Structural and Fractal Characterizations of Nanopores in Middle-Rank Tectonically Deformed Coals – Case Study in Panguan Syncline

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ABSTRACT: The reservoir properties of tectonically deformed coals (TDCs) differ significantly compared with their neighboring primary coals which are also known as unaltered or underformed coals. However, the heterogeneity of nanopores in TDCs under the syncline control has been seldom reported, and also the middle-rank level was minimally investigated to date. Thus, in this paper, the structures and multiscale fractal characteristics of nanopores in middle-rank TDCs under the controlling effect from Panguan Syncline were investigated via high-pressure mercury injection (HPMI), low-pressure CO$_2}$/N$_2$ adsorption (LPCO$_2}$/N$_2$GA), and fractal theory. The results show that both the pore volume (PV) and specific surface area (SSA) of macropores increase significantly in the stage of cataclastic−schistose coal. For ductile deformed coals, the PV increases, while the SSA remains stable. The SSA of mesopores increases slightly in the brittle deformation stage, but significantly in the ductile deformation stage. For micropores, both the PV and SSA for TDCs are significantly higher than primary coals. Moreover, the ductile deformation has a more significant promotion effect for the microporous PV and SSA than the brittle deformation. The fractal dimension of the adsorption pore (induced from the Sierpinski model) increases; however, that of seepage pores (Sierpinski model) decreases with the enhancement of tectonic deformation. The fractal dimension for mesoporous (induced from the FHH model, Frenkel−Halsey−Hill) at 2−6 nm keeps stable in the stage of cataclastic−schistose coal but significantly increases in the ductile deformation stage. For mesopores of 6−100 nm, their heterogeneities were also enhanced in the ductile deformation stage. The fractal dimension of 0.3−0.6 nm micropores is close to 3 and changes slightly with the enhancement of tectonic deformation, indicating that the heterogeneity of smaller micropores is stronger than that of larger micropores. The results are of broad interest for CBM exploration and gas outburst prediction.

1. INTRODUCTION

Coal is a complicated porous material with heterogeneous pore structures which have an obvious impact on the enrichment and exploitation of coalbed methane (CBM). Previous investigations have suggested that the rank, structural features, macerals, and composition (e.g., moisture, ash, fixed carbon, inertinite, and vitrinite) had a critical influence on the pore size distribution (PSD), pore shape (PS), pore volume (PV), and specific surface area (SSA). The block of West Guizhou and East Yunnan is located in the southwest margin of the South China plate, which is the main target area for CBM exploration of medium- and high-rank coals in China. However, because of the influence from the tectonic movements of multistages, especially Yanshanian tectonic movement, the coal seams in this area have undergone strong deformation, forming different types of tectonically deformed coals (TDCs). TDCs of different structural characteristics and types vary significantly in physical structure, chemical structure, and optical character-

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istics under the action of one or more stages of tectonic stress. They are prevalent in the main coal-producing countries internationally, such as North and South China. As the PSF, PS, PV, and SSA of TDCs are significantly different from their neighboring primary coals, the CBM enrichment and migration properties differ greatly correspondingly, also affecting the CBM exploitation potential and prominence of coal and gas outburst. Therefore, it is of great significance to reveal the heterogeneity of pore structures in TDCs.

The difference in CBM properties for TDCs of various types is resulted from the joint action of heterogeneities of structure and PSD. Therefore, in recent years, a lot of researches have been carried on to reveal the heterogeneity of pore structures in TDCs. The methods utilized to examine the porous properties in unconventional reservoirs can be classified into image analysis, fluid injection, spectroscopy analysis, and physical probe, where the fluid injection has been the most successful method applied to quantitatively detect the nanopores in coals. Additionally, the fractal theory can innovatively provide new insights into methane adsorption, desorption, and seepage through quantitative evaluation of the heterogeneity for nanoporous structures in TDC reservoirs. Different single fractal models exhibited their corresponding segmentation characteristics, resulting in the discrepancies of fractal dimension. These fractal dimensions of different intervals could quantify the heterogeneity of nanopores and were widely adopted in quite recent years.

Based on the high-pressure mercury injection (HPMI) experiment, Li et al. calculated the multifractal analysis of Hg PSD in cataclastic, mortar, and mylonitic coals and discovered that the tectonic deformation can lead to narrower Hg PSD and greater volatilities in PS. Song et al. highlighted the fractal characteristics of adsorption pores (<100 nm) for TDCs of different TDCs and the relationship between the fractal dimension (Frenkel–Halsey–Hill, FHH method), as well as gas adsorption capacity. The gas adsorption of coal increased with the increasing fractal dimension, and high fractal dimension suggests the more complexity of the pore structure. Both SAXS (small-angle X-ray scattering) and LPN2GA (low-pressure N2 adsorption) are used to further calculate the surface fractal dimension, indicating that the surface fractal dimension of cataclastic, schistose, and mortar coals increases with the increasing deformation intensity. Pan et al. investigated the nanoporous structure of TDCs by atomic force microscopy (AFM) and proposed that the TDC surface, especially for ductile TDCs, was characterized by the creep flow. Through the HPMI PSD and Sierpinski model, Yao et al. discussed the heterogeneity of seepage pores and proposed that the fractal dimension of the microfractures increased linearly with the enhancement of the coal deformation degree. Then, via the Menger model, Yao studied the heterogeneity characteristics of seepage and diffusion pores and concluded that the fractal dimension tends to increase slowly in the brittle deformation stage and significantly in ductile deformation. Song et al. comprehensively analyzed the applicabilities of Menger, thermodynamics, Sierpinski, and FHH fractal models for various TDCs, and further revealed the fractal characteristics of pores. Li et al. also calculated the fractal dimension of various TDCs based on the surface fractal model and proposed that wrinkle coal with higher pore fractal dimensions (D > 2.9, FHH model) are characterized by more diversities in pore morphology, larger amount of SSA, and have a stronger heterogeneity in the pore structure because of the contribution of the ink bottle-type and slit-type pores.

