Carbon 124 (2017) 271–280

Contents lists available at ScienceDirect

Carbon

journal homepage: www.elsevier.com/locate/carbon

Temperature dependence of water adsorption on highly graphitized carbon black and highly ordered mesoporous carbon

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ARTICLE INFO

Article history:
Received 25 June 2017
Received in revised form
28 August 2017
Accepted 29 August 2017
Available online 30 August 2017

ABSTRACT

In previous work [1] we showed an unusual temperature dependence for water adsorption in porous activated carbons, and hypothesized that the pore size plays a critical role in water adsorption in mesopores. In this paper, we shed further light on water adsorption in mesopores by investigating its dependence on temperature for a highly graphitized non-porous carbon black and a highly ordered mesoporous carbon, Hex. They were chosen because of their distinctly different structures, with the former representing an open graphitic surface, while the latter having highly structured and graphitic mesopores of hexagonal shape. Analysis of the isotherms for these systems shows that adsorption proceeds by nucleation of water molecules around functional groups (*FG*) to form an embryo *FG*-water complex, which grows with increasing pressure to form a cluster. If the clusters are closer than a critical separation, they agglomerate to form a condensate, and provided that the pore size is small enough, the adsorbate fills the confined space. Interestingly, the amount adsorbed in the mesopores at 298 K is greater than that at 263 K, which is attributed to the formation of larger clusters at 298 K, facilitating the agglomeration of clusters followed by condensation in the mesopores.

1. Introduction

The great significance of water and its interactions with other matter are indisputable. Although the molecule is very simple, its collective properties, even as a single phase in a bulk material, can be of seemingly endless complexity. This complexity is even further enhanced in the presence of other components. The crucial feature of the molecule, which gives rise to this abundance of collective behaviour, is the uniquely strong electrostatic interaction between a pair of water molecules, which is a consequence of the combination of the very small hydrogen atom and the very large displacement of electrons towards the oxygen atom. The extraordinarily strong electrostatic interaction between water molecules, or between water and other charge centres, has a distinct directional character, and is commonly described as hydrogen bonding, since the strength of the electrostatic link is similar to that of a weak chemical bond, although no electron exchange is involved.

Many carbon adsorbents can acquire, or be decorated with oxygen containing functional groups, and when exposed to water vapor these groups also form hydrogen bonds with the water molecules. Typically, the functional groups are attached at sites where there are unsaturated electrons, such as edges or defects in a graphene plane. Since, even in the most perfect graphitic structure, graphene planes must terminate somewhere, and functional groups are therefore likely to be present in any high surface area carbon adsorbent. In the presence of water, functional groups become centres for the nucleation of water clusters, which may grow and merge in suitable geometrical configurations such as crevices or pores. The presence of water vapor can therefore hamper the efficiency of separation processes in real carbon materials where the growth of water clusters can significantly reduce adsorption capacity and hinder transport through pore spaces. Some researchers have reported the adsorption of organic-water system on activated carbons (AC) with experimental studies and computer simulation, the results clearly shows the organic adsorbed amounts are influenced by the presence of water [2,3]. Functional groups or very tight pore spaces are an essential prerequisite to water adsorption in graphitic materials at ambient temperatures, since interactions between water molecules are

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http://dx.doi.org/10.1016/j.carbon.2017.08.067
0008-6223/

stronger than those between water and a graphitic surface, and the system is non-wetting [4,5].

An understanding of the part played by functional groups in water adsorption is an essential step in the application of carbon adsorbents in processes involving mixtures of water/air and or organic species. Insight can be gained by carrying out water adsorption at very low loadings, where the intrinsic interaction between a water molecule and a functional group can be analyzed and quantified [5–7].

Studies of adsorption on carbons dates back more than 200 years, and has generated an extensive literature covering a wide range of adsorbates and carbon materials, having a variety of pore structures and surface chemistry [8–15]. Computer simulation studies of water adsorption on carbon surfaces are now frequently used to understand how water adsorbs at the microscopic level [4,16–26]. Recently, we reported simulation and experimental results for water adsorption on graphite with attached functional groups [4–7,15], and showed that water adsorbs initially on functional groups to form an adsorbed complex, which then acts as nucleation sites for further water molecules to form clusters which then grow in size with increasing pressure. We have found that the order of interaction is water-functional group » water-water » water-graphene surface [4–6]. In a recently paper on water adsorption in microporous and mesoporous carbons, we showed that the water cluster needs to reach a certain size before water can adsorb inside a pore [12]. This finding was further substantiated in our investigation of the effects of temperature on water adsorption in microporous and mesoporous carbons, where we observed that, at a given reduced pressure, the amount adsorbed in mesopores is lowered when temperature is decreased [1]. In porous carbons in which only micropores are present, the adsorption uptake occurs as a single step, and isotherms at sub-critical temperatures are superimposable at all temperatures, when plotted against the reduced pressure [1,6]. On the other hand, water isotherms at 298 K for carbons having distinct micropore and mesopore distributions, show a two-step uptake, in contrast to the single step uptake at 263 K which is almost the same as the first step of the 298 K isotherm. We attributed the first step to adsorption in micropores and the second one to adsorption in mesopores. However, we were not able to determine the threshold pore size above which water does not adsorb for a given temperature, nor the temperature dependence of the water cluster growth [1]. Some researchers have measured water hysteresis scanning curves in desorption from porous carbon materials in attempts to gain a better understanding of water adsorption phenomena [15,27,28].

