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Alteration of graphene based slit pores and the effect on hydrogen molecular adsorption: A simulation study

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ABSTRACT

In this paper we investigate the effect of graphene pores' alterations on hydrogen molecular adsorption. The alterations take place in three ways: insertions at different amount of oxygen functional groups on the graphene structure, carbon atoms substitution by boron ones, and insertion of three alkyl groups. Totally one graphene pore model, six oxygenated models, two boron substituted models and three alkyl models were constructed. Hydrogen physical adsorption process was simulated via Molecular Dynamics at 77 K. Our results show that there is optimum oxygen and boron percentage for adsorption energy and gravimetric adsorption of hydrogen. On the other hand the insertion of alkyl groups leads to loss of adsorption capacity and reduction of adsorption energy for all three models.

1. Introduction

Hydrogen has been the focus of much research in the past decades, due to its potential use as a clean energy carrier. During this long time, one of the greatest obstacles for its efficient use, is the lack of an ideal storing technology for it. Different methods have been proposed and tested for its storage, such as liquefaction, compression, physical and chemical adsorption, formation of metal hydrides, etc.

All of the above have their disadvantages, namely high costs (liquefaction and metal hydrides), safety concerns (compression), lack of an ideal storage medium (adsorption). The most promising method from the above seems to be physical or chemical adsorption in solid adsorbents. Adsorption has been the subject of numerous investigations, experimental [1–33] and theoretical [34–98]. A wide range of materials have been tried and designed in the quest of the ideal storage medium, the most successful of them being activated carbons (AC) [61–65,68,70], carbon nanotubes (CNT) [64,87,88], metal organic frameworks (MOF) [7,31–33,94–100], and some curved carbonaceous structures [89–93,101,102].

Most of the experimental and theoretical works have been carried out at 77 K, whilst the adsorption of hydrogen should fulfill certain goals at room temperature. The internationally accepted goal for hydrogen gravimetric adsorption is 4.5% w/w for 2015, as set by DOE. The most important factor for a potential adsorbent is the energy of adsorption, which should be high enough to ensure satisfying gravimetric adsorption at high (room) temperatures but low enough to allow for desorption as well.

Most potential adsorbents for physical adsorption exhibit low adsorption energies, in the range 2–7 kJ/mol. The usual strategy for the enhancement of these energies is either the substitution of carbon atoms with metals (mainly) [24,59,64,66,67,73,76–78,91,96,103] or the decoration of the whole structures (with metals) [13,25,26,28,57,58,68,69,73,79,80,85,86,89,92,104], or the insertion of functional groups [29,84], or structural modification [67,105–108]. Such actions have provided some highly optimistic results especially for CNT and MOF.

This work tries to investigate the effect of a series of graphene alterations, namely carbon atoms substitution by boron ones, the insertion of oxygen functional groups at different percentages and the insertion of alkyl groups, on gravimetric adsorption and adsorption energy.

2. Simulations

All simulations and calculations took place in HyperChem, HyperCube Inc. software, on an eight-core server. The modeling work was divided into two parts: the development of the models and the set up and running of physical process simulation.

Our choice for the simulation method was Molecular Dynamics, due to the nature of physical adsorption (no bond breaking or formation). The chosen force field was the popular MM+. We present a swift presentation of the MM+ interaction equations:

Van der Waals interactions are not calculated by the standard 12-6 Lennard–Jones, but rather by:

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$$r_{ij}^{*} = r_i^{*} + r_j^{*}$$

$$\varepsilon_{ij} = \sqrt{\varepsilon_i \varepsilon_j}$$

$$E_{\mathrm{vdW}} = \sum\nolimits_{ij\in \mathrm{vdW}} \varepsilon_{ij}(2.9\times 10^5 \exp(-12.5\rho_{ij}) - 2.25\rho_{ij}^{-6})$$

where $\rho_{ij} = \frac{R_{ij}}{r_{ij}^{*}}$

At short distances [$r_{ij} < 3.311$] the interaction vdW equation is replaced by:

$$E_{\mathrm{vdW}} = 336.176 \sum\nolimits_{ij\in \mathrm{vdW}} \varepsilon_{ij}\varepsilon_{ij}^{-2}$$

The dihedral angle or torsional ener interaction is given by:

$$E_{\mathrm{dihedral}} = \sum_{\mathrm{dihedrals}} \frac{V1}{2}(1-\cos 2\varphi) + \frac{V2}{2}(1-\cos 2\varphi) + \frac{V3}{2}(1 - \cos 2\varphi)$$

The values of $V1$, $V2$, $V3$ [kcal/mol] are supplied as a Supplementary document.

Bond stretch and angle bending cross term are calculated by:

$$E_{\mathrm{stretch-bond}} = 2.51118 \sum_{\mathrm{angles}} K_{\mathrm{sb}}(\theta-\theta_0)_{ijk}[(r-r_0)_{ik} + (r-r_0)_{jk}]$$

If atom j or k is hydrogen, $r-r_0$ equals zero. In any other case, $K_{\mathrm{sb}} = 0.120$ for XR_2 and $K_{\mathrm{sb}} = 0.090$ for XRH (where X is an atom of the first row) and $K_{\mathrm{sb}} = 0.250$ for XR_2 and $K_{\mathrm{sb}} = -0.400$ for XRH (where X is an atom of the second row).