The above investigations demonstrated the distinct differences in heterogeneity for different TDCs based on these mono-fractal approaches. Li et al. had first explored the variability and heterogeneity within PSDs in cataclastic, granulated, and mylonitic coals and found that for irregular PSDs of coals, a single fractal dimension would describe the irregularity within limited size intervals, that is, different pore size intervals exhibit different types of self-similarity. Furthermore, for shear and ductile TDCs, the multifractal structures are complex with high heterogeneity and significant internal differences within PSD for wrinkle and mylonitic coals, indicating their most clustered distribution for inner PSD, followed by schistose, and scaly coals. Therefore, the fractal dimension of nanopores in TDCs can be divided into: D1 (>100 nm), D2 (<100 nm), D3 (>8 nm), and D4 (<8 nm) based on the distinct evolution trends with the increasing intensity.

Above efforts have clearly indicated that there exists significant differences in heterogeneity within various PSD intervals. While because of different fractal models used in previous work and the limited TDC types used in Li et al., it is still not clear what are multiscale fractal characterizations for full sequential, various TDCs using the same fractal dimension, and the response of these multiscale fractal dimensions to the tectonic deformation. As TDCs were primarily formed and extensively developed under the extrusion and/or shear stress, they can be developed along the strong deformation sites, which were typically exhibited as a fault (especially for the thrust fault and layer slip fault) and folds. However, the main groups of TDCs have mainly concentrated on the nanopores under the effects from nappe, monocline, and fault. The structure and heterogeneity of nanopores for TDCs formed in the syncline-deformed zone have been rarely reported to date. On the other hand, previous publications have mainly investigated the low and high ranks. The middle ranks have received relatively few attentions. Thus, there exist great theoretical and practical significances to investigate the multiscale fractal properties for middle-rank TDCs formed under the syncline-deformed zone, which was minimally reported in previously.

Here, concerning the compressibility effects on HPMI results, the corrected HPMI and LPN2/CO2GA were comprehensively utilized to investigate the nanoporous structures. Then, multiscale fractal characterizations and the response to tectonic deformation were revealed combining the Sierpinski model, FHH model, and the surface fractal model. The quantitative characterization method for PSDs here may provide relevant information which can be used to deepen our understanding on how the tectonic deformation affects PSD heterogeneity in coal. Following the recommendations of the international unit of pure and applied chemical (IUPAC), pores are classified according to their diameter size as micropores (<2 nm), mesopores (2–50 nm), and macropores (>50 nm). In addition, based on the interaction of the gas molecular and pore size, pores of >100 nm in size are called seepage pores, where gas laminar flow occur during production, while pores of <100 nm in size are assigned to adsorption pores, in which gas diffusion and physical adsorption occur.
2. GEOLOGICAL BACKGROUND AND SAMPLING

Panguan Syncline lies in western Guizhou. Tectonically, it belongs to rotational-torsion deformation area of Puan, Liupanshui fault depression, western Guizhou upwarp, and Yangtze paraplatform. The syncline was narrow in the south and wide in the north and protrudes to the west, exhibiting an arc plunge character. It has an axial of $30^\circ - 45^\circ$ (NE, North-East) with 45 km in length and 5–20 km in width (Figure 1a).

The exposure strata were Maokou Formation of Lower Permian, Emeishan Formation of Upper Permian, Longtan Formation of Upper Permian, Changxing-Dalong Formation of Upper Permian, Feixianguan Formation of Lower Triassic, Yongningzhen Formation of Lower Triassic, Guanling Formation of Middle Triassic, and Quaternary. The Changxing-Dalong Formation of Upper Permian was the main coal-bearing strata (thickness, 246 m in average). The superposition and transformation induced from the tectonic movements of multiple periods destroyed the primary coal basin. Compared with the East China region, this area is more obviously affected by Himalayan tectonic movement which was superimposed on the Indosinian and Yanshanian structures, resulting in the more complicated syncline structures and widely development of TDCs. The 10 samples here were all from Longtan Formation collected from Yueliangtian Colliery (Figure 1b), Shanjiaoshu Colliery (Figure 1c), and Huopu Colliery (Figure 1d) (Table 1).

3. SAMPLES, EXPERIMENTS, AND FRACTAL DIMENSIONS

3.1. Samples. The 10 samples are composed of the types of primary, cataclastic, schistose, and wrinkle coals (with the...
increasing deformation intensity, in duplicate) based on the division scheme proposed by Jiang et al.,12 where the cataclastic and schistose coals were formed in the brittle deformation environment; however, the wrinkle coals are formed in the ductile deformation environment. The macro- and micro-deformation characteristics of the selected samples are shown in Figure 2. The elemental analysis for these samples was conducted using a Vario EL elemental analyzer. The vitrain band was also sorted by hand to eliminate the maceral inclusions, and volatile matter were obtained on a 5E-MAG6600 automatic proximate analyzer according to GB/T 31391-2015. The industrial analysis and element analysis results of primary coal and TDC are shown in Figure 2. The elemental analysis for these samples was conducted using a Vario EL elemental analyzer. The proximate analysis results including ash yield, moisture content, and volatile matter were obtained on a SE-MAG6600 automatic proximate analyzer according to GB/T 30732-2014. The 10 middle-rank (R_{max} = 0.92–1.02% according to GB/T 31391-2015) coal samples were low volatile (14.42–42.55, 30.79% in average) with an ash yield of 0.53–1.46% (0.93% in average) (Table 2), indicating that the primary coals and TDCs here are “low-moisture and low-ash” coals in the ASTM (American Society of Testing Materials) scheme. The vitrain band was also sorted by hand to eliminate the maceral influence on the HPMI and LPN$_2$/N$_2$GA results. The minimum variations in coal rank, moisture content, and maceral composition can efficiently eliminate their influences on pore structures and heterogeneity according to the literatures.

