

# Ab initio study of hydrogen chemical adsorption on platinum surface/carbon nanotube join system

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The process of hydrogen chemical adsorption on platinum cluster/single wall carbon nanotube (CNT) join surfaces is modelled at various temperatures and pressures. For that, the adsorption energy of hydrogen atoms on surfaces of both platinum (111) plate and CNT (5,5) or (8,8) types is calculated by density functional theory with the PBE approximation. At various temperatures the hydrogen atom hopping rate on both platinum and CNT surfaces is calculated by the transition state theory. Furthermore the hydrogen hopping rate from the platinum surface to the attached nanotube is obtained by calculation of the total energy profile. It is proved that hydrogen atoms can migrate easily at the platinum surface at all temperatures, but at the CNT surface they can mi-

grate beginning at 400–500 K. By calculation of chemical potentials of hydrogen in gas or on CNT or platinum cluster surfaces the equilibrium density of adsorbed hydrogen was calculated at different temperatures and pressures. It is established that for all temperatures in the range 300–900 K and for all pressures less than 500 bar, the hydrogen is dissociated and chemically adsorbed on the platinum surface very effectively, but surface site occupation by hydrogen on attached CNT surface is rather small. But if CNT vacancies are present in the tube structure and the temperature is lower than 450 K, hydrogen atoms can be adsorbed effectively enough on these vacancies.

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**1 Introduction** For at least a decade, fuel-cell-powered transport has been recognized as a much-needed technology to ameliorate environmental problems associated with hydrocarbon combustion. Currently, the hydrogen technology for powering vehicles (i.e. fuel cells) is significantly more advanced than the technology for storing the hydrogen. One basic merit for hydrogen storage is the ratio of weight percent (wt%) hydrogen stored relative to the weight of the storage medium. According to the United States Department of Energy (DOE) requirement, this ratio should be at least 6–7 wt% for a viable ground transportation technology [1]. Hydrogen storage in lightweight carbon materials would therefore be particularly attractive. Carbon nanotubes (CNTs) seem to be an alternative for this, since nanotubes are chemically stable and have low mass density. Moreover the homogeneous curved

surfaces of CNTs are especially important for surface science, because adsorption phenomena have been focused on atomically flat surfaces before nanotube discoveries.

Despite much in the literature concerning hydrogen adsorption in CNTs, the experimental data in this field are very contradictory. For example, in the pioneering work by Dillon et al. [2], it was noted that the hydrogen content in single-wall carbon nanotubes (SWCNTs) can reach 5–10 wt% at room temperature and a pressure of  $4 \times 10^4$  Pa. Ye et al. [3] and Liu et al. [4] reported that the content of adsorbed hydrogen reaches 8.25 wt% at a temperature of 80 K under a pressure of 10 MPa and decreases to 4.2 wt% at room temperature under the same pressure. According to Nutzenadel et al. [5] and Rajalakshmi et al. [6], the content of electrochemically adsorbed hydrogen inside SWCNTs lies in the range from 0.4 wt% to 4.0 wt%. Zhu et al. [7]

produced SWCNTs in which the content of adsorbed hydrogen was approximately 3.5 wt%.

In theoretical studies [8, 9] a new method for calculation of the equation of state of hydrogen molecules adsorbed in SWCNTs was proposed. This method took into account quantum mechanical effects that are responsible for the discrete energy levels of hydrogen molecules and their movement between nearest neighbours. It was shown that the limit of physical adsorption of hydrogen on CNT surfaces is  $\sim 1.8$  wt% (at a temperature of 150 K and pressure of 450 bar). Such a low physical adsorption value is explained by the low adsorption energy of  $H_2$  molecules on the CNT surface ( $E_{\text{ads}} \approx -0.09$  eV, according to [10]).

Another possible way of hydrogen adsorption is its adsorption in some d-metals forming hydrides, especially palladium or its alloys. In this case adsorption effectively occurs at temperatures above 300 K and pressures up to 30–40 bar. But the large atomic weight of these metals is not conducive to their use as storage in transport. Moreover such compounds are too expensive [11].

