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The interplay between molecular layering and clustering in adsorption of gases on graphitized thermal carbon black – Spill-over phenomenon and the important role of strong sites

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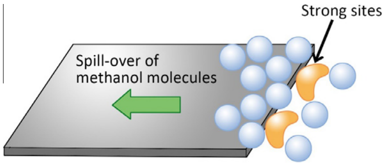
GRAPHICAL ABSTRACT



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ABSTRACT

We analyse in detail our experimental data, our simulation results and data from the literature, for the adsorption of argon, nitrogen, carbon dioxide, methanol, ammonia and water on graphitized carbon black (GTCB), and show that there are two mechanisms of adsorption at play, and that their interplay governs how different gases adsorb on the surface by either: (1) molecular layering on the basal plane or (2) clustering around very strong sites on the adsorbent whose affinity is much greater than that of the basal plane or the functional groups. Depending on the concentration of the very strong sites or the functional groups, the temperature and the relative strength of the three interactions, (a) fluid-strong sites (fine crevices and functional group) (F-SS), (b) fluid-basal plane (FB) and (c) fluid–fluid (FF), the uptake of adsorbate tends to be dominated by one mechanism. However, there are conditions (temperature and adsorbate) where two mechanisms can both govern the uptake. For simple gases, like argon, nitrogen and carbon dioxide, adsorption proceeds by molecular layering on the basal plane of graphene, but for water which represents an extreme case of a polar molecule, clustering around the strong sites or the functional groups at the edges of the graphene layers is the major mechanism of adsorption and there is little or no adsorption on the basal planes because the F-SS and FF interactions are far stronger than the FB interaction. For adsorptives with lower polarity, exemplified by methanol or ammonia, the adsorption mechanism switches from clustering to layering in the order: ammonia, methanol; and we suggest that the bridging between these two mechanisms is a molecular spill-over phenomenon, which has not been previously proposed in the literature in the context of physical adsorption.

1. Introduction

Adsorption of gases on carbon black at sub-critical temperatures, has been generally regarded as being a molecular layering

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process. Graphitized thermal carbon black (*GTCB*) is considered to be an especially appropriate adsorbent in this respect because of the energetic homogeneity of the graphite basal plane. Langmuir [52] was the first to describe the sub-monolayer adsorption process, and the theory was later extended by Brunauer et al. [15] to multilayer adsorption, widely known as the *BET* theory. In Langmuir's theory, interactions amongst adsorbate molecules are ignored, and in the *BET* theory it is assumed that these interactions are equivalent to those in the liquid state in the adsorbate beyond the first adsorbed layer. Since the pioneering work of Langmuir and Brunauer and co-workers, many modifications to the multilayer theory have been proposed [25]. Cassel [19] was perhaps the first to highlight one of the limitations of the *BET* theory by pointing out that if the lateral interactions are ignored the surface tension becomes negative and even infinitely negative. With the introduction of molecular simulation the potential energy of interaction between adsorbate molecules, and between adsorbate molecules and the adsorbent surface can be specifically accounted for. The mechanism of adsorption can now be probed in microscopic detail and many simulation results have been achieved which are in agreement with the experimental data.

GTCB particles have a polyhedron shape [96,38,110,108,109], and despite its homogeneous basal plane it possesses high energy sites at the junctions between the adjacent basal planes [30,29]. These sites could be due to functional groups which are not removed in the process of graphitization but very fine crevices (defects) at these junctions may also make a contribution. The importance of functional groups has been highlighted in many papers, for example: Bandosz et al. [3], Taqvi and LeVan [104], Salame et al. [92], Salame and Bandosz [93], Tóth and László [105], Seredych et al. [98]. Irrespective of their origin, these strong sites can act as locations for anchoring adsorbate molecules. If the strong sites are due to functional groups, which always carry fixed partial charges, interaction with associating fluids, such as water and ammonia, will be primarily associated with electrostatic interactions. The combination of the defects and the functional groups will enhance the initial interaction of associating fluids with the carbon surface, no matter how low their adsorption capacity. This results in the formation of a physically bound complex, which then acts as a nucleating site for further adsorbate molecules to adsorb and grow into a cluster. This is the clustering mechanism, that has been reported in the literature (for example, Cassel [19]). In the case of highly graphitised carbons, explanations of the observed isotherms based on a high concentration of narrow pores can clearly be ruled out, nevertheless these adsorbents exhibit strong water uptake [8] in the form of type III isotherms. Graphitisation at extremely high temperature (approaching 3000 K) destroys or removes most functional groups as well as increasing particle size and reducing surface area per unit mass. However, the very large number of edge sites per particle is likely to ensure that residual electrostatic charge and breaks in the basal planes will be present at the edges. Although there are reports stating that highly graphitized carbon blacks have no oxygen-containing groups on the surface, because they are decomposed at high temperatures, evidence suggests that a small quantity of these groups remains even after graphitization at high temperature [17,16,113,41,101,111].

