

## Theoretical comparative study on hydrogen storage of BC<sub>3</sub> and carbon nanotubes

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**Abstract.** We have applied the grand canonical Monte Carlo method (GCMC) to investigate the physisorption properties of hydrogen storage in BC<sub>3</sub> and carbon nanotubes, respectively. Some important physical amounts under different temperatures and pressures, such as adsorption isotherms and adsorption amounts were studied. The results show that, the physisorption properties of BC<sub>3</sub> nanotube are superior to those of carbon nanotube at all conditions. The main reasons causing such different results between them were analyzed from the interaction energies among nanotubes and H<sub>2</sub> molecules.

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## 1 Introduction

Hydrogen energy is a reproducible and clean energy source, which has attracted extensive attentions in recent years. The efficient storage of hydrogen is significant for its utilization as the future energy carrier; however, it is also the bottleneck for the development of hydrogen energy. The main reason is that the amounts of hydrogen stored are not satisfied with the requirement of the development of hydrogen energy [1-3]. Therefore, some researchers are still exploring new hydrogen storage materials.

Since the discovery of carbon nanotubes (CNTs) by Iijima in 1991[4], a large number of experimental and theoretical studies have been devoted in order to explore hydrogen storage of CNTs due to its large specific area and tubular structure[5,6]. However, data on the hydrogen storage capacity of CNTs are still in dispute because some experiments

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are not reproducible. The current point is that the hydrogen storage capacity of CNTs is small at room temperatures and moderate pressures and that CNTs are not superior to other carbon nanostructures for hydrogen storage[7]. The discovery of CNTs sets off a tremendous explosion for obtaining novel one-dimensional nanostructures [4]. Shortly, some new nanotubes originating from hexagonal compounds, such as BC<sub>3</sub> and BN [5,6], have been proposed. Their geometries, electronic properties and possibilities for technical applications have been investigated theoretically [8,9]. However, to our knowledge, the hydrogen storage in BC<sub>3</sub> nanotube is an open question. Therefore, we investigated the hydrogen adsorption in this nanotube using density functional theory (DFT) recently [10], and the physisorption of molecular hydrogen in BC<sub>3</sub> nanotube including both external and internal adsorption sites was compared with CNTs. The studied results show that BC<sub>3</sub> nanotube may be a better candidate for hydrogen storage than CNTs.

Based on this, the physisorption process of H<sub>2</sub> in BC<sub>3</sub> nanotube in different temperatures and pressures is investigated quantitatively using grand canonical Monte Carlo (GCMC) method. Some important physical amounts, such as adsorption isotherms under different conditions and the total interaction energies of BC<sub>3</sub>(8,0)/C(8,0) nanotube and H<sub>2</sub> molecules were studied in this paper. The GCMC simulations show that the physisorption amounts of H<sub>2</sub> in BC<sub>3</sub> nanotube are superior to those of CNTs. Some reasonable explanations causing different behavior of hydrogen storage in these two nanotubes are given. These results may help experimental explorations of new possible hydrogen storage materials.

## 2 Grand canonical Monte Carlo (GCMC) method

For the hydrogen adsorption on BC<sub>3</sub> and carbon nanotubes, we have used compass force field. It is the ab initio forcefield that enables accurate and simultaneous prediction of structural, conformational, vibrational, and thermophysical properties for a broad range of molecules in isolation and in condensed phases, and under a wide range of conditions of temperature and pressure[11]. Because the nanotube host has been treated as a rigid structure, with fixed atom positions obtained from the minimized structure, only the non-bond interaction energy is calculated for hydrogen adsorption. The total host-guest interaction energy consists of the sum of a long-rang coulombic term and a short-range van der Waals (vdW) term

$$E_{total} = E_{cou} + E_{vdW}, \quad (1)$$

$$E_{cou} = \sum_i \sum_{j>1} \frac{q_i q_j}{r_{ij}}, \quad (2)$$

where  $q_i$  and  $q_j$  are the net atomic charges of the  $i$ th and  $j$ th atoms, respectively, and  $r_{ij}$  is the distance between the  $i$ th and  $j$ th atoms. Since the electrostatic interaction is long-range interaction and the model systems are periodic, Ewald sums are used for  $E_{cou}$ . The

Lennard-Jones potential energy function has been used to describe the vdW interactions as follows

$$E_{vdW} = \sum_i \sum_{j>i} D_{ij} \{ (\sigma_{ij}/r_{ij})^{12} - 2(\sigma_{ij}/r_{ij})^6 \}, \quad (3)$$

where  $D_{ij}$  and  $\sigma_{ij}$  are the LJ potential parameters and  $r_{ij}$  is the interaction distance between the  $i$ th and  $j$ th atoms. The geometric combination rule is applied for the vdW interaction parameters.

