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Effects of temperature on methanol adsorption on functionalized graphite: Saturation of functional groups

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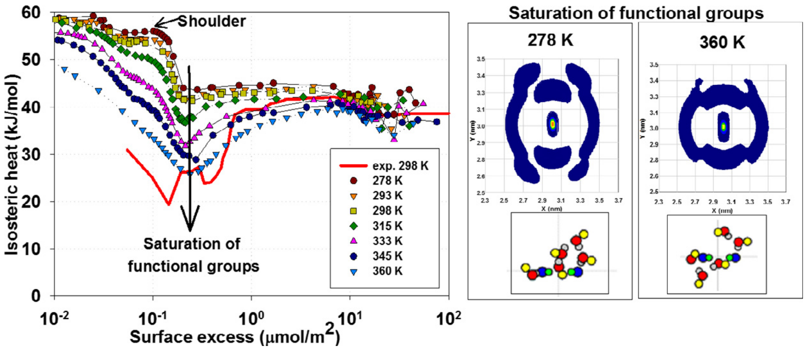
HIGHLIGHTS

- Adsorption of methanol on *GTCB* with two grafted hydroxyl groups was studied.
- Contribution heats, local density and angular distributions were analyzed.
- A minimum in the isosteric heat vs. loading is observed in experiment and simulation.
- The minimum heat is attributed to the saturation of functional groups.
- The minimum heat (the cusp) is more pronounced at higher temperatures.

GRAPHICAL ABSTRACT



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ABSTRACT

Grand Canonical Monte Carlo simulation of methanol adsorption on a graphite model with two hydroxyl groups grafted on the surface has been carried out to investigate the effects of temperature in the range of 278–360 K. The spacing between the OH groups was chosen so that two hydrogen bonds could be formed with the first methanol molecule. In the Henry law region, the isosteric heat at zero loading is greater than the condensation heat. When the loading is increased, the isosteric heat at low temperatures decreases slightly and exhibits a shoulder, which is associated with the formation of a cluster of methanol molecules around one OH group. On further increase in loading, the adsorbate–adsorbate interactions decrease because methanol begins to adsorb on the other OH group, resulting in a sharp decrease in the isosteric heat to a minimum, at which point both OH groups are covered with methanol molecules. At higher temperatures the isosteric heat at zero loading decreases but remains higher than the condensation heat. The shoulder heat is progressively diminished with temperature because methanol molecules are distributed over the two OH groups, due to the entropic effects. Interestingly, the minimum heat still occurs when the functional groups are covered and is even more pronounced at high temperatures.

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1. Introduction

Physical adsorption of non-polar gases is commonly used to characterize the physical properties of porous materials (Joyner Emmett, 1948; Gregg and Sing, 1982; Roberts et al., 1987; Yin et al., 1999; Thommes et al., 2005; Morishige, 2006; Rasmussen et al., 2010; Fan et al., 2011; Reichenbach et al., 2011; Nguyen et al., 2013a, 2013b; Klomkliang et al., 2014, 2015a, 2015b; Alabadi et al., 2015; Zelenka, 2016; Cychosz et al., 2017) because of the absence of electrostatic interactions. Attention has also been paid to the use of polar fluids, such as water and methanol, for the characterization of surface chemistry because of their stronger interactions with functional groups than with the basal plane of carbon (Morimoto and Miura, 1985; Sing et al., 1985; Bandosz et al., 1996; Easton and Machin, 2000; Ohba and Kaneko, 2007; Wongkoblap and Do, 2007; Nguyen et al., 2011; Nguyen et al., 2013a, 2013b; Factorovich et al., 2014; Kaneko, 2015; Zeng et al., 2015; Klomkliang et al., 2016; Kowalczyk et al., 2017; Sarkisov et al., 2017).

