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Micro-pores and fractures of coals analysed by field emission scanning electron microscopy and fractal theory

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HIGHLIGHTS

- Nanoscale pores were analysed by FESEM and fractal theory.
- Nanopores in coal matrix can be categorised as micro-pores or micro-fractures.
- Micro-pores are round or elliptical and micro-fractures are irregular bending.
- As coalification, the average width of micro-pores changes very small.
- With increasing coal rank, the average width of micro-fractures changes regularly.

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ABSTRACT

In this study, the micro-pores and fractures of six coal samples with different metamorphic degrees ($R_{o,m}$ = 0.75–2.80%) were analysed using field emission scanning electron microscopy (FESEM). The micro-fractures and pores were quantitatively classified based on fractal theory. Our results show that pores in coal matrix can be categorised as either micro-pores or micro-fractures according to fractal theory. Micro-pores exhibit round or elliptical shapes, whereas micro-fractures are bent and exhibit irregular shapes, which are connected with other micro-fractures via round or elliptical channels. With increasing metamorphic degrees, the distribution of the total surface porosity of micro-pores and micro-fractures is characterised by an inverted "U" shape. The total surface porosity is at its greatest during the high-rank bituminous coal stage. However, the correlation between coal metamorphic degree and surface densities of micro-pores and micro-fractures varies. During the low- and medium-rank stages, the surface frequency and the average width of micro-pores and fractures increase with increasing coal rank. During the high-rank coal stage, with increasing coal rank, the surface frequency of micro-pores and fractures rapidly increases but as a whole is lower than those during the low- and medium-rank stages. The average width of micro-fractures decreases with increasing average surface frequency in a logarithmic relationship; in contrast, the average width of micro-pores increases logarithmically with increasing average surface frequency.

1. Introduction

Coal is a medium with complicated dual-structure system composed of a large number of pores and fractures of different scales [1]. Micro-pores in coal have extremely large specific surface areas [2,3]. The micro-pore system in coal is the primary storage space for coalbed gas, where the amount of absorbed coalbed methane can reach 90–95% [4,5]. The characteristics of pores and fractures in coal are the basis to study absorption, desorption, diffusion, and seepage of coalbed methane [6–12].

A number of methods have been applied to study pores and fractures in coal, including mercury intrusion porosimetry [13], liquid nitrogen absorption [14], atomic force microscopy (AFM) [15], small-angle X-ray scattering (SAXS) [16] and small-angle neutron scattering (SANS) [17]. These different test methods have different advantages. Mercury intrusion porosimetry and liquid nitrogen absorption methods can be used to indirectly analyse the pore volume and specific surface area of coal [14,18–21]. Scanning electron microscopy (SEM) and AFM can determine the shape of coal surfaces and the characteristics of pores and fractures on the

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micrometre and nanometre scales. Compared with indirect observation methods, the advantage of FESEM is being able to directly observe the shapes of pores and fractures and quantitatively analyse the structures of pores and fractures because in situ and true images of sample surfaces can be obtained by FESEM with high resolution (magnification of 900,000×). In addition, FESEM has no specific requirement for samples (such as very fine powder sample) and working environment (such as high pressure). FESEM has been widely applied to study non-coal material surfaces [22–24].

In the 1970s, Mandelbrot [25] proposed fractal theory to characterise complicated graphs and processes. Fractal theory has been widely applied in studies on pores and fractures in coal. For example, Cai et al. [26] used fractal theory to show the correlation between the fractal dimension of coal surfaces and coal rank and the evolution of the fractal dimension of coal surfaces under heating and high-pressure conditions. Based on mercury intrusion porosimetry and gas absorption study, Wang et al. [27] concluded that seepage and absorption pores in coal increase with increasing metamorphism of coal; coalification results in rough pore surfaces and more complicated pore structures, and the fractal dimensions of large pores are greater than those of small pores. Luo et al. [28] conducted a methane absorption experiment to study activated carbons with four different micro-pore structures and found that the pore size is linearly correlated with fractal dimension based on the unimodal distributed activated carbons. According to a mercury porosimetry experiment and the expansion and diffusion characteristics of coalbed methane, Fu et al. [29] compared fractal studies that investigated specific pore volumes and pore diameter structures and categorised coal pores as either diffusion pores or seepage pores. However, there have been extremely few studies that investigate the characteristics of nanoscale pores and fractures in coal and their corresponding factors by combining the FESEM technique and fractal theory. Thus, in this study, based on the high-resolution imaging technique FESEM, we quantitatively characterised nanoscale pores and fractures in coals using fractal theory and further discuss the effects of the coalification on the distribution of nanoscale pores and fractures in coal, which is of great importance for understanding the storage, diffusion, and transport mechanisms of coalbed methane.