Because the GCMC method[12] is the most common technique for predicting the microporous materials adsorption equilibria with fixed chemical potential and temperature, we carried out the GCMC method assuming the structure of host nanotube to be rigid during the sorption process. We don't treat the possibility of cation migration, although some redistribution of cations can be occurred by hydrogen adsorption. Only the sorbate hydrogen molecules are placed at random locations inside the nanotube cavity. The metropolis scheme is used at a constant pressure and temperature. Any random molecular configuration is accepted with a probability that decreases exponentially with total energy between the nanotube and the molecular hydrogen. The periodic boundary conditions are applied in all three dimensions. All average energies were obtained over  $2 \times 10^7$  steps. In order to describe the interactions between nanotube and  $H_2$  molecule, we use spline cut-off to describe van der Waals interaction and Ewald summation to describe electrostatic interaction.

### 3 Results and discussion

#### 3.1 The adsorption of $H_2$ molecules in CNTs

In order to validate the feasibility of compass forcefield, the physisorption process of  $H_2$  molecules in C(7,7) was simulated. We obtained the relationships of total interaction energies and total adsorption amounts of C(7,7) and  $H_2$  molecules with simulation times, as shown in Fig. 1. From this figure, we can see that, with the increase of simulation times, the number of adsorbed hydrogen molecules comes to equilibrium. When simulation times reach  $2 \times 10^6$  steps, this system is basically balanceable. The 4.32  $H_2$  molecules were adsorbed in each cell and the total interaction energy of this system is -4.56 KJ/mol. Other nanotubes in different pressures and temperatures have the similar trends. Therefore,  $1 \times 10^7$  steps used in this study may ensure that all systems can reach equilibrium. And the simulated results are correct and reliable.

In a given temperature, by varying pressures of the system, we may obtain the relationships between physisorption amounts of hydrogen and pressure, i.e. adsorption isotherm. The adsorption isotherms of C(7,7) in a broad range of temperature (77 K-300 K) are shown in Fig. 2. We can see that the adsorption amounts increase and saturate with the increase of pressure and the decrease of temperature. Compared our results with those which were investigated by Cabria *et al.*[13] using quantum-thermodynamic model method, our calculated hydrogen adsorption amounts are 2.38wt% and 0.59wt% at 77 K

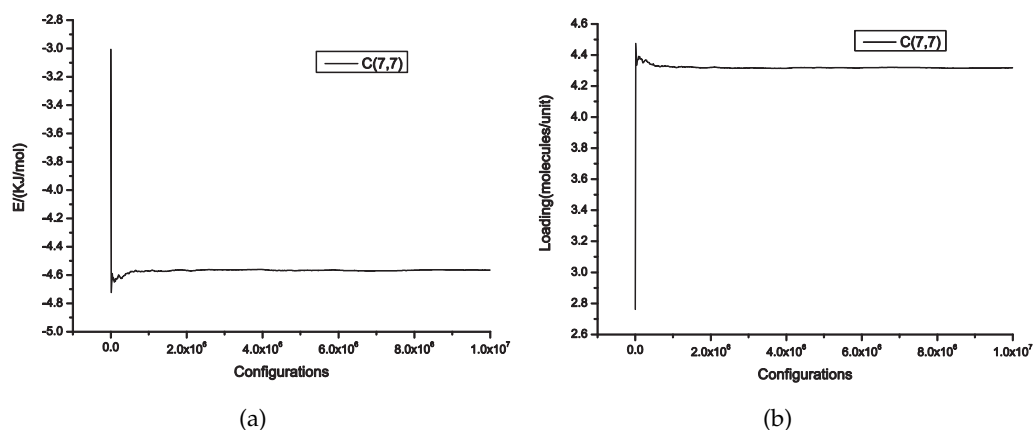


Figure 1: (a) The relationship of total interaction energies of C(7,7) and H<sub>2</sub> molecule with simulation times; (b) The relationship of total adsorption amounts of H<sub>2</sub> molecule in C(7,7) nanotube with simulation times.

and 300 K with a pressure of 10 MPa, which are consistent with 2.5wt% and 0.6wt% in Ref.[13]. Thus the forcefield parameters and model used in this study are reliable.

