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Influence of Coalification on the Pore Characteristics of Middle–High Rank Coal

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ABSTRACT: The pore size distribution, pore shape and connectivity, and fractal characteristics are investigated to determine the pore characteristics of three different samples of middle—high rank coal. Pores of more than and less than 10 nm were measured using mercury intrusion porosimetry (MIP) and gas adsorption, respectively. The pore size distribution was verified with the initial methane diffusion rate and CH_4 desorption. Fractal dimensions of seepage pores and adsorption pores were counted using the results from MIP and gas adsorption, respectively. First, the results show that micropores and transition pores occupy the most volume and specific surface area. Micropores and transition pores, as well as porosity, gradually increase as coal rank increases. Second, the fractal dimensions of seepage pores and adsorption pores gradually increase with increasing coal rank, which shows that coalification makes pore structure more complex and pore surface rougher. Additionally, the fractal dimensions of bigger pores are greater than those of smaller pores, implying that the surface and structure of bigger pores is rougher and more complex than those of smaller pores, respectively. Finally, the connectivity of coal has a close relationship with macropores rather than coal rank.

1. INTRODUCTION

Coal is a complex, porous organic rock.¹⁻⁵ The pores in coal act as storage and diffusion channels for gases.^{6,7} The pore characteristics of coal, including pore volume, specific surface area, porosity, shape, connectivity, and fractal characteristics, affect the capability of gas adsorption and gas flow in coal. They also have important effects on the gas transportation pattern and the mechanisms of gas adsorption and storage in coal seams.⁸⁻¹³ There is plenty of methane stored in the pores of coal. As a low-carbon energy resource, methane is also one of the main factors causing gas explosion and coal-gas outburst. Because of the adsorption capability of pores of coal, CO2 geosequestration in coal seams also becomes more attractive. Therefore, the pores characteristics of coal play an important role in the production of coal, coal bed methane (CBM), and CO₂ geosequestration.¹⁴ In consideration of characteristics of coal, a classification system is adopted in this paper: macropores (≥1000 nm in diameter), mesopores (100-1000 nm in diameter), transition pores (10-100 nm in diameter), and micropores (≤ 10 nm in diameter).^{15,16} Macropores and mesopores are named as seepage pores, through which highvelocity gases and low-velocity gases form laminar/turbulent infiltration and laminar flow infiltration, respectively.^{17,18} Thus, they are the main channels of gas flow during CBM production and CO₂ injection. Transition pores and micropores, also known as adsorption pores, have extremely large internal surfaces. The pore surface has a strong adsorption ability for certain gases, for example, CH_4 and CO_2 . This means that they are the main systems for gas adsorption and diffusion.^{19,20}

Coalification is a long and complex process. During coalification, peat gradually transforms into bituminous coal, which then transforms into anthracitic coal through complicated physical and chemical reactions. Coal rank is the standard to measure the coalification degree of coal, which is quantified by the parameters of vitrinite reflectance or volatile matter yield. During coalification, the properties and pore characteristics of coal change through complicated physical and chemical reactions.²¹⁻²³ There are a number of studies on the pore characteristics of coal, but most of them only focus on the size distribution of coal pores and fractal characteristics of seepage pores or adsorption pores.^{24–30} Additionally, there are few published analyses on the fractal characteristics of both seepage pores and adsorption pores. In this paper, fractal characteristics of both seepage pores and adsorption pores in coal together with the pore shape and connectivity were analyzed. The pore size distribution was further verified with the initial methane diffusion rate and CH₄ desorption. As closed pores cannot be entered into by gas and have little relationship with gas adsorption and flow in coal, thus we only studied open pores in this paper. Because of the limitation of coal samples, we only discuss the pore characteristics of middle-high rank coal.

2. EXPERIMENTAL WORK

Three different samples of middle—high rank coal were collected directly from the working faces of the northern China mining area, carefully sealed in the canister to prevent samples from oxidization, and then instantly carried to the laboratory for experiments. The collected samples were dried at 60 °C for 24 h in a vacuumed oven, sieved to five size fractions of 0.074-0.2, 0.2-0.25, 0.2-0.5, 1-3, and 5-10 mm, and dried again in the same way.

