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IMPROVING HYDROGEN PHYSISORPTION ENERGY USING SWCNTS THROUGH STRUCTURE OPTIMIZATION AND METAL DOPING SUBSTITUTION

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ABSTRACT

The effect of metal doping on the hydrogen physisorption energy of a single walled carbon nanotube (SWCNT) is investigated. Unlike many previous studies that treated metal doping as an ionic or charged element, in this study, lithium and magnesium are doped to an SWCNT as a neutral charged by substituting boron on the SWCNT (Boron substituted SWCNT). Using ab initio electronic structure calculations, the interaction potential energies between hydrogen molecules and adsorbent materials were obtained. The potential energies were then represented in an equation of potential parameters as a function of SWCNT diameters in order to obtain the most precise potential interaction model. Molecular dynamics simulations were performed on a canonical ensemble to analyze hydrogen gas adsorption on the inner and outer surfaces of the SWCNT. The isosteric heat of the physical hydrogen adsorption on the SWCNT was estimated to be 1.6 kcal/mole, decreasing to 0.2 kcal/mole in a saturated surface condition. The hydrogen physisorption energy on SWCNT can be improved by doping lithium and magnesium on Boron substituted SWCNT. Lithium-Boron substituted SWCNT system had a higher energy physisorption that was 3.576 kcal/mole compared with SWCNT 1.057–1.142 kcal/mole. Magnesium-Boron substituted SWCNT system had the highest physisorption energy that was 7.396 kcal/mole. However, since Magnesium-Boron substituted SWCNT system had a heavier adsorbent mass, its physisorption capacity at ambient temperature and a pressure of 120 atm only increased from 1.77 wt% for the undoped SWCNT to 2.812 wt%, while Lithium-Boron substituted SWCNT system reached 4.086 wt%.

Keywords: Adsorption; Hydrogen; Metal Doping; Physisorption energy; SWCNT

1. INTRODUCTION

Two major problems facing world societies today are limited fossil fuel energy resources and environmental pollution. Research and development scientists in this area of technology are currently searching for sustainable and environmentally friendly alternative energy sources (Aceves et al., 2010). The use of hydrogen gas for fuel-cell fuel holds potential for implementation in vehicle transportation technology. Successful implementation of hydrogen fuel-cells in vehicles would mean the realization of the dream of living in carbon pollution-free urban areas (Alhamid et al., 2016).

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Researchers are still encountering various problems in the implementation of fuel-cell fuels in vehicles, one of which is hydrogen storage and distribution. With a very low density under standard conditions for temperature and pressure (STP), hydrogen gas requires a great deal of storage space. Therefore, a number of studies have been devoted to storing high density hydrogen gas effectively and efficiently.

Several options for hydrogen gas storage exist, including high-pressure (Jones, 1924), low temperature tanks or cryogenics (Lin et al., 2009) metal hydride (Mahdizadeh & Goharshadi, 2014), or chemically binding in a covalent or ionic component (Møller & Plesset, 1934). However, these technologies are hampered by safety issues (dangerously high pressure), low storage efficiency (high operational costs for storage technology at low temperatures), and heavy storage systems (metal hydrides have high density).

Various single walled carbon nanotube SWCNTs structures exhibit different hydrogen gas storage performances. Therefore the influence of SWCNT structure on the performance of hydrogen gas storage by physical adsorption was studied in this paper. The energy of hydrogen adsorption on SWCNTs is estimated using first-principle quantum mechanics calculations. Furthermore force-matching method is applied to determine the equilibrium distance between two particles (σ) and the lowest potential energy (ε). These parameters are required to conduct molecular dynamics simulation to investigate the capacity and characteristics of hydrogen gas adsorption on SWCNTs. The similar procedures are conducted to investigate hydrogen physisorption capacity on boron-substituted SWCNT with lithium and magnesium doping.

