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Full Length Article

Thermodynamic analysis of high-pressure methane adsorption on coal-based activated carbon

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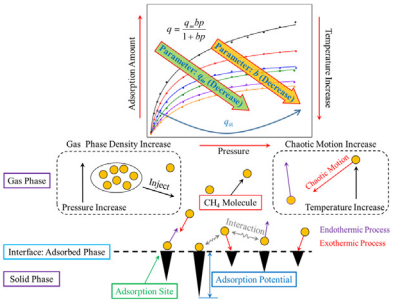
GRAPHICAL ABSTRACT



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ABSTRACT

In this work, three different activated carbons were prepared from low-rank bituminous coal by KOH activation method. High-pressure methane adsorption tests were conducted to these three different activated carbons from 273.15 to 373.15 K. Experimental results show that 313.15 K seems to be the critical temperature point for methane adsorption. When the adsorption temperature is lower than 313.15 K, methane adsorption amount would be rapidly decreased with the increase of temperature. The maximum-monolayer adsorption capacity q_m, which is fitted by adsorption experimental result of activated carbon, would be gradually decreased with the increase of temperature. The adsorption equilibrium constant b also presents the similar law as the temperature changes. Thermodynamic parameters show that methane adsorption on activated carbons are nonspontaneous ($\Delta G^\circ > 0$) and exothermic ($\Delta H^\circ < 0$) physisorption (the magnitude of $\Delta H^\circ < 20$ kJ/mol) under high-pressure conditions. And, with increase of temperature, the adsorption feasibility would be decreased. The isosteric heat of adsorption (q_{st}) of methane on the activated carbons are 15.78–16.72 kJ/mol, 15.94–18.26 kJ/mol and 15.83–16.97 kJ/mol, respectively. With increase of the adsorption amount, isosteric heat of adsorption present a first decreasing and then increasing rules under the influence of temperature and pressure. The minimum value of q_{st} appears near the adsorption amount of 3 mmol/g. The higher temperature would increase the thermal motion of methane molecules and the higher pressure would increase the density of methane molecules in the fixed space, which would result in the intermolecular interactions of methane that have been ignored are gradually appeared.

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1. Introduction

As an accessory product of coal production, coal-bed methane is not only an important source of coal mine safety accidents (such as gas explosion, mine fire, rock burst and coal dust) [1–4], but also a kind of potent greenhouse gas. However, the gas is also a clean energy with high calorific value and attracting more attention [5–8]. Due to various geological conditions (like water blocking effect [9,10], high ground stress [11,12], and coal-rock deformation [13–15]), the methane concentration of a large amount of gas which is extracted from coal seams in China is too low to be utilized (the average methane concentration of the drilling gas less than 30% in China because of the low permeability of coal seams [16–18]), as a consequence, low concentration methane extracted from Chinese coal mine was usually discharged directly into the air, which caused serious air pollutions and greenhouse effects.

The extracted coal-bed methane is mainly consisting of methane, nitrogen, some oxygen and a small amount of other gases [19]. Up to now, the pressure swing adsorption (PSA) process is an efficient and convenient method to separate and purify methane from coal-bed methane for use as a clean energy or chemical raw material [20,21]. Besides, other separation techniques, such as temperature swing adsorption (TSA) and vacuum swing adsorption (VSA), were also adopted to purify methane from gas mixture. Fakhroleslam and Fatemi [22] have simulated the PSA, VSA, and TSA processes for purification of methane from CO_2. Pahinkar et al. [23] investigated the feasibility of the use of adsorbent-coated micro channels in TSA processes for natural gas purification. Raganati [24] and Ammendola [25] tested capture and recovery of CO_2 by means of the TSA process. The key factor of these technologies is to study the properties of adsorbents. Activated carbons as cheap adsorbents have been more widely used in the PSA field due to their well-developed pore structure and excellent thermal stability [26–28]. At present, coal is widely used as a major raw material for the preparation of activated carbon [29,30]. Lillo–Ródenas et al. [31–33] conducted a series of experiments on the preparation of activated carbons by using anthracite as precursor and adopted KOH activation method, finally found that when the activation temperature was controlled above 700 °C, the activation process preferentially generates micropores that then expanded to form mesopores and macropores. Hüttinger et al. [34] suggest that the KOH excellent activation effect results from the metallic potassium, which is generated during activation process, having a good wettability to the carbon surface in a molten state, thereby reducing the tension of KOH on the carbon surface and being able to react more fully with the carbon surface. Therefore, KOH was chosen as activator to prepare activated carbon from three kinds of coal samples in this work.

