Isothermal characteristics of methane adsorption and changes in the pore structure before and after methane adsorption with high-rank coal

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Abstract
The pore structure is an essential factor that influences the isothermal characteristics of methane adsorption of coal, and the pore structure is altered after methane adsorption. In this study, a high-rank coal sample was investigated via methane adsorption isothermal measurement, and changes in the pore structure were studied using low-pressure N₂ adsorption and low-pressure CO₂ adsorption before and after the methane adsorption. The excess adsorption capacity exhibits a rapid increase at low pressure, reaching a maximum when the test pressure is approximately 8 MPa. Following that, the excess adsorption capacity of the high-rank coal tends to decrease. After the methane adsorption, the pore volume and specific surface area of the micro-, meso-, and macropores increase as compared to those before the methane adsorption, especially for micropores with apertures greater than 0.8 nm and mesopores with apertures below 10 nm. This is mainly caused by high pressure in the methane adsorption, indicating a pressure effect on the pore structure after the methane adsorption. After the methane adsorption, the ratio of pores with various sizes in the high-rank coal is enhanced, but the connectivity for meso- and macropores presents a slight decrease.
Keywords
High-rank coal, methane adsorption, pore structure, fractal characteristics, pressure effect

Introduction
Coal is compounded of organic matters and minerals, and is a typical porous medium. It has intense heterogeneity in the pore structure. In the field of coalbed methane development, pores with pore apertures <10 nm are the most dominant in methane adsorption (Cai et al., 2013; Jin et al., 2016; Zhao et al., 2016a). When the pore aperture exceeds 100 nm, it will favor the seepage of methane (Cai et al., 2013; Yao et al., 2009). The isothermal characteristics of methane adsorption of coal are commonly influenced by the mineral types and content, macrolithotypes, macerals, coal particle sizes, moisture, and so on (Clarkson and Bustin, 1999; Lutynski and Gonzalez, 2016; Zhang et al., 2013, 2018a, 2018b; Zhao et al., 2016b). Essentially, all these factors can be summarized as the pore structure (Clarkson and Bustin, 1999; Yao et al., 2009). The pore specific surface area (SSA) ultimately influences the methane adsorption capacity, especially for micropores (Faiz et al., 2007).

There are various minerals in coal, including calcite, pyrites, clay minerals, quartz, and feldspar (Liu et al., 2018a). These minerals may reduce the connectivity between the pores and fractures. Besides, a high content of minerals will reduce the pore volume (PV) (Clarkson and Bustin, 1996), which has an influence on the adsorption, diffusion, and seepage of the methane. Micro-fractures are developed in the vitrain and clarain, and with massive micropores, they present a favorable methane adsorption capacity (Clarkson and Bustin, 1999; Zhao et al., 2016b). The vitrinite features large micropore volumes, which present high adsorption capacity (Adeboye and Bustin, 2013; Clarkson and Bustin, 1999; Faiz et al., 2007; Sing and Williams, 2004). With the growth of coalification, the adsorption pore SSA firstly decreases and then increases, and this is mainly owing to newborn micropores and the physical and chemical changes of the coal structure (Gürdal and Yalçın, 2000, 2001; Laxminarayana and Crosdale, 1999). For high-rank coal, the macropores are converted to micropores. This is derived from the orientation of the coal molecule (Zhao et al., 2016a), and the thermal maturity will accelerate the specific development of the micropores (Liu et al., 2019). Due to the moisture, the occurrence of moisture in coal pores compete the adsorption sites with the gases, leading to the decreased adsorbed volume (Zhang et al., 2018c; Zhao et al., 2018).

The coal swells with the adsorption of methane, and then shrinks during desorption of gases (Pan and Connell, 2007). Commonly, the larger the adsorption capacity is, the greater matrix swelling of coal would be. The research on coal swelling and shrinkage corresponding to the adsorption and desorption of methane show that the volumetric changes of the coal is not total reversible (Zhang et al., 2018c), meaning the deformation of the coal during the adsorption and desorption process is inhomogeneous (Nie et al., 2018). When the coal adsorbs the gases, its deformation path just fits the Langmuir equation (Lin and Zhou, 1986; Zhang et al., 2018c). As for the procedures of desorption gases, the shrinks may follow the exponential equation (Lin and Zhou, 1986), Langmuir-type equations (Zhang et al., 2018c), and power function (Zhang et al., 2014), and this difference may relate to the maturity (Lin and Zhou, 1986; Reucroft and Patel, 1986), strength (Lin and Zhou, 1986), porosity (Lin and Zhou, 1986), moisture content (Zhang et al., 2018c), lithotypes (Karacan, 2007),...
and so on. With the increased adsorption–desorption cycles, the deformation of the coal would decrease (Zhou et al., 2017).