2. RESEARCH METHODOLOGY

The present research is a theoretical study of hydrogen gas adsorption on an SWCNT using a molecular thermodynamic approach. The theoretical study includes analysis of specific surface area (SSA), estimated adsorption energy calculations ab-initio quantum mechanics, and molecular dynamics simulations of the hydrogen adsorption equilibration process on an SWCNT. The results of this study were analyzed with the developed monolayer adsorption approach and desorption kinetic theory, which is based on the statistical mechanics of molecular dynamics simulations.

2.1. Research Flowchart

As shown in Figure 1, the method for hydrogen storage capacity enhancement using lithium-magnesium doped on Boron substituted SWCNT combines the results from quantum mechanics calculations with classical molecular dynamics simulations. The research begins with some preliminary studies, such as a review of the literature, formulation of the research problem, and a research design concept. To conduct the main research, we prepared hardware and software to support the computation of the molecular dynamics simulation.

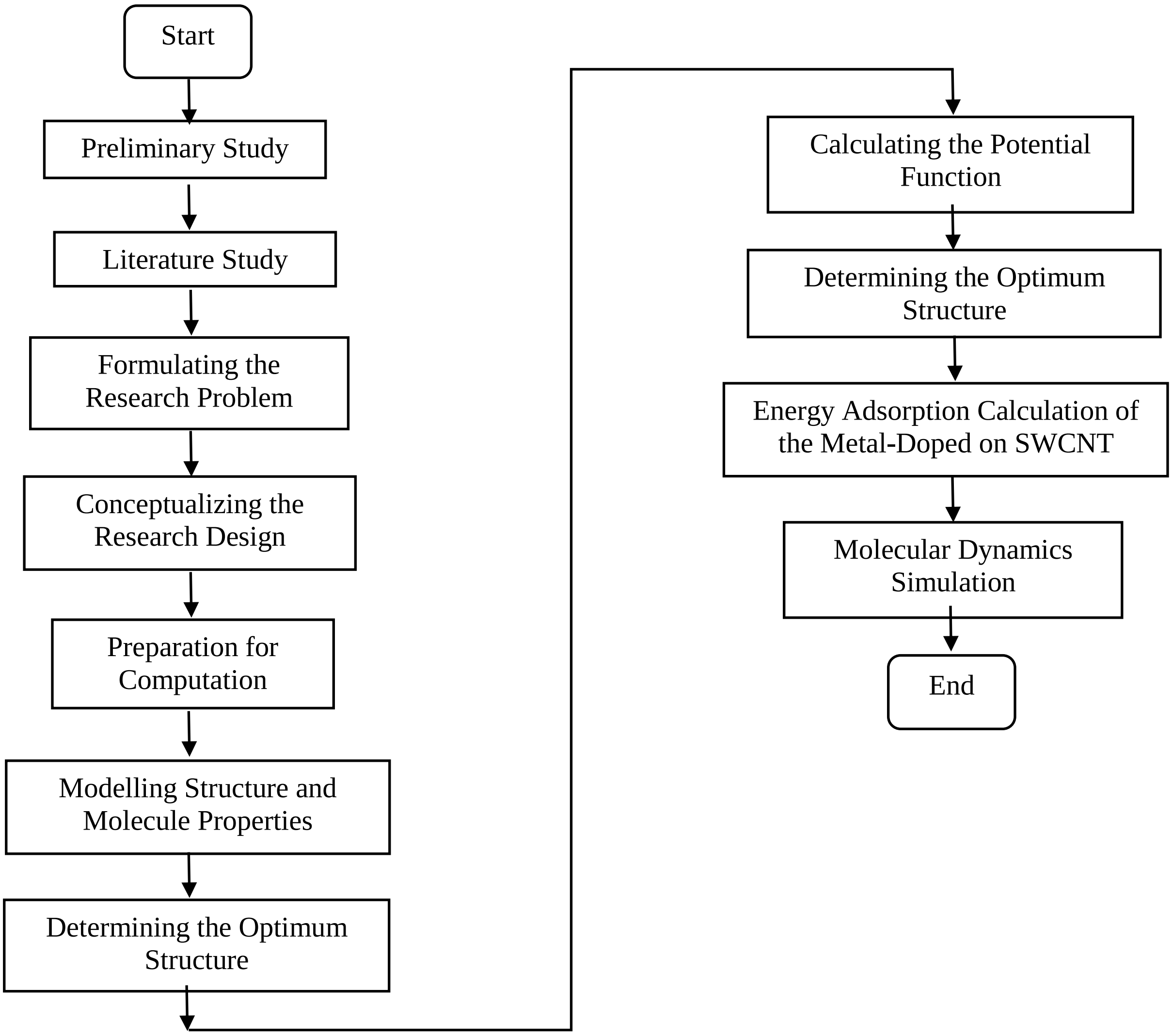


Figure 1 Research flowchart

Adsorbent material models vary based on their characteristics such as chirality, and the diameter and length of the nanotube. The composition and doping ratio of lithium and boron on nanotubes are investigated using density functional theory (DFT) to estimate the hydrogen adsorption energy of those materials. The estimated adsorption energy is used to predict its hydrogen sorption capacity. DFT is used to produce data on the forces acting on the atoms. These data are used to construct more realistic potential functions using a numerical optimization procedure. The potential functions are then used in the molecular dynamics simulation, which is conducted on a larger system containing more atoms and longer simulation times.

2.2. Quantum Mechanics Calculations

The calculation of the interaction energy between molecules using the quantum mechanics theory approach is often referred to as the study of first-principle ab-initio or calculation. Ab-initio is derived from the Latin word meaning "of origin." In other words, ab-initio calculations are those based on the quantum mechanics theory. Ab-initio calculations are the calculation of the electronic structure of a molecule. By estimating the molecular orbital shape, ab-initio calculations can determine the total energy of a molecular system. For the ab-initio calculations in this study, we used Psi4 software, which has been trusted and used in several other studies (Nasruddin et al., 2016a).

