CODEN IEJMAT Internet Electronic Journal of Molecular Design **2007**, *6*, 302–310 ISSN 1538–6414
BioChem Press http://www.biochempress.com

Internet **Electronic** Journal of
Molecular Design

September 2007, Volume 6, Number 9, Pages 302–310

Editor: Ovidiu Ivanciuc

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Received: August 4, 2007; Revised: September 24, 2007; Accepted: September 25, 2007; Published: September 30, 2007

Citation of the article:
A. A. Kuzubov, R. P. Avramov, M. A. Raimova, T. A. Kozhevnikova, J. M. Milyutina, and P. O. Krasnov, Theoretical Study of Atomic Hydrogen Diffusion on the Surface of Carbon Nanotubes of Various Diameters and Chiralities, *Internet Electron. J. Mol. Des.* **2007**, *6*, 302–310, http://www.biochempress.com.

Inter*net* Electronic Journal of Molecular Design

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Theoretical Study of Atomic Hydrogen Diffusion on the Surface of Carbon Nanotubes of Various Diameters and Chiralities

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Abstract

Density functional theory calculations in a basis of plane waves were preformed to determine diffusion process characteristics for atomic hydrogen chemically adsorbed on the surface of (5,5), (8,8) and (8,0) single–walled carbon nanotubes. It has been determined that carbon nanotubes can be used for the storage hydrogen in a chemically bound atomic state. The saturation process of carbon nanotubes with hydrogen should be carried out at high temperatures and in the presence of catalyst that would decompose hydrogen into atomic form. High temperatures aid the diffusion process leading to uniform distribution of hydrogen atoms on carbon nanotube surface. At standard temperatures the migration of hydrogen atom on the nanotube surface is hindered significantly.

Keywords. Carbon nanotubes; hydrogen storage; potential barriers.

Abbreviations and notations

ax, axial bond	NT, nanotube
CNT, carbon nanotubes	*pax*, perpendicular bond to the axial direction
DOE, Department of Energy	VASP, Vienna Ab–initio Simulation Package
nax, non–axial bond	SWNT, single–walled nanotubes
npax, non–perpendicular bond to the axial direction	T, temperature

1 INTRODUCTION

Recently, due to increased costs of hydrocarbon based fuels and ecological problems created by the use of those, the attention has been turned to ecologically clean hydrogen energy sources. The most prominent but still unsolved problem in that area is the mechanism of hydrogen storage. One

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of the scenarios ways could be the use of sorbents that can reversibly store hydrogen. The well known limit for adsorbed hydrogen storage for industrial and transportation use is 6.5 % according to DOE [1].

One of the possible cases of hydrogen adsorption is the formation of hydrides with *d*–metals, especially with Pd and its alloys. Nevertheless, due to high atomic weights of *d*–metals, such hydrogen storage technique cannot be used in automotive transportation. In addition to that, these compounds can be quite costly [2,3].

Other possible hydrogen sorbents are carbon nanotubes (CNT) that were firstly discovered in 1991 by Iijima group [4]. Their nanometer–scaled size and quasi–one–dimensionality give rise to outstanding chemical and transport properties [5]. One of the perspective applications of CNTs is adsorption of various atoms and molecules on their surface. Specific area of CNTs of up to 1000 m^2/g provides the possibility of holding large amounts of hydrogen as well s noble gasses or water vapors etc. The first famous work on that topic discussed possible adsorption of HF molecules on a nanotubes [6]. Nevertheless, the experimental results on hydrogen adsorption are still controversial. For example, experimental works of Dillon *et al.* [7] have reported the possibility of 5–10 %% hydrogen storage in single–walled nanotubes (SWNT) at room temperature and the pressure of $4 \cdot 10^4$ Pa. In [8,9] it was shown that the amount of adsorbed hydrogen can reach 8.25 (weight)% at 80 K and 10 MPa and 4.2 % at room temperature and 10 MPa. According to [10,11] it is possible to store only 0.4 to 4 % of hydrogen in CNTs using electrochemical processes. In [1] the density of stored hydrogen was reported to be ~3.5 %. In theoretical works such as [12] and its sequel, [13], the mechanism of phys–adsorption of hydrogen has been presented taking into account thermal and quantum effects. It was shown that even though quantum effects are usually neglected in the description of phys–adsorption of hydrogen, these effects become important when such light molecules are involved. In these works it was determined that the limit for the amount of hydrogen phys–adsorbed on the surface of CNTs is actually ~1.8 % (at T = 150 K and pressure of 450 bars).The small percentage of phys–adsorbed hydrogen can be explained by relatively weak adsorption of H_2 molecule on the surface of SWNTs (~0.09 eV according to [14]).

