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Adsorption capacity, adsorption potential and surface free energy of different structure high rank coals

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A B S T R A C T

Methane adsorption capacity of coal is one of the major factors influencing total gas-in-place and it is linked to coal structure, while our knowledge of it is still limited. In this study, coal structures were classified into five categories, including integrated, blocky, cataclastic, granulated and mylonitized. The integrated and blocky coals are intact and the other three are deformed. To investigate the methane adsorption capacity, adsorption potential and surface free energy of different structure coals, four high rank coal samples were collected from No.3 coal seam of the Zhaozhuang coal mine in Southeastern Qinshui Basin China, and a series of methane isothermal adsorption experiments and pore distribution measurements were carried out in the laboratory, and then the adsorption potential and the surface free energy were analyzed. It turns out that, there are no obvious differences in the methane adsorption capacity for the various structure coals when the equilibrium pressure is below 2 MPa; while there are significant differences when the pressure is above 2 MPa. The higher the gas pressure is, the greater the difference is. Methane adsorption capacity of different structure coals can be arranged in a descending order: mylonitized > granulated > cataclastic > intact. That is, the methane adsorption capacity is higher for the deformed coal samples than for the intact ones. Both the specific surface area and the pore volume increase with the increase of deformation degree. Mesopores contribute most to the total pore volume; while the adsorption pores have the greatest contribution to the total specific surface area. The adsorption potential and surface free energy for different-structure coals under the same adsorption space volume increase with the increase of deformation degree. Adsorption potential decreases with the increase of adsorption space, and the adsorption potential of micropore is considerably higher than that of mesopore and macropore. As the temperature rises, the cumulative reduction of surface free energy decreases and the surface free energy decreases significantly at each equilibrium pressure. Methane adsorption in coal is dominated by adsorption potential and surface free energy.

1. Introduction

Almost all of the late Paleozoic coal-bearing basins in China experienced one or a few tectonic movements of various scales in geological history and thereby the coal seams were tectonically deformed to various extents (Meng et al., 2010; Hou et al., 2012; Zhou et al., 2014; Jia et al., 2015). According to "Regulations on the Prevention and Cure of Coal and Gas Outburst", an official standard document in China, coal structures are classified into five categories including type I- nondestructive coal, type II- destructive coal, type III - strongly destructive coal, type IV - sheared coal and type V- pulverized coal. Type III, IV and V are collectively referred as deformed coals and Type I and II as intact ones. The intact coals have well-preserved sedimentary structures. Nearly all of the coal and gas outburst accidents occur in the deformed coal seams. Gas drainage neither from surface nor from underground has ever achieved a good result. Therefore, the research on adsorption mechanism in various-structure coals encompasses theoretical and practical significances for coalbed methane (CBM) development.

Methane adsorption capacity in various-structure coals has been widely discussed by many researchers. Guo et al. (1996) summarized the characteristics of coal and gas outburst that occurred in the deformed coals in the Pingdingshan mining district, China. Zhang et al. (2007), Chikatamarla and Peter (1999), Yves

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Nomenclature

ε	is the adsorption potential, J/mol;
P_0	is the saturation vapor pressure of the adsorbate at temperature T, MPa;
P_i	is the equilibrium pressure of ideal gas under a constant temperature, MPa;
P	is the equilibrium pressure, MPa;
R	is the Universal Gas Constant, J/(mol K);
T	is the absolute temperature, K;
P_c	is the critical pressure of adsorbate, MPa; for methane, P_c is 4.62 MPa;
T_c	is the critical temperature of adsorbate, K.; for methane, T_c is 190.6 K.
w	is the adsorption volume, cm^3/g;
M	is the molecular mass of adsorbate, g/mol;
V_{ad}	is the volume of adsorbate in adsorbed state, mol/g;
ρ_{ad}	is the density of adsorbate in adsorbed state, g/cm^3.
σ	is the surface tension, J/m^2;
Γ	is surface excess concentration, mol/m^2; it is the methane concentration difference between the surface and inside of the coal;
V	is methane adsorption volume, L;
V_0	is the molar volume of gas under standard condition, 22.4 L/mol;
S	is the pore surface area of coals, m^2/g;
V_L	is Langmuir volume, cm^3/g;
P_L	is Langmuir pressure, MPa;
$\Delta\gamma$	is the variation of surface free energy of coals after gas adsorption, J/m^2.