Meanwhile, methane is the main component of coal-bed methane and natural gas. The energy released by complete combustion of a unit volume of methane is only 0.11% of the gasoline [35]. Thus the storage and transportation of methane are also the keys to its efficient use. So far, there are mainly three kinds of natural gas storage methods, namely liquefied natural gas (LNG), compressed natural gas (CNG) and adsorbed natural gas (ANG) [36–38]. Among them, ANG has been widely studied due to its low maintenance cost, safety and reliability. Liu et al. [39] adopted KOH to activate corn cobs for the preparation of activated carbons with high specific surface area and conducted methane adsorption experiments, found that when the methane pressure is lower than 3.5 MPa, the methane emissions decreased rapidly. Policicchio et al. [40] prepared activated carbons from cellulose crystals and tested its methane storage capacity at 298 K. The results show that at 3.5 MPa, the commercial methane storage volume specified by the U.S. Department of Energy (DOE) can be approached. Antoniou et al. [41] studied methane storage performance of zeolitic carbon materials at three different temperatures and found that at 298 K and 3.5 MPa, methane storage capacity was up to 8 wt% and the variation of adsorption heat on the prepared materials was different. Beckner and Dailly [42] compared the methane storage capacity of activated carbons and metal–organic frameworks on a laboratory scale and pilot scale. The results show that the intergranular porosity is not conducive to the storage of methane by MOFs. However, reducing the intergranular porosity to increase methane storage capacity, in turn, leads to a decrease in the average gas flow rate. Therefore, the gas flow rate and gas volumetric capacity are important parameters for the use of ANG technology. The research on the methane adsorption mostly focuses on the different types of activated carbons at normal room temperature,

Table 1
Proximate and vitrinite reflectance analysis of coal samples.

Sample	Proximate analysis (w/w %)				Vitrinite reflectance $R_{0,max}$(%)
	FC_{ad}	V_{daf}	A_{ad}	M_{ad}	
DF	55.38	23.20	17.07	4.35	0.70
SM	58.71	28.60	3.12	9.57	0.65
XB	56.31	27.62	5.37	10.70	0.58

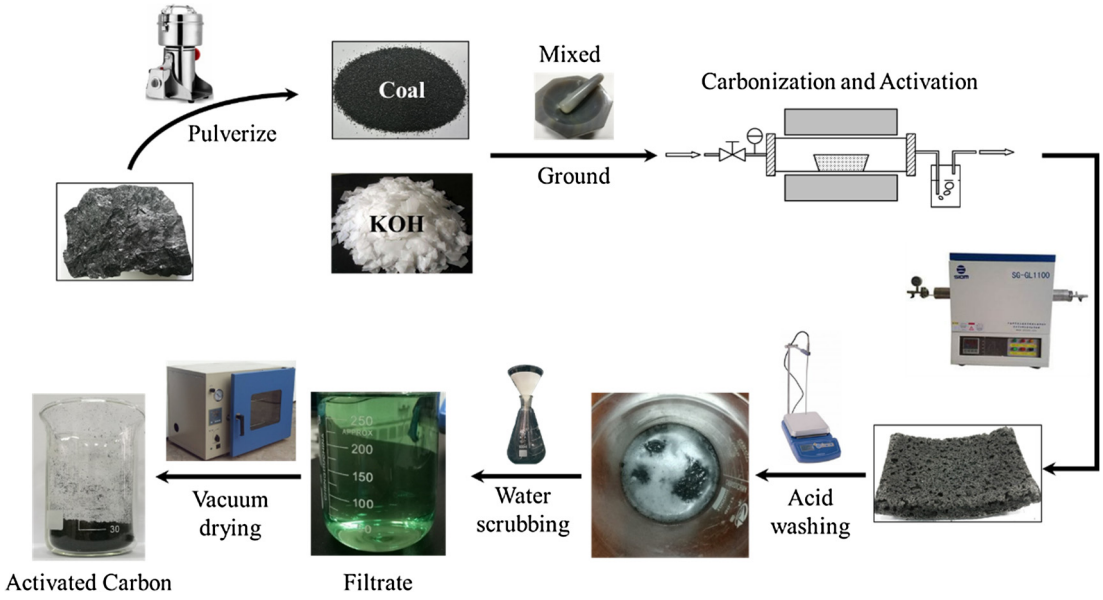

Fig. 1. The flow diagram of preparation of coal based activated carbon.