### 3.2 The adsorption of H<sub>2</sub> molecules in BC<sub>3</sub> nanotube

Using GCMC method, we studied the physisorption properties of the BC<sub>3</sub>(8,0) composite nanotube under different temperatures (77 K-300 K) and pressures (0-10 MPa) and compared with those of CNTs. Fig. 3 shows the relationships of total adsorption amounts of H<sub>2</sub> molecules in these two nanotubes with simulation times at 300 K and 10 MPa. When simulation times reach  $1 \times 10^6$  steps, the two systems are both basically balanceable. At equilibrium, the number of H<sub>2</sub> molecules adsorbed in BC<sub>3</sub>(8,0) and C(8,0) nanotubes are

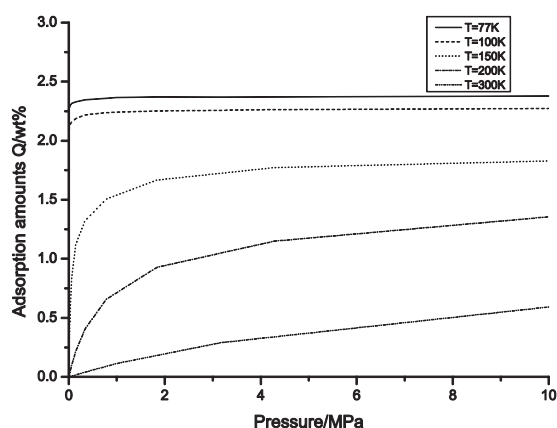


Figure 2: The H<sub>2</sub> adsorption isotherms of C(7,7) nanotube in different temperatures from this study.

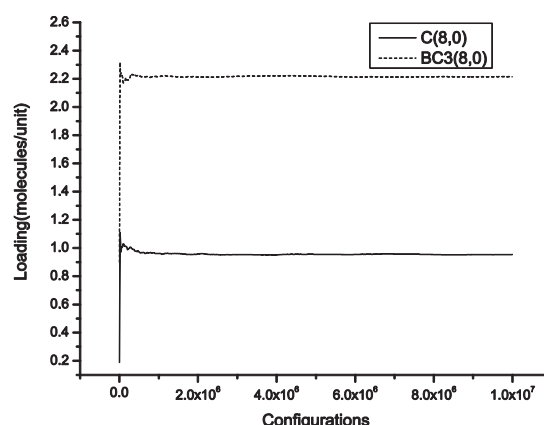


Figure 3: The relationship of total adsorption amounts of H<sub>2</sub> molecule in BC<sub>3</sub>(8,0) and C(8,0) nanotubes with simulation times.

0.955 and 2.215, respectively. Therefore,  $1 \times 10^7$  steps may ensure that all systems can reach equilibrium at all conditions.

### 3.3 Comparative study of physisorption amounts of hydrogen between BC<sub>3</sub> and carbon nanotubes

We studied the adsorption isotherms of the BC<sub>3</sub>(8,0) and the C(8,0) in a broad range of temperature (77 K-300 K) and pressure (0-10 MPa) using GCMC method, as shown in Fig. 4. Their physisorption amounts under different temperatures and pressures were obtained, which may compare their hydrogen storage capacity. We can see that the adsorption amounts increase and saturate with increasing pressure, which are in agreement with experiments on porous carbons [14,15]. And the adsorption amounts correspondingly increase with decreasing temperature. However, there is a maximum adsorption limit. For the BC<sub>3</sub>(8,0) nanotube, the adsorption limit is 1.602wt% which may be reached at 10 MPa and 200 K, 0.5 MPa and 77 K, respectively; however, this limit is not reached at room temperature 300 K, which is the temperature of interest. Comparably, the C(8,0) nanotube will reach its adsorption limit 0.520wt% at 5MPa and 200K, 0.2 MPa and 77 K, respectively; and this limit is also not reached at 300 K.

