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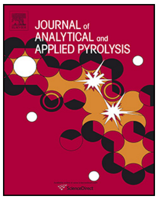

Effect of nitrogen-containing groups on methane adsorption behaviors of carbon spheres

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ABSTRACT

Methane adsorption behaviors of surface treated carbon spheres were studied in this work. Nitrogen-containing groups containing carbon spheres were prepared by urea, ammonia aqueous solution and NH_3 treatments, respectively. The textural properties were characterized by N_2 adsorption/desorption isotherm at 77 K. Their surface morphologies were analyzed by scanning electron microscopy (SEM). The surface properties of carbon spheres were confirmed by ultimate analysis and X-ray photoelectron spectroscopy (XPS). The adsorption characteristics of methane onto carbon spheres were measured at 298 K and pressures up to 5.0 MPa by a volumetric method. The D–A model fitted the experimental data well. As a result, the functionalized carbon spheres led to a decrease in adsorption capacity as compared with pristine CS, and there was a positive correlation between the saturated adsorption capacity and the BET SSA and total PV of samples. When the BET SSA and total PV were considerable, the surface properties, such as nitrogen-containing groups, were the more sensitive factors. Meanwhile, a higher nitrogen content, especially a higher pyridine nitrogen content, provided more positive adsorptive sites for methane adsorption. Therefore, the more appropriate the textural structure and the surface properties, the better the methane adsorption capacity.

1. Introduction

Carbon spheres (CS) is one of the most excellent carbon materials widely developed for various industries. As a sort of well developed solid porous structure, the carbon spheres results in energy storage systems, such as specific adsorption capacity of gases, and electrochemical applications [1–4]. The gas adsorption capacity requires the information of the adsorbent characteristics [5]. As a main component of adsorbed natural gas (ANG) and coal seam gas (CSG), methane is viewed as a beneficial source [6]. Methane adsorption over carbon materials [7], such as carbon spheres, is a satisfied strategy for gas storage, which enhances the adsorption density, lowers the storage pressure and the temperature comparing with conventional storage process [3,8]. The storage of methane employing adsorption has recently become attractive as a possible alternative to the conventional storage methods such as compressed natural gas (CNG) and liquefied natural gas (LNG) [5].

Besides, plenty of investigations were committed into the relationship between the microstructure of carbon materials and their adsorption capacities [3,4]. The adsorption ability of carbon materials is associated with their physical and chemical properties [9]. The surface characteristics of carbon materials depend on the content of heteroatoms [10–14], such as oxygen or nitrogen which determine the charge and hydrophobicity of the carbon surface [10]. Various carbon materials, which are suitable active materials for methane adsorption, have surface functional groups containing many heteroatoms, such as oxygen, nitrogen, and sulfur [15]. Among them, oxygen-containing groups negatively affect the adsorptive performance [10,15]; it not only leads to the destruction of surface structure but also effectively approaches toward attaining a changing adsorption capacity [16,17].

However, to our knowledge, little current research has focused on introducing nitrogen-containing groups to investigate their influences on methane adsorption. To address this concern, the factors affecting methane adsorption still call for further investigation, and the relationship between methane adsorption capacity and the surface nitrogen-containing groups of carbon materials is still required in detail.

Nitrogen-containing carbon materials could be effectively prepared through carbonization using nitrogen-rich carbon

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precursors, such as polyacrylonitrile, melamine, quinoline pitch, urea, and so on [17–25].

In the present study, we investigated the effect of nitrogen-containing groups on the carbon spheres prepared using a series of methods with urea, ammonia aqueous solution and NH_3 as the nitrogen precursors, respectively. The nitrogen complexes on carbon sphere surface were characterized by X-ray photoelectron spectroscopy (XPS). The texture was determined by N_2 adsorption/desorption at 77 K. Detailed analyses of the texture allowed the investigation of pores in which the adsorption behaviors took place. The data of methane adsorption equilibrium were measured by a volumetric method and fitted to the Dubinin–Astakhov (D–A) model. Furthermore, the results were discussed with regard to the content of nitrogen, the type of nitrogen functionalities, pore structure, and methane adsorption capacity.

2. Experimental

2.1. Sample preparation

The RF resins spheres were typically synthesized by using resorcinol and formaldehyde solution as precursors, similarly described in the previous literature [2]. 6 mL of the ammonia aqueous solution (NH_4OH, 25 wt%) was mixed with a solution containing 480 mL of absolute ethanol (EtOH) and 1200 mL of deionized water, then stirred for more than 1 h. Subsequently, 12 g of resorcinol was added and continually stirred for 10 min; and followed by adding the formaldehyde solution (16.8 mL) to the reaction solution and stirring for 24 h with the speed of 300 r/min at 30 °C; and then heated for 24 h at 100 °C under a static condition in a Teflon-lined autoclave. The solid product was obtained by centrifugation and air-dried at 100 °C for 24 h. Lastly the RF resin spheres were heated to 350 °C under Ar atmosphere with a heating rate of 5 °C/min, then kept at 350 °C for 2 h, and subsequently heated to 950 °C with a heating rate of 5 °C/min and maintained at 950 °C for 2 h (named as CS) for carbonization [2].