The idea of doping the surface of CNTs with light metal atoms to create centers of physical adsorption of hydrogen is well known in the scientific world. For example, Chen *et al.* [15] report the possibility of 10 to 20 %% storage of hydrogen on the surface of CNTs doped with Li atoms. Using infrared spectroscopy (FTIR) authors have uncovered the preference in formation of Li–H bonds as opposed to C–H bonds. That shows that Li atoms act as catalytic centers physical and dissociative adsorption of hydrogen. In the case of using potassium atoms the amount of hydrogen adsorbed on CNTs can reach 21 %, although such nanotubes would be chemically unstable [16]. It in unclear, though, if metal adsorbed on the surface of CNTs will stay in the form of single atoms. Some works [17] propose that metal would form clusters on the surfaces of carbon nanostructures that would decrease abruptly the amounts of adsorbed hydrogen.

In this work we will investigate one of the aspects of using metals as catalysts for dissociation of hydrogen molecules and their spillover on the surface of CNTs. Such idea of utilizing secondary surface to aid adsorption process has been widely used before: the very term spillover was invented long ago [18]. The idea is that if the probability of absorption of certain molecules on the surface of a material is low (due to low dissociation probability or high potential barrier), the more beneficial secondary adsorption surface can be used to speed up the process. For example, in the case of molecular hydrogen, it can be first dissociated on a surface of metal catalyst particles and then spilled over to the surface where it would be adsorbed and stored. An effective spillover of hydrogen in depends on its diffusion on the surface of CNTs, which was studied in the present work.

2 MATERIALS AND METHODS

In our studies the model of infinite carbon nanotubes of (8,8), (5,5) and (8,0) types was used. Due to the fact that the nanotubes produced in experiments are mostly 10–12 Å in diameter, the diffusion of hydrogen was studied on the surface of (8,8) SWNT with the diameter of 10.84 Å. The diameter (curvature) dependence of the effect was studied by considering (5,5) SWNT with the diameter of 6.78 Å in our calculations, whereas the chirality dependence was investigated through (8,0) nanotube.

All calculations were made within DFT formalism [19,20] using VASP (*Vienna Ab–initio Simulation Package*) software [21–23]. This program for *ab initio* calculation employs the method of pseudopotentials and the expansion of wave functions in the basis of plain waves. Vanderbilt pseudopotentials [24] were used in the program for the purpose of decreasing the number of basis functions and speeding up the calculations. The “nudged elastic band” method [25] was used to find transition states and energy barriers in the process of hydrogen atom hopping on the surface of CNT.

Rate constants of hydrogen atom hopping were calculated through the theory of transition states considering E_0 as zero point energy for atomic oscillations with frequencies v_i:

$$k = A\exp\left(-\frac{E_{barrier}}{k_B T}\right), \tag{1}$$

where

$$A = \frac{k_B T}{\hbar}\frac{\prod_{i=1}^{3N-7}\left[1-\exp\left(-\frac{\hbar v_i^{\#}}{k_B T}\right)\right]}{\prod_{i=1}^{3N-6}\left[1-\exp\left(-\frac{\hbar v_i}{k_B T}\right)\right]}, \tag{2}$$

T − temperature, $E_{barrier}$ − the height of potential barrier for atom hopping. The product in the denominator of (2) was calculated for most favorable state of hydrogen in local minima, and the product in the numerator of (2) was calculated for transition states. Potential barrier height was determined as a difference in energy between the top of the barrier and the minimum. Zero point energy was also taken into account for transition states:

$$E_0 = \sum_{i=1}^{3N-7} \frac{\hbar \nu_i^{\#}}{2} \tag{3}$$

and for energy minimum:

$$E_0 = \sum_{i=1}^{3N-6} \frac{\hbar \nu_i}{2}. \tag{4}$$

The oscillation frequencies of hydrogen atoms on the surface were calculated with numerically defined dynamic matrix of displacements of hydrogen and neighboring carbon atoms.

