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On the isosteric heat of adsorption of non-polar and polar fluids on highly graphitized carbon black

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ABSTRACT

Isosteric heat of adsorption is indispensable in probing the energetic behavior of interaction between adsorbate and solid, and it can shed insight into how molecules interact with a solid by studying the dependence of isosteric heat on loading. In this study, we illustrated how this can be used to explain the difference between adsorption of non-polar (and weakly polar) fluids and strong polar fluids on a highly graphitized carbon black, Carbopack F. This carbon black has a very small quantity of functional group, and interestingly we showed that no matter how small it is the analysis of the isosteric heat versus loading can identify its presence and how it affects the way polar molecules adsorb. We used argon and nitrogen as representatives of non-polar fluid and weakly polar fluid, and methanol and water for strong polar fluid. The pattern of the isosteric heat versus loading can be regarded as a fingerprint to determine the mechanism of adsorption for strong polar fluids, which is very distinct from that for non-polar fluids. This also allows us to estimate the interplay between the various interactions: fluid–fluid, fluid-basal plane and fluid-functional group.

1. Introduction

Physical adsorption of gas on surfaces or in porous solids is associated with a release of energy, resulted from the interactions between the adsorbate and the surface and among adsorbed molecules. The amount of heat released per unit molecule added to the adsorbed phase at constant temperature and loading is commonly known in the literature as the isosteric heat (the correct thermodynamic term is the negative of the change in the enthalpy of adsorption [1]). Experimentally the isosteric heat can be measured with an adsorption calorimeter [2–4], or calculated using two adsorption isotherms which were measured at different (close enough) temperatures by Clausius–Clapeyron equation [5,6]. The experimental isosteric heat gives the overall heat released from the process [2–6], and its dependence on the extent of loading can provide insight into how molecules interact with various parts of the system as well with themselves. Together with computer simulation this can give detailed contributions of various interactions: fluid–fluid, fluid-basal plane and fluid-functional group [7,8]. In this paper we presented an interpretation of the experimental heat versus loading, calculated from the adsorption isotherms at different temperatures. To determine the role of functional group (strong sites) on adsorption data were collected at very low pressure, and we investigated its role with two groups of adsorbate: argon and nitrogen were used to represent non-polar and weakly polar fluids, and methanol and water as representative of strongly polar fluids. Water, in particular, has received interest from many groups in the quest to understand how it interacts with a carbon surface [9–16]. The pattern of the heat curve versus the extent of loading is sensitive to the magnitudes of various interactions: fluid–fluid, fluid-basal plane and fluid-functional group, and by carefully analyzing this pattern we can deduce the adsorption mechanism.

2. Experimental

2.1. Materials

A highly graphitized carbon black, Carbopack F (supplied by Supelco, USA) was used in this study. TEM image and the nitrogen isotherms and the properties of Carbopack F are shown in Fig. 1 and Table 1. The concentrations of functional groups, S_0, such as phenolic, lactonic, and carboxylic groups were measured with Boehm titration [17], and only phenolic and carboxylic groups were detected. We also used Carbopack Y and B, which are less

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graphitized carbon black than Carbopack F, to study the effects of surface heterogeneity (Supplemental Table S1).

2.2. Measurement

Nitrogen and argon adsorption on Carbopack F, Y and B were measured at 77 K and 87 K using a high resolution volumetric adsorption apparatus (BELSORP-max, BEL Japan). Water and methanol adsorption on Carbopack F were measured at 283 K and 298 K using the same apparatus. The samples were degassed at 473 K for 5 h under vacuum at pressure less than 0.1 mPa to remove any physically adsorbed amount before each measurement.

2.3. Isosteric heat of adsorption

The isosteric heats of adsorption for each adsorbate were 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. [18]):

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

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.