The potential interaction energy between molecules can be calculated using the following equation (Nasruddin et al., 2016b):

$$E_{A-B}(r) = E_{(A+B)}(r) - (E_A + E_B) \tag{1}$$

where $E_{A-B}(r)$ is a large potential interaction energy between molecules of A and B at a certain distance r; $E_{(A+B)}(r)$ is the total energy of large systems containing molecules A and B, which interact at a certain distance r; $E_A$is a large total energy system containing only molecule of A; and E_B is a large total energy system containing only molecule of B.

2.3. Force-matching Method

After obtaining the calculation results for the potential interaction energy between hydrogen molecules and the molecules (carbon and hydrogen) in the SWCNT, a force-matching method is applied to obtain an accurate potential model for implementation in the molecular dynamics simulations (Plimpton, 1995). Simplified hydrogen molecule united-atom models, also called isotropic models, have been previously used (Sakintuna, 2007). The potential function model used is the Lennard-Jones potential (Turney et al., 2012), as in the following equation:

$$\Delta E(r) = 4\varepsilon\left\{\left(\frac{\sigma}{r}\right)^{12} - \left(\frac{\sigma}{r}\right)^{6}\right\} \tag{2}$$

where, ΔE (r) is the potential interaction energy at distance r; ε is the lowest energy potential; σ is the distance at which the potential interaction energy value is equal to zero; and r is the distance between the particles.

The force-matching method is performed by totaling all the interactions in the particle model and matching it to the large value of the potential interaction energy from the ab-initio calculation results. The sum of all interactions in Equation 2 produce yields the total potential interaction energy with can be represented in the following equation (Turney et al., 2012):

$$\Delta E_{total}(r) = 4\varepsilon \sum_{j>i}^{N} \sum_{i=1}^{N-1} \left\{\left(\frac{\sigma}{r}\right)^{12} - \left(\frac{\sigma}{r}\right)^{6}\right\} \tag{3}$$