One interesting possibility is to use CNTs with attached metal atoms. For example, in one study [12] it was concluded that the capacity of a K–CNT complex can reach 21%, but such tubes are chemically unstable. Unfortunately, the question about the opportunity of stable adsorption of single metal atoms on the surfaces of CNT systems still remains unclear [13]. Some authors have shown (e.g. [14]) that the atoms of metals tend to cluster on the surface of carbon nanostructures with a significant reduction of the hydrogen adsorption value.

In this work we theoretically investigate the possibility of CNTs to adsorb hydrogen atoms which are produced by chemical dissociation of hydrogen molecules on attached platinum cluster surfaces. We further investigate hydrogen atoms hopping to the CNT surface and their subsequent ‘spillover’ on the CNT surface.

The idea of using extrinsic surfaces for adsorption facilitation is not new. The term ‘spillover’ was introduced more than half a century ago [15]. If molecules are adsorbed on a surface with low probability (for example, because of low probability of their dissociation or large value of potential energy barrier), for simplification of this process another material can be used as an intermediate agent. Molecules ‘spill over’ from the intermediate agent to a final surface. For example, in the case of molecular hydrogen, it can be dissociated to the atomic state on a metallic surface (dissociation catalyst being Pt, Pd, etc.) and after that the hydrogen atoms can transfer to another surface. Thus, it is possible to assume that the process of chemical adsorption of hydrogen on a CNT surface can be considerably facilitated if one uses some metal cluster attached to the CNT as the catalyst and uses an extra large CNT surface to hold the hydrogen atoms. Moreover, it is known from many experiments that CNTs are often synthesized with already attached platinum or other d-metal clusters.

In this work an investigation of this process of hydrogen chemical adsorption on CNTs with attached metal

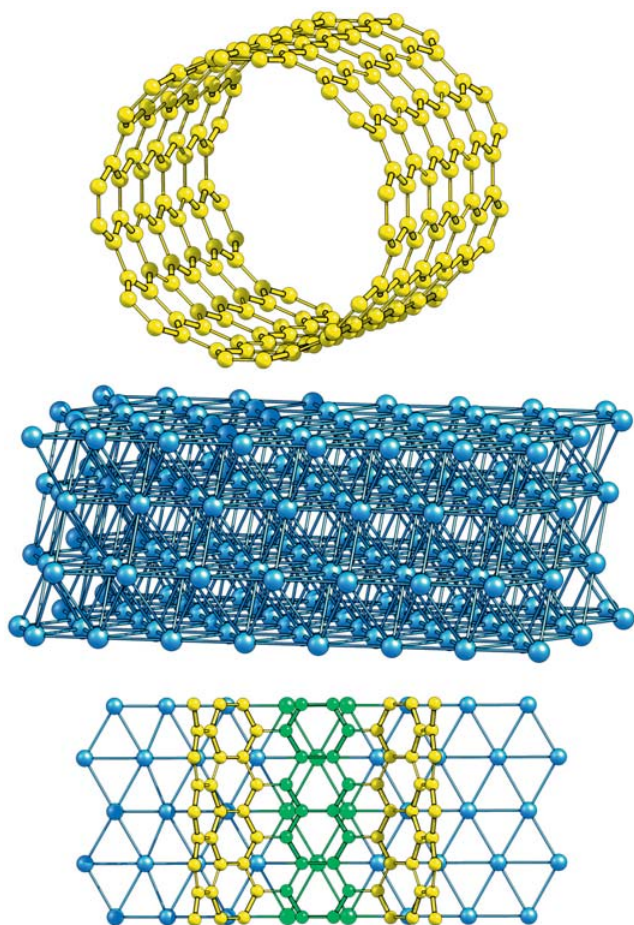
clusters has been carried out. Platinum plate was chosen as the metal cluster because it has good catalytic properties for hydrogen dissociation and because it is used frequently as a substrate in experiments with CNTs [16, 17].

**2 Method and model** Here we perform an investigation of hydrogen adsorption onto outer walls of SWCNTs of (8,8) and (5,5) types connected to a platinum cluster. We used the first-principles density functional method [18, 19] (VASP software [20–22]) with the PBE generalized gradient approximations [23] for the exchange–correlation potential and plane wave basis set. The electron–ion interaction is taken into account via ultrasoft Vanderbilt-type pseudopotential formalism [24]. Because one uses periodical boundary conditions (PBC) we simulate an infinite CNT connected with an infinite platinum (111) slab (see Fig. 1).