3. Results and discussion

3.1. Noble and non-polar gases adsorption on graphite

Argon and nitrogen adsorptions on graphite are perhaps the most widely studied systems in the literature, where reliable isotherms and isosteric heats can be found [2–5,19–25]. Fig. 2 shows the isosteric heats of argon and nitrogen adsorption on Carbopack F which we calculated using the isotherms at 77 K and 87 K. The heat curve is typical for noble gases and many simple adsorbates. Although this pattern of the heat curve has been thoroughly explained in the literature, we shall present briefly here for the purpose of comparison with the more interesting patterns of water and methanol presented in Section 3.2. We take argon in Fig. 2a as an example: at very low loadings, argon adsorbs dominantly on the basal plane due to the stronger fluid–solid (FS) interaction than the interaction with the functional group. The strength of this FS interaction is 10 kJ/mol, which is the isosteric heat at zero loading. As the loading is increased (still less than the monolayer concentration), molecules, not only interact with the surface, but also with the previously adsorbed molecules, resulting in the isosteric heat as the sum of the FS interaction (~10 kJ/mol) and a contribution from the fluid–fluid interaction, which is proportional to the loading. This yields an approximately linear increase of the heat versus loading. As the first layer is completed, there is a sharp decrease in the isosteric heat because molecules start to adsorb in the second layer which is further away from the surface. After many layers have been formed on the surface, the isosteric heat approaches the heat of liquefaction because the adsorbates in the higher layers are liquid-like.

Table 1
Characteristic pore and surface properties of Carbopack F.

	S_{BET} (m^2/g)	V_{micro} (ml/g)	V_{meso} (ml/g)	S_0 (mmol/g)
Carbopack F	4.9	0.00	0.00	0.07

The heat curve versus loading shows one interesting feature of a spike in the region where the first layer is about to be completed. We observed this for both argon and nitrogen, and this is in agreement with the calorimetric measurements [4,25], and a number of our computer simulation studies [8,26,27]. The heat spike observed is lower than the calorimetric heat measured by Rouquerol and co-workers [4,25], and this is because our isosteric heat was calculated using the 77 K and 87 K isotherms, and therefore our heat curve corresponds to a temperature between these temperatures.

The explanation of the heat spike for adsorption of gases on a homogenous graphite surface has been given elsewhere [7]; we briefly described it graphically in Fig. 3:

(a) after the first layer is formed and relatively dense, molecules begin to adsorb on the second layer, resulting in a decrease of the isosteric heat,
(b) as chemical potential (or pressure) is increased molecules have high enough chemical potential to squeeze into the first layer and at the same time all previously adsorbed molecules are rearranged to accommodate new molecules. This gives rise to the high heat spike because (i) molecules are close to the surface, (ii) molecules interacting with neighbors and (iii) restructuring of all adsorbed molecules in the first layer,
(c) adsorption continues in the second layer.

It is worthwhile to emphasize that the heat spike is only observed when the surface is homogeneous. Adsorption of argon and nitrogen adsorption on heterogeneous surfaces do not show any spike in the heat curve (supplemental Figs. S2 and S3).

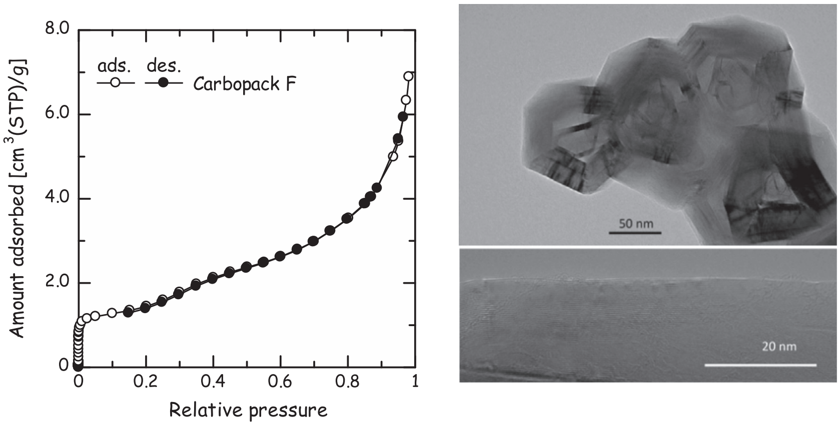

Fig. 1. Nitrogen adsorption isotherm for Carbopack F at 77 K, and TEM images of Carbopack F.