CHEMICAL PHYSICS
OF NANOMATERIALS

Calculation of the Energy of Binding of Titanium and Scandium Complexes to the Surface of Carbon Nanotubes

A. A. Kuzubov[a,b,c], P. O. Krasnov[b,c], T. A. Kozhevnikov[a], and M. N. Popov[b]

[a] *Institute of Natural and Humanitarian Sciences of Siberian Federal University, Krasnoyarsk, 660041 Russia*
[b] *Kirenskii Institute of Physics, Siberian Division, Russian Academy of Sciences, Akademgorodok, Krasnoyarsk, 660036 Russia*
[c] *Siberian State Technological University, Krasnoyarsk, 660049 Russia*
e-mail: kaa@iph.krasn.ru
Received July 31, 2008

Abstract—Complexes of zigzag-type carbon nanotubes (CNTs) with transition metal atoms, scandium and titanium, were studied. It was demonstrated that the energy of binding of both atoms with a carbon surface decreases whereas the rate of diffusion along the surface increases with increasing nanotube diameter. The rate constant of migration of scandium atoms over a CNT surface are several orders of magnitude higher than that for titanium atoms, because the CNT surface–Sc atom binding energy is substantially lower.

INTRODUCTION

Molecular hydrogen is an economically more efficient and ecologically cleaner fuel than various hydrocarbons.

Despite obvious advantages of hydrogen energetics, there remain a number of problems on the way to its industrial realization, notably the absence of effective methods for storing molecular hydrogen with favorable volumetric and gravimetric relations between the gas and the material used to retain it. In the last decade, carbon nanotubes (CNTs) have received considerable attention as a storage material [1–3]. It is known, however, that the energy of physical adsorption of molecular hydrogen on a CNT surface is too low (~0.03 eV) to make them suitable for accumulating considerable amounts of hydrogen [4].

The works [5–11] in which carbon nanostructures (fullerenes, nanotubes, etc.) coated with a layer of transition metals were proposed to be used as hydrogen adsorptions. The idea behind this proposition is that molecular hydrogen interact with such materials in a specific way, resulting in the formation of the so-called Kubas complexes [5, 12, 13]. In such complexes, hydrogen has a structure close to the molecular one, since it virtually does not dissociate into atoms. In this case, the energy of binding of hydrogen molecules with individual metal atoms at the CNT surface energy lies within 0.2–0.5 eV [5–7], values an order of magnitude larger than the energy typical of physical adsorption but smaller than the typical energy of a chemical bond, which suggests that hydrogen desorption can occur under mild conditions. These works were stimulated by experimental [14, 15] and simulation [16–19] studies, which demonstrated the possibility of coating of CNTs with transition metals. Note

that only titanium and possibly scandium can directly interact with a CNT surface, forming a metal layer on it. Atoms of the other transition metals cannot interact with CNTs in this way, so that they can be deposited only onto an intermediate scandium or titanium layer.

The known studies of the interaction of molecular hydrogen with the proposed materials have a serious drawback, since they ignored the possibility of aggregation of metal atoms into clusters on the surface of the nanostructure and gas molecules were postulated to interact with individual metal atoms. Clearly, the characteristics of metal clusters differ from those of individual atoms. It was demonstrated [20] that the aggregation of scandium on a CNT surface seriously worsens the properties of these structures as hydrogen storage materials. First, nearly all bound hydrogen molecules dissociate. Second, the fraction of gas adsorbed diminishes drastically. Third, the energy of adsorption of undissociated hydrogen molecules decreases significantly, to values typical of physical adsorption.

The fundamental reason why metal atoms aggregate on a CNT surface is a high energy of their interaction with each other, comparable with the energy of their interaction with the CNT surface, and low energy barrier heights to their motion along the carbon surface. The present work was motivated by the desire to understand the effects of these two factors through theoretically examining the energies of binding of scandium and titanium to nanotubes with various diameters and chirality indices $(n, 0)$ and the energetic and kinetic characteristics of the migration of atoms of these metals along a CNT surface.