From the distribution of the brittle and ductile TDCs, the axis zone of the syncline possesses the stronger deformation than the wing zone, which is attributed to the longitudinal bending folding effects under the action of bedding compression stresses. The ductile TDCs in the axis zone were generated via the extrusion stress above the neutral plane of the syncline. Additionally, because of the influence from bedding shear between the coal seam and roof and the floor strata and bending folding of coal seam, the coal matrix in the syncline zone has a relatively strong structural deformation. The deformation intensity increases with the enhancement of the folding deformation degree, forming ductile TDCs such as wrinkle coal and/or mylonite coal. In the wing zone of the syncline, the local bedding shear stress is formed because of bedding shear sliding between the coal seam and its roof and floor strata. The dense bedding shear joints are developed in the coal seam, thus forming a bedding bending sliding shear zone and the development of the cataclastic coals and schistose coals.

### 3.2. Experiments

The HPMI can continuously measure the pore fracturing in the micron and nano scale.19–41 The LPN$_2$GA and LPCO$_2$GA can quantitatively detect the PSD information of nanopores and micropores, respectively. Thus, the pore structure information of the nanoscale and micronscale can be obtained via the comprehensive utilization of HPMI and LPCO$_2$/N$_2$GA. Here, HPMI was conducted in the Shanxi Institute of Geology and Mineral Resources. The LPN$_2$GA was conducted in the Key Laboratory of Coalbed Methane Resources and Reservoir Forming Process, Ministry of education, China University of Mining and Technology. The LPCO$_2$GA was conducted in the Key Laboratory of Carbon Materials, Chinese Academy of Sciences. Matrix compression occurs in the high-pressure section (>20 MPa, corresponding pore diameter <100 nm). The amount of mercury input was induced from both the PV and matrix compression,19,40,44 and thus, the matrix compression correction is required. Both the LPCO$_2$GA and LPN$_2$GA were nondestructive experiments. The specific test conditions of these three experiments are as follows.

#### 3.2.1. High-Pressure Mercury Injection

To exclude the effect of moisture on experimental results, the block samples of <6 g were first vacuum-dried at 353 K in an oven for 24 h. Then, the HPMI was conducted using a PoreMaster 33 mercury porosimeter. The maximum pressure is 204 MPa. As the pores of >100,000 nm in size are induced by the effects of particle accumulation, rather than the natural pores in coal, thus, the maximum HPMI pore diameter is defined at 100,000 nm in size in this paper.13,27,30 Given that the compressibility of coal has a significant effect on HPMI results when >20 MPa,13,40,44 thus, the HPMI results of >20 MPa should be corrected.13

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**Table 2. Industrial Analysis and Element Analysis Results of Primary Coal and TDC**

| sample no. | TDC type     | R$_{max}$ (%) | M$_{ad}$ | A$_{ad}$ | V$_{ad}$ | FC$_{ad}$ | S$_{ad}$ (%) | O$_{ad}$ | C$_{ad}$ | H$_{ad}$ | N$_{ad}$ |
|------------|--------------|---------------|----------|----------|----------|-----------|--------------|----------|----------|----------|----------|
| SJS2       | primary      | 0.98          | 1.46     | 6.12     | 14.42    | 80.34     | 3.19         | 5.92     | 85.33    | 3.73     | 1.62     |
| SJS3       | cataclastic  | 0.98          | 0.86     | 10.59    | 35.36    | 57.8      | 0.69         | 7.2      | 84.57    | 5.42     | 2.05     |
| YLT2       | schistose    | 0.92          | 0.53     | 32.09    | 42.55    | 39.02     | 0.84         | 17.68    | 75.91    | 3.91     | 1.26     |
| YLT4       | wrinkle      | 0.97          | 0.92     | 9.16     | 34.18    | 59.79     | 0.52         | 6.67     | 85.62    | 5.27     | 1.87     |
| HP1        | mylonitic    | 1.02          | 0.88     | 5.33     | 27.44    | 68.69     | 0.26         | 6.91     | 85.93    | 4.88     | 2.00     |

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*Note: M$_{ad}$-moisture content; A$_{ad}$-ash content; V$_{ad}$-volatile content; FC$_{ad}$-fixed carbon content; TDC-tectonically deformed coal; R$_{max}$-maximum vitrinite reflectance; ad-ash dried basis; and daf-dried ash-free basis.*
3.2.2. \( \text{LPN}_2\text{GA} \). The \( \text{LPN}_2\text{GA} \) was conducted on a Quantachrome Instruments Version 5.0 specific surface analyzer. The samples (~2 g of <200 mesh) were first outgassed at 105 °C for >12 h to remove air, free water, and other gases. The adsorption and desorption isotherms were obtained at a relative pressure \( (P/P_0) \) where \( P \) is the equilibrium pressure and \( P_0 \) is the saturated vapor pressure) range of 0.01–0.995 with the normal boiling temperature of liquid nitrogen.