From Fig. 4, we can also see that, the adsorption amounts of the BC<sub>3</sub>(8,0) are larger than those of the C(8,0) for all temperatures examined. Table 1 shows the adsorption amounts of BC<sub>3</sub>(8,0) and C(8,0) and the differences between them at 300K, 200K, 77K with a pressure of 200 atm, respectively. From this table, we can see that, the adsorption amounts of the former are 1.182wt%, 1.589wt% and 1.602wt% at 300 K, 200 K and 77 K, respectively; while the adsorption amounts of the latter correspond to 0.497wt%, 0.520wt% and 0.520wt%, respectively. Furthermore, the differences between them are becoming larger with the increase of temperature. Concretely, the difference is only 0.685%

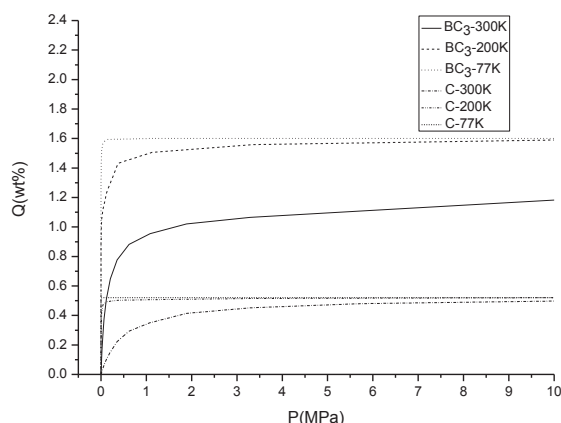


Figure 4: The adsorption isotherms of  $BC_3(8,0)$  and  $C(8,0)$  nanotube in different temperatures.

Table 1: The physisorption amounts  $Q$  of hydrogen in  $BC_3(8,0)$  and  $C(8,0)$  nanotubes and the differences  $\Delta Q$  between them at 10 Mpa and different temperatures.

$T$	$Q_{BC_3}(\text{wt}\%)$	$Q_c(\text{wt}\%)$	$\Delta Q(\text{wt}\%)$
300	1.0182	0.497	0.685
200	1.0589	0.520	1.069
77	1.602	0.520	1.082

at 300 K; however, when temperature lowers to 77 K, it increases to 1.082%. Therefore, the GCMC results suggest that the  $BC_3$  nanotube has a higher hydrogen storage capacity than the CNTs, which are consistent with those obtained using DFT [10].

In order to analyze the reason causing such different physisorption properties between  $BC_3(8,0)$  and  $C(8,0)$ , we studied the total interaction energies of these two nanotubes and  $H_2$  molecules, as shown in Fig. 5. From this figure, we can see that, the energy distribution of  $BC_3(8,0)$  presents a single peak and the largest energy is -3.55 KJ/mol; however, for the  $C(8,0)$  nanotube, the energy distribution is dispersed and the energies are -2.25 KJ/mol, -1.45 KJ/mol and 0.15 KJ/mol, respectively. The reasons may be that, in the same temperature and pressure, the difference of hydrogen storage mechanism between  $BC_3$  and CNTs mainly originates from the van der Waals (VDW) interactions of nanotubes and  $H_2$  molecules which are weak themselves. The VDW interaction of  $BC_3$  with  $H_2$  molecules is greater than that of CNTs with  $H_2$  molecules because of ionicity of B-C bond in  $BC_3$ , thus the physisorption capacity of the former is superior to that of the latter. Furthermore, we can see from Fig. 5 that, the interaction energies of  $BC_3(8,0)$  nanotube with  $H_2$  molecules are indeed larger than those of  $C(8,0)$  nanotube with  $H_2$  molecules. On the other hand, the kinetic energies of  $H_2$  molecules becomes smaller with decreasing temperature, thus the interactions among  $H_2$  molecules are weaker; however the ionicity of B-C bond in  $BC_3$  weakly depends on temperature. Therefore, comparing with the CNTs, the VDW interaction of  $BC_3$  with  $H_2$  molecules becomes stronger

