Quantum chemistry study on H_2 entering the middle defects on carbon nanotubes vertically*

Wang Baojun, Ling Lixia, Zhang Riguang, Zhao Qingyan

Key Laboratory of Coal Science & Technology, Ministry of Education and Shanxi Province, Taiyuan University of Technology, Taiyuan 030024, Shanxi, China

Introduction

Nowadays, a great deal researches are interested in studying hydrogen fuel due to its abundance and friendliness to environment, but how to store hydrogen is a key question. Carbon nanotubes (CNTs) provide a new and efficient material for storing hydrogen due to its unique structure[1]. It has been reported that CNTs were found to be able to uptake a certain amount of hydrogen[2], and the defects on CNTs played important role[3]. We have ever studied the cohesive energy of hydrogen adsorbing on three kinds of CNTs with defect using molecular dynamics and quantum chemistry method. The results showed that the energy was the lowest when the center of H_2 stay at "Semi-entrance" to the defect of CNTs[4]. But the definite position of H_2 entering the defect CNTs has not been known. In this paper, the cohesive energies, bond orders and net charges were calculated by quantum chemistry calculation method ZINDO, the optimal position of H_2 vertically entering into the two mid-defects of CNTs were obtained.

Construction of CNTs with Defect and Calculation Method

The two kinds of defects on CNT chair (5,5) were designed (Fig. 1). The first defect was the elimination of one carbon atom, the second defect was the elimination of one C-C bond. The semi-empirical INDO/1 method in MSI·Cerius^2·ZINDO software was applied in this paper. The single point energies of the CNTs with defects, H_2 and the complex structures constructed by vertically putting H_2 in the defects were denoted respectively by E_i, E_H and E, the cohesive energy could be obtained by following equation: $E_c = (E_i+E_H)-E$

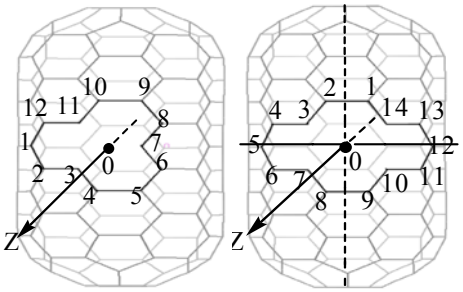

Fig. 1. The construction of defects on CNT chair (5,5)

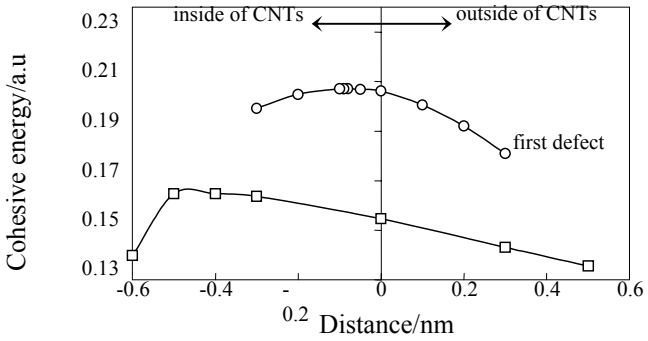

Fig. 2. The cohesive energy of H_2 entering the center of two defects vertically

* Supported by the National Basic Research Program of China (2005CB221203) and the National Natural Science Foundation of China (20576087)

Results and Discussion

The cohesive energies of H_2 and CNTs with two kinds of defects were calculated when H_2 entered into the defect along the Z-axis. The Horizontal abscissa in Fig.2 represents the distance between the middle of H-H bond and the O point. It is concluded that the cohesive energy of H_2 entering the first defect is greater than that of H_2 entering the second defect (see Fig. 2). From the position of the greatest cohesive energy on the Z-axis, H_2 moves in the several directions listed in Table. 1,and the moving distance was denoted using the distance between the middle of H-H bond and Z-axis. The greatest cohesive energies of H_2 and defect CNTs at several directions were listed in Table 1. In addition, the bond orders between H and C of defect, net charges distribution on the carbon atoms of defect were calculated when H_2 moves. The optimal position of H_2 entering the first defect CNTs is that the middle of H-H bond is located at the point of 0.2Å from the Z axis in the direction of O to C3 and O to C11, and the optimal position of H_2 entering the second defect is that the middle of H-H bond is located at 0.59Å from the Z-axis in the direction of diameter axis. Meanwhile, we also find that the microscopic structures of CNTs are influenced to different extent after adsorption of H_2 on the different defect CNTs.

Table 1. The cohesive energies of H_2 moving at several directions in two defects

The first defect			The second defect		
Direction	Distance (nm)	Cohesive energies (a.u)	Direction	Distance (nm)	Cohesive energies (a.u)
Toward:			Toward:		
C7	-0.20	0.2276	C5	0.59	0.2045
C3	0.20	0.2314	C12	0.59	0.2042
C11	0.20	0.2315			
middle point of C3-C6	0.17	0.2138	middle point of C1-C2	0.56	0.1735
middle point of C8-C11	0.17	0.2137	middle point of C8-C9	0.60	0.1718

References

1. H. W. Zhu, D. H. Wu, C .L Xu. Carbon Nanotubes. Machine Industry Press, Beijing, 2003: 258-259
2. X. B. Wu, P. Chen, J. Lin, K. L. Tan. Hydrogen Uptake by Carbon Nanotubes. International Journal of Hydrogen Energy, 2000, 25: 261-265
3. T. W. Ebbense, T. Takada, Topological and SP3 Defect Structures in Nanotubes. Carbon, 1995, 33(7): 973-978
4. B. J. Wang, Q. Y. Zhao, H. L. Wu, J. P. Li, K. C. Xie. Quantum Chemistry Calculation of Interaction of Hydrogen and Carbon Nanotube Defects. Journal of Chemical Industry and Engineering, 2005, 56(7): 1332-1337