3.2.3. \( \text{LPCO}_2\text{GA} \). For \( \text{LPCO}_2\text{GA} \), the adsorption isotherms were obtained at a relative pressure between \( 1.2 \times 10^{-4} \) and \( 3.3 \times 10^{-5} \) at 273.15 K on the TriStar II 3020 Version 3.02, whose corresponding absolute pressure ranged from 3.14 to 855.11 mm Hg in an ice/water bath with the glycol and water mixture.

3.3. Fractal Dimension. Because of the complexity of pore structures, the traditional Euclidean geometry was difficult to describe its heterogeneity, especially for the TDCs. However, the fractal theory can quantitatively describe the complexity of pore structures and PSD in coal. Because Pfeifer and Avnir proposed that the pores of reservoir rocks exhibited fractal properties, international scholars have widely used the fractal theory to characterize the heterogeneity of nanopore structure in the corresponding pore size range. Among these single fractal models, the Sierpinski, FHH, fractal models, SSA, and volume fractal model can all capture the heterogeneity of nanopore structure in the corresponding pore size range.

3.3.1. Sierpinski Model. The fractal dimensions (\( D \)) were calculated based on the Sierpinski model from the HPMI data.

\[
\ln(V) = (3 - D) \ln(P - P_i) + \ln \alpha
\]

where the \( P_i \) is the mercury inlet pressure (MPa), and \( V \) is the mercury injection amount (mL). Assuming the slope of the \( \ln \) \( (P - P_i) - \ln \) \( V \) curve is \( K \), then, \( D = 3 - K \).

3.3.2. FHH Model. For \( \text{LPN}_2\text{GA} \) data, the FHH fractal model was used to calculate the fractal dimension based on the following equation:

\[
\ln\left(\frac{V}{V_0}\right) = C + A \times \ln[\ln(p_0/p)]
\]

where \( V \) is the gas adsorption volume at \( p \), \( V_0 \) is the gas volume, \( p_0 \) is the saturated vapor pressure, and \( A \) is the slope of \( \ln(V/V_0) - \ln[\ln(p_0/p)] \) logarithmic curves. The \( C \) is a constant. Then, the fractal dimension is \( A + 3 \).

3.3.3. Surface Fractal Model. The surface fractal dimension can be calculated using the following equation:

\[
\ln S(r) = \ln(S_{r}K_0) + B \ln r
\]

where \( S \) (r) and \( B \) depicted the SSA distribution and the slope of the \( \ln(S) - \ln (r) \) curve, respectively. Then, the surface fractal dimension \( (D_s) \) is \( D_s = 2 + B \) or \( D_s = (B - 3)/3 \). The \( r \) is the pore diameter, and \( B \) is the fitting constant.

4. RESULTS AND DISCUSSION

4.1. Structural Characteristics of Pores. The \( \text{LPN}_2\text{GA} \) adsorption–desorption curves for the samples are shown in Figure 3a–e. As the principle of the \( \text{LPN}_2\text{GA} \) is in accordance with the theory of adsorption and condensation in porous media, thus, the variation characteristics of the adsorption–desorption curves can reflect the PS. The actual mesopore size at each relative pressure \( P_0/P \) can be calculated through the Kelvin equation. Most of the samples have hysteresis loops, indicating that the nanopores are overall in an open state. However, significant differences exist between the hysteresis loops of different types of TDCs, indicating that the PS of the nanopores has distinct differences with the primary coals.
The adsorption volume increases slightly at low pressures, while the increase speed accelerates greatly at the relative pressure is ∼1.0, indicating the concentration of N2 at a higher relative pressure. Then, the adsorption volume grows sharply. The steep rise at $P/P_0 \approx 1$, and the catastrophe point at $P/P_0 \approx 0.5$ (corresponding to the ink bottle-shape pores of about 6 nm) indicates that the physisorption isotherms are well-consistent with the type IV curves proposed by Sing, where the hysteresis loops are close to type B classified by De Boer. The overlap regions between the adsorption and the desorption curves at $P/P_0 = 0–0.50$ and the following catastrophe points indicate the existence of the pores of one side-closed and the ink bottle-shaped pores, respectively. However, the stable increase stage between the catastrophe points and the rapid increase indicate the existences of cylindrical shaped pores with two sides open. There exists three stages in the process of nitrogen adsorption, that is, monolayer adsorption, multilayer adsorption, and capillary condensation, indicating that the pores in middle-rank TDCs vary continuously and drastically (Figure 3). The variation characteristics of the hysteresis loops demonstrate that the tectonic deformation has a transformation function for the nanopore shapes. The hysteresis loops of the primary coals and TDCs here can be divided into three types (type A, type B, and type C) based on the characteristics of the catastrophe points incorporating division schemes proposed by De Boer and IUPAC.

For type A, there are only small or even no hysteresis loops. The adsorption curves are basically parallel to the desorption curves (Figure 3a,b), indicating that the relative pressures in adsorption concentration processes are the same to desorption evaporation processes for the nanopores. This kind of hysteresis loops are mainly induced from the semi-open pores with poor connectivity. This type covers primary coal.
and all TDC types here. The type B differs from type A by a relatively sharp decline point on the desorption curves at $P/P_0 \approx 0.51$ (sample HG1 and YLT2), which are composed of primary, schistose, and wrinkle coals (Figure 3b,c). The obvious yield point is mainly caused by the ink bottle-shaped pores. There are also plenty of the parallel plate pores of $>10$ nm similar to these in the primary coals. The type C is for cataclastic coal (sample HP1) and has a sharp inflection point at $P/P_0 \approx 0.51$. Unlike type B, the desorption branch decreased rapidly at a relative pressure slightly below the inflection point (Figure 3f). The pore shape characteristics of different TDCs are in line with the fact that the brittle TDCs are advantageous to CBM production, while the ductile TDCs are of high incidence for coal and gas outburst.

