

# The energetics of hydrogen adsorbed in nanoporous carbon: A simulational study

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## Abstract

Porous carbon is considered a promising material to store hydrogen. It can be visualized as a defective relaxed sample and therefore some of the methods we have developed to deal with porous silicon are presently applied to this material. Porous atomic structures with 50% porosity that, due to the size of the supercells fall within the regime of nanoporous carbon, are generated using our procedure. Two pure nanoporous samples of densities  $1.75 \text{ g/cm}^3$  and  $1.31 \text{ g/cm}^3$  were hydrogenated, relaxed and their total energy obtained. The hydrogenated samples were first stripped of the hydrogen atoms and their total energy obtained. Then the original samples were stripped of the carbon atoms and the total energy calculated. From these values the average energy per hydrogen atom was then deduced. We compare our results to CH bond energies; conclusions are drawn.

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## 1. Introduction

In a very recent publication, hydrogen adsorption in different carbon nanostructures was experimentally studied [1]. We had already started simulations to understand the adsorption of hydrogen in nanoporous (np) carbon [2], and the possibility of comparing our conclusions with experiment made the subject much more interesting.

Hydrogen has been considered the fuel of the future, but its use in large scale applications has been hindered because of the difficulty and potential danger in storage technologies. Different techniques have been reviewed [3,4] and some investigated [5] to develop an efficient and economically attractive way to store this element for fuel cell applications, and Refs. [1–5] contain a good number of interesting alternatives. We decided to study the porous

state of carbon since it is well known that activated carbon has been used for a long time as a reactive cleaning agent to get rid of unwanted byproducts in catalytic processes. This behavior merits the study of porous carbon as a potential material to store hydrogen or trap other contaminating substances. Due to its chemical valence carbon appears in a variety of atomic structures and the multiplicity of structures leads to activated carbon, amorphous and single walled nanotubes, nanoporous carbon and graphene nanostructures, to mention a few. Experiment shows that activated carbon with an average pore diameter of  $11.75 \text{ \AA}$  and a pore volume (for pores with radius  $< 6.5 \text{ \AA}$ ) of  $0.75 \text{ cm}^3/\text{g}$  is one of the best carbonaceous materials with a storing capacity of 4.5 wt% at 77 K [1]. Simulations that take into account the contribution of quantum effects to the free energy, suggest that the US Department of Energy specification (6.5% mass ratio and  $62 \text{ kg/m}^3$  volume density) can be approached in nano-graphite platelets (graphene) [5]. It is clear that there is much activity in this area and important results will be obtained in the future, foster-

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ing the use of hydrogen as an answer to an urgently needed clean fuel.

Much discussion exists concerning the way hydrogen is adsorbed in carbon. The experiments reported in Ref. [1] seem to indicate that hydrogen is physisorbed (physically adsorbed) rather than chemisorbed (chemically bound) which makes it more readily available by heating the carbon samples, but also more unstable. They argue that the process responsible for hydrogen adsorption in porous carbon materials is physisorption, which is due to weak van der Waals forces between adsorbate and adsorbent and that chemisorbed hydrogen would require more than ten times the enthalpy of adsorption observed. Also, measurements indicate that there is an occupancy of one hydrogen molecule per 17.5 Å of carbon surface which corresponds to a reticular distance of 4.5 Å between hydrogen molecules on the carbon surface [1].

Theoretical calculations indicate that hydrogen adsorption in SWCN is favored in small micropores [6,7] whereas experiment indicates that carbon materials ideal for hydrogen storage should possess a high microporosity with a small pore dimension.

It appears then that although physisorption seems to be the preferred adsorption process, a pore-size dependence

may alter the incorporation of hydrogen in porous carbon affecting the efficiency of the process. For that reason we decided to undertake a systematic simulational study of hydrogen adsorption in nanoporous carbon. We are here reporting a study of the hydrogenation of two supercells originally with 512 atoms, where a pore was carved converting them into 50% porous supercells (256 atoms). Two densities were considered, 1.31 and 1.75 g/cm<sup>3</sup>.

