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Scanning curves of water adsorption on graphitized thermal carbon black and ordered mesoporous carbon

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ABSTRACT

Adsorption isotherms of water on porous carbons generally show large hysteresis loops whose origin is believed to be different from simple gases adsorption in mesoporous solids. In this paper, we discussed in details the behavior of water adsorption isotherms and their descending scanning curves for two carbons of different topologies, a highly graphitized thermal carbon black, Carbopack F, and a highly ordered mesoporous carbon, Hex. For both solids, very large hysteresis loops are observed, but their behaviors are different. For Carbopack F, the loop extends over a very wide range of pressure and the loop is larger when the descending is started from a higher loading; while for Hex, the hysteresis loop shows distinct steps, the number of which depends on the loading where the descending starts. By carefully analyzing the scanning curves from different loadings, we established the mechanism of water adsorption in Hex as a sequence of three steps: (1) water molecules adsorb on functional groups located at the junctions between adjacent basal planes of graphene layers, (2) growth of water clusters around the functional groups, and (3) bridging of adjacent clusters to form larger clusters, followed by a complete filling of mesopores.

1. Introduction

Physical gases adsorption in porous materials has been considered as a promising technology for separation, for example, natural gas separation for energy supply [1] and carbon dioxide capture for environmental protection [2]. The adsorbents must meet a number of requirements: good affinity, selectivity, high capacity, good thermal and mechanical stability, good regeneration and acceptable cost. Porous carbon, such as activated carbon, molecular sieving carbon and carbon aerogel, is one of such classes of adsorbent [3], and most importantly this class of adsorbent can be tailored for the right pore size, volume and surface chemistry to suit specific applications. However, for it to perform well in separation, it must be able to deal with water as water always presents in most gaseous mixtures and it is very detrimental to the separation of desired substances because it competes for adsorption sites, resulting in a reduction in the efficiency of separation, especially when the humidity is greater than about 40% [4–7]. It is, therefore, very important to have a deeper understanding of how the porous structure and the surface chemistry affect the mechanism of water adsorption in porous carbon.

Water adsorption on activated carbon typically shows Type V, according to the IUPAC classification with a large H1 or H2 hysteresis loop [3,8–11]. Hysteresis in water adsorption in non-porous and porous carbons is one of the least understood phenomena in adsorption, due to the complex interplay between the various interactions: (1) intermolecular interaction among water molecules, (2) interaction between water and the strong sites, for example functional groups where water can form very strong electrostatic interactions with, and (3) interaction between water and the graphene layers. The term “hydrophobic” interaction is commonly used to refer to the last interaction because it is the weakest interaction among the three interactions. It is, however, important to make it clear that the notion that water does not like graphene surfaces is not correct, but rather water molecules simply prefer to interact with themselves and functional groups on the surface. By increasing the temperature or by doping the graphene surface with either nitrogen or oxygen (for example graphene oxide), water does

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indeed adsorb on the surface, rendering it "hydrophilic". Many activated carbons can adsorb water in their micropores and mesopores because of the high concentrations of functional groups located either at the edges of the graphene layers or on the graphene layers, mainly at the defects [8,12,13]. It is now believed that the hysteresis observed in water adsorption in microporous carbons is not due to capillary condensation and evaporation, which is typically observed in adsorption of simple gases in mesoporous materials [14]. Adsorption of water in carbon was first put forwarded by Dubinin and co-workers [15], who proposed an entirely different mechanism than the capillary condensation and evaporation of simple gases in mesoporous media, where the Cohan/Kelvin equation applies [3]. Not only hysteresis of water adsorption is observed in porous carbons, but it also occurs with non-porous carbon, even with graphitized thermal carbon blacks (GTCB) [16]. We have reported water adsorption on Carbopack F (a highly GTCB) [16,17] that the uptake is very small (almost insignificant) for pressures up to a relative pressure, P/P_0, of 0.9, at which the uptake begins to increase steeply. Upon reducing P/P_0 from 0.99, the desorption branch does not trace the adsorption branch, resulting in a very broad hysteresis loop, spanning over the full range of pressure, with a lower closure point at a relative pressure of less than 0.001. To understand the origin of the broad hysteresis loop, we need to describe the mechanism of water adsorption in Carbopack F: at very low loadings, water molecules adsorb around the functional groups at the edges of the graphene layers because of the strong electrostatic interactions compared to the intermolecular interactions and the interactions between water and the graphene layer. As the loading is increased water clusters are formed around the functional groups and grow in size because of the greater electrostatic interaction between water molecules than the dispersive water–graphene interaction [17]. This mechanism of adsorption was taken into account in the recent theories for water adsorption in porous carbon [12,18], and is also justified with molecular dynamics [19] and Monte Carlo simulations [20].

