Full Length Article

Characteristics of microscopic pore structure and fractal dimension of bituminous coal by cyclic gas adsorption/desorption: An experimental study

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ABSTRACT

The characteristics of micropore (0.32–2 nm), mesopores (2–50 nm) and fractal dimensions of bituminous coal during the process of cyclic gas adsorption/desorption were revealed by combining N_2 (77 K) and CO_2 (273 K) adsorption experiments from microscopic aspect. The results indicate that the pore structure characterization in the coal matrix are changed, resulting in decreased mesopore volumes and increased micropore volumes. The mesopore volumes are mainly constituted by the pores of 10–20, and 20–30 nm, and it will increase at first and then decrease with the increasing pressures. The maximum change of micropore volume reaches 65.6%, indicating a great effect on the micropores influenced by pressures. In addition, the main micropore size range, major peak and the model diameter of coals all increase with the increasing pressures, the higher the adsorb pressure is, the higher swelling is. With the help of the conceptual models, we then analyzed the variation reasons, which may be result from transformation of mesopores and the connection of the inaccessible pores. D_1 and D_2 in #1 and D_2 in #2 all increase with the increasing adsorption pressures, enhancing the roughness of surface and complexity of structure, while D_1 in #2 shows an opposite property. The study of variations of microscopic pore structure by cyclic adsorption/desorption was aimed at providing new understanding for the exploration of the changes of diffusion and permeability.

1. Introduction

Clear understanding of the variation of pore structure of coal induced by gas adsorption/desorption is of great importance for coalbed methane (CBM) [1]. Porous coal materials, as a kind of complex carbon-based C adsorbents, contain much micropores (less than 2 nm), mesopores (2–50 nm), and macropores (great than 50 nm) [2], which consist of slit-shaped pores connected by windows [3]. Gas is symbiotic with coal, which is stored in coal mainly by sorption and free states [4]. Bituminous coal from a wide range of sources (including China, Europe, Australia, South America, the US and Canada) usually has higher gas content and occurrence of coalbed methane. It is commonly believed that swelling and contraction occur in the process of gas adsorption and desorption of the coal, and the whole process is irreversible [5–7]. The first studies on coal swelling were proposed by Hargraves in 1958 [8], which showed an average linear swelling of 0.182% per MPa change in equivalent sorption pressure using CO_2 as the gas.

Recent years, with the development of technologies, a series of experiments were performed to observe the adsorption-induced coal swelling and changes of volume strain during adsorption of CH_4, CO_2 or other gases [9–11]. It is usually reported that the degree and rate of CO_2 induced swelling is greater than CH_4 and N_2 [12]; the greater the adsorb pressure is, the greater swelling is. The work of George and Barakat [12] demonstrated that CO_2 produced more strain (2.1%) with adsorption at 4 MPa, while CH_4 and N_2 were 0.4% and 0.2%, respectively. This finding has already named differential swelling and is identified as necessary to optimize the recovery of CH_4 technology during the sequestration of CO_2 [13]. In terms of microcosmic, the studies of Karacan [5] indicated the volumetric strains tend to compress any other region with higher porosity or any open fracture within the sample to create volume to expand. This phenomenon may be the reason for the changes of diffusion and permeability. Nie et al. [14] got the same conclusion by calculating strains induced by adsorption with a new measurement way of coal particle tracking method and the results showed that the expansion deformation tends to first squeeze the original pore or fracture inside them for more expansion space. Adsorption-induced coal

Nomenclature		D	the fractal dimension
		A	constant
M_{ad}	moisture content, %	μ	relative pressure, P/P0
A_d	ash content, %	$N(\mu)$	the amount adsorbed at a relative pressure μ, cc/g
V_{daf}	volatile content, %	N_{max}	the amount adsorbed when μ reaches the maximum 0.995,
F_{cd}	fixed carbon content, %		cc/g
f	protodyakonov coefficient	D_w	the fractal dimension
R_0	vitrinite reflectance, %	r	the radius of curvature of the meniscus, m
P	the gas adsorption equilibrium pressure, Pa	σ	the surface tension between liquid and gas of nitrogen, J/
P_0	saturated vapor pressure of gas adsorption, Pa		m
V	gas molecular volume adsorbed at equilibrium pressures	v	the molar volume, m^3/mol
	P, mL/g	R	the universal gas constant, J(mol·K)
V_0	the monolayer volume calculated by using the BET equation, mL/g	T	the absolute temperature, K

swelling depends on the internal structure of porous body. It is well known that pore structure in porous coal materials can be deemed as dual porosity media, consisting of matrix and fracture [15]. Due to the development of pore structure, especially microporous structure, the matrix will produce a significant swelling deformation after adsorbing gases. The swelling deformation cannot be completely restored after desorption gas, indicating the irreversible destructive effect of coal adsorption/desorption on microstructure. Theoretical and experimental studies have indicated that the differential swelling of coal is mostly explained by adsorption in micropores and the results are available in the literature [10,16]. Yang et al. [7] employed the quenched solid density functional (QSDFT) theory model to study the deformation of coal induced by methane adsorption at geological conditions. The results demonstrated that adsorption-induced deformation either swells or contracts depending upon the pore size distribution. Much work so far has focused on the relation between volumetric strain changes and adsorption-induced coal swelling and pressures, gas type and geological conditions, and the pore structure after adsorbing [17,18]. Little is known, however, about the variations of microscopic pore structure in the process of adsorption-induced coal swelling.