## 2. Results

Carbon displays a rich variety of bond types that makes it very versatile and these bonds lead to structures of molecules or solids not encountered in other elements belonging to group IV of the Periodic Table; therefore porous carbon should manifest some of this richness in structure. Porous carbon can be visualized as a defective relaxed sample and therefore some of the methods we have developed to deal with porous silicon can be applied to this material [8]. Using these techniques we first constructed a cubic supercell with 512 atoms for two different densities, one high, diamond-like (3.5 g/cm<sup>3</sup>) density and another low, graphite-like (2.62 g/cm<sup>3</sup>) density. Next we carved a pore by removing 256 atoms from within the sample in a ran-

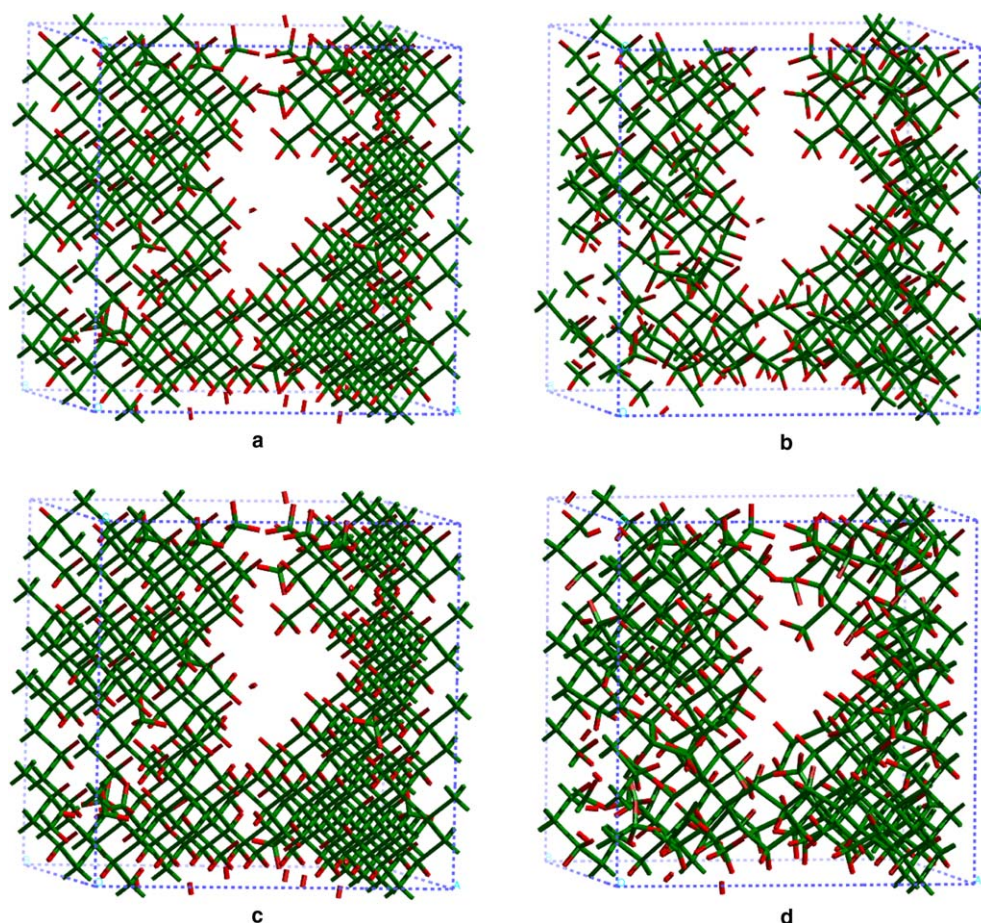


Fig. 1. Porous samples of hydrogenated carbon with 50% porosity: (a) 'crystalline', with a density of 1.31 g/cm<sup>3</sup> before hydrogenation; (b) relaxed, with a density of 1.31 g/cm<sup>3</sup> before hydrogenation; (c) 'crystalline', with a density of 1.75 g/cm<sup>3</sup> before hydrogenation and (d) relaxed, with a density of 1.75 g/cm<sup>3</sup> before hydrogenation.