The nanotube (8,8) with a diameter of 10.84 Å was chosen because in most experiments CNTs with similar diameters of 10–12 Å are usually obtained. For studying the influence of CNT curvature on the hydrogen adsorption rate the narrow (5,5) CNT with a diameter of 6.78 Å was also investigated.

To model the hydrogen adsorption on platinum cluster surface, a slab containing four atomic layers was chosen. It was found that four atomic layers are enough for a correct description of the electronic structure of thick platinum cluster. For neglecting the interaction between neighbour platinum slab with connected CNT and their periodical images (due to PBC) a vacuum space of  $\sim 7$  Å between them was chosen along the *c*-axis. In the case of (8,8) nanotube a supercell size of  $9.60 \times 19.39 \times 31.00$  Å<sup>3</sup> was used. This supercell value in the *XY*-plane enabled one to reach a coincidence of both platinum surface and CNT periodicities. For that, it was necessary to rotate the CNT relative to crystallographic vectors of the platinum surface by some angle (see Fig. 1, bottom). Also, it was necessary to stretch the CNT geometry by  $\sim 1.2\%$  along the axis. But during preliminary computations it was defined that such a longitudinal CNT deformation does not affect the CNT electronic structure significantly.

Due to the large supercell size for integration over the first Brillouin zone (BZ) we used 4*k*-points inside the BZ chosen along the CNT axis by Monkhorst–Pack *k*-point sampling [25] in all calculations. The geometry optimization was carried out until the forces acting on each atom become less than 0.05 eV/Å. To define the equilibrium distance between CNT and platinum cluster surface we made ab initio calculations of the CNT lying at different distances from the platinum cluster. It was defined that chemical bonds are not formed between both the nanostructures, so only weak van der Waals interactions are important for describing the CNT–Pt cluster system. To define an equilibrium distance between both nanostructures, van der Waals interactions were considered with the help of intermolecular Lennard–Jones (6–12) potential with parameters defined in [26].



**Figure 1** (online colour at: [www.pss-b.com](http://www.pss-b.com)) (8,8) CNT–Pt cluster join system (platinum atoms are grey (blue online), carbon atoms are white (yellow online)); at bottom, the top view projection of the system is shown. Nearest atoms of CNT and platinum surface are shown by light gray (green online).

After calculations of the platinum surface geometry optimization, no substantial changes in the geometry were observed, in agreement with experiments. For calculations of potential energy barriers and the transition state of the hydrogen atom during its movement on platinum slab and CNT surfaces and during its hop between these nanostructures, the nudged elastic band method [27] was used. The equilibrium density of hydrogen adsorbed on both surfaces was calculated using equality of chemical potentials,  $\mu = (\partial G / \partial N)_{p,T}$  (where  $G$  is the Gibbs energy and  $N$  the number of atoms in the given phase), of hydrogen atoms (or molecules) in the gas phase, and also on platinum and CNT surfaces.

The chemical potential of hydrogen molecules in the gas phase can be derived as

$$\mu_{\text{gas}} = \frac{F + PV}{N} = \frac{F}{N} + P\Omega, \quad (1)$$

where free energy  $F$  is defined as

$$F = -NkT \ln \left[ \frac{eV}{N} \left( \frac{2\pi mkT}{h^2} \right)^{3/2} \right] + F_{\text{vib}} + F_{\text{rot}}. \quad (2)$$

The vibration part of the free energy is defined by

$$F_{\text{vib}} = \frac{N\hbar\omega_{\text{vib}}}{2} + NkT \ln \left[ 1 - \exp \left( -\frac{\hbar\omega_{\text{vib}}}{kT} \right) \right], \quad (3)$$

where  $\omega_{\text{vib}}$  is the characteristic frequency of the hydrogen molecule which is equal  $T_{\text{vib}} \cong 6000$  K. The rotation part of the free energy is given as

$$\begin{aligned} F_{\text{rot}} &= -NkT \ln(z_{\text{rot}}) \\ &= -NkT \ln \left[ \sum_{j=0}^{\infty} (2j+1) \exp \left( -\frac{T_c j(j+1)}{T} \right) \right], \end{aligned} \quad (4)$$

where  $T_c \cong 85.4$  K is the characteristic temperature of hydrogen molecule rotation.