The objective of this paper is to systematically study water adsorption isotherms over the same range of temperatures as in our previous work [1] on a highly graphitized carbon black (Carbopack F) and on a highly ordered mesoporous carbon with hexagonal graphitic pores (Hex).

2. Experimental

A highly graphitized carbon black, Carbopack F (supplied by Supelco, USA) and a highly ordered mesoporous graphitized carbon, Hex, were used as adsorbents. The properties relevant to this work are summarised below; more details can be found elsewhere [5,15,29–31]. Carbopack F consists of polyhedral micro particles with dimensions of the order of several hundred nm (typically 200–300 nm) with homogeneous graphitic surfaces. Nitrogen adsorption at 77 K does not reveal any detectable pores [5,29]. Hex has hexagonal mesopores with a very narrow pore size distribution and a mean pore diameter of 9 nm [31]. The surfaces of the pores are composed of graphene patches of 5 nm in linear dimension [30]. Both these carbon samples are graphitized at temperatures greater than 2400 K, resulting in a significant reduction in the concentration of functional groups. The O/C ratio of both carbons by X-ray photoelectron spectroscopy (XPS) analysis is lower than 0.0500 [15].

Water adsorption measurements were made at 263 K–298 K using a high-resolution volumetric adsorption apparatus (BELSORP-max, MicrotracBEL). The adsorption temperature was maintained with a water bath containing 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 equilibrium; if the change was larger than ±0.3%, equilibration was continued for a further 300s until this criterion was met. The samples were degassed in the same apparatus at 473 K for 5 h under vacuum at pressures less than 0.1 mPa to remove any physically adsorbed gases before each measurement.

3. Results and discussion

3.1. Water adsorption isotherms on Carbopack F

Fig. 1a shows the water adsorption isotherms plotted with respect to the reduced pressure for non-porous Carbopack F at various temperatures from 263 K to 298 K. They are compared in Fig. 1b and c on linear scales and logarithmic scales respectively, plotted against the absolute pressure; the logarithmic plots magnify the Henry law region at low loadings.

A distinctive feature of the water adsorption isotherms on non-porous Carbopack F in Fig. 1a is the large hysteresis loop that spans nearly the full range of reduced pressure, with a lower closer point at less than 0.001 which is seen at all temperatures investigated in this study. We could not determine a lower closure point because desorption does not occur unless heating is applied [15] and is indicative of the very strong hydrogen bonding between water molecules and functional groups. To ensure that this is not due to any possible chemisorption, we cleaned the Carbopack F by heating and exactly the same isotherms were reproduced when measurements were repeated a number of times. At the very high graphitization temperatures used in the preparation of Carbopack F all highly reactive sites would have been completely removed. We note that the width of the hysteresis loop on the density scale is larger at higher temperatures, and is constant over nearly the full range of the reduced pressure. For example, this width is 2 μmol/m^2 at 298 K and is 1 μmol/m^2 at 293 K. This observation indicates that water is present as a highly metastable cluster, which does not disintegrate even at very low pressure. We hypothesize that as the temperature increases the water clusters become larger (because of the thermal fluctuation) and for a given reduced pressure, adjacent clusters, attached along the edges of the graphene layers, merge to form 1D strings of water occupying all the junctions along the micro-crystallite, and act as a mesh enclosing the crystal but leaving its surfaces exposed. Only when the pressure approaches the saturation vapor pressure (around $0.95P_0$) does condensate form in the interstices between the crystallites. We show below that this spacing is approximately 20 nm.

This proposed mechanism is supported by the experiments of Berzekina et al. (1969); in this work, water was preloaded onto a highly graphitized thermal carbon black at loadings up to the equivalent of 3.8 times the monolayer coverage. When this water-preloaded carbon was exposed to argon the argon isotherm was essentially the same as that for the clean carbon, indicating that water clusters are mainly formed at the junctions of the crystallites [32] and do not spread over the basal planes.

At a reduced pressure of 0.95 the water density has reached 4 μmol/m^2 which is well below the theoretical concentration required to form a monolayer over the carbon surface (15.4 μmol/m^2). The isotherms then increase sharply, due to the condensation in the interstices between the crystallites, where there is now sufficient adsorbed water to form a concave interface due to the