Proximate analysis was performed according to the China National Standard GB/T 212-2008 using a 5E-MAG6600 automatic industrial analyzer to measure ash, moisture, volatile material, and fixed carbon

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of coal. Vitrinite reflectance ($\%R_0$) was collected with a microscope photometer produced in Germany by Zeiss, following China National Standards GB/T 6948-2008. The initial methane diffusion rate was obtained using a WT-I rate tester produced by the Fushun Coal Science Research Institute following China Production Safety Industry Standards AQ 1080-2009. Mercury intrusion porosimetry (MIP) was performed following Chinese Oil and Gas Industry Standard SY/T 5346-2005 and using a Micromeritics AutoPore IV9500 porosimeter produced in the United States, which automatically registers the pressure and injection volume at the pressure range of 0–450 MPa and the pore radius range of 3–180000 nm. Gas adsorption was performed using a Quantachrome AUTOSORB-1 automated surface area analyzer following China National Standard GB/T 5751-2009 at the pore radius range of 0.614–24 nm.

MIP is a widely used technique to analyze the pore size distribution of porous materials, the principle of which is as follows. Mercury is not able to be injected into the pores of porous materials without external pressure. With external pressure increasing, mercury overcomes the surface tension and is injected into the pores of porous materials. The relationship of external pressure and pore radius meets the Washurn equation^{31–33}

$$r = -\frac{2\sigma \cos \alpha}{p} \tag{1}$$

where *r* is the pore radius of porous materials (in cm), σ is the surface tension of mercury, assumed as 0.48 N/m, α is the contact angle of mercury on the porous materials surface, assumed as 140° for intrusion and 107° for extrusion, and *p* is the external pressure. MIP is based on the gradual injection of liquid mercury into an evacuated pore system with external pressure. The higher the external pressure, the smaller the pores into which mercury can be injected. Smaller pores, for example, micropores, are easily compressed and broken. Therefore, MIP is not suitable for measuring smaller pores. Moreover, the mercury is not able to extrude completely from the pore system; therefore, the intrusion result of MIP was usually used to calculate the pore size distribution.

Gas adsorption is usually used to measure nanoscale pores, the principle of which is as follows: with porous materials as the adsorbent and N_2 as the absorbate, the volume of gas adsorption is registered while the gas pressure gradually increases to the saturated vapor pressure at a constant temperature of 77 K. The adsorption isotherm is obtained by drawing with the volume of gas adsorption and relative pressure (the gas pressure/the saturated vapor pressure). With the opposite course, the desorption isotherm is also obtained. The sorption isotherms are analyzed to obtain the specific surface and volume of pores in porous materials with gas sorption theory, for instance, the Langmuir model, BET model, Frenkel–Halsey–Hill (FHH) model, Kelvin equation, BJH model, DR model, and so forth.^{31,34–36}

3. RESULTS AND DISCUSSION

The results from proximate analysis, vitrinite reflectance measurements, and coal rank are summarized in Table 1. The table shows that R_0 and coal rank gradually increase from #1 to #3, while volatile matter decreases. The degree of coalification

Table 1. Results from Proximate Analysis, Coal Rank, and Vitrinite Reflectance

	proximate analysis					
sample	M _{ad} %	A _{ad} %	FC _{ad} %	V _{daf} %	vitrinite reflectance R_0 (%)	coal rank
#1	1.41	12.02	55.20	36.25	0.98	high volatile A bituminous
#2	0.77	8.01	74.59	18.24	1.67	low volatile bituminous
#3	1.06	17.05	73.58	10.17	2.75	anthracite

of the three coal samples rises in order from #1 to #3. Coal samples #1, #2, and #3 are high volatile A bituminous, low volatile bituminous, and anthracite coal following ASTM, respectively.

3.1. Pore Size Distribution. As shown in Table 2, the bulk density, apparent density, and porosity of the three coal

Table 2. Results from MIP

sample	total intrusion volume/ (mL/g)	total pore area/ (m^2/g)	bulk density at 0.99 psia /(g/mL)	apparent (skeletal) density/ (g/mL)	porosity/%
#1	0.0319	16.3690	1.2074	1.2559	3.8639
#2	0.0343	17.1550	1.2201	1.2741	4.2391
#3	0.0350	18.2660	1.2387	1.2943	4.2995
#3	0.0350	18.2660	1.2387	1.2943	4.2995

samples gradually increase with increasing coal rank, which shows that coalification makes the coal skeleton denser. This change in density occurs because polycondensation of coal molecules occurs with increasing coal rank during coalification, meaning that the density of coal increases. It leads to coal bulk compaction. Because of uneven bulk compaction, the internal stress of coal is greater than the strength of coal, and cracks gradually develop in coal. As a result, the porosity of coal increases with increasing coal rank in middle—high rank coal.

