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Adsorption equilibrium of hydrogen on graphene sheets and activated carbon

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ABSTRACT

For obtaining the technical data to evaluate the performance of hydrogen storage by adsorption on graphene sheets (GS), analysis of adsorption equilibrium of hydrogen on the GS and the activated carbon were carried out based on the hydrogen adsorption data covering a wide temperature range. The GS and SAC-02 activated carbon, which respectively had a specific surface area about 300 m^2/g and 2074 m^2/g, were selected as adsorbents. Six adsorption isotherms of excess amounts of high purity hydrogen were measured at temperature from 77.15 K to 293.15 K and pressure up to 6 MPa. Parameters of Langmuir, Langmuir–Freundlich and Toth equations were set by non-linear fit against adsorption data, predicting accuracy of the equations was then evaluated by the accumulated relative errors between experimental data and those from the equations under different pressure regions. Absolute adsorption amounts determined by the modified equation were used to calculate the isosteric heat of adsorption.

It shows that both adsorption isotherms of hydrogen on the GS and the activated carbon have the features of Type I, but the trend of isotherms varying over the pressure is different within the lower temperature region. Results from Langmuir equation have the largest error. Toth equation can much accurately predict the adsorption data with an overall accumulated relative error less than 4%. The value of the isosteric heat of hydrogen adsorption on the GS is about 5.06–6.37 kJ/mol, which is much higher than 4.05–5.52 kJ/mol for hydrogen on the SAC-02 activated carbon under the whole experimental condition. It reveals that interaction between hydrogen molecules and the graphene layer is stronger than that of hydrogen and carbon surface, and Toth equation could be appropriate to analyzing adsorption equilibrium for hydrogen on carbon based adsorbents.

1. Introduction

Recently, as a new kind of carbon materials, graphene materials in particular have attracted a great deal of interest as a promising hydrogen storage media due to the low atomic masses, relatively high chemical stabilities and tunable pore structures [1–3]. However, hydrogen storage densities on recent graphene materials are still far from the targets set by United States' Department of Energy (DOE) and International Association of Energy (IAE), some results are even smaller than those of hydrogen on other carbon-based adsorbents [4–6], it is therefore necessary to probe into the factors influencing the interaction between hydrogen molecules and the graphene layer.

In general, for supercritical hydrogen adsorption on carbon based adsorbents, physical properties such as the specific surface area and porosity as well as the functional group upon the adsorbent surface are the determinant factors to their hydrogen storage capacities, modification of the structure and composition of the adsorbent is therefore necessary [4,7–9]. Moreover, as physical adsorption of hydrogen on carbon adsorbents has been researching since 1960s due to the quick adsorption/desorption characteristic of the storage system under moderate conditions, the physical adsorption capacity should accordingly be fully developed while changing the composition of the adsorbent [10–12]. Recent researched results show that the contribution of physical adsorption of hydrogen is not enough to meet the DOE target unless the storage temperature is lowered down to cryogenic region [13], introduction of other kinds of interaction mechanism between hydrogen molecules and adsorbent surface is therefore needed [14,15,11], but this will bring about another question because the storage system should be maintained at a higher temperature region where the contribution of the physical adsorption will be inhibited [16,17]. Meanwhile, as a higher storage temperature always accompanies with a larger adsorption enthalpy, which will impair the capacity of physical adsorption, the compositional

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modification and selection of a storage temperature should thereby be matched while developing hydrogen storage medium from graphene materials.

The variation of the adsorption enthalpy is usually determined by adsorption isosteres from excess amounts employing Clausius–Clapeyron equation [18], but the result may be ambiguous if isotherms of excess amounts pass the maximums or are measured over a wide temperature range [19,20]. Moreover, in the viewpoint of practical application, it is the absolute adsorption amount that has a clear physical meaning in designing an adsorption storage system [21–23]. Hence, an approach, which can directly calculate the absolute adsorption amount without any assumption on the state of the adsorbed phase beforehand, should be preferentially emphasized.

The aim of this paper is to comparatively study temperature dependence of adsorptive performance of hydrogen on the GS and commercially available activated carbon. The study was commenced with the characterization of the adsorbent, then the measure of the adsorption isotherms and the thermodynamics analysis of the experimental data.