There are various methods for studying the pore structure of coal (Zhao et al., 2019), and the test scopes for pores with different methods have also been discussed detailed by Zhao et al. (2019). Low-pressure N₂ adsorption (LP-N₂A) is frequently used to quantitatively study the pore structure of coal. The particle size of 60–80 mesh is the most favorable for LP-N₂A (Mastalerz et al., 2017). When the coal particle size exceeds four mesh, it has difficulty in N₂ adsorption, and it can even present a negative effect on the micropore volume (Clarkson and Bustin, 1999). The result of LP-N₂A contains two curves (adsorption curve and desorption curve), and the adsorption curve is commonly used to analyze the pore size distribution (PSD) (Groen et al., 2003; Thommes and Cychosz, 2014). However, there is a defect in that the LP-N₂A cannot detect pore sizes less than 0.7 nm (Lee et al., 2006; Li et al., 2019; Thommes and Cychosz, 2014). It is known that the adsorption characteristics of gases on the surface of the porous medium can be featured as monolayer adsorption and multilayer adsorption; the monolayer adsorption mainly occurs in micropores, while the multilayer adsorption arises in the mesopores and macropores. The Barrett–Joyner–Halenda (BJH) model and the Brunauer-Emmett-Teller (BET) mode are commonly used to study the characteristics of the mesopores and macropores, which can be acquired from the LP-N₂A measurements. As for the micropores, which needs a shorter gas probe, in such case, low-pressure CO₂ adsorption (LP-CO₂A) should be added (Li et al., 2019; Thommes et al., 2015). The hysteresis loop of the LP-N₂A can be used to estimate the connectivity of the pore. Commonly, a smaller hysteresis loop indicates a better connectivity of the pore (Liu et al., 2010; Maex et al., 2006; Suuberg et al., 1995). If the pores of the coal have fractal features (Lee et al., 2006; Niu et al., 2017, 2019; Song et al., 2017; Yao et al., 2008; Zhao et al., 2018), then the pore fractal dimension can also be used to quantitative evaluate the heterogeneity of the pores (Wang et al., 2019), and the Frenkel–Halsey–Hill (FHH) model is frequently used (Yao et al., 2008; Zhou et al., 2018). A multi-fractal is an expansion of the fractal and can represent the pore structure more finely (Li et al., 2015; Song et al., 2018; Sun et al., 2016).

Due to the swelling of the coal matrix during the gases adsorption, there would be some deformation for the coal. Whether this deformation would lead to the change of the pore structure after the gases adsorption? The change of the pore structure would present an influence on the pore connectivity and the ratio of the micropore, mesopore, and macropore in the coal. Then, the methane adsorption isothermal of a high-rank coal sample with a particle size of 60–80 mesh (0.18–0.25 mm) was examined in this study, and the N₂ probe and CO₂ probe were also used to study the changes of pore structure before and after the methane adsorption.

**Geological setting**

The high-rank coal sample was collected from the Zhucang Syncline, Bide-Santang Basin, western Guizhou, China (Figure 1). The Upper Permian Longtan Formation is a transitional phase stratum and is mainly delta facies and tidal flat facies (Liu et al., 2018b). There are approximately 35 layers of coal seams with steady distribution. The thickness of the Longtan Formation is approximately 320 m, and the cumulative thickness of the coal seams reaches to 22.4 m. The No. 16 coal seam is one of the dominant coal seams in the area. The thickness of the No. 16 coal seam ranges from 0.35 to 3.64 m, with an average of 1.98 m.
The folds and faults are developments in the Zhucang Syncline, but the faults have little influence on the coal structure in the deep zone.