In this paper, we presented a detailed analysis of descending curves to shed even better light into the mechanisms of water adsorption and desorption from non-porous and porous carbons. Highly graphitized thermal carbon black, Carbopack F, and highly ordered mesoporous carbon, Hex [21], are used to represent these two classes of carbon.

2. Experimental

2.1. Materials

A highly graphitized carbon black, Carbopack F (supplied by Supelco, USA) and a highly ordered mesoporous carbon [21], Hex, were used as the model adsorbents. Some of their properties relevant to this paper will be briefly given below and more details can be found elsewhere [16,17,21,22]. Carbopack F consists of polyhedral micro particles (of the order of several hundred nm) with homogeneous graphene layers on the faces of the polyhedra, and nitrogen adsorption at 77 K does not reveal any detectable pores [16,17]. Hex has hexagon mesopores with a very sharp pore size distribution with a mean pore diameter of 9 nm [22], the length of channel is longer than several hundred nanometer [21], and its pore surface is composed of graphene patches of 5 nm in linear dimension [21]. Both carbon are graphitized at temperatures greater 2400 K, resulting in a significant reduction in concentration of functional groups. By way of Boehm titration, the concentration is 0.07 mmol/g in Carbopack F [16,17,23], which is grossly overestimated as concluded in our previous work [23]. In Table 1, the oxygen/carbon (O/C) ratio of samples is shown. The X-ray photoelectron spectroscopy (XPS) measurements were performed in a ULVAC PHI 5000 VersaProbe II spectrometer, with AlKα radiation (1486.6 eV) used for the excitation. All the binding energies were referenced to the C1s peak at 284.6 eV of C–C carbon. TEM images and the nitrogen isotherms of materials are shown in Supplemental data.

Table 1
Characteristic pore properties of Carbopack F [17] and Hex [21].

	S_{BET} [m2/g]	V_{micro} [ml/g]	V_{meso} [ml/g]	O/C ratio
Carbopack F	4.9	0.00	0.00	0.0404
Hex	205 [22]	0.00	0.43	0.0498

S_{BET} = BET area obtained with nitrogen adsorption at 77 K; V_{micro} = micropore volume; V_{meso} = mesopore volume obtained as nitrogen capacity at 0.98 and with an assumed liquid density.

2.2. Measurement

Water adsorption measurements were done at 298 K using a high resolution volumetric adsorption apparatus (BELSORP-max, MicrotracBEL). The adsorption temperature was maintained with a water bath using an antifreeze coolant. To obtain each point on the isotherm, the system was first allowed to equilibrate for 300s and if the pressure change was less than ±0.3%, the measurement was accepted as being at (quasi) equilibrium; if the change is larger than ±0.3%, equilibration was continued for a further 300s until this criterion was met. Before each measurement of a new isotherm, the solid was degassed at 473 K for 5 h under vacuum (<0.1 mPa) to remove any impurities. The descending scanning curves were measured from a predetermined pressure using the same apparatus.

2.3. Isosteric heat of adsorption

The isosteric heat was calculated by applying the Clausius–-Clapeyron (CC) equation on isotherm data at two temperatures (formal derivation of CC equation can be found in Pan et al. [24]) close enough so that the derivative in the CC equation is replaced by the difference:

$$q_{iso} = -\Delta_{ads}H_{diff} = \frac{RT_1T_2}{T_2 - T_1}\ln\left(\frac{P_2}{P_1}\right) \tag{1}$$

where R is the gas constant, T_1 and T_2 are the adsorption temperatures, and P_1 and P_2 are the respective absolute pressures at a given loading. In this study, we used isotherms at 283 K and 298 K to calculate the isosteric heats on Carbopack F and Hex.

3. Results and discussion

3.1. Water adsorption on Carbopack F and Hex

Water adsorption isotherms on Carbopack F and Hex at 298 K are shown in Fig. 1.

The water adsorption isotherms on Carbopack F have been discussed elsewhere [16], but we briefly describe here because they will form the basis for the subsequent discussion of descending curves in Carbopack F and Hex. The water adsorption amount increases slightly (almost insignificantly) for relative pressures up to 0.9, at which the uptake increases steeply (note the difference in the magnitude of the amount adsorbed in Carbopack F and that of Hex). The descending curve from a loading at a relative pressure of 0.99 (about 15 μmol/m^2) does not trace the adsorption branch, but rather forms a very large loop that spans over the full range of pressure. We could not determine the lower closure point because