The diffusion process was studied in (8,0), (8,8) and (5,5) nanotubes. From the topological standpoint, for every nanotubes it is possible to find two non–equivalently situated C–C bonds (Figure 1). For example, (8,0) nanotube is one of the ensemble of (*n*,0) SWNTs identified as zigzag conformers. In zigzag nanotubes one of the bonds is situated along the axis of the nanotube (axial − *ax* bond) where the other one is oriented at the angle of 60° to nanotubes axis (non–axial – *nax* bond). Likewise, in (*n*,*n*) nanotubes there are bonds perpendicular to nanotube axis (*pax*) and the ones that are not perpendicular (*npax*). Despite the number of non–equivalently situated axes, all the atoms on the carbon surface are equivalent to each other and bound to their neighbors by one axial and two non–axial bonds.

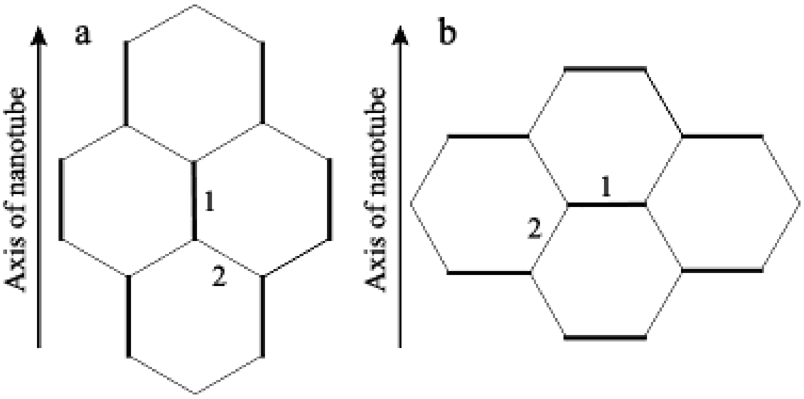

Figure 1. Positions of the non–equivalent C–C bonds in CNTs. **a**) NT (*n*,0): 1 – axial bond (*ax*), 2 – non–axial bond (*nax*); **b**) NT (*n*,*n*): 1 – perpendicular bond to the axial direction (*pax*), 2 – non–perpendicular bond to the axial direction (*npax*).

At first the geometry optimization was carried out for the initial system consisting of carbon nanotube and a single hydrogen atom. The results of such optimization have shown that in the state of equilibrium hydrogen should be positioned near the carbon atom (the distance between C and H atoms is about 1.1 Å). The geometry of the nanotube itself did not experience substantial changes.

Potential energy maps assuming stationary carbon structure were created to determine the pathway of hydrogen atom on the nanotube surface. The analysis of those maps shows that hydrogen will most probably diffusively migrate along the paths with minimum energy, i.e. along C–C bonds.

In further work we consider the hopping mechanism of hydrogen from one carbon atom to another along various bonds (Figure 2). The migration of hydrogen from inside and outside of the nanotube was calculated. In the case of the diffusion on the outer surface of SWNT the possibility of hydrogen atom hopping in the presence of other H atom on the neighboring nanotube site was modeled. Since, in the former case, the initial and final positions of hydrogen atom were not equivalent, the equilibrium constants determining the probability of coexistence of two hydrogen atoms on the neighboring sites of SWNT had to be found. These equilibrium constants were calculated as the ratio of the rate constants for the processes of approach and withdrawal of hydrogen atoms:

