Analysis and Research on Functional Groups of Coal Surface and its Physical Adsorption of CH_4

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Abstract: The characteristics of coal surface pore surface area were analyzed by mercury injection test so that we can obtain the types and distribution of different functional groups on coal sample surface through the method of infrared spectrum experiment and theoretical analysis. The physical adsorption processes and calorific values between different functional groups and CH_4 were studied based on different functional groups constructed by molecular simulation software so that we can put forward the coefficient concept of heat release rate in which can further perfect the adsorption theory of coal gas.

1. Introduction

Coal is a porous organic rock with a variety of mineral impurities and cut by cracks. It is an excellent natural adsorbent. In the coal seam, more than 90% of the gas exists in the form of adsorption on the inner surface of coal transition pores and micropores [1,2]. When adsorbing, free gas molecules must lose this energy to stay on the surface of the coal, so the adsorption is exothermic. The adsorbed gas molecules in the vibration equilibrium state should obtain the part of the energy lost at least during adsorption to become a free gas, so the desorption is endothermic. The unsaturation of the force on the surface of the coal body leads to a residual force field, which can adsorb gas [3].

The content of coal seam gas is a macroscopic result [4], which does not explain the coal's ability to adsorb gas and the difference in adsorption capacity. Most of the research is stagnant in the content of gas as the adsorption result [5], there is little research on the adsorption and desorption of coal by gas from the surface action of solids and gases. It is especially difficult to find the thermal effect of coal on gas adsorption process and the energy variation of coal-gas system in this process. In this paper, by studying the adsorption of methane molecules with characteristic functional groups on coal surface, the surface free energy of coal, the interaction of coal and methane on the surface explain the adsorption process of coal to methane gas, which is intended to clarify the characteristics and mechanism of coal adsorption gas, enrich coal-gas adsorption theory.

2. Analytical pore surface area of coal

In this paper, the surface area distribution characteristics of coal samples are analyzed by mercury intrusion method. The principle of mercury intrusion method is that the contact angle between mercury and solid is about 140º. It has no wetting ability to coal and needs to enter the pores of coal surface under pressure. According to the Washburn equation of the non-wetting capillary principle, the amount of mercury entering the pores of the coal surface under pressure is experimentally measured, then converted into pore volume and surface area under different pore sizes [6]. The conversion is based on the Young-Duper equation, which correlates the amount of

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work required to enter the mercury in solid volume (dV) with the amount of work required to form the mercury-solid interface area (dA). That can be written as:

$$\gamma \cos\theta dA = -PAdV \tag{1}$$

Assuming that the cross-sectional area of the pores is constant, the equation is integrated over the experimental pressure range to obtain the total surface area of the pores into the mercury enters as:

$$A(Hg) = -\frac{1}{\gamma \cos\theta}\int_0^{P_{max}} PdV \tag{2}$$

In this paper, the experimental results of coal surface area are obtained by mercury intrusion test. The pore surface area of coal sample is 18.88m^3/g, Its cumulative surface area and stage surface area with pore size distribution are shown in Figs 1 and 2.

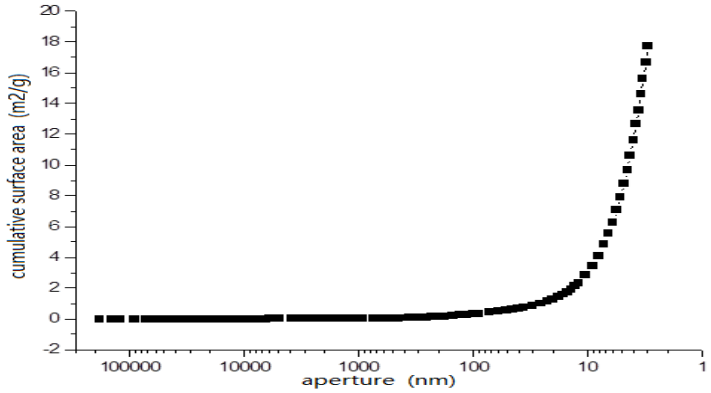


Fig. 1 the cumulative surface area distribution of coal with pore size

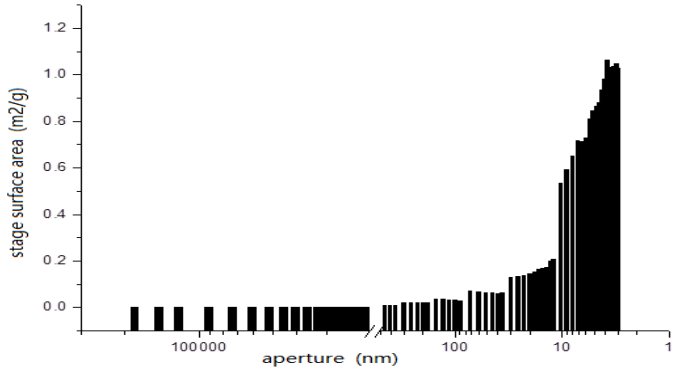


Fig. 2 the stage surface area distribution of coal with pore size

3. Study on the types and distribution of functional groups on coal surface

Fourier infrared spectroscopy (FTIR) is used to irradiate infrared light waves with different wavelengths onto the surface molecules of coal. The energy of lower infrared light waves causes the vibration and rotation of coal surface molecules, causing the infrared light waves of specific wavelengths to be absorbed, thus forming The infrared absorption spectrum of the measured molecule.