et al. (2013), Skoczylas et al. (2014) and Li et al. (2015) concluded, from the analyses of coal petrography, coal quality, and isothermal adsorption/desorption tests under equilibrium moisture condition, that the methane adsorption capacity of coal is greatly related to its physical and chemical structures, porous structure, and particle size and so on; with the increasing degree of coal deformation, Langmuir volume increases gradually; the deformed coals usually have a higher methane adsorption capacity and a higher risk level of coal and gas outburst than the intact ones. Wang and Yang (1980) proposed that there are no significant differences in methane adsorption property between the intact and the deformed coal samples and the tectonic stress do not affect the micropore volume or the specific surface area of coals. Based on the isothermal adsorption experiments for three coal samples of different deformation degrees in Huaibei mining area, China, Pan et al. (2012) considered that the adsorption capacity of coal at low temperature (30 °C) increases with the increasing deformation degree, and there are no significant differences in the adsorption capacity among various structure coals at high temperatures (50 °C, 70 °C).

CBM is mainly adsorbed on the inner surface of coal matrix. Knowledge of pore system and molecular structure of coal matrix is essential for the gas adsorption mechanism of coal. On the basis of detailed investigations on coal petrography, coal quality and isothermal adsorption lines, Faiz et al. (1992), Mastalerz et al. (2008) and Swanson et al. (2015) presented some conclusions: the pores in coal comprise micropores and mesopores; micropores provide the main adsorption space; pore volume and specific surface area are positively related to coal gas content and the adsorption capacity is positively related to coal rank, specific surface area, and fixed carbon content. Jiang and Ju (2004), Ju et al. (2009), and Hou et al. (2012), Pan et al. (2015) conducted experiments on the chemical structures of different types of deformed coals under the conditions of high temperature and high pressure and they considered that, with the rise of deformation degree, the basic structure unit of coal enlarges rapidly; aromatization and ring condensation enhance obviously; macromolecular structure deformation of coal would cause the change of nanoscale porous structure; in the same metamorphism environment, due to the tectonic stress, for the deformed coals, the amount of mesopores decreases significantly while the amount of micropores increases gradually.

Thermodynamics is a branch of physics and focuses on the heat and temperature and their relation to energy and work. Thermodynamic variation is a macroscopical representation of methane adsorption capacity on coals. And adsorption potential, surface free energy can be used to quantitatively characterize the thermodynamics. Coal decreases spontaneously its surface free energy by decreasing the surface tension during adsorption. Therefore, the adsorption capacity of coals can be illustrated by the variation of surface free energy during adsorption. Jian et al. (2014) calculated the surface free energy variation of coals with intact and tectonic structure at different temperatures, and analyzed the cause of energy variation from dynamic metamorphism perspective. Cui et al. (2003) and Bai et al. (2014) investigated the relationship between adsorption capacity and adsorption heat of various structure coals and illustrated the microcosmic mechanism of heat generation during methane adsorption on coals by thermodynamic theory. G.Q. Li et al. (2014), X.J. Li et al. (2014) and Liu and Feng (2012) characterized the methane adsorption behavior on coal surface by estimating the adsorption heat and forces between the methane molecules and coal surfaces.

Although a lot of efforts have been made on exploring the adsorption of different structure coals, our knowledge of it is still limited and there are still diverse viewpoints on it and the mechanism behind it is still obscure. This study was undertaken to investigate the methane adsorption behavior and thermodynamics in coals of different structures. The coal structures were first addressed, and then the measurement of pore distribution of coals of different structures and the methane isothermal adsorption experiments under different temperature-pressure conditions were carried out, and finally the thermodynamic characteristics were analyzed. The outcome of this research may deepen our understanding of the adsorption mechanism of coals and benefit the CBM exploration and development in the study area.

2. Coal structure and its classification

Coal structure refers to the geological structure features of a coal seam affected by tectonic movement. Moderate structural deformation can increase fractures in coal and lead to an improved permeability of the coal seam. However, excessively high level stress can break an intact coal seam into fine particles and destroy the coal cleat system and thereby result in a significant reduction in permeability (Meng and Li, 2013). According to the morphological features of coal under different tectonic stress regimes, coal structures can be classified into five types, including integrated, blocky, cataclastic, granulated and mylonitized structures (Table 1) (after the China national standard “Classification of coal-body structure” (GB/T 30050-2013), modified). The first two types are intact coals and the latter three are deformed coals. The deformed

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