dom manner creating porous atomic structures with a 50% porosity and a pore diameter of  $\approx 14$  Å for the low density structure and  $\approx 10$  Å for the high density structure, that, due to the size of the supercells, fall within the regime of nanoporous carbon. Two pure nanoporous ‘crystalline’ samples of densities  $1.31 \text{ g/cm}^3$  and  $1.75 \text{ g/cm}^3$  were hydrogen saturated with 266 hydrogen atoms (Fig. 1(a) and (b)), relaxed (Fig. 1(c) and (d)) and the total energy obtained. In order to calculate the average bond energy per hydrogen atom the relaxed hydrogenated samples were stripped of the hydrogen atoms and the total energy of the carbonaceous structure was obtained. Next we removed all the carbon atoms from the hydrogenated samples and the total energy of the hydrogenic structure was also computed.

Once the energies of these three different structures are known the average bonding energy per hydrogen atom can be obtained. For these relaxations and single point energy calculations a Harris functional based code known as Fast Structure SimAnn [9] (fast for short) was used.

Radial distribution functions (RDFs), total and partial, were also computed for both densities of the hydrogenated supercells in order to see the feasibility of our method to describe adsorption of hydrogen (Figs. 2 and 3). It is clear that an analysis of the position of the main peaks in the RDFs can give us information concerning the location of the atoms with respect to one another, and in particular the position of hydrogen with respect to carbon. Since

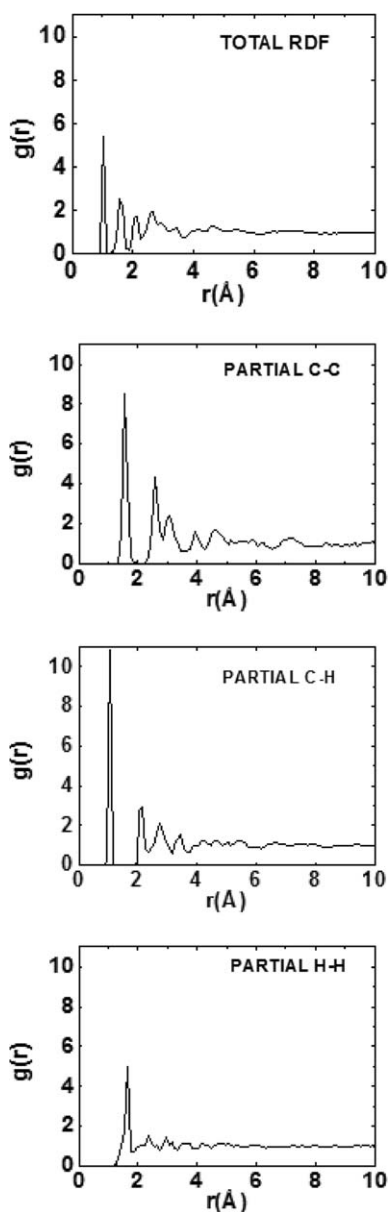


Fig. 2. Total and partial RDFs for the relaxed porous sample of hydrogenated carbon with a density of  $1.31 \text{ g/cm}^3$  before hydrogenation. No obvious sign of hydrogen physisorbed is detected.