The pore size distribution of the three coal samples from MIP is shown in Figure 1. The figure shows that micropores and transition pores of the three coal samples account for 78.69–88.54% of the volume and increase with increasing coal rank. Additionally, macropores and mesopores have few specific surface areas, while micropores and transition pores occupy nearly 100% and increase with increasing coal rank, illustrating that micropores and transition pores, especially micropores, determine the specific surface area of coal. The difference in specific surface area is because gelation matters form many polycondensate chain—chain pores during coalification, most of which are less than 10 nm.

Considering the compression effect of MIP at high pressure, we also measured micropores of the three coal samples using gas adsorption. The desorption isotherm was used to calculate the pore size distribution, and the range of P/P_0 is from 0.05 to 1. The result is shown in Figure 2.

As shown in Figure 2, the result range of gas adsorption is mainly 0.614–10 nm (micropores). The volume and specific surface area of the micropores in #3 are the largest, those in #2 are the second largest, and those in #1 are the smallest. The result from gas adsorption is similar to the data obtained from MIP.

The pore size distribution was verified with the initial methane diffusion rate. According to the basic principle of CH_4 desorption and diffusion, CH_4 is stored in bigger pores and smaller pores in the form of free gas and adsorbed gas, respectively. First, CH_4 in bigger pores, for instance, macropores and mesopores, diffuses to the surface of coal. Finally, CH_4 in smaller pores, for instance, transition pores and micropores, diffuses to the bigger pores and then to the surface of coal. ^{19,20,30,37–39} Additionally, smaller pores, especially micropores, are the main control of gas adsorption and storage. Hence, the bigger pores, macropores and micropores, control the initial speed of gas desorption and diffusion, and the smaller pores, transition pores and micropores, control the final volume of gas desorption and diffusion. Figure 3 shows that the initial volume of #2 is the largest, that of #3 is the second largest, and







Figure 2. Pore size distribution of the three coal samples from gas adsorption.



Figure 3. Initial methane diffusion rate of the three coal samples.

that of #1 is the smallest in the beginning, which agrees with the distribution of the macropores and mesopores from the three coal samples previously discussed. The final volume of #3 is the largest, that of #2 is the second largest, and that of #1 is the smallest, which agrees with the transition pores' and microspores' distribution of the three coal samples previously discussed. The result from the initial methane diffusion rate agrees with the pore size distribution from MIP and gas adsorption (Figures 1 and 2).

Because coalification mainly focuses on the micropores and transition pores, we further verified the distribution of micropores and transition pores of the three coal samples with 2-5 MPa of CH₄ desorption. The result is shown in Figure 4.

As shown in Figure 4, the desorption volumes of #1, #2, and #3 increase successively in pressures of 2-5 MPa, which shows that transition pores and micropores of the three coal samples gradually increase with increasing coal rank. These findings agree with the results from MIP and gas adsorption.

The pores of samples were determined with MIP, and the micropores of samples were also determined with gas adsorption in consideration of the compression in MIP. The bigger pores, macropores and mesopores, control the initial speed of gas desorption and diffusion, while the smaller pores, transition pores and micropores, control the final volume of gas desorption and diffusion. The pore size distribution of samples



Figure 4. Desorption volume of CH₄ under 2–5 MPa.



Figure 5. Types of pores.

was verified with the initial methane diffusion rate and 2-5 MPa CH₄ desorption.

To sum up, micropores and transition pores occupy the most volume and specific surface area. Micropores and transition pores, as well as porosity, gradually increase as coal rank increases. That is to say, the adsorption capability of samples gradually increases with coal rank increasing. Therefore, the risk of gas explosions and coal-gas outburst increases in coal production with increasing coal rank, while CBM reserves and the capability of CO₂ geosequestration increase.