4.2. PSD of Pores. 4.2.1. PSD from HPMI. Figures 4a–e and 5a–e depicted the typical mercury injection and withdraw curves and the corresponding HPMI PSD, respectively. The intrusive mercury curves composed of the injection and withdraw curves can be classified into three types, that is, parallel-, tip-edge-, and double S type based on the schemes proposed by Li (Figure 4a–e). For the parallel type, the mercury injection curves are basically parallel to the withdraw curves for most regions, resulting in the small differences between these two curves (primary and cataclastic coal) (Figure 4a,b). This indicates the weak tectonic deformation. The PV for the parallel types are dominated by the pores of 2–50 nm (39.57% in average), followed by these of 50–100 nm, and the percent of $>1000$ and 100–1000 nm are relatively low (Figures 5a, 4b).

For the tip-edge type, the mercury injection curves manifest as a reverse shape, and the withdraw curves decrease linearly for most regions (Figure 4c,g,h). The hysterisis loops are bigger than the parallel types, indicating that the percentages of semi-closed pores are still high, however, begin to decrease, which results in the decrease of the parallel plate pores and the increase of the fine bottleneck pores. Unlike the parallel types, the PV of the reverse S type are mainly dominated by the pores of $50–100$ nm, followed the 2–50 nm. Still, the percentages of $>1000$ and 100–1000 nm are low (Figures 5b,c, 4g,h). For the double S type, the injection and withdraw curves manifest as S shape and reverse S shape, respectively, resulting the most significant hysteresis loops than the other three types (Figure 5d,e).

The shapes of the hysteresis loops in these coals changes from the small angle shape of the tip-edge types to a large angle-opening shape (Figure 4d–f), indicating that the significant increase in the proportions of the fine bottleneck pores. These coals have a relatively weak pore connectivity because of the fine-grained or powdered coal matrix deformation effect. The PV is dominated by pores of $>1000$ nm, followed by these of 50–100 nm (Figure 4d–f). By comparison of these three types, it could be concluded that the shapes of the intrusive mercury curves provide an indicator for the coal deformation types. The percentage of the PV for pores of $>1000$ and 100–1000 nm increases significantly while that of the 2–50 nm decreases with the increasing deformation intensity, respectively (Figure 5f), indicating the decreasing...
transformation effect of the tectonic deformation on pore structures with the decreasing the geometric scale.

Figure 6a–c depicted the corresponding PV, SSA, and mean pore size for primary coal and different TDCs. All TDCs have higher PV and SSA than primary coals. Then, both the PV and SSA increase distinctly during the cataclastic–schistose stage and then slowly during the schistose–wrinkle stage. For ductile coals, the PV increases distinctly, while the SSA increases slowly with the enhancement of the ductile deformation (Figure 6a,b), indicating the scale effects induced from the microfractures. In wrinkle coal, the PV and SSA are 0.09–0.12 cm$^3$/g and 7.33–7.60 m$^2$/g, respectively. The mean pore size decreases significantly during the brittle stage and slightly during the ductile stage (Figure 6c), indicating that the mechanical crushing induced from the extrusion and shear stress could increase the number of macropores and microfractures. The ductile deformation has a relatively slight impact on the pore size of the macropores and microfractures compared with the mesopores and micropores.

4.2.2. PSD from LPN$_2$GA. The SSA (derived from BET) induced from the LPN$_2$GA data was mainly provided by the pores of <50 nm in diameter, and the proportions of pores of 50–200 nm are negligible (Figure 7b–f). The SSA of mesopores gradually increases during the brittle stage (0.77–1.82, 1.47 m$^2$/g in average), indicating that the brittle deformation increase the adsorption spaces. Then, the SSA of mesopores increases significantly at the ductile stage (1.22–4.02, 2.62 m$^2$/g in average), indicating the highest adsorption capacity for ductile TDCs (Figure 7a).

The BJH SSA of primary coals are dominated by the pores of 2–10 nm (48.86–61.63, 55.25% in average) and 10–20 nm (17.74–22.58, 20.16% in average) in size and the SSA proportion decreases with the increasing pore diameter, further indicating that the SSA are mainly provided by the pores of small apertures. For the cataclastic coals, the SSA proportion for the 2–10 nm (57.62–70.00, 63.81% in average) and 10–20 nm (15.41–23.99, 19.70% in average) in size are significantly higher than those of the primary coals (Figure 7b,c), which is also in line with their lower average BET diameters. For schistose, and wrinkle coals, the SSA proportion for the 2–10 nm was 47.65–54.21% (50.93% in average) and 51.19–55.86% (53.52% in average), respectively (Figure 7e–e). The relative equal SSA distribution in the cataclastic coals and schistose coals are beneficial for the methane diffusion and seepage.

Figure 8a–e depicted the BJH PV distributions of 2–100 nm for primary coals and different TDCs. The PV for pores of 2–100 nm in cataclastic, schistose, scaly, and wrinkle coals are 1.3383, 1.3275, 1.3424, and 1.0104 times larger than that of primary coals, respectively. The distributions for the PV differ distinctly with the SSA distribution, and the PV of pores of 2–100 nm gradually increases with the increasing pore diameter, indicating that the volume of the mesopores was mainly provided by the larger mesopores. The percentages of the 2–50 nm in the 2–200 nm for primary and cataclastic coal were 46.52–52.57% (49.54% in average) and 36.67–52.23% (44.45% in average), respectively. For schistose, and wrinkle coal, they were 40.47–46.69% (43.58% in average) and 29.64–45.24% (37.44% in average), respectively, lower than primary coals. However, for the mylonitic coal, this proportion was 49.07–57.93% (53.50% in average), indicating that the mylonitic coal has a higher percentages for the smaller mesopores. This can also be clarified by its higher adsorption capacity for the mylonitic coals. The average BJH diameters for the primary coals (13.30–15.90, 14.60 nm in average) are slightly higher than cataclastic coal (9.22–11.92, 10.57 nm in average) (Figure 9).