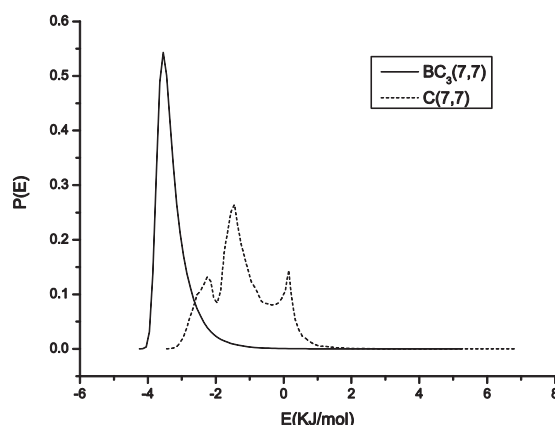


Figure 5: The total interaction energies of  $BC_3(8,0)/C(8,0)$  nanotube and  $H_2$  molecules.

when temperature decreases, and the difference of VDW interaction between CNTs and  $BC_3$  are becoming bigger, thus the difference of physisorption amounts between them are also becoming more noticeable. This is the reason why  $BC_3$  nanotube has a higher storage capacity of hydrogen than CNTs.

## 4 Conclusions

Using GCMC method, we have studied the physisorption properties of  $BC_3$  nanotube for different conditions, which were compared with CNTs correspondingly. Firstly, in order to validate correctness and accuracy of the model and compass parameters, the computed adsorption isotherms of  $C(7,7)$  for different temperatures and pressures were compared with corresponding reference. Then we studied the hydrogen storage of  $BC_3$  and carbon nanotubes using the GCMC method. The total interaction energies of  $BC_3(8,0)/C(8,0)$  nanotube and  $H_2$  molecules, the relationships of total adsorption amounts with simulation times and some isotherms for different temperatures were obtained, respectively. The studied results show that the hydrogen storage capacity of  $BC_3$  for all conditions examined is stronger than that of CNTs, and the differences of adsorption amounts between them are becoming more noticeable with the decreasing of temperature. The reasonable theoretical explanations are given.

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## References

- [1] Z. H. Zhou, X. M. Wu, Y. Wang, *et al.*, Acta Phys. -Chim. Sin. 18 (2002) 692 (in Chinese).

- [2] B. A. Hammel, T. P. Bernat, G.W. Collins, *et al.*, DOE Reports, No.UCRL-JC-130302 (1998).
- [3] C. Dillon and M. J. Heben, *Appl. Phys. A* 72 (2001) 133.
- [4] S. Iijima, *Nature* 354 (1991) 56.
- [5] A. C. Dillon, K. M. Jones, T. A. Bekkedahl, *et al.*, *Nature* 386 (1997) 377.
- [6] C. Liu, Y. Y. Fan, M. Liu, *et al.*, *Science* 286 (1999) 1127.
- [7] A. Zttel, *Mater Today* 9(2003) 24.
- [8] N. Hamada, S. Sawada, and A. Oshiyama, *Phys. Rev. Lett.* 68 (1992) 1579.
- [9] Y. Miyamoto, A. Rubio, M. L. Cohen, *et al.*, *Phys. Rev. B* 50 (1994) 4976.
- [10] X.Y. Liu, W. G. Sun, C. Y. Wang, *et al.*, *Eur. Phys. J. D* 10 (2009) 1140.
- [11] J. R. Hill and J. Sauer, *J. Phys. Chem.* 98 (1994) 1238.
- [12] M. Allen and D. Tildesley, *Computer Simulation of Liquids* (Oxford Universtiy Press, Oxford, 1981).
- [13] I. Carbria, M. J. López, and J. A. Alonso, *J. Chem. Phys.* 128 (2008) 144704.
- [14] Y. Gogotsi, R. K. Dash, G. Yushin, *et al.*, *J. Am. Chem. Soc.* 127 (2005) 16006.
- [15] M. Jordá-Beneyto, F. Suárez-García, and D. Lozano-Castelló, *Carbon* 45 (2007) 293.