SIMULATION METHOD
AND THE OBJECTS OF THE STUDY

Simulations of the characteristics of complexes of Sc and Ti with CNTs with chirality indices $(n, 0)$ $(n = 5–15)$ were performed under periodic conditions. The parameters of the supercell were chosen so as to exclude the interaction of structures belonging to different supercells: 14.5–17 by 14.5–17 Å (depending on the type of nanotube) in the plane perpendicular to the nanotube axis and 7–8 Å along the nanotube axis. Thus, the supercell contained a segment of the nanotube and a metal atom.

Calculations were performed within the framework of the density functional theory (DFT) [21, 22] implemented in the VASP (Vienna Ab-initio Simulation Package) [23–25]. This program for ab initio calculations is based on the pseudopotential method and the expansion of the wavefunctions in a plane wave basis. To substantially decrease the number of basis functions and to increase the rate of calculations, the program employed the Vaderbild pseudopotential [26] for all the atoms involved.

The energy of binding of metals to a CNT was calculated by the formula

$$E_{bond} = E_{CNT} - E_{CNT + Me} - E_{Me},$$

where $E_{CNT + Me}$ is the energy of the equilibrium state of the metal–CNT complex, E_{CNT} is the energy of the equilibrium state of the CNT, and E_{Me} is the metal energy.

The direction of diffusion of scandium and titanium atoms, reaction paths, and kinetic parameters (rate constant, preexponential factor, and activation energy were calculated for nanotubes with chirality indices of $(9,0)$ and $(10, 0)$.

To determine the characteristics of the transition state and potential barriers for metal atom jumps along a CNT surface, we used a nudged elastic band method [27]. The vibrational spectrum was calculated for the equilibrium and transition states. The vibrational frequencies of a metal atom at a CNT surface were determined based on numerically calculated dynamic matrix of its displacements and the nearest-neighbor atoms of the carbon surface.

The rate constant for metal atom jumps along the CNT surface was calculated within the framework of the transition state theory by the formula

$$k = A\exp\left(-\frac{E_a}{k_B T}\right),$$

where A is given by

$$A = \frac{k_B T}{h}\left\{\prod_{i=1}^{3N-7}\left[1 - \exp\left(\frac{h\nu_i^\#}{k_B T}\right)\right]\right\}$$

$$\times \left\{\prod_{i=1}^{3N-6}\left[1 - \exp\left(\frac{h\nu_i}{k_B T}\right)\right]\right\}^{-1}.$$

Here, T is the temperature, and ν and $\nu^\#$ are the vibrational frequencies for the equilibrium and transition states, respectively. The value of the denominator in the above expression was calculated for an optimal state of the metal atom in the local potential energy surface minima, whereas the numerator, for the transition state. The activation energy E_a was defined as the difference between the energies of the local minimum and the top of the potential energy barrier, with consideration given to the zero-point vibrations of the CNT–Me system in the ground,

$$E_0 = \sum_n \sum_{i=1}^{3N-6}\left(n + \frac{1}{2}\right)h\nu_i \approx \sum_{i=1}^{3N-6}\frac{h\nu_i}{2},$$

and transition

$$E_0^{TS} = \sum_n \sum_{i=1}^{3N-7}\left(n + \frac{1}{2}\right)h\nu_i^\# \approx \sum_{i=1}^{3N-7}\frac{h\nu_i^\#}{2},$$

states. Here, n is the vibrational quantum number. The validity of the $n = 0$ approximation used in these two formulas was supported by preliminary calculations with the use of the Gibbs distribution, which showed that, even at a temperature of 600 K, the population of the excited vibrational levels does not exceed 3%.

RESULTS AND DISCUSSION

Calculations of the most favorable positions of scandium and titanium atoms at a CNT surface demonstrated that the position of Me at the center of the hexagon formed by carbon atoms corresponds to the minimum energy. Since the hexagon is distorted, two carbon atoms aligned along the nanotube axis occur closer to the metal atom. Depending on the parameters of the CNT, the CNT–Sc distances lie within 2.17–2.24 and 2.42–2.54 Å for the shorter and longer bonds, respectively. The analogous distances for the CNT–Ti system are 2.07–2.15 and 2.29–2.43 Å, respectively.