4.2.3. PSD from LPCO$_2$GA. The CO$_2$ adsorption isotherms manifested as Type I proposed by IUPAC$^{51,52}$ indicative of micropore solids. The Figure 10a–f depicted the SSA and PV of the micropores induced from the BET model and the microporous size distribution of the primary coal and TDCs,

Figure 9. Variations of the average pore diameter induced from the BJH model for primary coals and different TDCs.
The SSA of micropores induced from the BET model in cataclastic (51.73–62.37, 57.05 m²/g in average), schistose (60.01–63.68, 61.85 m²/g in average), and wrinkle (59.72–64.83, 62.28 m²/g in average) coals are far larger than those of primary coal (33.25–39.43, 36.34 m²/g). It increases gradually during the brittle stage and keeps stable at the ductile stage (Figure 11a). The average width of micropores are obviously <1 nm (Figure 10b–f), especially for the wrinkle coals (0.40 nm in average), which also indicates that the SSA of micropores are mainly contributed by micropores of small widths.

The cumulative SSA of micropores was mainly provided by pores of <0.61 nm diameter (with a cumulative content range from 66.20 to 71.83% in SSA). As shown in Figure 10b–f, the microporous SSA was mainly concentrated at 0.51–0.61 nm (peak 1) and 0.80–0.87 nm (peak 2) segments. Both the locations of the peak 1 and peak 2 keep stable with the enhancement of the tectonic deformation. Additionally, Prinz and Littke have proved that the micropores of >0.4 nm in coal should correspond to the void space among macromolecules based on the XRD results. Thus, the peak 1 is corresponding to the BSU-layered pores. The peak 2 keeps essentially constant with the enhancement of the tectonic deformation, which is consistent with the stability of the aromatic diameter. Thus, the peak 2 was corresponding to the cylindrical pores. Ju et al. proposed that the widths of the micropores can be reduced through the preferential growths in the directions parallel to the stress and the priority collages in the directions perpendicular to the stress of the aromatic carbon nets. The DFT-average pore widths of the primary, respectively. The SSA of micropores induced from the BET model in cataclastic (51.73–62.37, 57.05 m²/g in average), schistose (60.01–63.68, 61.85 m²/g in average), and wrinkle (59.72–64.83, 62.28 m²/g in average) coals are far larger than those of primary coal (33.25–39.43, 36.34 m²/g). It increases gradually during the brittle stage and keeps stable at the ductile stage (Figure 11a). The average width of micropores are obviously <1 nm (Figure 10b–f), especially for the wrinkle coals (0.40 nm in average), which also indicates that the SSA of micropores are mainly contributed by micropores of small widths.

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cataclastic, and schistose coals are 0.3989, 0.3962, and 0.4003 nm, respectively, and close to the dynamic diameter of methane (0.414 nm), which is beneficial for the surface and configurational diffusion under the monolayer adsorption conditions based on our previous studies.

4.3. Fractal Dimensions.

4.3.1. Fractal Dimensions of Adsorption and Seepage Pores.

Figure 11a–e depicted the Sierpinski fractal curves based on the HPMI results, which could be distinctly divided into two segments, that is, a low-pressure region ($P < 8.35 - 46.33$ MPa) and a high-pressure region ($P > 8.35 - 46.33$ MPa). They were corresponding to the adsorption and seepage pores, respectively, indicating the variations in the heterogeneity between these two types of pores. The correlation coefficients between $\ln (P - P_t)$ and $\ln (V)$ were $>0.90$ for these two segments, indicating that the adsorption (the fractal dimension abbreviated as $D_{ap}$) and seepage pores (the fractal dimension abbreviated as $D_{sp}$) in primary coals and TDCs have good fractal characteristics. The $D_{ap}$ here was corrected and optimized using the methods proposed in our previous work until the value was eventually stabilized at the maximum pressure.

Figure 12a,b are the variations of the $D_{ap}$ and $D_{sp}$ with the increasing tectonic deformation intensity, respectively. It could be concluded that the $D_{ap}$ overall increases with the increasing deformation intensity and the wrinkle coals have the highest $D_{ap}$ (Figure 12a), indicating that the nanopores of the mylonitic coals (2.93–2.97, 2.95 in average) have the strongest heterogeneity than the primary coals (2.60–2.76, 2.69 in average) and other TDCs. This can provide more adsorption sites for methane and is in line with their highest SSA discussed in Section 4.2.2, which is also consistent with our previous work that the ductile TDCs have a significantly higher methane adsorption capacity than the brittle TDCs. The $D_{sp}$ keeps stable during the brittle stage and decreases significantly with the increasing deformation intensity, resulting in the lowest $D_{sp}$ in the mylonitic coal (2.54–2.65, 2.60 in average) (Figure 12b). For the primary, cataclastic, and schistose coals, the $D_{ap}$ is higher than $D_{sp}$, indicating that the heterogeneity of the adsorption pores is higher than that of the seepage pores in these coal types, which is beneficial for methane adsorption, however, a disadvantage to methane seepage. However, the opposite trend can be found in the wrinkle, and mylonitic coals. Thus, as mentioned above, the $D_{ap}$ and $D_{sp}$ can efficiently characterize the heterogeneity of the pores spanning from nanoscale to micron scale, providing an indicator for the ability of adsorption and seepage, respectively.