**Samples and test methods**

**Sample**

The coal sample was collected from the No. 16 coal seam of the Dayan coal mine in the Zhucang Syncline (Figure 1). The coal sample was acquired from a fresh working face in the underground mine, with a size of 20 × 20 × 10 cm. The fresh coal sample was immediately packaged with preservative film to avoid oxidation, and the coal sample was transported to the laboratory to take the measurements. The basic property characteristics are shown in Table 1.
To avoid potential deviations, the surface of the coal was removed before it was pulverized. With an agate mortar, the coal sample was pulverized to a particle size of 60–80 mesh. After that, the relative measurements were initiated using the coal sample.

**Measurements of the coal sample**

The heterogeneity of the coal is strong, and to avoid the uncertainty from the heterogeneity of the coal, all of the measurements are initiated with the same coal sample. The measurements were divided into three sections. First, the LP-N₂A and LP-CO₂A measurements were carried out with the coal sample. Following that, the methane adsorption measurement was conducted. Finally, the LP-N₂A and LP-CO₂A were repeatedly conducted.

**Methane adsorption measurement.** The methane adsorption measurement with the coal sample was conducted with the Sorption analysis under extreme conditions (ISOSORP)-GAS SC magnetic suspension gravimetric method methane adsorption isothermal instrument. Before the methane adsorption measurement, a blank test was carried out at 30°C. The blank test can not only check the magnetic suspension balance but also acquire the mass and volume of the sample container (Li and Wu, 2019). In the blank test, 12 test pressures were set: 0.5, 1, 1.5, 2, 2.5, 3, 3.5, 4, 4.5, 5, 5.5, and 6 MPa. The procedures of methane isothermal adsorption were introduced in detail by Li and Wu (2015), including preprocessing, buoyancy measurement, and adsorption measurement. The test temperatures for the buoyancy measurement and adsorption measurement are 30°C, with the maximum pressure of 6 and 20 MPa, respectively.

**Measurements of the pore structure.** The LP-N₂A measurement can acquire pores with apertures greater than 0.7 nm (Lee et al., 2006; Li et al., 2019; Thommes and Cychosz, 2014). For pores with the apertures less than 0.7 nm, the CO₂ probe was utilized (Li et al., 2019; Thommes et al., 2015).

The coal sample was dried for 12 h under 105°C before the LP-N₂A measurement, with the main purpose being the discharge of the moisture in the coal. Subsequently, the coal sample was voided for 12 h at 110°C to discharge any possible adsorbed gas on the surface of the coal. Thereafter, N₂ was selected as the adsorbate, and the LP-N₂A measurement was carried out at −196°C with relative pressure ranging from 0.01 to 0.995. Previous research indicates that there would be an underestimation of the PV by approximately 20–30% PV for pores with apertures less than 10 nm using the BJH model (Jin et al., 2016), and that the density functional theory (DFT) model can provide a more-refined and wider PSD (Thommes, 2010; Thommes and Cychosz, 2014). However, the fact that the DFT model can only represent pores with diameters less than 30 nm should not be ignored. Therefore, the BJH model is much more practical (Jin et al., 2016). The meso- and macropore PV and

| Sample            | $R_{o,\text{max}}$ (%) | $M_{ad}$  | $A_d$   | $V_{daf}$ | $F_{C_d}$ | Quartz | Feldspar | Pyrite | Clay |
|-------------------|------------------------|-----------|---------|-----------|-----------|--------|----------|--------|------|
| Dayan coal        | 3.13                   | 2.39      | 8.72    | 6.84      | 85.04     | –      | –        | 28     | 72   |
PSD were calculated with the BJH model in this study, and BET model was utilized to acquire the SSA. The LP-CO$_2$A was initiated at 0°C, and the measurement procedures were the same as those for the LP-N$_2$A measurement, with a maximum relative pressure of 0.03. The Dubinin–Astakhov (D-A) model was utilized to calculate the micropore volume; the micropore SSA was acquired with the Dubinin–Radushkevich (D-R) model, and the DFT model was applied to calculate the micropore PSD (Hou et al., 2017; Jin et al., 2016).

