



Adsorption of methanol on highly graphitized thermal carbon black effects of the configuration of functional groups and their interspacing



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ABSTRACT

Adsorption of methanol on a carbon black has been studied to investigate the effects of the separation distance and orientation of two functional groups on the adsorption isotherm and the isosteric heat. Monte Carlo simulation was carried out to study methanol adsorption on a graphene surface with two hydroxyl groups arranged in three different orientations: (1) outward, (2) co-directional, and (3) inward. Depending on the orientation and the spacing, the isosteric heat at zero loading is either greater or less than the heat of condensation, highlighting the importance of the interplay between the spacing and the orientation. As the loading is increased to the stage where the functional groups have been covered, methanol begins to adsorb on the graphite surface because of the methyl group-graphite interaction and the large surface area of graphite. At higher loadings adsorption proceeds by molecular layering on the graphite surface, and the isosteric heat approaches the heat of condensation, implying that the multi-layered methanol has a structure similar to the bulk fluid. The simulation results for the isotherm and for the isosteric heat versus loading are in agreement with experimental data for methanol on Carbopack F samples.

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1. Introduction

Physical adsorption of polar molecules on graphitized thermal carbon black (GTCB) has been extensively studied experimentally and theoretically [1–14] because understanding the intrinsic interaction between a polar adsorbate and a graphitic surface is of fundamental importance in optimising the design of mixture adsorption involving polar fluids on carbon adsorbents [15,16].

Experimental studies of adsorption of polar species, including water, ammonia, methanol and ethanol, on graphite have been reported [1,7–12]. The experimental isosteric heat at zero loading can be either higher or lower than the heat of condensation, λ , and the isosteric heat was found to approach λ at high loadings. As an example we consider the experimental data for water adsorption

on carbon black measured by Miura and Morimoto [8–10]. These authors varied the surface functional group by heating the parent carbon black at 400, 700, and 1000 °C, and found that the isosteric heat at zero loading of the sample treated at the highest temperature was lower than λ but that of the other two samples was greater than λ . This is evidence of the effect of modifying the concentration of the functional groups [17–20] which will be lower when the carbon is heated to a higher temperature. Several papers have reported studies of both non-polar and polar adsorbates on carbonaceous materials with various surface functionalities, including polar groups and metal-doping [21–24] [25,26]; a general result is that the adsorbed amount increases when functional groups are introduced.

Not only is the concentration a critical factor, but the configuration of adjacent functional groups also plays an important role in the directional hydrogen bonding between them and the polar molecules. Different types of functional group (for example carbonyl, hydroxyl and carboxyl) may be present in real materials [27,28], and they do not have a regular structure; therefore, it is not

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possible to make a precise specification for the contributions from concentration, and type of functional group. The aim of this paper is to assess the magnitude and relative importance of these contributions, using molecular simulation, which provides us with microscopic details of the adsorption mechanism.

The simulation results are supported by the experimental data on Carbo-pack F (GTCB) in both pristine and reduced forms.

2. Theory and experimental method

2.1. Experimental method

A highly graphitized carbon black, Carbo-pack F (supplied by Supelco, USA) was used as adsorbent. It was reduced under hydrogen to decrease the concentration of oxygen containing groups. Details of the treatment have been reported elsewhere [12,29]. Methanol adsorption was measured at 283 K, 293 K, and 298 K using a high resolution volumetric adsorption apparatus (BELSORP-max, Microtrac BEL). Before each measurement, the solid was degassed at 473 K for 5 h under vacuum (<0.1 mPa) to remove any impurities.

2.2. Fluid potential model

The criterion for choosing the intermolecular potential model was that it must be able to reproduce the vapour-liquid equilibrium accurately. The TraPPE-UA models [30], meet this requirement, and the relevant molecular parameters are listed in Table 1. This potential model was shown to give a good description of methanol adsorption at various temperatures on Carbo-pack F obtained from experimental work [31]. Therefore, the same choices of energy potentials are used in the present work.