4.3.2. Fractal Dimensions of Meso-macropores.

The FHH fractal curves are shown in Figure 13a–e. There are two
distinct linear segments at $P/P_0 = 0.5$, indicating that the fractal characteristics of these two intervals differ significantly. The first linear segment of $P/P_0 = 0.5–1$ is influenced by multiple layer coverage, where the monolayer coverage was used to determine the slope $A_{f1}$. The second linear segment of $P/P_0 = 0–0.5$ is induced from the capillary condensation and is used
to determine the slope $A_{12}$. Thus, two different fractal dimensions $D_{h1}$ and $D_{h2}$ can be derived from the region of $P/P_0 = 0.5-1$ and $P/P_0 = 0-0.5$, respectively, indicating the variations in the structural heterogeneities between $6-100$ and $2-6$ nm, while both the calculated $D_{v1}$ and $D_{v2}$ from the equation "3(1 + $A_1$)" and "3(1 + $A_2$)" is $<2$ for all samples, which deviates from the definition of fractal dimension. Thus, the equation "3 + $A_1$" and "3 + $A_2$" were used to calculate $D_{v1}$ and $D_{v2}$, respectively, which is further used to characterize heterogeneities of the adsorption pores in TDCs.

The $D_{v1}$ increases linearly during the cataclastic–schistose stage, then keeps stable during the schistose–wrinkle stage, and finally increases sharply at the mylonitic stage (Figure 14a). The $D_{v2}$, although discrete, overall increases with the enhancement of the tectonic deformation (Figure 14b). The $D_{v1}$ is higher than $D_{v2}$ for all the samples, which indicates that the inhomogeneity of nanopores is induced by the variations in the pore surface under tectonic deformation. The $D_{v1}$ and $D_{v2}$ of primary coals are lower than TDCs, indicating that the tectonic deformation has promoted the heterogeneity in pore surface and structures. The mylonitic coals have the highest $D_{v1}$ and $D_{v2}$, indicating that the nanopores of 2–100 nm have the highest heterogeneity, followed by the wrinkle and schistose coals. There exists a significant positive correlation between $D_{v1}$ and $D_{v2}$ ($R^2 = 0.64$) (Figure 14c), verifying the FHH model used here.

4.3.3. Fractal Dimensions of Micropores. The surface and volume fractal curves for the micropores were shown in Figures 15a–e and 16a–e, respectively. These fractal curves can be distinctly divided into two segments. The fractal dimensions for the larger micropores (0.6–1.4 nm) and smaller micropores (0.3–0.6 nm) are defined as $D_{s1}$ ($D_{v1}$) and $D_{s2}$ ($D_{v2}$), respectively. Their variations of the surface fractal and volume fractal dimensions are shown in Figure 17a–d. All the surface fractal dimensions are 2–3, consistent with the physical meaning of the fractal theory. The $D_{v2}$ for YLTS (3.03, mylonitic coal) was larger than 3, which differs from values of 2–3 from the conventional rocks. Cai et al. considered that when the fractal dimensions are >3, the coal reservoirs are either highly metamorphosed or highly fractured through deformation. Yao et al. proposed that the fractal dimensions of higher than 3 from the HPMI Menger model are induced by the high coal compressibility after 10 MPa, which results in the destruction of the original coal pore systems. Combining the fact that the $D_{v3}$ and $D_{v4}$ for the primary coals and the brittle TDCs are 2–3 and the above mentioned literatures, it could be concluded that the fractal dimensions >3 for some ductile TDCs are resulted from both the high heterogeneity of the micropores and the destruction effect from shear stress and ductile deformation for the micropores. Therefore, the $D_{v3}$ and $D_{v4}$ of >3 can also provide a theoretical basis for the micropore heterogeneity.

The $D_{v1}$ for the primary coals (2.31–2.36, 2.34 in average with a standard deviation $S_{3d}$ of 0.02) is significantly lower than those of the TDCs and the $D_{v1}$ gradually increases with the enhancement of the brittle and ductile deformation. For cataclastic, and schistose coal, the $D_{v1}$s were 2.35–2.83 (2.60 in average) and 2.36–2.48 (2.42 in average), respectively. The wrinkle coal (2.35–2.53, 2.44 in average) has a close $D_{v1}$ with those of the brittle TDCs. The mylonitic coal (2.52–2.53 with a $S_{3d}$ of 0.01) has a highest $D_{v1}$ than the other types of TDCs, indicating that the mylonitic coals have the highest degree of heterogeneity for the microporous surface. Ju et al. proposed that the growth of aromatic rings under the shear and ductile deformation may lead to the generation of the anisotropic small spheres through the aromatic nuclear dislocation and aroma layer slip, which further results in the increase of the aromatic regions. The increasing heterogeneity of these cylindrical pores is caused from the increase of irregular arrangements of these anisotropic small spheres among the local orientation- and non-directional perimeter range of the aromatic layers. The mylonitic coals have the highest $D_{v2}$ (2.65–2.76, 2.71 in average with a $S_{3d}$ of 0.05) (Figure 17b), indicating that the mylonitic coals have the
highest heterogeneity for the BSU layered pores of 0.3−0.6 nm, followed by the scalpy coals (2.70−2.73, 2.72 in average with a $S_{	ext{ad}}$ of 0.01), which may be induced by the Stone-Wales (SW) defect via in-plane rotation of C=C bonds by 90° as Han et al. indicated from the strong shear stress. Han et al. proposed that the slip between aromatic layers will generate a shearing component under the shear stress, which may result in bond rotation and further structure defects in shear- and the mylonitic coals. For the brittle TDCs, the $D_s$ was ranging 2.61−2.71 (2.67 in average with a $S_{	ext{ad}}$ of 0.02), slightly higher than primary coal, indicating the promoting effect for the microporous surface induced from the brittle deformation. For the wrink- and mylonitic coal, the $D_s$ were 2.70 and 2.65−2.76 (2.71 in average), respectively, significantly higher than the primary coal, indicating the ductile rheology could cause the highest degree of heterogeneity for the microporous surface. The $D_2$ for primary coals was significantly lower than those of the TDCs, indicating that the tectonic deformation could promote the heterogeneity for the pores of 0.3−0.6 nm. It increases slightly during the cataclastic-schistose-wrinkle deformation stage (Figure 17a,b) and significantly during the wrinkle-mylonitic stage. For all the coals here, $D_3$ was higher than $D_1$, indicating that the surface heterogeneity of the 0.3−0.6 nm was stronger than that of the 0.6−1.4 nm. The $D_4$ was lower than $D_3$ for all the TDCs, suggesting the volume heterogeneity for pores of 0.6−1.5 nm was stronger than that of the 0.3−0.6 nm. The $D_4$ was close to 3, suggesting the highest heterogeneity for the larger micropores. Both the $D_3$ and $D_4$ increases slightly during the brittle deformation stage and significantly at the ductile deformation stage (Figure 17c,d), indicating that the ductile deformation could exert a more significant transformation for micropores than the brittle deformation. The overall changing trend $D_4$ was also consistent with that of the $D_3$ when excluding the highest and lowest values, indicating the impact of the tectonic deformation on pore heterogeneity.