Figure 1 shows the calculated binding energies of the Me–CNT complexes as a function of their chirality. As can be seen, this dependence is of oscillating character. As the nanotube diameter increases, the binding energy increases whereas the oscillation amplitude decreases. For CNTs of large diameter, the energy of binding of the metal atom with the CNT is identical to the energy of binding with a graphite surface [20]. Local maxima in the binding energy are observed for complexes with nanotubes having a small energy gap width (for example, for nanotubes with chirality indices (9, 0), (12, 0), etc.).

The most probable mode of diffusion of a Me atom along (9, 0) absorbed (10, 0) CNT surfaces is hopping from the center of a hexagon to the center of another hexagon via two routes: across a C–C bond directed along the nanotube axis (ax) or across a C–C bond directed at an angle to the nanotube axis (nax) (Fig. 2).
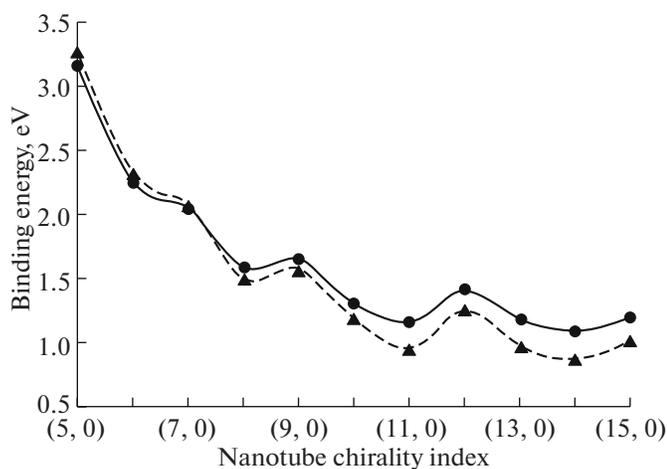
Fig. 1. Dependence of the energy of binding of (▲) Sc and (●) Ti atoms with nanotubes on the nanotube chirality index.

Fig. 2. Possible pathways of migration of metal atoms over a nanotube surface.

For each transition, we determined the reaction paths (Fig. 3) and calculated the kinetic parameters (the rate constants, preexponential factors and activation energies) (table). The reaction trajectory for the motion of the metal atom in the *ax* direction was cal-
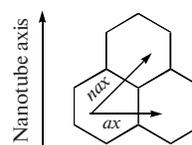
culated only up to the C−C bond, since this position (over the bond) corresponds to a local minimum.

A comparison of the rate constants suggests that the diffusion of a metal atom occurs most rapidly for a nanotube with a chirality index of (10, 0), since the energy of binding to the (9, 0) CNT is higher than that to the (10, 0) CNT, a factor that diminishes the mobility of metal atoms.