$$K = \frac{k_{approach}}{k_{removal}}. \tag{5}$$

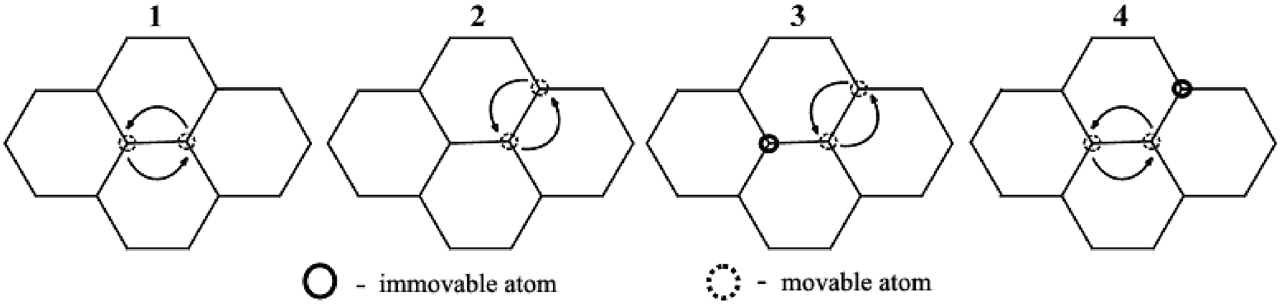

Figure 2. Possible reaction's paths of the hydrogen atom's migration on the surface of nanotubes along different bonds: 1, 2 – without neighboring hydrogen atoms; 3, 4 – with hydrogen atom on the neighboring site of NT.

3 RESULTS AND DISCUSSION

As a result, the energy barriers, rate and equilibrium constants were calculated for hydrogen atom diffusion on the surface of SWNT (Figure 3, Tables 1 and 2). The calculated rate constants show that the diffusion process at the standard temperature on the outer surface of SWNT is rather slow ($k_{\max} < 10^{-4}$), whereas on the inner surface the process goes significantly faster ($k_{\max} \sim 10^{5}$). Nevertheless, when the temperature is increased, the migration of hydrogen on the carbon surface speeds up. Also, it has been found that for nanotubes with the same chirality and different diameters, namely (5,5) and (8,8), the rate constant for the outer surface diffusion increases with diameter.