Chemical potentials of adsorbed atoms are calculated as follows:

$$\mu_{\text{adsorbed}} = kT \ln \left( \frac{\Theta}{1-\Theta} \right) + E_{\text{adsorbed}} + F_{\text{vib}}, \quad (5)$$

where  $\Theta$  is the filling ratio of the surface adsorbing states. The adsorption energy (per atom) of a hydrogen atom on CNT surface can be written as

$$E_{\text{adsorbed}}^{\text{CNT+H}} = E_{\text{tot}}(\text{CNT} + \text{H}) - E_{\text{tot}}(\text{CNT}) - E_{\text{tot}}(\text{H}), \quad (6)$$

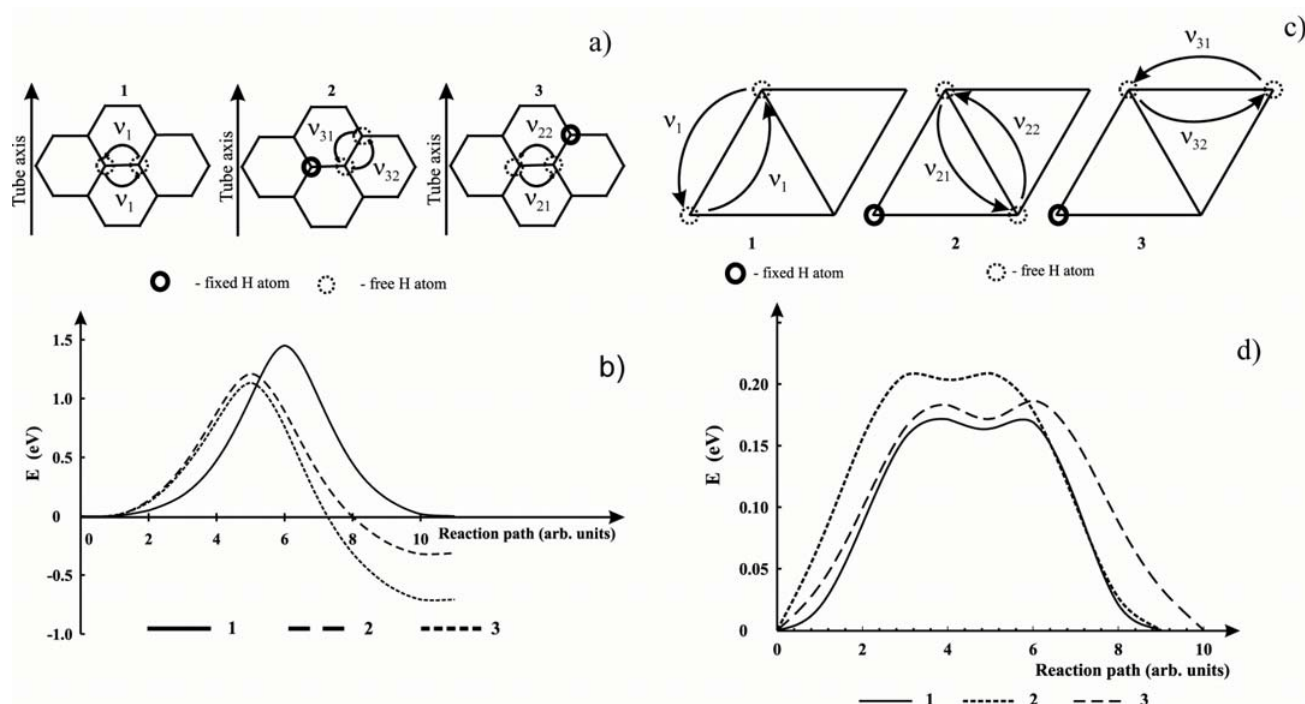
where  $E_{\text{tot}}(\text{CNT} + \text{H})$ ,  $E_{\text{tot}}(\text{CNT})$  and  $E_{\text{tot}}(\text{H})$  are the total energies of CNT with adsorbed hydrogen atom, CNT and single hydrogen atom, respectively.

