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Pore characterization of different types of coal from coal and gas outburst disaster sites using low temperature nitrogen adsorption approach

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ABSTRACT

To characterize the pore features of outburst coal samples and investigate whether outburst coal has some unique features or not, one of the authors, working as the member of the State Coal Mine Safety Committee of China, sampled nine outburst coal samples (coal powder and block) from outburst disaster sites in underground coal mines in China, and then analyzed the pore and surface features of these samples using low temperature nitrogen adsorption tests. Test data show that outburst powder and block coal samples have similar properties in both pore size distribution and surface area. With increasing coal rank, the proportion of micropores increases, which results in a higher surface area. The Jiulishan samples are rich in micropores, and other tested samples contain mainly mesopores, macropores and fewer micropores. Both the unclosed hysteresis loop and force closed desorption phenomena are observed in all tested samples. The former can be attributed to the instability of the meniscus condensation in pores, interconnected pore features of coal and the potential existence of ink-bottle pores, and the latter can be attributed to the non-rigid structure of coal and the gas affinity of coal.

1. Introduction

Coal and gas outburst is one of the most serious disasters in underground coal mines [1–3], which can be attributed to several factors: high methane pressure, high methane content, high in-situ stress, different coal properties, and complex geological conditions [4–7]. Generally, the methane content in the coal seam mainly consists of the adsorbed gas and the free gas; the adsorbed gas accounts for 80–90% of the whole methane content in the coal seam. Since the adsorbed gas plays a significant role in coal seams of high gas pressure and content, the adsorption properties of methane in coal are always the topic for researchers to explore techniques to prevent coal and gas outburst hazards, improve coal seam degasification, and enhance coalbed methane recovery [8–13]. As the methane storage matrix, the complex nanopore system and surface area feature of coal has a direct influence on methane sorption capacity and the interaction between methane and coal. Even though much research has been conducted to probe the pore and surface area properties of coal [14–20], few of these samples are from coal and gas outburst sites. This is because the coal and gas outburst site is inaccessible when coal and gas outburst occurs. Therefore, the pore characterization and surface area features of outburst coal from coal and gas outburst sites will provide important data for understanding the coal and gas outburst mechanism.

The low temperature nitrogen adsorption test (LT-NAT) is one of the commonly used tests for mesopore, macropore and surface area analysis of coal and shale. With the development of density functional theory and computer simulation approaches, the whole range of micro- and meso-pore can be probed with commercially available models such as non-local density functional theory (NLDFT) [21]. Generally, the nitrogen adsorption test is not the recommended approach to probe the porous media with micropore such as coal and shale (ISO 15901-3:2007). On the one hand, relatively low pressures of 10^{-7}–10^{-5} are needed to investigate the micropore filling process. On the other hand, the diffusion restriction under low pressure will prevent nitrogen molecules entering the narrowest micropore. Even though there are several limits for probing the micropores of porous media using the nitrogen adsorption test, the test results of micropore probing is still heuristic to some extent. In addition, combined with the BET theory, the BET

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surface area can also be obtained from nitrogen adsorption isotherms.

To probe the pore and surface area features of outburst coal from coal and gas outburst sites, low temperature nitrogen adsorption tests on nine outburst coal samples were conducted. Test data were processed using BET linear fitting for BET surface area and non-local density function theory (NLDFT) for pore size distribution and NLDFT surface area. The ad/desorption behaviors (hysteresis loop) of these test samples were also studied.

2. Introduction of coal and gas outburst disaster in underground coal mines

The tested outburst coals were sampled from five underground coal mines in China-Pingdingshan No. 13 mine, Guomin mine of Yichuan LLC, Sanyuandong mine of Zhengzhou LLC, Tonghua mine of Songzao LLC, and Jiulishang mine of Jiaozuo coal LLC. The proximate analysis of the coal samples tested is shown in Table 1 and the apparent feature in shown in Fig. 1.

A brief account of the coal and gas outburst disasters is shown below:

(1) On 13th June 2010, at 10:35 a.m., a coal and gas outburst disaster occurred in the degasification roadway of JI 15-17-11111 working face in Pingdingshan No. 13 mine. Eight people died in this disaster.
(2) On 31st March 2010, at 19:20 p.m., a coal and gas outburst disaster occurred at 21 working face in Guomin mine, in which 44 people died (39 people working underground and 5 people working on the surface) and 6 people were lost.
(3) On 2nd August 2010, at 22:47:56 p.m., a coal and gas outburst disaster occurred at Sanyuandong mine, in which 16 people died. The outburst coal mass was 675 tons and the outburst gas volume was 58,900 m^3.
(4) On 30th May 2009, at 10:55 a.m., a coal and gas outburst disaster occurred in a roadway in Tonghua mine, in which 30 people died. The outburst coal mass was 3000 tons and the outburst gas volume was 87,000 m^3.
(5) On 27th October 2011, at 0:36 a.m., a coal and gas outburst disaster occurred at the drilling site in the 16,031 roadway of Jiulishan mine, in which 18 people died and 5 people were injured. The outburst coal mass was 3246 tons and the outburst gas volume was 291,200 m^3.