**Results and discussion**

**Blank test**

According to gravity equilibrium, when gravity reaches an equilibrium state under various pressures, the mass balance equation is as follows

$$M_c = \rho_{He} V_c + M_{1b}$$  \hspace{1cm} (1)

where $M_c$ is the mass of the sample container, in g; $\rho_{He}$ is the density of helium during the blank test, in g/cm$^3$; $V_c$ is the volume of the sample container, in cm$^3$; $M_{1b}$ is the mass of the balance, in g.

From equation (1), there should be a negative relationship between $\rho_{He}$ and $M_{1b}$, the absolute of slope should be $V_c$, and the intercept should be $M_c$. It can be determined that the $M_c = 5.40856$ g, and $V_c = 0.68324$ cm$^3$ (Figure 2).

When equation (1) is improved, the dynamic change of the volume and mass can be calculated as follows

$$M_{c(i)} = \rho_{He(i)} V_{c(i)} + M_{1b(i)}$$ \hspace{1cm} (2)

where $M_{c(i)}$ is the mass of the sample container at various test pressures, in g; $\rho_{He(i)}$ is the density of the helium during the blank test at various test pressures, in g/cm$^3$; $V_{c(i)}$ is the

![Figure 2. Negative relationship between $\rho_{He}$ and $M_{1b}$ in the blank test.](image-url)
volume of the sample container at various test pressures, in cm³; \( M_{1b(i)} \) is the mass of the balance at various test pressures, in g; and \( i \) is the test pressure, from 1, 1.5, \ldots, 6 MPa.

\( V_c \) and \( M_c \) present a decrease with increased test pressure. When the test pressure exceeds 5 MPa, \( V_c \) and \( M_c \) tend to be stable (Figure 3). The dynamic change of \( V_c \) may have a relationship with the weak compression deformation under high pressure. The possible explanation for the dynamic change of \( M_c \) is that it is calculated with equation (2), with the dynamic change of \( V_c \) leading to the change of \( M_c \).

**Methane adsorption characteristics of coal sample**

**Buoyancy measurements of coal sample.** According to equation (1), the volume and mass of the sample and sample container can be calculated with equation (3). In that regard, negative relationships between the \( \rho_{He} \) and \( M_1 \) values for coal sample are acceptable (Figure 4)

\[
M_{c+s} = \rho_{He} V_{c+s} + M_1
\]  

(3)

**Figure 3.** Dynamic change of \( V_c \) and \( M_c \) under various test pressures in the blank test.

**Figure 4.** Buoyancy measurement of the coal sample.
where $M_{c+s}$ is the mass of the sample and sample container, in g; $\rho_{He}$ is the density of the helium, in g/cm$^3$; $V_{c+s}$ is the volume of the sample and sample container, in cm$^3$; and $M_1$ is the mass of the balance, in g.

With the increased test pressure, the $V_{c+s}$ values of the coal sample performances decrease, and they tend to be stable under high pressure (Figure 5). The sample container can be compressed under high pressure, and then the dynamic change of the $V_{c+s}$ cannot represent the dynamic change of $V_s$. Using equation (2), the $V_{c+s}(i)$ at various test pressures can be calculated, and then $V_s(i)$ can be acquired according to the subtraction between $V_{c+s}(i)$ and $V_c(i)$. With the increased test pressure, the $V_s$ of the coal sample presents a significant increase under low pressure, and then the $V_s$ tends to gradually become stable (Figure 5). Helium is thought to be nonadsorbed, and the micropore volume of the high-rank coal is high. Accordingly, the expansion of the sample volumes of the coal may be related to the quick filling of helium under low pressure (Li and Wu, 2019).

The density of the coal sample can be calculated using $M_s$ and $V_s$. For the coal sample, the densities initially show a sharp decrease under the low test pressure, and then present as stable (Figure 6). The dynamic change of the helium density of the coal is related to the dynamic sample volume.

**Methane adsorption isothermal of the coal sample.** The measured adsorption capacity is the excess adsorption capacity. Under low test pressures (< 5 MPa), the excess adsorption capacities of the coal sample show a rapid increase. When the test pressure reaches 8 MPa, the excess adsorption capacity of the sample reaches to maximum. With the increased test pressure, the excess adsorption capacity decreases (Figure 7).