3.2. Pore Shapes and Connectivity. The types of pores in coal can be classified as cylindrical, conical, slits, spherical

(ink bottle), and interstices depending on their pore shapes (Figure 5a).The types of pores in coal can be classified as interconnected, passing, dead end, and closed according to their pore connectivity (Figure 5b). The former three types are also called open pores.⁴⁰ Open pores have important effects on the transportation, adsorption, and storage of gas in coal seams.

Figure 6 shows the N_2 adsorption/desorption loop of the three coal samples at a low temperature (77 K). De Boer divided the adsorption/desorption loop into five types.⁴¹ The adsorption/desorption loops of #1 and #2 belong to type D, which corresponds to a type of wedge-shaped pore with all open sides formed by the accumulation of sloping sheets or



Figure 6. N₂ adsorption/desorption loop of the three coal samples.

film. This type of loop is formed because it is not parallel between sheets, and there is no steep period on the desorption curve. The space between both sides forms a meniscus interface by capillary condensation under lower relative pressure and is gradually filled with increasing relative pressure. The adsorption curve and desorption curve will then overlap. When the length of the narrow side between the sheets reaches the size of several or dozens of molecules, the loop will disappear. Therefore, there are a large number of wedge-shaped pores with all open sides in coal samples of #1 and #2. The adsorption/desorption loop of #3 belongs to type C, which corresponds to a type of tubular pore with a cone or double cones, whose radius is continuously changing from r (minimum radius) to R (maximum radius, $R \leq 2r$). When the relative pressure on an adsorption curve reaches a value corresponding to r, capillary condensation suddenly occurs, and the adsorption curve steepens in the adsorption process. N₂ begins to slowly desorb when the relative pressure reaches a value corresponding to R and ends when the relative pressure reaches a value corresponding to R and ends when the relative pressure reaches a value corresponding to r; therefore, the desorption curve is smooth. Therefore, there are a large number of tubular pores with a cone or double cones in the coal sample of #3.

As shown in Table 3, the threshold pressure and tortuosity of #1 is the highest, followed by #3 and #2. The opposite trend

 Table 3. Connectivity Parameters of the Three Coal Samples from MIP

coal sample	threshold pressure/Pisa a	tortuosity ^b	permeability/mdarcy ^c
#1	27.93	42.47	0.69
#2	4.37	14.69	13.51
#3	7.70	24.59	3.65

^{*a*}Threshold pressure means the minimum pressure of mercury able to enter into the pores. ^{*b*}Tortuosity is a property of the curve being tortuous and refers to the ratio of the length of the curve (L) to the distance between the ends (C). ^{*c*}Permeability means the ability of a material (for example, rocks) to transmit fluids or gas.

occurs for the permeability, meaning that the connectivity of #2 is the best, followed by #3 and #1. The connectivity has little relationship with coal rank and is positively correlated with macropores, which illustrates that the connectivity of middle—high rank coal has a close relationship with macropores rather than coal rank.

3.3. Pore Fractal Characteristics. Fractal geometry is a mathematical tool to deal with complex systems by self-similarity. A fractal dimension is a ratio providing a statistical index characterizing complicated geometric forms. There are obvious fractal characteristics in the pores of sedimentary rocks, especially coal. The fractal dimension between 2 and 3 for a fractal pore surface can characterize the roughness of the pore surface, meaning a stronger adsorption capability.^{9,42–46} To consider the compressibility of MIP and the measure range of gas adsorption, we analyzed the fractal characteristics of seepage pores and adsorption pores using MIP and gas adsorption, respectively.

Some research analyzed pore fractal characteristics using MIP with different methods and built a double-logarithm regression equation between the mercury intrusion volume and mercury pressure using the Washburn equation.^{47–50}

$$\ln\left[\frac{\mathrm{d}V_{P(r)}}{\mathrm{d}P(r)}\right] \propto (4 - d_{\mathrm{f}}) \ln r \propto (d_{\mathrm{f}} - 4) \ln P(r) \tag{2}$$

where P(r) is the mercury pressure (in MPa). $V_{P(r)}$ is the mercury intrusion volume into pores under P(r) (in mL), r is the pore radius of coal (in nm), and d_f is the fractal dimension of pores.

If a scatter diagram is drawn using $\ln[dV_{P(r)}/dP(r)]$ and $\ln P(r)$ from the intrusion result of MIP and a straight line is fitted, the slope K can be inferred, that is, $d_f = 4 + K$.