Coal is not a completely symmetrical molecule. The benzene ring, hydrocarbon group, carboxyl group and hydroxyl group are characteristic functional groups of the macromolecular structure on the coal surface. They have infrared activity and absorb the energy of light waves at a certain wavelength, which causes the infrared absorption spectrum. Different kinds of functional groups on the coal surface are with corresponding infrared spectra, and various specific functional groups in the infrared spectrum such as -CH_3，-OH，-COOH，-NH_2，-C≡C-，>C=C<, etc. The position of the characteristic absorption peaks their produce at a certain frequency remains substantially unchanged. The coal sample of weakly cohesive coal was selected for infrared spectroscopy, and the infrared

spectrum of the obtained coal sample is shown in Fig. 3.

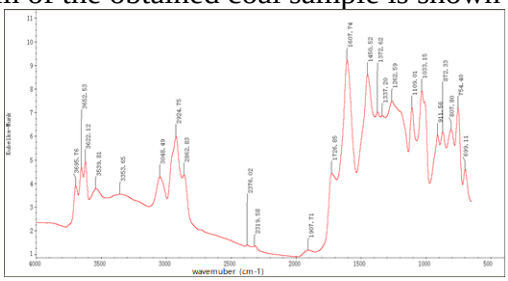


Fig. 3 the infrared spectrum of coal sample

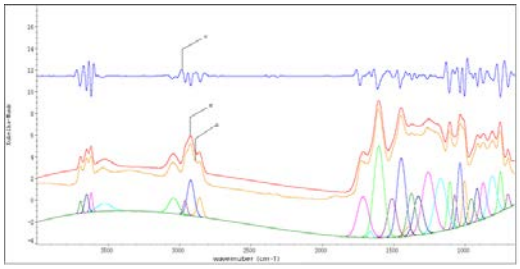


Fig. 4 the peak resolution map of coal sample

We use OMNIC software to conduct a preliminary analysis on the peak number of absorption spectrum by second derivative. The peak resolution function is used to separate the superimposed peaks, calculate the peak area of the corresponding peak of each functional group, and control the functional groups of different molecules on the surface of coal sample. By comparing The absorption position and intensity table in the infrared spectrum,we analyse the proportion distribution of the main functional groups semi-quantitatively, the peak resolution of the surface functional group is shown in Fig 4. From the results of statistical analysis, it is known that the main functional groups on the coal surface include alkyl side chains, aromatic rings and oxygen-containing functional groups.

The structure and quantity distribution of the main functional groups on the coal surface directly reflect the adsorption activity of the coal surface. By semi-quantitative analysis of the molecular infrared spectrum, the content of each functional group in the coal can be obtained.The Lambert-Beer law means that when a parallel monochromatic light wave is projected perpendicularly through a uniform non-scattering light absorbing material, the absorbance (A) is proportional to the thickness (b) and concentration (c) of the absorbing layer The Lambert-Beer law expression is written as follows:

$$A(\nu) = \lg \frac{1}{T(\nu)} = K(\nu)bc \tag{3}$$

Where $T(\nu)$ is transmittance. According to the software calculation, the proportion of different functional groups on the surface of the coal sample is shown in Fig. 5. The surface of the coal sample contains different functional groups such as oxygen functional groups, aromatic hydrocarbons and aliphatic hydrocarbons. The adsorption of various functional groups on methane molecules is different, which affects the physical adsorption of gas to some extent.

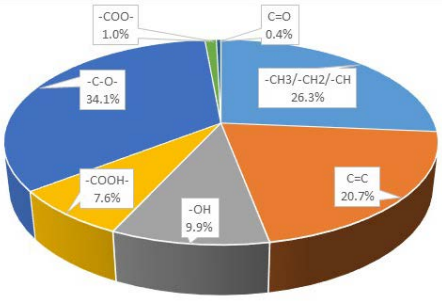


Fig. 5 the proportion of different functional groups on the surface of coal samples

4. Quantum chemical calculation of calorific value by adsorption

Based on the analysis of the characteristic functional groups and distribution of coal samples, according to the theory of quantum chemistry, the Gaussian-09 software was used to calculate the adsorption and exothermic characteristics of methane molecules by the main functional groups on coal surface [7]. And the exothermic phenomenon of its adsorption process opens up a new idea.

4.1 The calculation principle

The Schraedinger Equation is a basic equation describing the laws governing the motion of microscopic particles, as follows:

$$\hat{\mathrm{H}}\psi = \mathrm{E}\psi \tag{4}$$

Where $\hat{\mathrm{H}}, \psi$, E are the Hamiltonian of the system, the wave function of system state and the energy of the system in a steady state.