Angle bending energy is given by:

$$E_{\mathrm{bondangle}} = 0.043828 \sum_{\mathrm{angles}} \frac{1}{2} K_\theta(\theta-\theta_0)^2[1 + \mathrm{SF}(\theta-\theta_0)^4]$$

where $\mathrm{SF} = 7\cdot 10^{-8}$.

Dipoles interactions energy is given by:

$$E_{\mathrm{dipole}} = 14.39418\varepsilon \sum_{ij\in \mathrm{polarbonds}} \mu_i\mu_j \left[\frac{\cos x - 3\cos a_i \cos a_j}{R_{ij}^3}\right]$$

where ε is the dielectric constant [assumed to be 1.5 in HyperChem], the angle x is the angle between the two dipole vectors and the angles a_i, a_j are the angles between the R_{ij} vector and the two dipole vectors.

Bond stretching interactions are calculated by:

$$E_{\mathrm{bond}} = 143.88 \sum_{\mathrm{bonds}} \frac{1}{2} K_r(r-r_0)^2 \times [1 + switch(r-r_0, -\frac{1}{3}\mathrm{CS}, -\frac{4}{3}\mathrm{CS})\mathrm{CS}(r-r_0)]$$

The default value for CS is −2.0 in HyperChem.

2.1. Development of the models

Hydrogen was modeled as a cloud of two-centered molecules, based on the MM+ field of molecular mechanics. Three hundred molecules were constructed in a periodic box of $56\times 56\times 56$ Å^3, which is the maximum allowed dimension of the used software. The cloud underwent Molecular Dynamics simulations at 77 K, until the total energy of the system presented no fluctuations. This time period of the simulations was 200 ps. During the process, the total and the kinetic energy were recorded. Multiple MD simulations provided equivalent results. Geometry optimization calculations also provided equivalent results.

The solid models were constructed in two steps. First, normal 5×5, 6×6 and 9×9 graphene sheets were constructed (number of benzoic rings per sheet) using Geometry optimization algorithms and then the substitutions took place. Geometry optimizations were based on Polak–Ribiere algorithm (conjugate gradient) with termination conditions of an RMS gradient 0.01 kcal Å^{-1} mol^{-1}. The used algorithm does not have any effect on the results of the simulation. The chosen algorithm needs logical amount of computational time to reach the asked precision. Other algorithms could be used, in a different kind of investigation, such as conformational search [larger or smaller 'jumps'].

Two models based on carbon substitution with boron were constructed, namely 16B and 32B, standing for the substitution of 16 and 32 carbon atoms on a 6×6 graphene, respectively. The new models underwent an additional geometry optimization process, with the same operating and termination conditions as mentioned above. The finalized structures and their properties are presented in Fig. 1 and Table 1, respectively.

Six oxygenated models were also constructed, as presented in Table 1 and shown in Fig. 2, by inserting different oxygen functional groups that are commonly met in AC, at different amounts in a 9×9 graphene. After the insertion of the oxygen groups, new geometry optimizations were carried out as well. The six models were named oxy1 to oxy6, and their respective oxygen gravimetric ration was set in the range 2.62% (for oxy6) to 8.38% (for oxy1). The oxy models were based on a heavier edition of a slit shaped pore, with three graphene sheets per pore wall.

The final three models (named $R1$, $R2$ and $R3$) used in this investigation resulted from the insertion of alkyls $-CH_3$, $-CH_2CH_3$ and $-CH_2CH_2CH_3$ on a 5×5 graphene sheet, in the way depicted in Fig. 3. Properties also reported in Table 1.

All twelve models were constructed under the slit pore assumption. The oxy models' walls were created by setting three parallel graphenes at 3.34 Å apart. For all models, a slit shaped pore of 7 Å was used, for comparison reasons with our previous work.

2.2. Adsorption simulations of hydrogen molecular adsorption on the altered graphene based slit pore models, at 77 K

Initially, the two systems (hydrogen cloud and a solid model) were merged into a new one, inside the same periodic box. Any hydrogen molecules that happened to be in a place inside the solid or too close to it were removed from the box. Possible presence of these molecules would lead to system explosion due to extremely high temperatures and kinetic energies.

During the MD simulations only the hydrogen molecules were allowed to move, in the stable environment of the solid. The solid models are used to create the potential energy surface (PES) of the system. The MD simulations were set up as following: the run time was set to 900 ps, which proved to be more than enough for the completion of the process. When equilibrium was achieved the simulation was terminated. The temperature was set constant at 77 K with a bath relaxation time of 0.01 ps. The MM+ field (molecular mechanics) was used throughout the simulations. Energy and its major components were recorded and graphed during the simulations. The used potential is the Lennard–Jones 12–6 potential. Hydrogen molecules are depicted as two-centered molecules.

MD simulations provide a specific advantage compared to MC ones: MD simulations provide 'real time' depiction of the physical process, in contrast to MC which provides statistical snapshots. This is important when you want to clarify a process mechanism, as in the present case.

The adsorbed quantity, the adsorption pressures, the adsorption energies were all calculated at the end of the simulations using actual calculations [no models, empirical or semi-empirical], providing high accuracy results. To be explicit:

Adsorption quantity was measured from the actual number of hydrogen molecules present in the interior of the models' pores. Adsorption energy was calculated as the difference [E[solid model + adsorbed molecules] − E[solid model] − E[initial hydrogen