
\]

\[
\frac{i}{N}
\]

\[
\text{data, exp, data, cal, data}
\]

\[
(14)
\]

where \( N_{\text{data}} \) means the number of data points and \( V_{\text{ad,exp}, i} \) and \( V_{\text{ad,cal}, i} \) mean the absolute adsorption quantity at equilibrium \( P_i \) by experiments and calculation, respectively, cm\(^3\)/g.

In addition, the deviations of \( V_{\text{ad,cal}} \) showed no significant differences between different types of TDCs, indicating that the obtained prediction models of methane adsorption quantity can effectively eliminate the differences between different samples of the same TDC type and reflect the overall characteristics of the TDCs of the same type.

These pieces of knowledge will provide data support for the evaluation of deep CBM reserves and the prediction of coal and gas outburst risks of deep coal seams.

### 4.3. Surface Free Energy

Figure 10 shows the variations of surface free energy of primary structure coal (a) and TDCs (b–d) with pressure and temperature.

\[
\text{ARD} = \frac{1}{N_{\text{data}}} \sum_{i=1}^{N_{\text{data}}} \left( \frac{V_{\text{ad,exp}, i} - V_{\text{ad,cal}, i}}{V_{\text{ad,exp}, i}} \right) \times 100\%
\]

\[
\text{SD} = \sqrt{\frac{1}{N_{\text{data}}} \sum_{i=1}^{N_{\text{data}}} \left( \frac{V_{\text{ad,exp}, i} - V_{\text{ad,cal}, i}}{V_{\text{ad,exp}, i}} \right)^2}
\]

with equilibrium pressure. In the low-pressure stage, the differences in the \( \Delta \gamma \) between different temperatures were insignificant. However, in the high-pressure stage, the \( \Delta \gamma \) mostly decreased with temperature rise, and the differences between different temperatures gradually increased with increasing equilibrium pressure. According to the lowest energy theory, the less energy the adsorption system has, the more stable the system is. As the surface free energy of coal is reduced by adsorbing methane molecules during methane adsorption, a greater \( \Delta \gamma \) means the coal has greater potential to adsorb methane and exhibits a higher methane adsorption capacity. Therefore, the \( \Delta \gamma \) can be used to represent the methane adsorption capacity of coal. As the increase in equilibrium pressure promotes methane adsorption on coal, the \( \Delta \gamma \) increases with equilibrium pressure. Similarly, as temperature rise inhibits the adsorption of methane on coal by increasing the kinetic energy of methane molecules, the \( \Delta \gamma \) showed a decreasing trend with the increase in equilibrium pressure. Therefore, in the low-pressure stage, the equilibrium pressure is the main factor controlling the methane adsorption capacity of coal. As the increase in equilibrium pressure promotes methane adsorption on coal, the \( \Delta \gamma \) increases with equilibrium pressure. Moreover, Figure 10 shows that the reduction in surface free energy at each pressure point (\( \Delta \gamma \)) decreased with the increase in equilibrium pressure, indicating that the reduction rate of surface free energy gradually decreased. During
methane adsorption, methane molecules preferentially occupy the high-energy adsorption sites. With the increase in equilibrium pressure, the low-energy adsorption sites in coal begin to be occupied by methane molecules. As the energy released by methane adsorption on low-energy adsorption sites is less than that on high-energy adsorption sites, the decreasing rate of surface free energy gradually decreases with the increase in equilibrium pressure. The decreasing trend of surface free energy variations with temperature rise indicates the negative effects of temperature rise on methane adsorption. Moreover, differences existed in the change in surface free energy between primary structure coal and different TDCs (Figure 9). The brittle TDCs mostly showed higher $\Delta \gamma$ and $\Delta \gamma_P$ values, indicating that the brittle TDCs exhibit a higher methane adsorption capacity than the primary structure coal. Besides, the highest $\Delta \gamma$ values were mostly observed in the mortar and granulitic coal, indicating that the methane adsorption capacity of the mortar and granulitic coal is higher than that of the cataclastic coal. These findings are in accordance with the adsorption characteristic curves. Besides, the differences in surface free energy variations between different TDCs gradually decreased with the increase in temperature, indicating that the positive effects of coal deformation on methane adsorption were weakened due to the negative effects of temperature rise.

5. CONCLUSIONS

(1) The pressure is the main factor influencing the methane adsorption quantity in the low-pressure stage, while the negative effects of temperature rise gradually increased with equilibrium pressure. At 30 °C, the brittle TDCs showed a higher methane adsorption capacity than the primary structure coal, and the methane adsorption capacity of TDCs increased with the enhancement of coal deformation. With the increase in temperature, the positive effects of coal deformation gradually decreased, whereas the negative effects of temperature rise gradually increased. Therefore, in shallow-buried coal seams, strongly deformed coals mostly show the highest methane adsorption capacity and have the highest risks of coal and gas outburst. However, in deep coal seams, weakly deformed coal (cataclastic coal) exhibits a higher methane adsorption capacity than the strongly deformed and undeformed coal.

(2) The adsorption potential of coal decreased with the increase in equilibrium pressure and increased with temperature rise. On the contrary, the adsorption space of coal increased with the equilibrium pressure and decreased with temperature rise. The adsorption space of brittle TDCs was higher than that of primary structure coal and generally increased with the enhancement of coal deformation. Each TDC type exhibited a distinct adsorption characteristic curve that is independent of temperature and pressure. Based on the adsorption characteristic curves, the prediction models of methane adsorption quantity were constructed, which can be used to calculate the methane adsorption quantity of TDCs at any temperature and pressure.

(3) With the increase in equilibrium pressure, the cumulative reduction of surface free energy ($\Delta \gamma$) gradually increased, while the surface free energy reduction at each pressure point ($\Delta \gamma_P$) gradually decreased. As the temperature increases, both the $\Delta \gamma$ and $\Delta \gamma_P$ decreased. The brittle TDCs mostly showed higher $\Delta \gamma$ and $\Delta \gamma_P$ values than the primary structure coal, and the surface free energy reductions in mortar and granulitic coal were mostly higher than that of cataclastic coal. Moreover, with the increase in temperature, the differences in surface free energy variations between different TDCs decreased, indicating that the positive effects of coal deformation on the methane adsorption capacity were weakened under the negative effects of temperature rise.

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Notes

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