In isotropic models, the interaction of the hydrogen molecule will ignore the effects of the interaction orientation. This model is not very accurate and will produce different errors at different simulation temperatures. It deals with the basic theory of statistical mechanics— the probability of a particle occupying an energy level, as in the following equation:

$$p(E_i) = \frac{e^{\frac{-E_i}{kT}}}{\sum_{i=1}^{N} e^{\frac{-E_i}{kT}}} \tag{4}$$

Thus, the effects of orientation error are influenced by temperature, so that the potential model should be designed as a function of temperature simulation. However, in the present study, this effect is negligible. Abandonment is still acceptable, given that the level of accuracy of the ab-initio calculations for the interaction energy between hydrogen molecules with SWCNTs is not very high because it only uses an MP2 level method and base-type double-zeta sets (Veziroğlu & Şahi, 2008). Therefore, the potential model is used according to the calculation of the energy interaction on the orientation, and the perpendicular orientation is believed to be the most stable interaction with a deeper potential energy than other orientations. The SWCNT cluster models used in the ab-initio calculations can be simplified by removing a hydrogen atom from each end of the SWCNT model. This is based on the assumption that the contribution of hydrogen atoms to the interaction of the model is too large given the considerable distance of the hydrogen molecule (Zheng et al., 2012).

3. RESULTS AND DISCUSSION

3.1. The Potential Interaction Energy between Hydrogen Gas and SWCNTs

The calculation of the potential interaction energy between molecules of hydrogen gas with SWCNTs was conducted with (5.0), (10.0), (20.0), and (1280.0) SWCNTs; the (1280.0) SWCNT has a structure similar to that of graphene. This shows that the larger the diameter of the SWCNT, the closer its structure is to the structure of graphene.

To illustrate how the curvatures of the SWCNTs affect the potential interaction energy between hydrogen molecules and SWCNTs, isosurface visualization of the highest occupied molecular orbital (HOMO) on the molecular structure of SWCNTs with different diameters are presented in Figures 2 and 3.

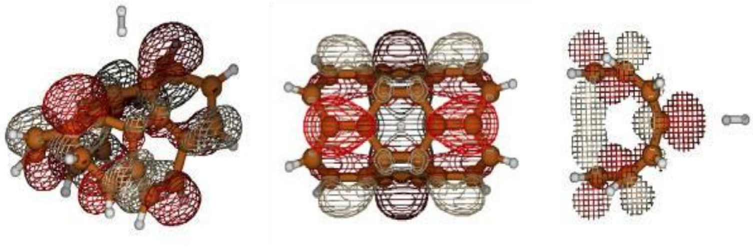


Figure 2 Isosurface (electron density: 0.02 a.u.) for the HOMO on the (5.0) SWCNT model interacting with hydrogen molecules. From left to right: 3-dimensional view, front view, and side view

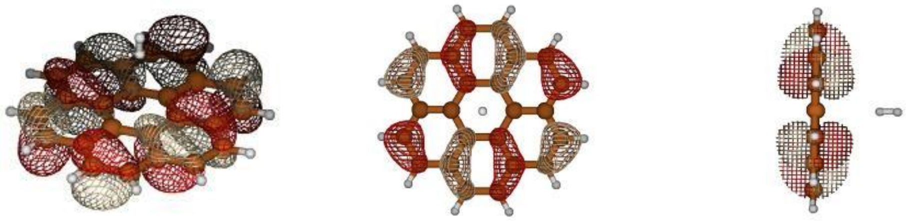
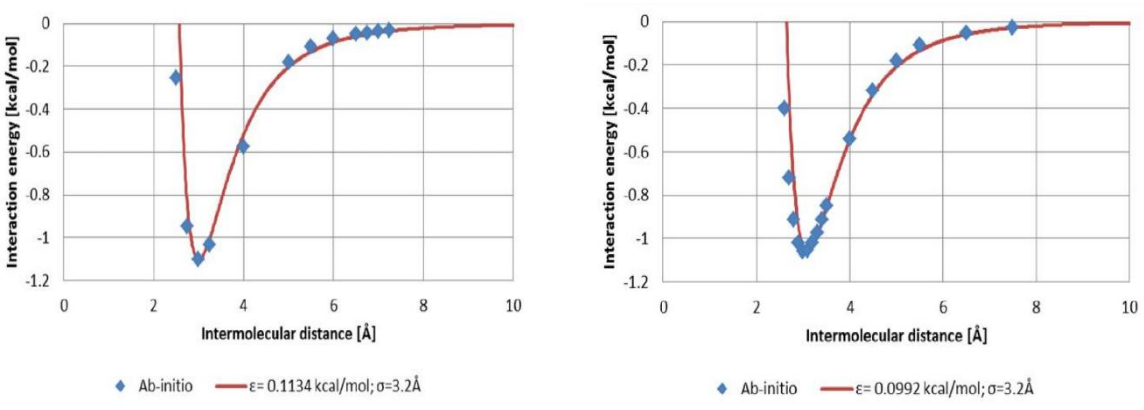