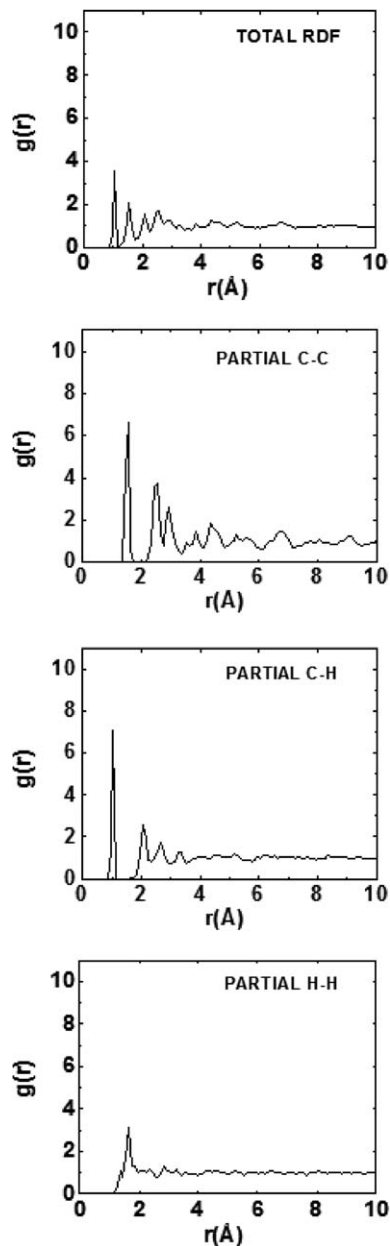


Fig. 3. Total and partial RDFs for the relaxed porous sample of hydrogenated carbon with a density of  $1.75 \text{ g/cm}^3$  before hydrogenation. No obvious sign of hydrogen physisorbed is detected.

chemisorption is essentially due to chemical bonding this position should be closer to the C–H distances in chemical compounds. On the contrary, if adsorption is due to physisorption then the distance C–H should be larger than for chemisorption.

### 3. Discussion

In this work, the calculations are carried out at 0 K and therefore do not include possible restructuring of the hydrogenated carbon supercells due to thermal effects. The effect of temperature is the subject of work underway.

As mentioned before, three single-point energy calculations using fast are involved. First we calculate the total energy of the relaxed hydrogenated carbon system; then we remove all the hydrogens and, without altering the geometry of the system, we calculate the total energy of the carbons. Finally, we remove the carbons only and calculate the total energy of the hydrogens without altering their positions. Then the average energy of the hydrogens bonded to the carbons can be obtained by subtracting both the total energy of the hydrogen system and of the carbon system from the total energy of the complete system. To obtain the average bonding energy of a hydrogen to a carbon we divide the result by the number of hydrogens. The energies per hydrogen atom are 2.74 eV for the sample with high density (1.75 g/cm<sup>3</sup>) and 3.10 eV for the sample with low density (1.31 g/cm<sup>3</sup>). By comparing these results to typical values reported in textbooks (4.26 eV in Ref. [10]) one can see that we obtain numbers below the normal C–H bond energies. Since energy differences are involved in our procedure, our present results should be close to the real values expected, and therefore they indicate that because of the way the porous structures were constructed, and because we are at 0 K, chemisorption is the way the hydrogen was adsorbed. This low value may also indicate that not all hydrogens are chemisorbed.

The RDFs may give us an answer to the last possibility [11], namely, that some hydrogens are physisorbed. An analysis of the position of the peaks, Figs. 2 and 3, do not clearly reveal the presence of an important number of hydrogens at typical van der Waals distances from carbon (the graphite interplanar distance is 3.4 Å).

### 4. Conclusions

To summarize, two samples of hydrogenated porous carbon with two different densities, have been analyzed to investigate whether, under the particular conditions considered in this work, the predominant adsorption process for

hydrogen in carbon is physisorption or chemisorption. We find that the average bonding energy C–H obtained is below the typical value reported for C–H bonds in molecules and compounds. An analysis of the RDFs for these systems indicate that there is no clear sign of hydrogens linked to carbons at distances typical of van der Waals forces. We then conclude that because of the way we hydrogenated the porous carbon samples, and because we are doing our calculations at 0 K the predominant type of adsorption is chemisorption. Work is under way to study thermal effects in the adsorption processes.

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