Our aim in this paper is to study variations of microscopic pore structure during cyclic adsorption/desorption for bituminous coals on the basis of the study of macroscopic adsorption volume expansion by previous scholars. Meanwhile, the micro-mechanism and the conceptual model are used to explain the changes in micropores, mesopores and inaccessible pores in this process, aiming to provide new understanding for the exploration of the changes of diffusion and permeability. In this work, a systematic adsorption study has been performed including (i) N_2 (77 K) and CO_2 (273 K) adsorption experiments of original state coals, (ii) cyclic adsorption/desorption scanning experiments after different adsorption pressures (0.5, 0.74, 1.5 and 3.0 MPa), and (iii) accurate pore structure analysis by applying different methods. The results indicate that in original state and each cycle of gas adsorption/desorption the structure of coals are different. Conceptual models are applied to explain the reasons for variations of microscopic pore structure. (iv) fractal Characteristics analysis obtained from the N_2 adsorption data with the Frenkel–Halsey–Hill (FHH) model.

2. Coal samples and methods

2.1. Coal samples

To study the effect of cyclic gas adsorption/desorption on pore structures, two kinds of coal samples were collected from the same seam of Wolong Hu colliery, in China, representing different deformation extents of coal, which is bituminous coal. The coal samples were collected from a freshly exposed mining face, immediately sealed and sent to the laboratory for the next step. Before the test, some excess

material in coal samples were selected, such as rocks and so on. The coal samples were then placed in a pulverizer to get a particle size of 0.2–0.25 mm. Each grinding step time was less than 30 s to avoid the coal temperature rising and possible structural and surface reactivity changes. Proximate analysis of moisture, ash, volatile and fixed carbon content were performed with a 5E-MAG6600 proximate analyzer (Changsha Kaiyuan Instruments, China). The detailed sampling locations and basic parameters of samples are listed in Table 1.

2.2. Experimental methods

The pore structure, pore volume and specific surface area (SSA) of coal samples were analyzed by the physical adsorption methods (N_2 adsorption and CO_2 adsorption) [19], using an Autosorb2 instrument (Quantachrome Instruments, United States). Before the test, the coal samples were outgassed for 5 h under 120 °C to remove gases, moisture and so on. Firstly, coal samples were analyzed by the N_2 (77 K) adsorption and CO_2 (273 K) adsorption at the original state, respectively. Then, ensuring that the each filling gas pressure was less than or equal to 0.5 MPa until the pressure reached the experimental pressure (0.5 MPa) after a long period of time (5 days). After that, the gas of coal samples was desorbed. Finally, N_2 (77 K) adsorption and CO_2 (273 K) adsorption experiments were performed again. Repeating the above steps, the adsorption pressure is gradually increased to 0.74 MPa, 1.5 MPa, 3.0 MPa, and then the experiments were performed, respectively. The Diagrammatic sketch of the experimental equipment and procedures are shown in Fig. 1.

The mesopore results were obtained from N_2 adsorption isotherms at liquid nitrogen temperature (77 K) and relative pressures from 0.001 to 0.995. N_2 adsorption data were analyzed using the Brunauer–Emmett–Teller (BET) analysis for SSA and QSDFT methods analysis for pore size distribution (PSD) [20,21]. For the micropore analysis, the CO_2 adsorption isotherms at 273 K was used to interpret micropore SSA and micropore volume and relative pressures from 3×10^{-5} to 0.0289 by using the Dubinin–Radushkevich (D-R) equation

Table 1
Locations, proximate analysis and basic physical parameters of coal samples.

Sample	Sampling location	R_0 (%)	Proximate analysis (%)				f
			M_{ad}	A_d	V_{daf}	F_{cd}	
#1	No. 8 coal seam, Wolong Hu colliery, Anhui Province	1.36	1.31	7.24	9.95	83.45	0.72
#2	No. 8 coal seam, Wolong Hu colliery, Anhui Province	1.41	1.72	11.05	11.78	77.9	0.21

M_{ad} = Moisture content; A_d = Ash content; V_{daf} = Volatile content; F_{cd} = Fixed carbon content; f = Protodyakonov coefficient.