Figure 3 Isosurface (electron density: 0.02 a.u.) for the HOMO on the (1280.0) SWCNT model interacting with hydrogen molecules. From far left to right: looks 3dimensional, front view, and side view

Using Equation 1, the value of the monolayer adsorption potential energy is calculated as a function of the distance between the hydrogen molecules and the walls of the SWCNTs. The results of the ab-initio calculations and force-matching for SWCNTs (5.0) and (10.0) are presented in Figure 4.



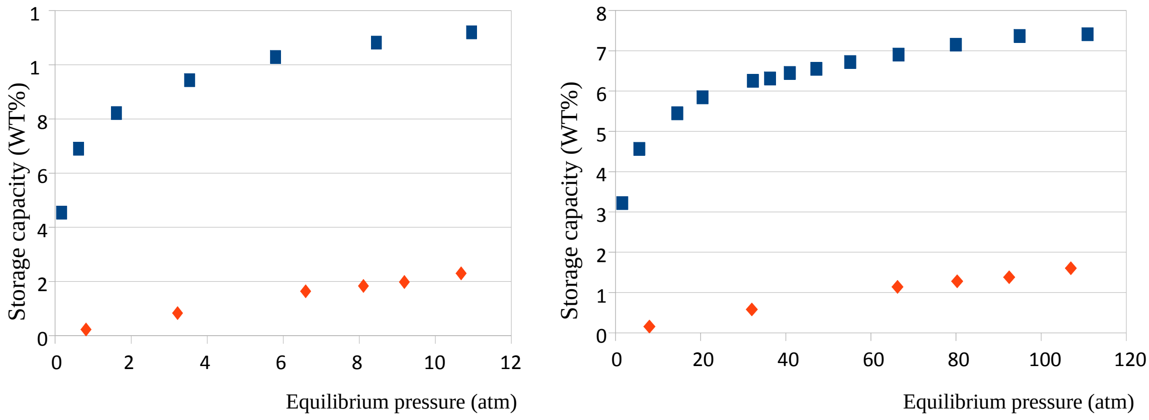
(a) (b)

Figure 4 The results of the ab-initio calculations and force-matching for the interaction between hydrogen molecules and the surface of: (a) the (5.0) SWCNT; and (b) the (10.0) SWCNT

These results indicate that the potential interaction energy between hydrogen molecules is affected by the diameter of the SWCNT, although not significantly; the values ranged from 1.057 to 1.142 kcal/mole. Nevertheless, the influence of the diameter was dominant in the potential parameter values, creating a fairly wide range from 0.0899 to 0.1134 kcal/mole.

3.2. Simulation Results for the Hydrogen Adsorption Capacity of SWCNTs

Using statistical averaging, the simulation results for the adsorption capacities of the various equilibrium pressures are summarized in Figure 5.