**Pore structure characteristics before and after the methane adsorption**

The International Union of Pure and Applied Chemistry (IUPAC) pore classification method is adopted in this study, including the micropore (<2 nm), mesopore (2–50 nm), and macropore (>50 nm). The PSD values of the meso- and macropores were acquired using LP-N$_2$A, whereas that for micropores was measured using LP-CO$_2$A.

**Adsorption isothermals of LP-N$_2$A and LP-CO$_2$A.** There is an interval between the adsorption curve and desorption curve of the LP-N$_2$A for some range of the relative pressure, and it is known as the hysteresis loop. The different pore sizes and pore shapes of porous materials produce
various hysteresis loops. According to the concept of a hysteresis loop, the connectivity of pores in the coal can be determined preliminarily (Liu et al., 2010; Maex et al., 2006; Suuberg et al., 1995).

Before the methane adsorption, the LP-N₂A results show that the adsorption content of the coal sample increases gradually at a low relative pressure. When the relative pressure exceeds 0.9, the adsorption content increases rapidly. The desorption curve is almost coincident with the adsorption curve at a high relative pressure. As for the decrease in the relative pressure, the hysteresis loop emerges, and when the relative pressure decreases to approximately 0.5, there is a sharp reduction. Following that, the desorption curve is almost

Figure 6. Dynamic change of the helium density of the coal sample.

Figure 7. Methane adsorption isothermal curve of the coal sample.
parallel to the adsorption curve under a lower relative pressure. The hysteresis loops presents as H$_3$ type, meaning the pores in the coal are mainly parallel plate pores (Figure 8).

The pore radius of the porous medium can be calculated with the Kelvin equation (Liu et al., 2018a), which is shown as

$$r = \frac{2\gamma M}{\rho RT \ln(p/p_o)}$$

where $r$ is the radius of the pore, in nm; $\gamma$ is the surface tension of the liquid nitrogen, at $23.6 \times 10^{-3}$ N/m; $M$ is the mole molecular mass of the liquid nitrogen, at 28.1 g/mol; $\rho$ is the density of the liquid nitrogen, at 0.81 g/cm$^3$; $R$ is the gas constant, at 8.314472 cm$^3$·MPa/mol/K; and $T$ is the thermodynamic temperature of the liquid nitrogen, at 77.3 K.

According to the Kelvin equation, a relative pressure of 0.4 corresponds to a pore aperture of 3.3 nm. The dominant pores in the coal sample are semi-closed pores with one side open, and the shape and size of these capillary pores show various changes. When the relative pressure reaches 0.5, the pore aperture is approximately 4 nm. The coal sample presents a sharp decrease for the desorption curve, indicating that there are certain amounts of ink bottle pores and fine bottle neck pores (Song et al., 2017). As the relative pressure rises to 0.8, the pore aperture reaches 10 nm, and cylindrical pores with the two ends opened are dominant. As for pores $>$10 nm, parallel plate pores are developed.

After the methane adsorption, the LP-N$_2$A measurements are repeatedly initiated, and as shown in Figure 8, the adsorption curve and desorption curve feature the significant change. When the relative pressure is less than 0.9, the adsorption content presents faintly increase, following that the adsorption content increases sharply. And it can be also found that the maximum adsorption content is also decreased. The Hysteresis loop presents as H$_4$ type, indicating the pores in the coal feature as narrow slit-shaped pores. Although there is no evident change of shape and size of the hysteresis loop for the coal sample, the adsorption

Figure 8. Adsorption curves and desorption curves of coal sample form the LP-N$_2$A measurements before and after the methane adsorption.
The adsorbed quantity increases with the increased relative pressure for the coal sample, and the adsorption curves of the LP-CO$_2$A present a logarithmic growth (Figure 9). After the methane adsorption, the adsorbed quantity of the coal sample shows a certain increase (Figure 9).

PV and SSA of coal sample. The micro-, meso-, and macropore PV and SSA values increase after the methane adsorption (Figures 10 and 11), especially those for mesopores. The increase of PV may be relative to a transformation of the closed pores in the coal under the repetitively increased test pressure (Wang et al., 2018).