The Schrödinger equation is a wave function that describes the state of a material. The wave function contains the microscopic properties possessed by the material. The calculation of the Schrödinger equation can be used to describe the multi-electron architecture around the molecule and the interaction of electrons. However, accurate calculation of the Schrödinger equation is still impossible, so it is inevitable to use the approximate and hypothetical methods.

4.2 The calculation method

It can be known that the coal surface functional groups and their distributions have the following five functional groups: -CH_2-, -CH_3, -OH, -C=O and -COOH. In this paper, the molecular model of the above functional groups on the surface of coal is established. The exothermic values of these groups and methane molecules are studied, and the heat generation of these five functional groups in the process of adsorbing methane molecules is obtained.

Due to the complexity of the coal structure, coal is a mixture of macromolecular structures containing a large number of aromatic rings. It is assumed that a macromolecular model of coal is established and the adsorption heat release of methane by the main functional groups on the model is calculated. This calculation process is very complicated, and it is easy to cause the calculation does not converge. Therefore, a simplified molecular model of typical characteristic functional groups is established, mainly to investigate the adsorption of simple molecules of a single functional group with methane molecules. The characteristic functional groups such as aliphatic hydrocarbon chain and oxygen-containing functional group are connected to a benzene ring to form a simplified coal molecule, and the adsorption process of methane molecules by these simplified coal molecules is calculated respectively, that is, the system composed of simple coal molecules and methane molecules is most stable status.

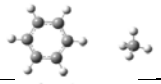
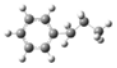
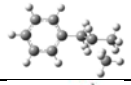
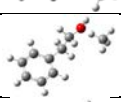
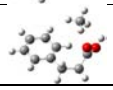
Since the main functions of the coal surface previously analyzed are mainly five groups of -CH_2-, -CH_3, -OH, C=O and -COOH. Referring to the related literature, the length of the functional group side chain has a certain influence on the adsorption exothermal. In order to simplify the calculation process, this section selects the typical functional group with moderate exothermic heat to represent the typical functional group on the coal surface.

4.3 The calculation process

1) Establishing molecules of pre-adsorption methane molecules and typical functional groups, and optimize calculations to obtain optimized molecular structure and optimized energy E_a.

2) Establishing a model for the adsorption of coal molecules and methane of the above functional groups, optimize the calculation, and obtain an optimized adsorption system and optimized energy E_b, and calculate the change in energy, that is, the heat release $\Delta E = E_b - E_a$ as shown in Table 1.

Table 1 the molecular mechanism and optimization energy of typical functional groups of methane molecules and coal surface before adsorption

Optimized molecular structure before adsorption	Optimized energy E_a(kJ/mol)	Optimized molecular structure after adsorption	Optimized energy E_b (kJ/mol)	Adsorption heat release ΔE (kJ/mol)
	-106386.90			
	-609767.49		-716154.39	0.006
	-919419.31		-1019582.61	262.509
	-1001123.75		-1113343.37	5832.725
	-1295483.80		-1416676.77	14806.075

4.4 The calculation of adsorption heat proportional coefficient

We introduced the adsorption heat proportional coefficient, which can be used as an index of coal sample adsorption performance and it is a specific attribute of coal type. The adsorption capacity is evaluated by the amount of heat release during coal adsorb gas. Through the above analysis, the pore surface area S_1 and the functional group proportionality coefficient S_2 are obtained, and the exothermic value ΔE obtained by adsorbing methane from each functional group molecule is calculated in the following formula:

$$Q = \sum_{i=1}^{5} q_i = S_1 \cdot S_2 \cdot \Delta E \quad (5)$$

Where the Q is the adsorption heat proportionality coefficient of coal sample. The calculation procedure of the adsorption heat proportional coefficient of the coal sample is shown in Table 2.

Table 2 the calculation process of adsorption heat proportional coefficient of coal sample

	Benzene ring C=C	$-CH_3$	-OH/-O-	-COOH/-COO-/ =O	superficial area S_1(m^2/g)	Exothermic proportionality Q (m^2/g)·(kJ/mol)
Functional groups heat ΔE(kJ/mol)	0.006	262.509	5832.719	14806.075		
Functional group ratio S_2(%)	21	26	44	9	18.888	79729.215
heat emission coefficient q_i (m^2/g)·(kJ/mol)	0.00219	3460.49	48474.09	25169.132		

5. Summary

Through the peak resolution analysis of the surface functional group of the coal sample, we found that the coal surface contains three kinds of functional groups: the oxygen-containing functional groups (-OH, -COOH-, -CO-, -COO-, C=O), the aromatic hydrocarbons (aromatic ring C=C), aliphatic hydrocarbons ($-CH_3$/$-CH_2$/-CH), and get their proportional relationship. By using Gaussian-09 software, the adsorption and exothermic characteristics of the main functional group molecules on the coal surface to methane molecules were calculated, and the coal-to-gas adsorption exothermic proportional coefficient was proposed. In this paper, the adsorption heat release coefficient of coal sample is 79,729.215 (m^2/g)·(kJ/mol). As an intrinsic property of coal, the difference of coal adsorption capacity can be explained from the aspect of energy change.

Acknowledgments

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