ADSORPTION OF MOLECULAR HYDROGEN ON PURE AND LITHIUM-DOPED CARBON NANOTUBES

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Carbon nanotubes are considered as candidate materials to store hydrogen for onboard automotive applications. A hydrogen storage capacity of 6 weight % is the 2010 target stablished by the Freedom CAR Hydrogen Storage Technical Team to allow for the use of electric cars based on fuel cells equivalent to the present gasoline-powered cars in terms of safety, performance and driving range. Another practical requirement is that hydrogen has to be easily adsorbed and desorbed at room temperature and normal or moderate pressures. However, the experiments of hydrogen adsorption on pure carbon nanotubes and another graphitic materials have shown that the adsorption is very small (2-3 weight % in the most optimistic cases) and is due to hydrogen physisorption on the surface. Thermodynamic estimations [1] indicate that an adsorption binding energy of 300-400 meV per hydrogen molecule is necessary to obtain efficient cyclic adsorption/desorption at room temperature and normal pressures. This binding energy is about 3-4 times larger than typical hydrogen physisorption energies on graphitic materials [1-3], which explains the low hydrogen adsorption on pure carbon nanotubes and another graphitic materials. On the other hand, some experiments have reported an adsorption of 14-20 weight % in Li- and K-doped carbon nanotubes at ambient pressure and moderate temperatures [4].

We have performed Density Functional calculations of the adsorption of molecular hydrogen on single wall carbon nanotubes. The adsorption is weak and molecular physisorption is favorable with respect to dissociative atomic chemisorption. The chemisorption barrier is about 2.5 eV. Physisorption binding energies are about 100 meV/molecule in the most stable configurations. It has been argued that physisorption would be more intense on metallic than on semiconducting nanotubes, but according to the present calculations the physisorption energies are similar. When the nanotube surface is fully covered, with one molecule per graphitic hexagon, the binding energy per molecule decreases for some nanotubes (with respect to the binding energy of an isolated molecule) because repulsive interactions between the adsorbed molecules develop when neighbor molecules are very close to each other. For the same reason, direct adsorption of a single hydrogen layer with coverages of more than one molecule per graphitic hexagon are not possible, even at low temperatures. Adsorption of a second layer (14.3 weight per cent of hydrogen when all the surface is covered) is possible, although the molecules of the outer layer are more weakly bound compared to those of the inner layer. The small binding energies calculated for all the nanotubes and all the configurations and coverages studied indicate that substantial adsorption is only possible at very low temperatures.

Similar calculations have been performed for pentaheptite nanotubes, generated by rolling up a two-dimensional three-fold coordinated carbon network composed of pentagons and heptagons. The results are similar to those obtained for hexagonal carbon

nanotubes: physisorption energies are also about 100 meV/molecule on pentagons, heptagons and other sites of the surface, and the chemisorption barrier is about 2 eV.

Finally, we have performed calculations of the physisorption of molecular hydrogen on Li-doped graphene layers and carbon nanotubes. In the doped systems the lithium atom finds its equilibrium position above the center of carbon hexagons. The binding energy of the hydrogen molecule in the Li-doped systems increases by a factor of 2 with respect to the pure undoped ones. The hydrogen molecule can be physisorbed on top of a Li atom or next to it in a lateral position, and the binding energy increases in both configurations. These results indicate that Li-doping increases the binding energy of molecular hydrogen to graphitic materials, and will then enhance their hydrogen storage capacity, giving qualitative support to the experimental findings.

References:
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Figures:
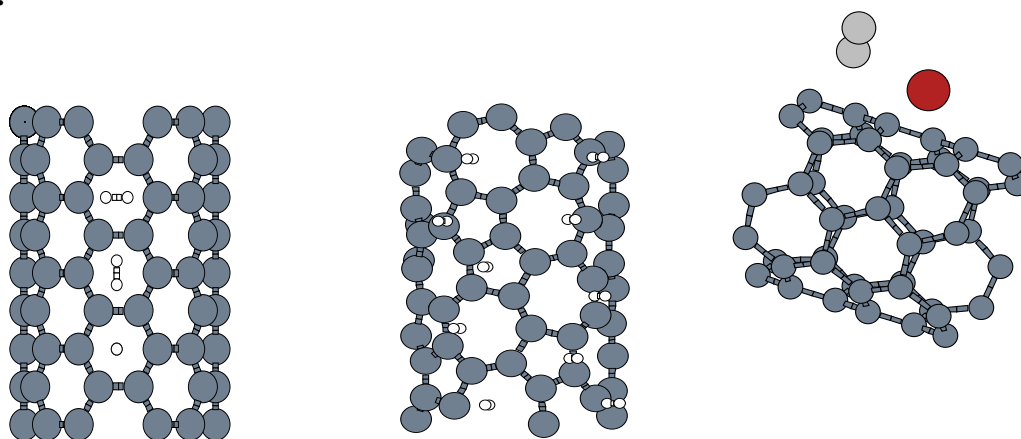
Figure 1 Left panel: Different adsorption configurations for a hydrogen molecule on the external surface of a carbon nanotube. Center panel: Adsorption of molecular hydrogen on the external surface of a pentaheptite carbon nanotube, formed by pentagons and heptagons. Right panel: Adsorption of a hydrogen molecule near a Li impurity adsorbed on the surface of a carbon nanotube.