For a polyatomic molecule with M site centres, the potential energy of interaction between a site a on a molecule i with a site b on a molecule j was calculated from the following LJ 12–6 equation:

$$U_{ij}^{(a,b)} = \sum_{a=1}^M \sum_{b=1}^M 4\epsilon_{ij}^{(a,b)} \left[\left(\frac{\sigma_{ij}^{(a,b)}}{r_{ij}^{(a,b)}} \right)^{12} - \left(\frac{\sigma_{ij}^{(a,b)}}{r_{ij}^{(a,b)}} \right)^6 \right] \quad (1)$$

where $r_{ij}^{(a,b)}$ is the separation distance between the LJ site a on molecule i and the LJ site b on molecule j , $\sigma_{ij}^{(a,b)}$ and $\epsilon_{ij}^{(a,b)}$ are the cross collision diameter and the cross well-depth of the interaction energy, respectively, and are calculated from the Lorentz–Berthelot mixing rules.

The interaction energy due to the electrostatic force between a charge α on a molecule i and a charge β on a molecule j were calculated from the Coulomb law of electrostatic interaction

$$U_{q;i;j}^{(\alpha,\beta)} = \sum_{\alpha=1}^{M_q} \sum_{\beta=1}^{M_q} \frac{1}{4\pi\epsilon_0} \frac{q_i^\alpha q_j^\beta}{r_{ij}^{(\alpha,\beta)}} \quad (2)$$

where M_q is the number of charges on the molecule, ϵ_0 is the permittivity of free space [$\epsilon_0 = 10^7/(4\pi c^2) = 8.8543 \times 10^{-12} \text{ C}^2\text{J}^{-1}\text{m}^{-1}$, c is the speed of light], $r_{ij}^{(\alpha,\beta)}$ is the distance between two charges α and β on molecules i and j , respectively, and q_i^α is the value of charge α on molecule i .

2.3. Fluid-basal plane interaction energy

The potential energy between an adsorbate molecule and the graphite surface is calculated from the 10–4–3 Steele equation [32]:

$$U_{i,s} = 2\pi \sum_{a=1}^M \epsilon_i^{(a,s)} \rho_s [\sigma_i^{(a,s)}]^2 \left[\frac{2}{5} \left(\frac{\sigma_i^{(a,s)}}{z_i^a} \right)^{10} - \left(\frac{\sigma_i^{(a,s)}}{z_i^a} \right)^4 - \frac{[\sigma_i^{(a,s)}]^4}{3\Delta (z_i^a + 0.61\Delta)^3} \right] \quad (3)$$

where z_i^a is the distance of site a of molecule i from the graphite surface, $\epsilon_i^{(a,s)}$ and $\sigma_i^{(a,s)}$ are the adsorptive-graphite interaction potential well-depth and collision diameter, respectively (calculated with the Lorentz–Berthelot mixing rule), ρ_s is the surface density of carbon atom in a graphene layer (38.2 nm^{-2}), and Δ is the spacing between two adjacent graphene layers (0.3354 nm). The molecular parameters for a carbon atom in the graphene layer are $\sigma_i^{(s)} = 0.34 \text{ nm}$ and $\epsilon_i^{(s)}/k_B = 28 \text{ K}$.

2.4. Surface functional group potential model

Even after thermal treatment at very high temperature, carbon black retains some functional groups, although their concentration decreases [8,10]. These functional groups are positioned either at the edges of the graphene layers or on the top surface, probably at defects on the surface [5,27,33–36]. The common functional groups are carboxylic, hydroxyl, and carbonyl [20]. Miura and Morimoto [8–10] have shown that heat treatment at 1000°C under vacuum leaves no trace of carboxyl groups but small quantities of carbonyl and hydroxyl groups remain. In this paper we chose two hydroxyl groups (whose molecular parameters [37] are listed in Table 1), positioned on the graphite surface with three different configurations of the hydrogen atoms as shown in Fig. 1: (1) pointing outward, (2) pointing in the same direction (co-directional) and (3) pointing towards each other. The solid-fluid potential energy around the two functional groups is shown as a potential energy surface. Since the collision diameter of the O-atom of the hydroxyl

Table 1
TraPPE-UA potential parameters for methanol and hydroxyl group models.

Fluid/Functional group	x (nm)	y (nm)	z (nm)	o (nm)	δ/k_B (K)	q (e)
Methanol						
CH ₃	0.14300	0	0	0.375	98.0	+0.265
O	0	0	0	0.302	93.0	−0.700
H	−0.02998	0.08961	0	–	–	+0.435
Hydroxyl group						
C _a	0	0	0	–	–	+0.20
O	0	0	0.13640	0.307	78.2	−0.64
H	0	0.08992	0.17002	–	–	+0.44

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