After the methane adsorption, the pore structure of the coal sample has changed and presents as an increase in the PV and SSA for pores with all apertures. However, the increase...
of the mesopore PV and SSA is more significant than that for the micro- and macropores. The results of the incremental PV and SSA indicate that mesopores with apertures below 10 nm feature significant increases, but when the pore aperture is greater than 10 nm, there is only a slight increase for the PV and SSA (Figure 12). As for the micropores in the coal, the incremental PV and SSA increase when the pore aperture exceeds 0.8 nm (Figure 13).
Multi-fractal characteristics of the pore. The pores of the porous medium present typical multi-fractal features, and a multi-fractal can characterize the pore structure of the coal. Previous studies have introduced the multi-fractal theory (Li et al., 2015; Song et al., 2018), which is directly utilized in this study. A generalized fractal dimension is commonly used to describe the pore structure, and is characterized as (Li et al., 2015; Song et al., 2018)

$$D_q = \lim_{\varepsilon \to 0} \frac{1}{q-1} \frac{\ln \chi(q,\varepsilon)}{\ln \varepsilon} = \lim_{\varepsilon \to 0} \frac{1}{q-1} \frac{\ln \left( \sum_{i=1}^{N(\varepsilon)} p_i^q(\varepsilon) \right)}{\ln \varepsilon}$$

(5)

where $D_q$ is the generalized fractal dimension; $\varepsilon$ is the equal length; $q$ is the moment order, which ranges from -10 to 10 in this study with a step of 1; $\chi(q,\varepsilon)$ is the partition function; $N(\varepsilon)$ is the number of boxes with the sizes of $\varepsilon$; and $p_i^q(\varepsilon)$ is the probability density distribution.

The linear relationships between the $\ln(\varepsilon)$ and $\ln(\chi(q,\varepsilon))$ values of the various coal particle sizes before and after the methane adsorption show that the pores (including micro-, meso-, and macropores) in the coal present multi-fractal characteristics (Figure 14). $D_{-10}$-$D_{10}$, $D_{-10}$-$D_0$, $D_0$-$D_{10}$, $D_1$, and $D_2$ are commonly used to analyze the pore structure in multi-fractal theory. $D_{-10}$-$D_{10}$, $D_{-10}$-$D_0$, and $D_0$-$D_{10}$ are the spectra of $D_q$, and the wider $D_{-10}$-$D_{10}$, $D_{-10}$-$D_0$, and $D_0$-$D_{10}$ indicate the complexity and heterogeneity of the distribution of the pore sizes (Li et al., 2015). $D_1$ is the information fractal dimension and represents the concentration degree of the pores (Li et al., 2015). $D_2$ is the correlation fractal dimension, which can provide a correlation of the distribution of the pores (Li et al., 2015).
After the methane adsorption, the spectrum of $D_q$ for various pore apertures presents a decrease, indicating that the complexity and heterogeneity of the PSD have become weaker (Table 2). However, the dynamic changes of pores with various pore apertures are different. For the meso- and macropores, the spectrum of $D_{-10}^0 - D_0$ features a significant decrease, whereas that for $D_0 - D_{10}$ increases, indicating the various changes of the meso- and macropore structures in the coal. As shown in Figure 12, the incremental PV and SSA of mesopores with apertures below 10 nm feature an approximately exponential decrease. Then, the PSD of these pores is apparently uniform, and the pore structure characteristics correspond to the decreased spectrum of $D_{-10}^0 - D_0$. Figure 10 shows that the incremental values of the macropore PV is evidently higher than that of the SSA, indicating that the complexity in the pore shapes of the macropores lead to the increase of the spectrum of $D_0 - D_{10}$. For the micropores, the incremental PV and SSA is almost the same when the pore aperture is less than 0.8 nm after the methane adsorption. Then, the spectrum of $D_{-10}^0 - D_0$ features no change, and the decrease of the spectrum of $D_0 - D_{10}$ indicates that the pore structures of pores with the apertures greater than 0.8 nm are enhanced. The $D_1$ and $D_2$ of the meso- and macropores decrease after the methane adsorption, but $D_1$ is close to 1, indicating that the equilibrium of the meso- and macropores in the high-rank coal has been enhanced. The decrease of the $D_2$ may have a relationship with the increase of the mesopore PV and SSA. The $D_1$ and $D_2$ of the micropores increase after the methane adsorption, indicating that the equilibrium and connectivity of the micropores have been increased.