Early experiments on the adsorption of water and methanol on carbonaceous materials were made by Pierce and Smith, 1950. Since then there have been many reports in the literature highlighting the important role of polar fluids in characterizing surface chemistry; for example (Morimoto and Miura, 1985, 1986; Zeng et al., 2015; and Salame et al., 1999, Salame Bandosz, 2000). An interesting observation in the adsorption of methanol on graphitized carbon black is the existence of a minimum in the plot of the isosteric heat at the loading where the functional groups are covered with adsorbate molecules (Klomkliang et al., 2016). When the pressure is increased beyond this point, methanol spills over onto the basal plane at sub-monolayer coverage, because there is a strong dispersion force interaction between the methyl group and the basal plane. Beyond this multilayers are formed. However, the part that the configuration of functional groups plays in this phenomenon, has not been elaborated. Recently, Klomkliang et al., 2017 studied the effects on methanol adsorption, of the orientation and separation of two hydroxyl groups mounted on a graphite surface, and showed that orientation modifies the isosteric heat curve over the range of loadings where the functional groups are progressively covered with methanol molecules. The isosteric heat curves were classified into two groups depending on whether the initial isosteric heat was greater or less than the condensation heat. When the two hydroxyl groups are separated by 0.5 nm and their respective hydrogen atoms point toward each other, the isosteric heat at zero loading is highest. This is because two hydrogen bonds can be formed between one methanol molecule and the two hydroxyl groups. When the functional groups are covered, the isosteric heat decreases to a minimum, and we shall refer to this as the saturation of the functional groups.

The behaviour of the isosteric heat versus loading is a result of the interplay of two interactions between methanol and the adsorbent: (1) an electrostatic interaction with the functional groups and (2) a vdW interaction with the graphite. The latter becomes more significant as temperature increases, because of the large area of the graphite surface (entropic effects). In this paper we extend the previous work of Klomkliang et al., 2017 to investigate the microscopic origin of the effects of temperature on the minimum heat.

2. Theory and method

2.1. Fluid-Fluid potential energy

The intermolecular interaction energy between the two adsorbate molecules is calculated as the sum of the pairwise dispersive, electrostatic and repulsive potential energies (Klomkliang et al., 2017). Many potential models for methanol have been proposed in the literature; here we chose the TraPPE-UA model (Chen et al., 2001) because it gives a good description of the vapor-liquid equilibrium, which has been found as the prerequisite to correctly describe adsorption. Its molecular parameters are shown in Table 1.

2.2. Fluid-Solid potential energy

The interaction between an adsorbate molecule and the graphite surface was calculated by the 10-4-3 potential equation (Steele, 1973) for a homogeneous surface, using an atomic surface density of 38.2 nm^{-2}, and a spacing between graphene layers of 0.3354 nm. The molecular parameters for a carbon atom in the adsorbent are $\sigma_i^{(s)} = 0.34$ nm and $\varepsilon_i^{(s)}/k_B = 28$ K.

2.3. Surface functional group potential model

There is no doubt that the surface chemistry of real materials is very complex. Even when two samples are prepared from the same precursor under the same preparation conditions, the identity, concentration and configuration of functional groups may be different. Here we have used a simple model that captures the main physical features of real materials. Hydroxyl groups were chosen as the functional group, because they are found in many carbon materials after heat treatment (Morimoto and Miura, 1985, 1986; Miura and Morimoto, 1991; Klomkliang et al., 2017) and were grafted onto a graphite surface.

We mounted two hydroxyl groups on top of the graphite surface separated by 0.5 nm with their respective hydrogen atoms pointing toward each other (Fig. 1a). With this configuration, two hydrogen bonds can form between one methanol molecule and the two OH groups which gives the maximum heat at zero loading (Klomkliang et al., 2016, 2017). The molecular parameters for the hydroxyl group model (Mooney et al., 1998) are listed in Table 1.

2.4. Grand Canonical Monte Carlo simulation

Grand Canonical Monte Carlo simulation was used to obtain adsorption isotherms and isosteric heats with 5×10^6 cycles in the equilibration and sampling stages. The standard Metropolis scheme (Allen and Tildesley, 1989) was adopted with 1000 insertion, deletion and displacement moves with equal probability for each cycle. The x- and y-dimensions of the graphite surface are 6 nm × 6 nm, the cut-off radius is 3 nm and the graphitic surface is positioned at the bottom ($z = 0$) of the simulation box, and the opposite side in the z-direction is treated as a hard wall. The box height is 8 nm.

The average surface excess density was calculated from the following equation:

$$\Gamma_{avg} = \frac{<N> - \rho_b V_{acc}}{A} \tag{1}$$

where $<N>$ refers to the average number of adsorbate particles, ρ_b is the bulk molecular density, V_{acc} is the accessible pore volume of the bulk phase (Do et al., 2008) and A is the surface area of graphite.

The isosteric heat was calculated from fluctuation theory (Nicholson and Parsonage, 1982)

$$q_{x-y} = \frac{<U_{x-y}><N> - <U_{x-y}N>}{<N^2> - <N><N>} \tag{2}$$

where U_{x-y} is the configuration energy of interaction between x and y entities. The isosteric heat is calculated as the sum of contributions from the following interactions: fluid-fluid (F-F), fluid-