Compared with the low-rank TDCs, the heterogeneity of nanopores differs significantly. Yu et al. have investigated the multiscale heterogeneity characteristics of nanopores in low ranks and highlighted the fractal dimensions. For the adsorption and seepage pores, their fractal dimensions have similar variations for the low and middle ranks. However, for the low ranks, the variations of the heterogeneity of the adsorption and seepage pores changes distinctly compared with the middle ranks, which was attributed to the differences in macromolecules. This is due to the fact that the nanopores were macromolecular genesis. The organic molecules of the low ranks are rich in the aliphatic side chains and functional groups, resulting in their higher sensitivities compared with the middle ranks. On the other hand, the seepage pores or even the micro fractures of the weak and strong deformation stages were primarily attributed to mechanisms of friction heat and strain energy, respectively. The low-rank TDCs possess lower mechanical strength and, thus, exhibit higher sensitiveness of heterogeneity to the brittle deformation.

For the mesopores, the variations of the fractal dimensions induced from the FHH model were consistent for the middle and low ranks, indicating transformation effects of the tectonic deformation for the nanoporous heterogeneity. However, the fractal dimensions of the mesoporous in the low ranks were higher than those in the middle ranks, although there is a lack of mylonitic coals here, which may be attributed to the compaction-dehydration effects during the coalification proc-ess. For both the surface and volume heterogeneity, their fractal dimensions increases gradually with the enhancement of the tectonic deformation. This was attributed to the fact that the micropores were generated from the inner BSUs, which keeps stable during the coalification process and increases in order in some extent.

5. CONCLUSIONS

As the TDCs can be primarily formed under the extrusion and/or shear stresses, the main controlling structures were frequently exhibited as the fault (especially for the thrust fault and layer slip fault) and folds. Previous publications have mainly focused on the nappe, monocline, and fault. Here, to reveal the heterogeneity properties of nanopores in middle-rank TDCs formed in the syncline deformation zone, the HPMI and LP$\text{CO}_2$/N$_2$GA were utilized to investigate the PSD and heterogeneity characteristics combining the Sierpinski, FHH, and surface/volume fractal models. The main conclusions were derived as follows.

1) The distribution of the brittle and ductile TDCs suggests that the axis zone of the syncline possesses stronger deformation than the wing zone, which is attributed to the longitudinal bending folding effects under the action of bedding compression stresses. The deformation intensity increases with the enhancement of the folding deformation degree, forming ductile TDCs such as wrinkle coal and/or mylonite coal in the axis zone. In the wing zone of the syncline, local bedding shear stress is formed because of bedding shear sliding between the coal seam and its roof and floor strata. The dense bedding shear joints are developed in the coal seam, thus forming a bedding bending-sliding shear zone and the development of the cataclastic coals and schistose coals.

2) The morphology of the hysteresis loops for HPMI curves was indicative of the tectonic deformation. The PV percentage for pores of >1000 and 100−1000 nm in diameter increases with the enhancement of tectonic deformation. The PV of the macropores increases significantly during the primary—cataclastic stage and becomes stable during the cataclastic—schistose—wrinkle stage. The average diameter for mesopores decreases significantly for the brittle deformation stage and slightly during the ductile deformation stage, indicating that the mechanical crushing effect from the extrusion and shear stress could increase the number of the mesopores. The BET SSA from the LP$\text{N}_2$GA data was primarily contributed by those of <50 nm in diameter.

3) The $D_4$ increase slightly during the primary—cataclastic—schistose deformation stage and sharply during the ductile deformation stage, indicating that ductile deformation could enhance the heterogeneity of the adsorption pores. However, the opposite variations can be found for the seepage pores. For brittle TDCs, the adsorption pores possess stronger heterogeneity than the seepage pores. Both the $D_3$ and $D_4$ increases with the enhancement of the tectonic deformation, indicative of the transformation effects of the tectonic deformation for micropores. The deformation has a consistent transformation effect for various size intervals of micropores. From the comparison in the variations of the fractal dimension, it could be concluded that the tectonic transformation on the nanoporous hetero-
neity become weaker with the decreasing geometrical scale.

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Notes
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