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Improved analytic methods for coal surface area and pore size distribution determination using 77 K nitrogen adsorption experiment

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ABSTRACT

77 K nitrogen adsorption was the most widely used technique for determining surface area and pore size distribution of coal. Brunauer–Emmett–Teller (BET) and Barrett–Joyner–Halenda (BJH) model are commonly used analytic methods for adsorption/desorption isotherm. A Chinese anthracite coal is tested in this study using an improved experimental method and adsorption isotherm analyzed by three adsorption mechanisms at different relative pressure stages. The result shows that the micropore filling adsorption predominates at the relative pressure stage from 6.8E−7 to 9E−3. Theoretically, BET and BJH model are not appropriate for analyzing coal samples which contain micropores. Two new analytic procedures for coal surface area and pore size distribution calculation are developed in this work. The results show that BET model underestimates surface area, and micropores smaller than 1.751 nm account for 35.5% of the total pore volume and 74.2% of the total surface area. The investigation of surface area and pore size distribution by incorporating the influence of micropore is significant for understanding adsorption mechanism of methane and carbon dioxide in coal.

1. Introduction

Considerable interest has been shown over the past years in the study of coal surface area and pore size distribution, which are critical for the adsorption/desorption of methane and CO_2. The influence of coal rank, maceral and destructive type on coal surface area, pore structure and pore size distribution has been investigated by extensive experimental and analytical studies, and among all the test methods, 77 K nitrogen adsorption remains the most widely used technique due to its following advantages: high chemical stability when the nature of adsorbent–adsorbate is taken into account, higher precision, lower test range and non-destructive compared with mercury intrusion method, and simple operation compared with visual observation, e.g., scanning electron microscope (SEM) [1–11].

In this research, the classification of pore size proposed by the IUPAC is adopted, and micropores, mesopores and mcaropores are defined, respectively, as pores with effective widths, $\omega < 2$ nm, $\omega = 2–50$ nm and $\omega > 50$ nm [8]. BET model and BJH model are the most commonly used analytic procedures of 77 K nitrogen adsorption for the determination of surface area and pore size distribution of coal, respectively [12]. However, both methods have advantages and limitations, thus inappropriate application will either overestimate or underestimate the surface area and pore volume of coal.

In this study, an improved experimental measurement of 77 K nitrogen adsorption isotherm on a Chinese anthracite coal is conducted, and the applicability of BET model and BJH model is discussed. Two new analytic procedures for coal surface area and pore size distribution calculation are developed.

2. Experimental

A sample of an anthracite coal is used from Qianqiuer Coal Mine in Yima city, Henan province, and the experimental work is prepared in China. The powder coal sample has a size of 40–60 mesh, which is considered to be large enough to preserve the coal mircropore. Prior to testing, the sample is dried at 60 °C in the oven with air for 2 days to remove the pre-existing moisture, and then put into the sample cell of Autosorb IQ gas sorption system by Quantachrome Instruments Co., Ltd.

When evacuating the sample cell during loading, it is firstly evacuated slowly using a fine vacuum for a minimum time and then, once the pressure is low enough, the course vacuum is opened. The sample is evacuated below 10 Pa for 8 h. 130 adsorption and

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desorption equilibrium points and lower relative equilibrium relative pressure range ($p/p_0 = 10^{-7}$, where p_0 is the saturated vapor pressure of liquid nitrogen at 77 K) are conducted in the experiment, which is different from 50–60 adsorption and desorption equilibrium points and lowest equilibrium relative pressure, $p/p_0 = 0.01$, usually adopted in the test. Equilibrium at each point is assumed to have been achieved if the pressure is constant over a 30 min interval. The nitrogen adsorption/desorption isotherm of the coal sample at 77 K and partial enlarged detail is shown as Fig. 1.

An in-depth description of the adsorption/desorption isotherm is provided in the following sections.

3. Isotherm and adsorption mechanism analysis

3.1. Isotherm analysis

Coal has a polymeric character, consisting of macromolecules of different sizes, with various types and degrees of crossing-link [13]. The physical structure of this assembly of molecules contains interconnecting pores of different shapes and sizes, from micropore to mcaropore, and normally lacks an ordered regularity [2,14]. The interaction between liquid nitrogen and coal due to surface free energy of coal surface, both interior and exterior surface, creates Van der Waal's force which adsorbs nonpolar gas molecule on coal surface, and belongs to physical adsorption.