The adsorption energy  $E_{\text{adsorbed}}^{\text{Pt+H}}$  of a hydrogen atom on the platinum surface is defined similarly. The contribution of  $F_{\text{vib}}$  to the free energy of a hydrogen atom on a surface due to its vibrations was defined like the same contribution for  $\text{H}_2$  molecules. The vibration frequencies of a H atom on the platinum or CNT surface were calculated from numerically obtained dynamic matrix for a small displacement (0.01 Å) of the H atom relative to three neighbouring surface atoms.

To compare the chemical potentials of adsorbed H atoms on both surfaces and  $\text{H}_2$  molecules in the gas phase, half of the binding energy of  $\text{H}_2$  molecule in the gas phase was added to the chemical potentials of adsorbed H atoms on the surfaces. The  $\text{H}_2$  molecule binding energy  $E_{\text{bind}}^{\text{calc}} = -4.54$  eV was calculated, in good agreement with the experimental value of  $E_{\text{bind}}^{\text{exp}} = -4.57$  eV.

The ratios  $k$  of hydrogen atom hopping on the surfaces were calculated by the transition state theory with taking into account zero-point motions  $\nu_i$  of H atoms above the surfaces:

$$k = A \exp \left( -\frac{E_{\text{barrier}}}{kT} \right), \quad (7)$$



**Figure 2** a) Possible trajectories of H atom hopping on the (8,8) CNT surface (1, without neighbouring H atoms; 2, 3, with neighbouring H atom adsorbed on the nearby C atom). b) Reaction path for 1–3 of a). c) Possible trajectories of H atom hopping on a platinum surface (1, without neighbouring H atoms; 2, 3, with neighbouring H atom adsorbed on the nearby platinum atom). d) Reaction path for 1–3 of c).  $v_i$  are the frequencies of H atom hopping (for both single H atom and H atom near to another H atom) on surfaces from one minimum (above surface atom) to the next one.

where

$$A = \frac{kT}{\hbar} \frac{\prod_{i=1}^{3N-7} [1 - \exp(-\hbar v_i'/kT)]}{\prod_{i=1}^{3N-6} [1 - \exp(-\hbar v_i/kT)}, \quad (8)$$

in which  $T$  is the temperature and  $E_{\text{barrier}}$  is the potential barrier value for atom hopping. The product  $\prod_{i=1}^{3N-6} [1 - \exp(-\hbar v_i/kT)]$  and total energy of zero vibrations

$$E_0 = \sum_{i=1}^{3N-6} \frac{\hbar v_i}{2},$$

were calculated for local minimum position of the hydrogen atom on the surface. The product  $\prod_{i=1}^{3N-7} [1 - \exp(-\hbar v_i'/kT)]$  was obtained from hydrogen atom transition state, i.e. for the hydrogen atom position matched to the maximum total energy.

**3 Results and discussion** We investigated the interaction of armchair (5,5) and (8,8) nanotubes with platinum surface and with hydrogen. We found that CNT binds with platinum surface only via intermolecular forces; at the

same time the shape of both nanotubes was distorted appreciably (see Fig. 1). Also, it was defined that  $\text{H}_2$  molecules are effectively dissociated on the platinum surface with Pt–H binding energy  $E_{\text{bind}} \sim 3.08$  eV. Further the potential profile and rate of hydrogen atom hopping from the CNT to platinum surface have been calculated. This profile is monotonic and the binding energy of hydrogen atoms on CNT (8,8) surface is 1.18 eV higher ( $E_{\text{bind}} = -1.90$  eV) than that for the platinum surface.

Also, the potential profiles and ratios of hydrogen atom hopping on the platinum (Fig. 2a and b) and CNT (8,8) (Fig. 2c and d) surfaces were calculated in the limits of both low and high density of atomic hydrogen on the surface. The calculated potential profile of a hydrogen atom on the CNT surface (see Fig. 2b, path 3) is very close to results from [28] where hydrogen adsorption on graphene was investigated, see also [29]. The calculated hydrogen hopping ratios from one minimum above a surface atom to the next one (in the limit of both low hydrogen density and when the hopping hydrogen atom adjoins with the same neighbour) on platinum and CNT (8,8) surfaces are given in Table 1.