Three different methods were used to modify the carbon spheres (CS).

Synthesis of U-CS. The carbon spheres (CS) were treated with urea in deionized water and stirred for 7 h at room temperature. Then the samples were dried at 70 °C for 12 h and thermally decomposed in Ar atmosphere at 950 °C and kept for 2 h. The product was washed out to neutral pH in boiling distilled water to eliminate decomposed urea. The sample was named as U-CS.

Synthesis of NH_2-CS. The carbon spheres (CS) were modified with ammonia aqueous solution (NH_4OH, 10 wt%) and stirred for 7 h at room temperature, and then the samples were washed out in distilled water and dried at 70 °C for 24 h (denoted as NH_2-CS)[23,24].

Synthesis of N-CS. N-CS was prepared by the carbon spheres at 550 °C under NH_3 gas flow. Briefly, 3 g of carbon spheres was put into a tube furnace with 5% NH_3 in Ar flow of 50 mL/min, then heated to 550 °C with a heating rate of 5 °C/min and maintained at this temperature for 1 h. The products were washed repeatedly with distilled water, and dried at 70 °C for 24 h. The resultant sample was represented by N-CS [24].

2.2. Characterization

The textural characterization of the four samples was obtained by N_2 adsorption/desorption isotherms, determined at 77 K with a NOVA1000e surface area and pore size analyzer (Quantachrome Company). Samples were degassed at 473 K for 180 min prior to the analysis. Specific surface area and pore size distribution of the samples were measured from the Brunauer–Emmett–Teller (BET) method and D–A method, respectively. The total pore volume was evaluated at $p/p_0 = 0.98–0.99$ [1,3,10].

Surface morphology was investigated by scanning electron microscopy (SEM) (Hitachi S-4800, Japan) [1,10].

The ultimate analysis of samples was performed in a CARLO ERBA 1106 element analyzer (Italy). The oxygen content was calculated by difference [1,10].

The composition state over the CS surface as a function of surface treatment was confirmed with X-ray photoelectron spectroscopy (XPS) using XSAM 800 spectrometer equipped with an EA-125 hemispherical multichannel electronics analyzer operating in an Al Kα X-ray source. Charging effects were corrected by adjusting the binding energy of C 1s peak from carbon contamination to 284.6 eV [10,26,27]. The XPS spectra peaks were curve-fitted by using XPS peak fit software [1,10,28].

2.3. Methane adsorption

Methane adsorption measurements were conducted using a volumetric method similar to that previously described [1,3,10]. A schematic arrangement was shown in Fig. 1. As He cannot be adsorbed at pressures below 10 MPa, it was used for the calibration of the free volume of the adsorption cell in the adsorption setup. The purities of He and methane were 99.999% and 99.99%, respectively. The methane adsorption measurement was similar to that of helium calibration. Before the measurement, the sample was degassed for about 3 h. After degassing, methane adsorption measurement was conducted under pressure ranges from 0 to 5.0 MPa at 298 K. This process was repeated three times to ensure the validity of the experiment [1,3,10].

2.4. Data reduction

With the methane adsorption proceeding, the difference between excess adsorption amount (n_{excess}, in mg/g) and the absolute adsorption amount (n_{absolute}, in mg/g) become more evident when the adsorption pressure became higher. Since the n_{absolute} cannot be directly measured, the n_{excess} measured from the experiments is used for the calculation of n_{absolute}:

$$n_{\text{absolute}} = \frac{n_{\text{excess}}}{1 - (\rho_{\text{gas}}/\rho_{\text{adsorbed}})} \tag{1}$$

where ρ_{gas} and ρ_{adsorbed} (in g/cm^3) are the density of the free gas phase and the adsorbed phase, respectively.

Since ρ_{adsorbed} cannot be determined directly, we use the following method to calculate the density of the adsorbed phase (ρ_{adsorbed}).

$$\rho_{\text{adsorbed}} = \rho_b \exp[-\alpha(T - T_b)] \tag{2}$$

$$\alpha = \frac{1}{\upsilon_{\text{adsorbed}}}\left(\frac{\partial \upsilon_{\text{adsorbed}}}{\partial T}\right) \tag{3}$$

where ρ_b is the density of methane at the boiling point (0.424 g/cm^3); T_b is the boiling point of methane (111.5 K); $\upsilon_{\text{adsorbed}}$ is the specific volume of the adsorbed phase; and α is the thermal expansion coefficient of the adsorbed phase. In our work, α was determined by the empirical value of 0.0025.

2.5. Isotherm regression analysis

The D–A equation was applied to fit the adsorption data. The relevant equation is expressed as,

$$n = n_0 \exp\left\{-\left[\frac{RT}{E}\ln\left(\frac{p_0}{p}\right)\right]^t\right\} \tag{4}$$