There are several computational methods on the fractal dimension of adsorption pores, including the Langmuir model, BET model, FHH model, and so forth.^{46,51} The Langmuir model, BET model, and FHH model are for adsorbent adsorbate interactions in monolayer coverage, near-monolayer coverage, and multilayer coverage, respectively.⁵² In this paper, the fractal dimensions are determined using an analysis of multilayer adsorption of N₂ to a fractal surface; therefore, the FHH model is more suitable.^{53–55} The FHH equation is shown as follows

$$\ln\left(\frac{V}{V_0}\right) = \text{constant} + (d_f - 3)\ln\left[\ln\left(\frac{P_0}{P}\right)\right]$$
(3)

where V/V_0 is the relative adsorption volume and V_0 and V are the volumes of monolayer coverage and adsorbed gas molecules at equilibrium pressure, respectively (in m³/t). P_0 and P are the saturation and equilibrium pressures of the gas, respectively (in MPa).

According to eq 2, in the plot of $\ln(V/V_0)$ versus $\ln[\ln(P_0/P)]$, the slope (*K*) of the straight line should be equal to $d_f - 3$. Therefore, the fractal dimension d_f is obtained by $d_f = 3 + K$.

If a scatter diagram is drawn with $\ln(V/V_0)$ and $\ln[\ln(P_0/P)]$ from the result of the desorption isotherm in gas adsorption and a straight line is fit, the slope *K* can be inferred, that is, $d_f = 3 + K$. The line is divided into two sections according to the curve of the linear trend, high pressure and low pressure. The result is given in Table 4 and Figure 8.

Table 4. Fractal Dimensions of Seepage Pores andAdsorption Pores from MIP and Gas Adsorption

coal sample	coal rank	$d_{ m f1}$	d_{f2}	d_{f3}
#1	high volatile A bituminous	2.8668	2.8212	2.1644
#2	low volatile bituminous	2.8886	2.8816	2.2335
#3	anthracite	2.9209	2.8990	2.2764

Figures 7 and 8 and Table 4 show that the fractal dimensions of both seepage pores and adsorption pores increase with increasing coal rank, which shows that coalification makes the pore surface rougher and pore structure more complex in middle-high rank coal. The rougher and more complex the pore surface and structure are, the more the protuberance and concaveness on the pore surface are. Hence, the pores with larger fractal dimension have a more specific surface area and have a stronger adsorption capacity. Additionally, $d_{\rm fl}$ is the maximum, d_{f2} is the second, and d_{f3} is the minimum, which illustrates that the bigger the pores, the larger the dimensions of the pores. There are numerous smaller pores in bigger pores, that is, the surface of bigger pores consists of the surfaces of the smaller pores. Therefore, the surface and structure of bigger pores are rougher and more complex than those of smaller pores, respectively.

4. CONCLUSIONS

The pore size distribution, pore shape and connectivity, and pore fractal characteristics of middle—high rank coal were analyzed using MIP, gas adsorption, and so forth in this paper. Finally, the following three conclusions are inferred:

(1) Micropores and transition pores of middle-high rank coal occupy the most volume and specific surface area. Micropores and transition pores, as well as porosity, gradually increase with increasing coal rank in middle-high rank coal. These increases occur because coalification intensifies the polycondensation of coal molecules, which encourages the



Figure 7. Fractal dimensions of seepage pores from MIP.

formation of a large number of micropores and transition pores in the coal.

(2) There are a large number of wedge-shaped pores with all open sides in coal samples #1 and #2 and many tubular pores with a cone or double cones in coal sample #3. The connectivity of #2 is the best, #3 is the second best, and #1 is the worst, illustrating that the connectivity of middle-high



Figure 8. Fractal dimensions of adsorption pores from gas adsorption.

rank coal has a close relationship with macropores rather than coal rank.

(3) The fractal dimensions of seepage pores and adsorption pores of the three coal samples gradually increase with increasing coal rank. Coalification makes pore surfaces rougher and pore structure more complex in coal. The fractal dimensions of bigger pores are greater than the dimensions of smaller pores, meaning that the surface and structure of bigger pores are rougher and more complex than those of smaller pores, respectively.

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Notes

The authors declare no competing financial interest.

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