Because for the tube in the low-density limit the hopping rates in different directions relative to the tube axis are varied weakly, the corresponding hopping rate only for the single direction is given in Table 1. It was established that results for adsorption on CNT (5,5) were very close to the results for adsorption on CNT (8,8), so they are not



**Table 1** Adsorption energy of hydrogen atoms (see Fig. 2a and c) adsorbed on CNT (8,8) and platinum surfaces at various temperatures and at a pressure of 500 bar, with and without neighbour H atoms present.

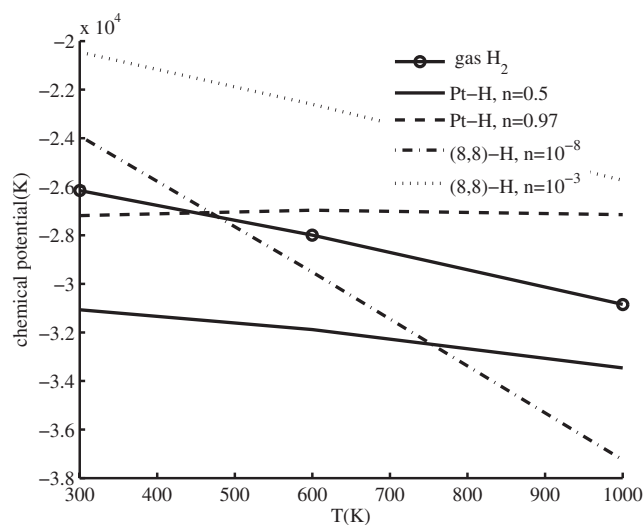
system	adsorption energy (eV)	frequency H atom hopping (s <sup>-1</sup> )														
		300 K					600 K					900 K				
		V <sub>1</sub>	V <sub>22</sub>	V <sub>31</sub>	V <sub>32</sub>	V <sub>1</sub>	V <sub>21</sub>	V <sub>22</sub>	V <sub>31</sub>	V <sub>32</sub>	V <sub>1</sub>	V <sub>21</sub>	V <sub>22</sub>	V <sub>31</sub>	V <sub>32</sub>	
Pt-H	-3.08	4.5 × 10 <sup>11</sup>	-	-	-	2.6 × 10 <sup>12</sup>	-	-	-	-	4.9 × 10 <sup>12</sup>	-	-	-	-	
Pt-H-H	-2.56	6.22 × 10 <sup>9</sup>	6.22 × 10 <sup>9</sup>	5.65 × 10 <sup>10</sup>	1.27 × 10 <sup>11</sup>	3.07 × 10 <sup>11</sup>	3.07 × 10 <sup>11</sup>	9.0 × 10 <sup>11</sup>	1.5 × 10 <sup>12</sup>	1.14 × 10 <sup>12</sup>	1.14 × 10 <sup>12</sup>	1.14 × 10 <sup>12</sup>	2.3 × 10 <sup>12</sup>	3.5 × 10 <sup>12</sup>		
(8,8)-H	-1.90	2.8 × 10 <sup>10</sup>	-	-	-	94.0	-	-	-	6.5 × 10 <sup>5</sup>	-	-	-	-		
(8,8)-H-H	-2.25	-	1.3 × 10 <sup>16</sup>	3.0 × 10 <sup>5</sup>	2.0 × 10 <sup>6</sup>	2.4 × 10 <sup>11</sup>	7.0 × 10 <sup>2</sup>	2.7 × 10 <sup>4</sup>	7.0 × 10 <sup>3</sup>	27.7	5.4 × 10 <sup>3</sup>	2.6 × 10 <sup>7</sup>	0.8 × 10 <sup>7</sup>	2.9 × 10 <sup>5</sup>		

shown here. However, due to bigger curvature of the (5,5) tube the binding energies of hydrogen atoms on the CNT surface are equal -2.04 and -2.23 eV for the cases of adsorption of single hydrogen atom and hydrogen atom adsorbed near another one, respectively.