**Analysis of the changes in pore structure after the methane adsorption**

The coal used in this study is high-rank coal, and the same coal sample was used for all measurement procedures in this study. Thus, the pore structure should not be changed after the methane adsorption. However, the pore structure changed after the methane adsorption. In reviewing the measurement procedures, there are two variable quantities, i.e., temperatures and pressures. The temperatures can change the pore structure of the coal, from both the decrease of the moisture and the change of the coal molecular structure. Before the methane adsorption measurement, the LP-N$_2$A and LP-CO$_2$A measurements were initiated, and the maximum test pretreatment temperature was 110°C, which is only slightly higher than that of the water boiling point temperature. Therefore, the free water held by the physic-mechanical forces in the coal can be removed; the reduction of the chemically bonded water and the adsorbed water requires a higher temperature (Arisoy and Akgun, 1994). In addition, while the temperature can decompose the side chains and oxygen functional groups in low-rank coal (Jian et al., 2015, 2018; Xin et al., 2019), the coal used in this study is high-rank coal, and thus, this effect can be ignored. The test pressure reaches 20 MPa in the methane adsorption measurement, and this high pressure may contribute to the change of the pore structure. After the methane adsorption, the LP-N$_2$A curves show

| Sample | Conditions | Adsorbate | $D_{-10}$ | $D_0$ | $D_1$ | $D_2$ | $D_{10}$ | $D_{-10}^0$ | $D_0 - D_{10}$ | $D_{-10}^0 - D_0$ |
|--------|------------|-----------|-----------|-------|-------|-------|---------|-------------|----------------|----------------|
| Dayan coal Before | N$_2$ | 1.35 | 1 | 0.96 | 0.92 | 0.86 | 0.49 | 0.14 | 0.35 |
| | CO$_2$ | 1.23 | 1 | 0.85 | 0.69 | 0.50 | 0.73 | 0.50 | 0.23 |
| After | N$_2$ | 1.08 | 1 | 0.94 | 0.88 | 0.68 | 0.40 | 0.32 | 0.08 |
| | CO$_2$ | 1.23 | 1 | 0.87 | 0.73 | 0.52 | 0.70 | 0.48 | 0.23 |
a significantly change, and the pores in the coal sample changes from the parallel plate pores to narrow slit-shaped pores, meaning the shape of the pores is changed. Besides, the maximum adsorption content is also decreased, indicating the pore volume is also changed. Moreover, in this study, the PV also increases after the methane adsorption, and this may also have a relationship to the closed pores (Niu et al., 2019). When the test pressure increases during the methane adsorption measurement, this high pressure would compress the closed pores in the high-rank coal to semi-closed and open pores, ultimately increasing the PV of the coal. The original closed pores are mainly mesopores, with the apertures below 10 nm. Besides, the previous studies show that the coal matrix would swell during the gases’ (CH₄, CO₂, and N₂) adsorption; there would emerge various deformation paths on the coal (Nie et al., 2018; Pan and Connell, 2007; Zhang et al., 2018c); this may also contribute to the change of the pore structure for the coal. When the adsorption of the gases completed, the desorption of the gases would lead to the shrinkage of the coal, but the swelling and shrink-age of the coal with the same path do not totally coincident (Zhang et al., 2014, 2018c), meaning some change of the coal during the gases adsorption is irreversible.

Conclusions

1. The methane adsorption on the high-rank coal would lead to the change of the pore structure, and the LP-N₂A and LP-CO₂A can detect the change of the pore structure effectively. The PV and SSA of the high-rank coal are all increased after the methane adsorption, and the significantly change mainly occurs for the micropores and meso-pores, especially that for the micropores with the apertures greater than 0.8 nm and mesopores with apertures below 10 nm.

2. The differences of the pore structure before and after the methane adsorption indicating that there is a certain deformation for the coal during the methane adsorption is irreversible. Besides, the high pressure also contributes to the change of the pore structure. The high pressure would change the shape and volume of the pores, the ratio of the micropore, mesopore, and macropores in the coal would be enhanced, which finally enhanced the pore connectivity of the pores, especially that for the micropores.

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