(a) (b)

Figure 5 The data capacity of hydrogen adsorption on the function of the equilibrium pressure on: (a) the (5.0) SWCNT; (b) the (10.0) SWCNT; ■ (temperature 77 K); ♦ (temperature 298.15 K)

3.3. Calculation of the Hydrogen Physisorption Energy of the Metal-doped SWCNT

First, the equilibrium distances between lithium or magnesium and the boron-doped SWCNT surface are calculated. For lithium, the most stable position is located at 2 Å above and below the bond of the diborene-like structure. For magnesium, the most stable position is located at 1.9 Å above and below the hollow hexagonal structure of the two diborene-like structures. To calculate the physisorption energy of hydrogen adsorption on the Li-B-SWCNT, the hydrogen molecules are placed above the lithium atom in parallel orientation to the graphene surface (SWCNT with infinitive diameter). The results show that the most stable position for the hydrogen molecule is at 4 Å above the graphene surface or 2 Å above the lithium atom, with a hydrogen physisorption energy of 3.576 kcal/mole.

To calculate the physisorption energy of hydrogen adsorption on the Mg-B-SWCNT, the hydrogen molecules are placed above the magnesium atom in parallel orientation to the graphene surface (SWCNT with infinitive diameter). The results show that the most stable position for the hydrogen molecule is at 3.8 Å above the graphene surface or 1.9 Å above the magnesium atom with a hydrogen physisorption energy of 7.369 kcal/mole. The magnesium-doped SWCNT has a higher physisorption energy than the lithium-doped SWCNT because of the existence of more dispersed electron orbitals, whereas the physisorption energy on the lithium-doped SWCNT is only dominated by the attractive force of the positive partial charge of lithium. Figures 6 and 7 provide illustrations of the molecular orbitals of the lithium-doped and magnesium-doped SWCNTs.

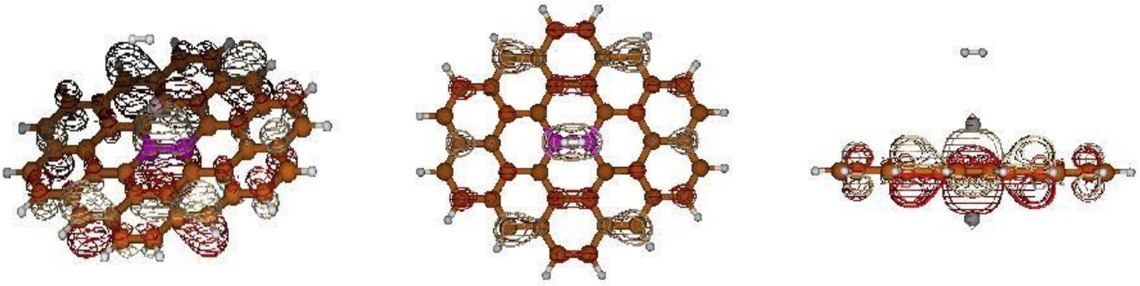


Figure 6 Isosurface (electron density 0.02 a. u.) of the HOMO on the lithium-doped boron-substituted graphene models that interact with hydrogen molecules. From left to right: 3-dimensional view, top view, and side view

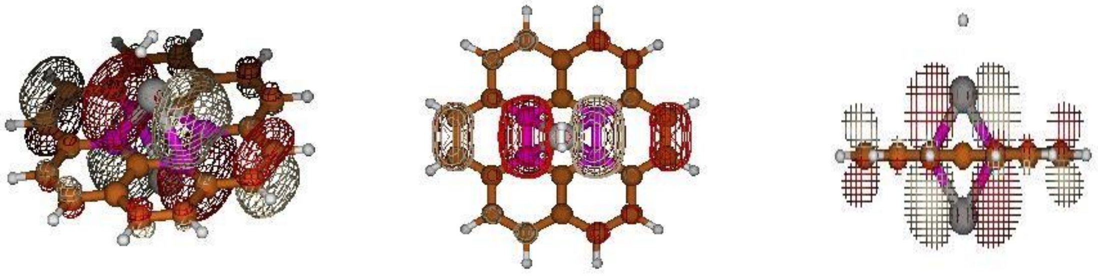


Figure 7 Isosurface (electron density 0.02 a. u.) of the magnesium-doped boron-substituted grapheme models that interact with hydrogen molecules. From left to right: 3-dimensional view, top view, and side view