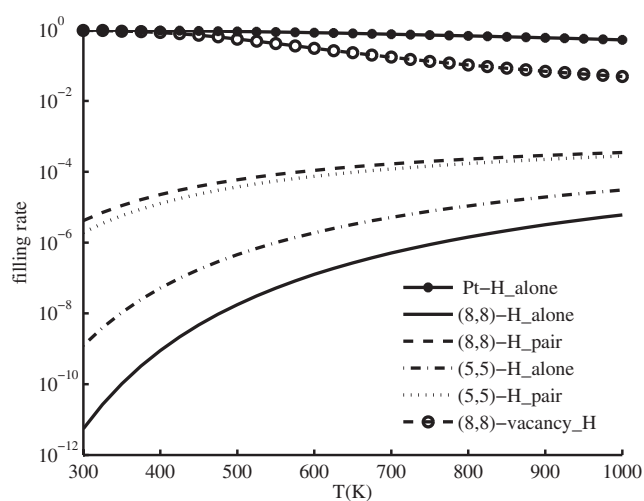
As for hydrogen adsorption on platinum surface, it is established that hydrogen migrates on the platinum surface practically freely at any temperature but sufficient hydrogen diffusion on CNT surface starting with temperature  $T > 450-500$  K, i.e. such systems can be used as hydrogen storage starting with working temperatures  $T > 450$  K. Also, we conclude that the hydrogen atom location in the inter-layer space between the CNT and the platinum surface is less energetically favourable than that outside this region.

Using equality of the chemical potentials of hydrogen atoms adsorbed on platinum and CNT surfaces as well as molecular hydrogen in the gas phase in thermodynamic equilibrium, the hydrogen density adsorbed on both surfaces in equilibrium have been calculated (see Figs. 3 and 4). In Fig. 3 chemical potentials of hydrogen atom on platinum and CNT (8,8) surfaces at various temperatures (300-900 K) and at a pressure of 500 bar are shown. One can see that chemical potentials of hydrogen in the gas phase and on platinum surface at a concentration of 0.97 and at temperature ~450 K are practically compared. The chemical potentials of hydrogen atoms on CNT surface up to a concentration  $C \sim 10^{-8}$  are considerably higher, so the equilibrium concentration of hydrogen atoms chemically adsorbed on CNT surface is very small at all reasonable temperatures (~10<sup>-3</sup> wt% at 1000 K).

We have calculated the energy of vacancy formation in CNT (8,8) and also the energy of hydrogen atom adsorption on this vacancy. The calculated energy of the vacancy is  $E_{vac}^{CNT} = -8.05$  eV which is close to the experimental value for graphite  $E_{vac}^{graphite} = -7.5$  eV [30]. We suppose that



**Figure 3** Chemical potentials of H atoms on platinum and CNT (8,8) surfaces as well as the potential of H<sub>2</sub> molecule (with counting on the one H atom) in the gas phase at various temperatures and at a pressure of 500 bar.



**Figure 4** Equilibrium densities of single and paired hydrogen atoms adsorbed on CNT (8,8) and (5,5) surfaces at various temperatures and at a pressure of 500 bar.

the difference in these quantities is the effect of surface curvature. The value of hydrogen adsorption energy on CNT vacancy is  $E_{\text{vac-adsorbed}}^{\text{CNT+H}} = -2.68$  eV. Due to the large hydrogen adsorption energy on CNT vacancies, the value of hydrogen adsorption on CNT vacancies has a significant value in comparison with defect-free CNT surface (see Figs. 3 and 4). The equilibrium hydrogen densities for both single and paired hydrogen atoms adsorbed on CNT (8,8) and (5,5) surfaces at various temperatures are shown in Fig. 4. Also shown in this Fig. is the equilibrium concentration of hydrogen atoms adsorbed on (8,8) CNT vacancies.

**4 Conclusions** A detailed analysis of chemical hydrogen adsorption in systems composed of CNT and attached platinum cluster has been carried out. It was shown that hydrogen easily dissociates on the platinum surface and diffuses over the surface. It can diffuse to the attached CNT surface by the spillover effect, but the equilibrium concentration of hydrogen adsorbed on the surface of CNTs with different diameters is very small due to low hydrogen adsorption energy. For example, hydrogen concentration  $n/n_{\text{max}} \sim 10^{-8}$  for (8,8) CNT at  $T = 500$  K when surface hydrogen diffusion value becomes essential. So it can be concluded that the chemical adsorption of hydrogen on CNT surface with metal catalysts clusters does not satisfy to the requirement of hydrogen energetics. But hydrogen can be effectively adsorbed on CNT vacancies at temperatures above 450 K when hydrogen diffusion on the CNT surface is large enough and the rate of filling by hydrogen atoms of surface sites is  $\theta = 0.5$ .

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