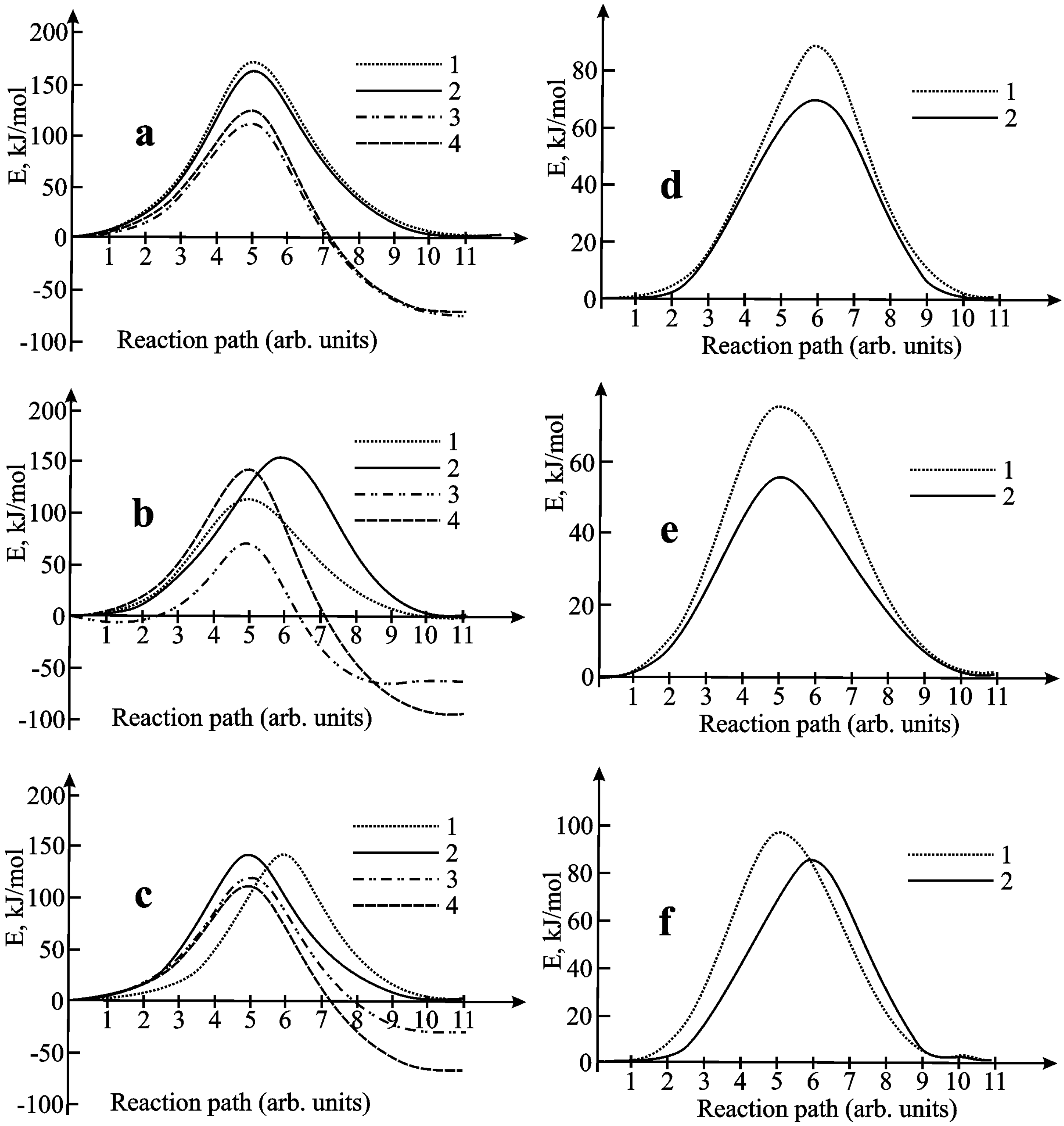

Figure 3. Energetic barriers of the hydrogen atom's migration on the surface of nanotubes along different bonds (**a**, **b**, **c** – external surface of NT; **d**, **e**, **f** – internal surface of NT). **a**) NT (5,5): 1 and 2 – along the *npax* and *pax* bonds, accordingly, without neighboring hydrogen atoms; 3 and 4 – along the *npax* and *pax* bonds, accordingly, with the second hydrogen atom on the neighboring site of NT. **b**) NT (8,0): 1 and 2 – along the *nax* and *ax* bonds, accordingly, without neighboring hydrogen atoms; 3 and 4 – along the *nax* and *ax* bonds, accordingly, with the second hydrogen atom on the neighboring site of NT. **c**) NT (8,8): 1 and 2 – along the *npax* and *pax* bonds, accordingly, without neighboring hydrogen atoms; 3 and 4 – along the *npax* and *pax* bonds, accordingly, with the second hydrogen atom on the neighboring site of NT. **d**) NT (5,5): 1 – along the *npax* bond, 2 – along the *pax* bond; **e**) NT (8,0): 1 – along the *ax* bond, 2 – along the *nax* bond; **f**) NT (8,8): 1 – along the *pax* bond, 2 – along the *npax* bond.

As for the inner surface, the diffusion rate constant decreases with increasing nanotube diameter. In SWNTs with the same diameter but different chiralities, namely (5,5) and (8,0), the diffusion speed is different (it is larger for zigzag (8,0) nanotube). For small diameter SWNTs the diffusion rate constants vary for different types of bonds and for (8,0) zigzag nanotube the difference is more significant then for (5,5) SWNT. However for large diameter (8,8) nanotube the variations of diffusion rate constant for nonequivalent bonds were not observed.

Table 1. Activation Energies (E_a, kJ), Preexponential Factors ($A\cdot10^{12}$, s^{-1}) and Velocity Constants (k, s^{-1}) for the Migration of Hydrogen Atoms along the CNT Surface