3. Experimental approach and data processing

The LT-NAT is conducted using a Micrometrics ASAP 2020 Analyzer, which employs the static volumetric method; the volume adsorbed is calculated by the measured pressure of the test tube caused by changes in pressure. Prior to the test, the prepared coal sample is degassed under vacuum at 200 °C for at least 12 h. After degassing, the degassed sample is exposed to N_2 at −196 °C in a relative pressure (p/p_0) ranging from 0.001 to 0.995, where p is the equilibrium pressure and p_0 is the saturation pressure. The equilibrium time for the test ranges from 10 s to 30 s. The LT-NAT test was carried out following the test procedure of ISO 9277:2010 and ISO 15901-2: 2006.

3.1. BET surface area analysis

Since the total surface area of the sample is covered by a complete monolayer of nitrogen molecules, the BET surface area is calculated with the widely used linear BET plot based on the monolayer capacity estimation shown below:

$$\frac{p/p_0}{a(1-p/p_0)} = \frac{1}{a_m C} + \frac{C-1}{a_m C}(p/p_0) \tag{1}$$

where a is the amount of gas adsorbed at corresponding relative pressure p/p_0, a_m is the monolayer amount of gas adsorbed, and C is an indicator of the force between the adsorbents and adsorbate interaction but cannot be used to calculate the adsorption enthalpy.

The BET equation is not applicable if the linear fitting curve cannot be obtained or the C value is negative. The recommended relative pressure (p/p_0) range of BET linear fitting is (0.05–0.35) for a man-made material with mesopores. However, this range does not apply for materials with micropores, such as coal. Since coal has a complex pore system containing pores from super-micropores to macropores, this unique feature makes it hard to evaluate its surface area using the common BET relative ranges [22,23]. The BET linear fitting should be in a lower pressure range because of the existence of micropores. For the adsorbents with micropores, Rouquerol et al. [22] provided a modified BET approach to assess the surface area in a reproducible and an objective way, which is also adopted in ISO 9277:2010. Two criteria should be met in his method: (a) C should be positive and (b) the application of the BET equation should be limited to the pressure ranges where the term $n_a\,(1-p/p_0)$ continuously increases with p/p_0. Once the pressure ranges for the linear BET relationship are obtained using Rouquerol's approach, the BET surface area can be calculated by the following equation:

$$S_{BET} = n_m a_m L \tag{2}$$

where a_m is the monolayer volume, N is the Avogadro number; A_{N2} the atomic surface area of N_2 (0.162 nm^2 at 77 K).

3.2. NLDFT model for pore size distribution

According to the International Union of Pure and Applied Chemistry (IUPAC), pores are classified into three types: macropores (⩾50 nm), mesopores (2–50 nm), and micropores (⩽2 nm) [24]. Generally, the LT-NAT is more accurate for estimating the pore size ranging from 2 nm to 100 nm, which covers both mesopore and macropore. Density function theory (DFT) model brings the gap for analyzing the pore size distribution (PSD) for micro-, meso- and macro-pore where the conventional approaches such as BJH

Table 1
Proximate analysis of outburst sample.

Sample name	Coal type	Apparent feature	f value	Moisture (M_{ad})	Ash (A_{ad})	Volatiles (V_{daf})
Pingdingshan No. 13 (PDS#1)	Lean coking coal	Block	0.26	0.70	15.16	19.32
Pingdingshan No. 13 (PDS#2)		Block	0.34	0.59	23.12	22.06
Guomin mine (GM#1)	Lean coal	Powder		0.73	18.40	11.94
Guomin mine (GM#2)		Block		0.68	5.83	12.61
Sanyuandong (SYD#1)	Lean coal	Powder		1.10	10.08	11.37
Sanyuandong (SYD#2)		Block	0.11	0.87	7.42	10.52
Tonghua (TH)	Anthracite	Powder		2.67	14.88	9.57
Jiulishan (JLS#1)	Anthracite	Powder	0.19	2.88	10.25	7.00
Jiulishan (JLS#2)		Block	0.19	2.62	12.74	7.07