2. Experimental

2.1. Structural characterization

The GS sample was prepared from the thermally expanded graphite oxide (GO) which was synthesized by the modified Hummer method [24]. The microstructure and morphology of the sample was characterized by scanning electron microscopy (SEM) and high-resolution transmission electron microscopy (HRTEM), which is respectively shown in Fig. 1(a and b). Fig. 1(a) reveals that the GS has a pocket-like morphology with wrinkled paper structure on the surface, and the image in Fig. 1(b) indicates that the GS has wrinkles at the edge of each layer and layers are linked by transparent membranes. The selected activated carbon SAC-02 synthesized from granular coconut shell was supplied by Ningde Xinsen Activated Carbon Co.

N_2 adsorption isotherm at 77.15 K on both samples was measured on Micromeritics ASAP 2020 to determine the specific surface area and the pore size distribution (PSD). Results from BET plot and the PSD determined by non-local density functional theory (NDFT) calculation are respectively shown in Fig. 2 and Table 1.

2.2. Adsorption measurement

About 0.5740 g of the GS and 0.6915 g of SAC-02 were selected as the adsorbent. Volumetric method was used to measure adsorption equilibrium data on PCTPro E&E, a fully automated Sievert instrument for measuring gas sorption properties of materials, especially for hydrogen storage materials. The instrument includes 5 built-in and calibrated reservoir volumes, here the reference cell used is 4.52 mL in volume and the adsorption cell is a standard Microdoser (MD) from HyEnergy. The measuring system also includes 4 capacitance pressure transducers. Two transducers are for PID gas pressure regulation, and the other two are for measuring at high-pressure 20 MPa and low-pressure 0.5 MPa. The transducer accuracy is 1.0% of reading.

The used gases, which include hydrogen, nitrogen and helium, were all ultra-high-purity grade supplied by Air Liquide Xiamen Co Ltd. Prior to each adsorption test, the sample experienced

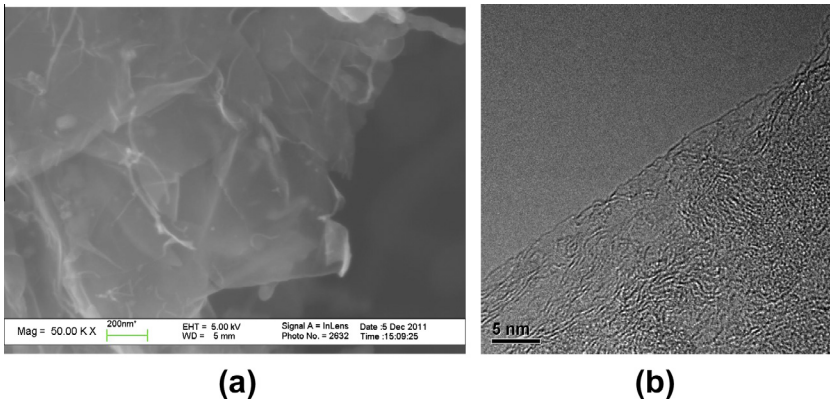

Fig. 1. The SEM image (a) and HRTEM images (b) of the GS sample synthesized by thermally exfoliated GO.

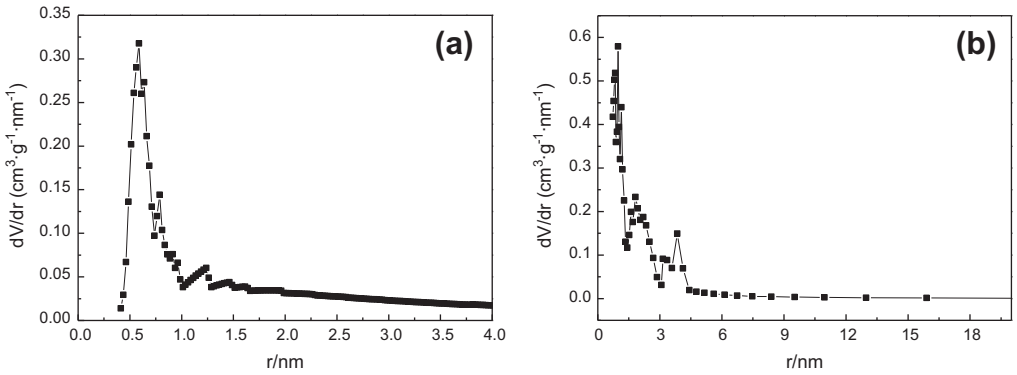

Fig. 2. PSD of the GS (a) and activated carbon SAC-02 (b) determined by adsorption data of nitrogen at 77.15 K.