A comparison of the probabilities of migration of Sc and Ti atoms shows that the rate constants for Sc are several orders of magnitude higher than for Ti, and, hence, the transition occurs more readily. This can be explained by a substantially lower energy of binding of Sc with the CNT and, consequently, a lower energy barrier height, a factor that leads to an increase in the transition rate.
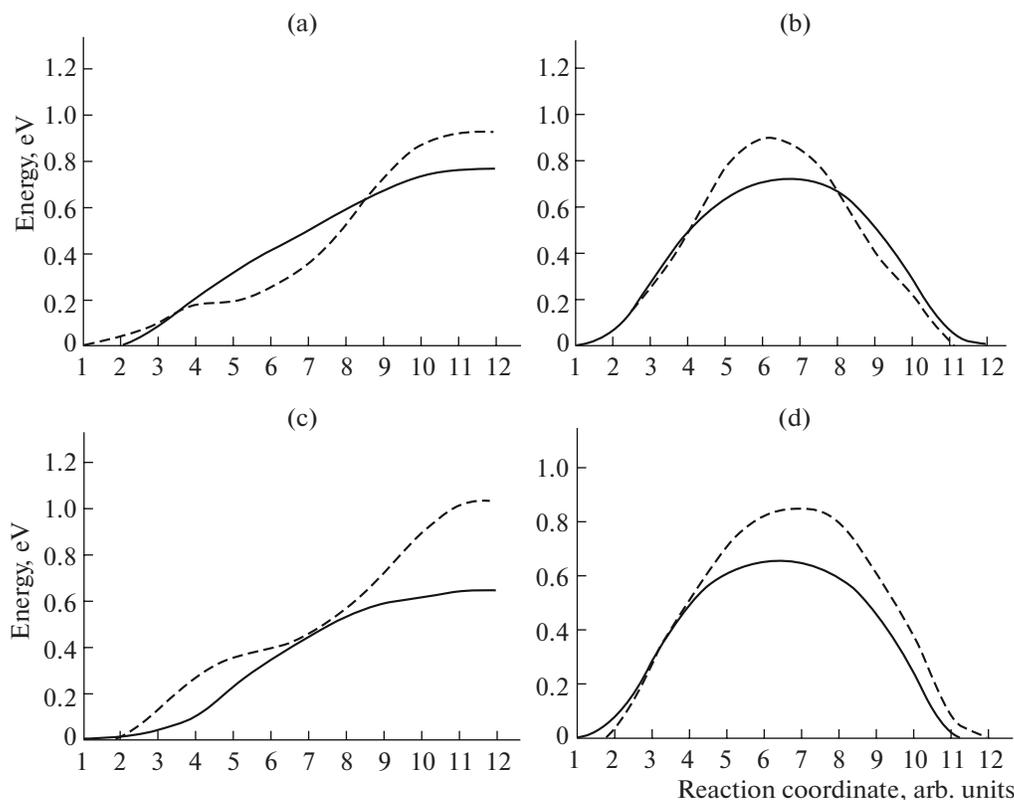

Fig. 3. Energy barrier heights to the transition of Sc (solid line) and Ti (dashed line) across different C−C bonds for nanotubes with different chirality indices: (a) (9, 0), transition across the C−C bond directed along the nanotube axis (*ax*); (b) (9, 0), transition across the C−C bond directed at an angle to the nanotube axis (*nax*); (c) (10, 0), transition across the C−C bond directed along the nanotube axis (*ax*); and (d) (10, 0), transition across the C−C bond directed at an angle to the nanotube axis (*nax*).

Kinetic parameters of the migration of transition metal atoms along (9, 0) and (10, 0) CNT surfaces

CNT	Me	Transition direction	A, s^{-1}	E_a, eV	k, s^{-1}
(9, 0)	Sc	ax	1.07×10^{13}	0.79	0.5984
		nax	8.35×10^{12}	0.73	4.1794
	Ti	ax	1.55×10^{13}	0.87	0.0312
		nax	2.28×10^{13}	0.84	0.1397
(10, 0)	Sc	ax	1.67×10^{13}	0.66	3.60×10^9
		nax	9.26×10^{12}	0.66	1.94×10^9
	Ti	ax	1.09×10^{13}	1.03	2.06×10^7
		nax	8.76×10^{12}	0.86	1.46×10^8

When analyzing the directions of diffusion of metal atom, one can conclude that the transition across the C–C bond oriented at an angle to the nanotube axis is generally more probable (except for Sc on a (10, 0) CNT) than across the C–C bond orientated along the nanotube axis. That the behavior of Sc atoms drops out of this pattern can be explained by the trapping of the Sc atom in the local minimum located just above the bond. This increases the lifetime of the system in the given state, causing a decrease in the migration rate constant. This assumption was confirmed by calculations of the vibrational spectrum, which turned out to contain no imaginary frequencies, a feature indicative of the existence of a local minimum above the bond.