For micropore width less than 1.5–2.0 nm, depending on the pore structure, the calculation of adsorption heat and theoretical arithmetic indicate that gas adsorption is micropore filling adsorption due to interlaping of surface free energy of adjacent pore surface [15,16]. Thus, the nitrogen molecule fills micropores firstly if they exist in coal sample because of the lager adsorption potential at low relative pressure. As for the mesopores and macropores, the surface free energy of adjacent pore surface is independent, and with the increasing relative pressure, monolayer adsorption occurs after the micropore filling adsorption completed. When the nitrogen molecule monolayer is basically full, multilayer adsorption occurs from some surface tension area. At the same time, in some relatively small mesopores, capillary condensation occurs when the relationship between relative pressure and pore width suits Kelvin equation [17]. With further increase of relative pressure, capillary condensation occurs in relatively large mesopores and macropore, and the adsorption volume increases rapidly. Desorption isotherm is achieved by reversing adsorption process, releasing liquid nitrogen and decreasing equilibrium relative pressure.

Fig. 1 shows that adsorption volume does not return to zero in desorption process. Due to the different relative pressure between capillary condensation and decondensation, the separation of the isotherms of adsorption and desorption at higher relative pressure can be observed, however they fail to overlay eventually. It is believed that the nitrogen molecule filled in micropores cannot obtain enough energy for overcoming barrier potential created by micropores under the experimental condition. It can be concluded that the micropore filling adsorption of Qianqiuer Coal is quasi-irreversible in the test.

3.2. Adsorption mechanism analysis

Numerous adsorption isotherm models are developed in recent years, and three widely applied models for gas adsorption in coal, Dubinin-Radushkevich (D-R) model, Langmuir model and BET model, which represent micropore filling adsorption, monolayer adsorption and multilayer adsorption respectively, are discussed in this section together with their applicability for different relative pressure stages of adsorption isotherm. These three models can be mathematically represented in the following forms:

$$\log V = \log V_0 - D\left(\log \frac{p_0}{p}\right) \tag{1}$$

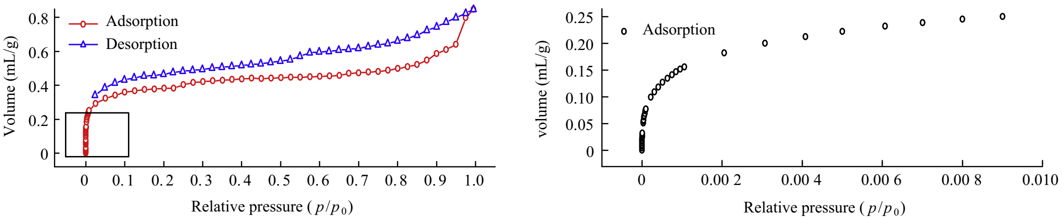
$$\frac{p}{p_0} \times \frac{1}{V} = \frac{1}{BV_\mathrm{m}} + \frac{p}{p_0} \times \frac{1}{V_\mathrm{m}} \tag{2}$$

$$\frac{1}{V(p_0/p - 1)} = \frac{1}{V_\mathrm{m}C} + \frac{C-1}{V_\mathrm{m}C} \times \frac{p}{p_0} \tag{3}$$

where V is the adsorption volume of nitrogen; V_m the monolayer saturated adsorption volume of nitrogen; V_0 the volume of micropore in coal sample; p/p_0 the relative pressure; D the constant related to micropore structure; B the constant associated with the energy of adsorption; and C is the BET constant related to the net heat of adsorption.

It is obvious that high linear correlation coefficients between $\log V$ and $[\log(p_0/p)]^2$, p/p_0V and p/p_0, $1/[V(p_0/p - 1)]$ and p/p_0 are the characteristics of monolayer adsorption, multilayer adsorption and micropore filling adsorption respectively [18–22]. For investigation of adsorption mechanism of different relative pressure stages, the adsorption isotherm is divided into 8 groups, the initial 14 adsorption equilibrium points are the first group while other every 10 continuous equilibrium points make up one group as shown in Fig. 2 and Table 1.

It can be seen from the Fig. 2a that both Langmuir and BET plot decrease in the initial stage which goes against the normal positive correlation, and a possible reason for this phenomenon may be due to nonphysical adsorption at very low relative pressure. The Langmuir and BET plot starts to increase in the latter part of Fig. 1a and the linear correlation coefficient of the two plots keep rising in the relative pressure stage from 3.8E−6 to 9E−3 but is still lower than of the D-R plot. The linear correlation coefficient of D-R plot which remains greater than 0.999 indicates that the Qianqiuer Coal contains micropores of less than 2 nm and the main adsorption in the relative pressure stage from 6.8E−7 to 9E−3 belongs to micropore filling adsorption. From the relative pressure point of 9.0E−3, as shown in Fig. 1e, the linear correlation falls sharply, it could be concluded that the micropore filling adsorption almost finishes at this stage. If the last adsorption point which deviates from the Langmuir plot distinctly is eliminated, the linear correlation coefficient is 0.99964, and the linear correlation coefficient of BET plot is 0.99706. It illustrates that monolayer adsorption predominates in



(a) Nitrogen adsorption/desorption isotherm at 77K

(b) Partial enlarged detail

Fig. 1. 77 K nitrogen adsorption/desorption isotherm and partial enlarged drawing of coal from Qianqiuer Mine.