Process	Parameters		NT (5,5)		NT (8,8)		NT (8,0)	
			pax	*npax*	*pax*	*npax*	*ax*	*nax*
Single hydrogen atom's migration outside of the NT	E_a		153.833	147.924	127.601	125.913	99.741	139.481
	A	T=298 K	6.084	6.186	6.070	6.211	6.126	6.341
		T=600 K	16.088	16.093	16.631	16.214	15.648	17.690
	k	T=298 K	$7.1\cdot10^{-15}$	$7.8\cdot10^{-14}$	$2.8\cdot10^{-10}$	$5.4\cdot10^{-10}$	$2.1\cdot10^{-5}$	$2.4\cdot10^{-12}$
		T=600 K	$1.9\cdot10^{4}$	$4.2\cdot10^{4}$	$6.5\cdot10^{5}$	$8.3\cdot10^{5}$	$2.6\cdot10^{7}$	$1.5\cdot10^{5}$
Single hydrogen atom's migration inside of the NT	E_a		58.156	76.651	74,438	86,933	44.234	59.460
	A	T=298 K	6.142	6.145	5.603	5.699	6.001	5.817
		T=600 K	11.468	11.681	11.270	11.826	10.981	10.900
	k	T=298 K	405.568	0.235	0.034	$1.4\cdot10^{-4}$	$1.0\cdot10^{5}$	227.1
		T=600 K	$1.0\cdot10^{8}$	$2.5\cdot10^{6}$	$3.8\cdot10^{6}$	$3.3\cdot10^{5}$	$1.6\cdot10^{9}$	$7.4\cdot10^{7}$
Hydrogen atom's migration at a presence of another hydrogen atom (they approach)	E_a		111,651	98.969	98.867	105.567	58.054	129.507
	A	T=298 K	6.043	5.967	5.944	5.993	5.317	6.107
		T=600 K	11.011	10.772	10.593	10.783	8.910	11.349
	k	T=298 K	$1.7\cdot10^{-7}$	$2.8\cdot10^{-5}$	$2.9\cdot10^{-5}$	$2.0\cdot10^{-6}$	366	$1.3\cdot10^{-10}$
		T=600 K	$2.2\cdot10^{3}$	$2.7\cdot10^{4}$	$2.7\cdot10^{4}$	$7.0\cdot10^{3}$	$8.0\cdot10^{7}$	62
Hydrogen atom's migration at a presence of another hydrogen atom (they retire)	E_a		185,951	185.951	163.910	133.740	114.606	221.602
	A	T=298 K	6.352	6.190	6.290	6.206	6.083	6.446
		T=600 K	12.516	11.789	12.170	11.760	11.083	13.117
	k	T=298 K	$1.8\cdot10^{-20}$	$1.4\cdot10^{-17}$	$1.3\cdot10^{-16}$	$2.4\cdot10^{-11}$	$5.3\cdot10^{-8}$	$1.0\cdot10^{-26}$
		T=600 K	$8.5\cdot10^{-4}$	$2.2\cdot10^{-2}$	0.068	27	$1.2\cdot10^{3}$	$7.1\cdot10^{-7}$

Table 2. Equilibrium Constants (K) for the Process of Hydrogen Atom Approach–removal to the Site of the NT Surface that is Occupied by Another Hydrogen Atom

Kind of the NT and the bond	T	K
(5,5) *pax*	298	$9{,}66\cdot10^{12}$
	600	$2{,}54\cdot10^{6}$
(5,5) *npax*	298	$2{,}00\cdot10^{12}$
	600	$1{,}20\cdot10^{6}$
(8,8) *pax*	298	$2{,}30\cdot10^{11}$
	600	$3{,}93\cdot10^{5}$
(8,8) *npax*	298	$8{,}26\cdot10^{4}$
	600	$2{,}54\cdot10^{2}$
(8,0) *ax*	298	$6{,}94\cdot10^{9}$
	600	$6{,}57\cdot10^{4}$
(8,0) *nax*	298	$1{,}25\cdot10^{16}$
	600	$8{,}79\cdot10^{7}$

The analysis of rate constants for the process of approach–withdrawal of hydrogen atom to the nanotube surface side occupied by another hydrogen have shown that independently of the nanotube's diameter and chirality it is more preferable for hydrogen atoms to stay on the neighboring sites of SWNT surface. However, at higher temperatures this effect looses its power and all of the nanotube sites tend to become equivalent. That signifies that equilibrium constant values decrease with rising temperature.

Calculated activation energies are comparable with the results got for hydrogen diffusion along unirradiated (1,04 eV) and neutron–irradiated (1,60 eV) graphite sheet [26].

4 CONCLUSIONS

As a preliminary conclusion of the current work, it has been determined that carbon nanotubes can be used for the storage hydrogen in a chemically bound atomic state. The saturation process of CNTs with hydrogen should be carried out at high temperatures and in the presence of catalyst that would decompose hydrogen into atomic form. High temperatures aid the diffusion process leading to uniform distribution of hydrogen atoms on CNT surface. At standard temperatures the migration of hydrogen atom on the nanotube surface is hindered significantly.

For the successive extraction of hydrogen from the system it is necessary to rise the temperature increasing the diffusion rate and, therefore, the probability of associative desorption.

Acknowledgment

Authors are thankful to the Institute of Computer Modeling of SB RAS (Siberian Branch of Russian Academy of Science) for the exploitation of computer cluster that was used to perform calculations described above.

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