3.4. Comparison of Hydrogen Adsorption Capacity

The potential parameters of lithium and magnesium are approximated by treating boron similar to carbon with the same potential parameters. The potential parameter between lithium and hydrogen molecules is approximated to be 1.79 Å for σ and 2.932 kcal/mole for ε. The potential parameter between magnesium and hydrogen molecules is approximated to be 1.7 Å for σ and 6.82995 kcal/mole for ε.

To estimate the effect of metal doping on hydrogen adsorption capacity, molecular dynamics simulations are performed in the (10.0) SWCNT at ambient temperature and in the pressure range of 1–120 atm. The results of the molecular dynamics simulations are summarized into isothermal curves for three different adsorbents, as shown in Figure 8.

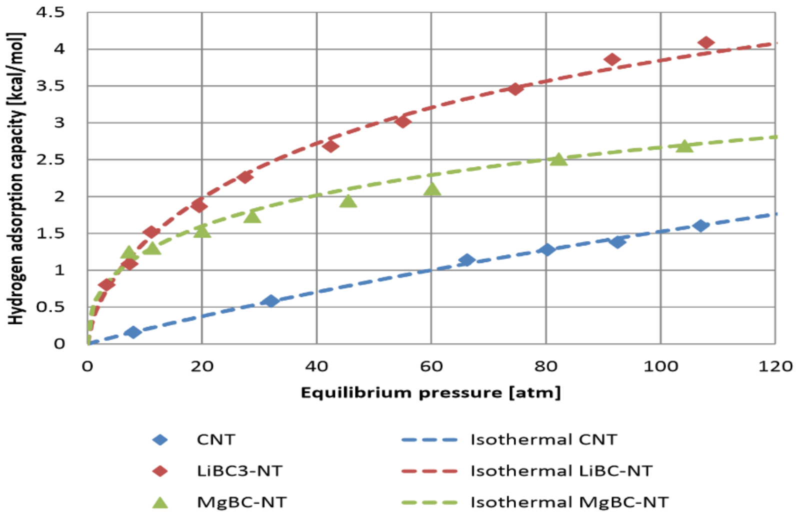


Figure 8 Isothermal curves for hydrogen adsorption on an SWCNT and the lithium/magnesium doped boron SWCNTs

In Figure 8, the molecular dynamics simulations show that even though the magnesium-Boron subtituted SWCNT system has the highest physisorption energy, its hydrogen adsorption capacity is lower than the lithium-doped Boron substituted SWCNT sistem. This is due to the heavier mass of the magnesium atom than lithium.

4. CONCLUSION

Obtained from the results of the calculation for the adsorption energy using ab initio electronic structure, the interaction potential energies between hydrogen molecules and SWCNT were 1.057–1.142 kcal/mole. The adsorption energy generated by smallest diameter (5, 0) SWCNT model is 1.101 kcal/mole. Meanwhile for (10, 0) SWCNT model had a lower adsorption energy of 1.057 kcal/mole and then goes up to 1.142 kcal/mole for graphene with infinity diameter. The physisorption energy of hydrogen was enhanced by lithium or magnesium doping. Lithium enhanced the physisorption energy of hydrogen to 3.576 kcal/mole, whereas magnesium enhanced the physisorption energy to 7.396 kcal/mole. The hydrogen adsorption capacity was increased to 4.08 wt% by lithium doping and to 2.812 wt% by magnesium doping. However, since Magnesium-boron substituted SWCNT has a heavier adsorbent mass, its physisorption capacity at ambient temperature and a pressure of 120 atm only increased from 1.77 wt% to 2.812 wt%, while for lithium-boron substituted SWCNT reached up to 4.086 wt%.

5. ACKNOWLEDGEMENT

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