CONCLUSIONS

The results obtained suggest that the energy of binding of scandium and titanium atoms with zigzag-type nanotubes exhibit an oscillating dependence on the nanotube diameter, more specifically, the binding energy increases and oscillation amplitude decreases with increasing nanotube diameter. Nanotubes with chirality indices of $(n, 0)$, where n is a multiple of three can interact with transition metals to form strong complexes. The rate of diffusion of a metal atom along a CNT surface increases with the CNT diameter. The rate of migration of scandium atoms is substantially higher than that of titanium atoms. In all probability, jumps of metal atoms occur across the C–C bond directed along the CNT axis.

ACKNOWLEDGMENTS

REFERENCES

1. A. C. Dillon, K. M. Jones, T. A. Bekkedahl, et al., Nature **386** (6623), 377 (1997).
2. C. Liu, Y. Y. Fan, M. Liu, et al., Science **286** (1127), 1127 (1999).
3. Y. Ye, C. C. Ahn, C. Witham, et al., Appl. Phys. Lett. **74**, 2307 (1999).
4. G. Vidali, G. Ihm, H.-Y. Kim, and M. W. Cole, Surf. Sci. Rep. **12**, 135 (1991).
5. Y. Zhao, Y.-H. Kim, A. C. Dillon, M. J. Heben, and S. B. Zhang, Phys. Rev. Lett. **94**, 155504 (2005).
6. T. Yildirim, J. Iñiguez, and S. Ciraci, Phys. Rev. B **72**, 153403 (2005).
7. T. Yildirim and S. Ciraci, Phys. Rev. Lett. **94**, 175501 (2005).
8. E. Durgun, S. Ciraci, W. Zhou, and T. Yildirim, Phys. Rev. Lett. **97**, 226102 (2006).
9. W. H. Shin, S. H. Yang, W. A. Goddard III, and J. K. Kang, Appl. Phys. Lett. **88**, 053111 (2006).
10. S. S. Han and W. A. Goddard III, J. Am. Chem. Soc. **129**, 8422 (2007).
11. Q. Sun, P. Jena, Q. Wang, and M. Marquez, J. Am. Chem. Soc. **128**, 9741 (2006).
12. G. J. Kubas, R. R. Ryan, B. I. Swanson, P. J. Vergamini, and H. J. Wasserman, J. Am. Chem. Soc. **106**, 451 (1984).
13. G. J. Kubas, Acc. Chem. Res. **21**, 120 (1988).
14. Y. Zhang and H. Dai, Appl. Phys. Lett. **77**, 3015 (2000).
15. Y. Zhang, N. W. Franklin, R. J. Chen, and H. Dai, Chem. Phys. Lett. **331**, 35 (2000).
16. O. Gulseren, T. Yildirim, and S. Ciraci, Phys. Rev. Lett. **87**, 116802 (2001).

17. C. K. Yang, J. Zhao, and J. P. Lu, Phys. Rev. B **66**, 041 403 (2002).

18. E. Durgun, S. Dag, V. M. Bagci, et al., Phys. Rev. B **67**, 201 401 (2003).

19. S. Dag, E. Durgun, and S. Ciraci, Phys. Rev. B **69**, 121 407 (2004).

20. P. O. Krasnov, F. Ding, A. K. Singh, and B. I. Yakobson, J. Phys. Chem. C **111**, 17 977 (2007).

21. P. Hohenberg and W. Kohn, Phys. Rev. B **136**, 864 (1964).

22. W. Kohn and L. J. Sham, Phys. Rev. A **140**, 1133 (1965).

23. G. Kresse and J. Hafner, Phys. Rev. B **47** 558 (1993).

24. G. Kresse and J. Hafner, Phys. Rev. B **49**, 14 251 (1994).

25. G. Kresse and J. Furthmuller, Phys. Rev. B **54**, 11 169 (1996).

26. D. Vanderbilt, Phys. Rev. B **41**, 7892 (1990).

27. G. Henkelman, B. P. Uberuaga, and H. Jónsson, J. Chem. Phys. **113**, 9901 (2000).