Thus it is clear that there are two distinct groups of sites for adsorption on the surface of *GTCB*: (1) the basal plane and (2) the defects and the functional groups. In this paper, we analyse the extensive experimental data for a number of adsorptives to show the interplay between molecular layering and clustering (that are commonly known in the literature), and an intermediate state between these two extremes which we introduce as a previously unrecognised phenomenon: spill-over in physical adsorption. We discuss argon, nitrogen, carbon dioxide, methanol, ammonia and water as adsorptives to cover a range of different hydrogen bond strengths in the order: argon, nitrogen $\ll$ carbon dioxide $\ll$ methanol < ammonia < water.

Argon and nitrogen are chosen to demonstrate the dominance of the fluid-basal plane interaction as one extreme, and water to show the dominance of the functional group at the other. The adsorptives with intermediate electrostatic strength (methanol and ammonia) exemplify the spill-over phenomenon.

We shall use two theoretical tools to study the behaviour of adsorption for these gases. The first is the Henry law constant, which is a measure of the strength of the affinity between an adsorbate molecule and the strongest sites on the surface. This helps to distinguish between the molecule-basal plane interaction and the interaction of a molecule with strong sites. For solids in general, the energy of adsorption sites can be widely distributed, and complications can arise because of uncertainties about the spatial arrangement of these sites. This is outside the scope of this paper. The second tool we use to analyse adsorption on *GTCB* is Monte Carlo simulation over the region of monolayer coverage and beyond. This gives a direct insight into the way in which the cohesive forces between adsorbate molecules order molecular clustering.

Gases adsorbed on the very homogeneous basal plane of *GTCB* are expected to be mobile, while adsorption on defects and/or functional groups is localised. Those gases that do not interact specifically with strong sites will adsorb on the basal plane according to a molecular layering mechanism and, at zero loading, we can quantify them with the theoretical Henry constant and isosteric heat [28]. On the other hand, for adsorptives that form associating fluids, adsorption on functional groups dominates the value of the Henry constant. Once a gas-functional group complex has been formed it acts as an anchor for further adsorption through co-operative hydrogen bonding.

Chemical heterogeneities [45], often as functional groups attached to the graphene surface, [11,60,55,56,69] have been invoked as an explanation for the experimental observations of water (and other associating fluids) adsorption on carbon material. However, theoretical considerations suggest that attachment to the surface of the basal plane is improbable, and that the dangling bonds at edge sites, leading to localised charge density are a more probable location for functional groups [64–68], or indeed it is possible that the edge charges alone are sufficient to nucleate water adsorption [71,97,80].

2. Theory

The development of a theory for the Henry constant was described in detail in Do et al. [28] and here we briefly present its features for a solid composed of a basal plane and functional groups (together with defects at the edges to form strong sites) attached to the edges of the graphene layers.

2.1. Adsorbate potential

Argon is modelled as a simple Lennard-Jones (LJ) molecule. Its collision diameter and reduced well depth are 0.3405 nm and 119.8 K, respectively. The intermolecular potential energy of interaction of the weakly polar nitrogen is described by the TraPPE model, which has two LJ sites and three electrostatic sites [87]: the collision diameter and reduced well depth for the nitrogen model are 0.331 nm and 36 K, respectively. One positive charge (0.964e) was placed at the centre of the molecular axis joining the centres of nitrogen atoms and two symmetric negative charges (−0.482e) on two nitrogen atoms at a bond length of 0.11 nm. For carbon dioxide, we used the TraPPE model [87], which has three LJ sites and three fixed partial charges. The C=O bond length is 0.116 nm, and the collision diameter, the reduced well depth of