2. Samples and methods

2.1. Samples

Coal is primarily composed of four lithotypes (such as vitrain, bright coal, durain, and fusain) with different pore and fracture characteristics. To avoid the effect of different coal compositions and degree of deformation, the vitrain was chosen for this study. The samples that were analysed in this study are obtained from the early Permian (P_1^1) coal measures in typical coal mines from North China, which include the Baode Colliery, Sihe Colliery, and Zhaozhuang Colliery in Shanxi Province, Shenjiazhuang Colliery in Hebei Province, and the Hebi Fourth Colliery in Henan Province. Quantitative analyses of coal rank and petrographic characteristics were performed on the polished sections of the samples using a standard polarising microscope and a microdensitometer (MPV-3). We also measured the average reflectance values of vitrinite, the percentage composition of vitrinite, inertinite, exinite, and the mineral content. General information regarding the coal samples is listed in Table 1.

2.2. Experimental methods

(1) The equipment used was a ZEISS SUPRA 55 high-performance FESEM: Acceleration Voltage: 0.1–30 kV; resolution: 1.0 nm at 15 kV, 1.7 nm at 1 kV, and 4.0 nm at 0.1 kV; Magnification: 12×–900,000×; high-resolution imaging and analysis of non-conductive samples. Sample preparation: a sample with an area of 0.5–1 cm^2 was cut from a large piece of coal. Relatively complete samples with fresh cross-sections were chosen for this study. Surface attachments of the samples were blown away, and the samples were fixed on sample mounts using conductive adhesive, which were then sputter coated with gold. The images of the samples were processed with Image-Pro Plus software (American Media Cybernetics Company).

(2) Measurement of pore and fracture diameters: According to the pore and fracture shapes observed in the FESEM images and the fractal results, diameters of the micro pores and widths of the micro fractures were calculated using the equivalent circle diameter and the equivalent ellipse minor axis, respectively. Details are given as follows: to increase the clarity of pore and fracture boundaries and to increase the accuracy of the information, images were first processed using the Gaussian filtering method. The processed images were then converted to binary images to measure the pore and fracture areas (images obtained in the experiment are raster images, where the area of each pixel is approximately 2 nm^2 to recognise correct objects; the area threshold value was set to 10 nm^2), and long axis (maximum distance between the centre of an image and its contour line); by multiplying the long axis, the rectangular length and long axis of the elliptic were obtained, and then calculated the pore and fracture width.

3. Results and discussion

3.1. Micro-pores and micro-fractures in coal

Fig. 1 shows the FESEM image of a coal sample. In Fig. 1(a) (1000× magnification), the sample surface is flat. However, after a portion of the image is magnified by 80,000×, as shown in Fig. 1(b), large quantities of micro-pores and micro-fractures can be observed. The micro-pores are generally round or elliptical. They are independently distributed, and some of the pores are connected with micro-fractures. The micro-fractures are irregularly bent and densely, randomly distributed with local connections. The lengths vary within a large range: although the length of micro-fractures with good connections can reach 1 μm, and the

Table 1
General information of the coal samples.

Sample ID	Location	Geological age	Vitrinite (%)	Inertinite (%)	Exinite (%)	Mineral (%)	$R_{o,m}$ (%)	Coal rank
BD01	Baode Colliery	P_1^1	60.90	23.50	15.10	0.50	0.75	Low-rank bituminous coal
SJZM04	Shenjiazhuang Colliery	P_1^1	86.38	12.85		0.78	1.11	Middle-rank bituminous coal
HBM05	Hebi Colliery	P_1^1	91.64	2.79		5.56	1.60	
HBM01	Hebi Colliery	P_1^1	93.51	2.53		4.01	1.91	High-rank bituminous coal
ZZ02	Zhaozhuang Colliery	P_1^1	89.85	1.31		8.86	2.31	Semi-anthracite
SHE02	Sihe Colliery	P_1^1	95.31	4.69			2.80	Anthracite