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## Interaction of Scandium and Titanium Atoms with a Carbon Surface Containing Five- and Seven-Membered Rings

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**Abstract**—The use of carbon nanotubes coated by atoms of transition metals to store molecular hydrogen is associated with the problem of the aggregation of these atoms, which leads to the formation of metal clusters. The quantum-chemical simulation of cluster models of the carbon surface of a graphene type with scandium and titanium atoms has been performed. It has been shown that the presence of five- and seven-membered rings, in addition to six-membered rings, in these structures makes it possible to strongly suppress the processes of the migration of metal atoms over the surface, preventing their clustering.

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### 1. INTRODUCTION

The search and creation of materials that could store molecular hydrogen in order for its further use as a fuel have been on the focus of attention of researchers for almost two decades. Carbon nanotubes have been considered for a long time as potential objects for this aim [1–3]. It is commonly accepted now that these structures cannot tightly bind hydrogen molecules in view of low physical sorption energy, which prevents storage required amounts of hydrogen in them [4].

As one of the methods for increasing the sorption energy, the authors of [5–7] proposed to use carbon nanotubes coated with transition metal atoms. The essence of this approach is that hydrogen molecules, together with these atoms, can form stable Kubas complexes [8, 9], where hydrogen molecules do not dissociate, and the complex formation energy is lower than the energies characteristic of chemical bonds, but is higher than the intermolecular interaction energies. These properties increase the efficiency of storage of required numbers of hydrogen molecules; in this case, their inverse extraction should occur under nonrigid conditions due to desorption. For the formation of such compounds on the surface of carbon nanotubes, metal atoms should form a uniform coating when one metal atom is over the center of each six-membered carbon ring. These compounds can be of interest not only for storage of hydrogen, but also as materials used as conducting filaments in molecular electronics. In particular, Huang et al. [10] showed that fullerene C<sub>60</sub> with one or two titanium atoms on the surface can be

a catalyst of the dissociation of water molecules and can store hydrogen released in this process.

Our previous studies [11, 12] showed that the formation of the uniform transition-metal coating of carbon nanotubes is a difficult problem mainly because of their aggregation with the formation of metal clusters. This is due to the high energy of the interaction between these atoms and low potential barriers of their displacement along the surface. The diameter of carbon nanotubes insignificantly affects the indicated parameters. This leads to the impossibility of creating a uniform metal layer both on graphene and on small-cross-section nanotubes, i.e., on objects consisting of the six-membered carbon rings (hexagons). At the same time, some authors reported on the formation of stable compounds of fullerene C<sub>60</sub> with transition metals that are located both over five-membered carbon rings (pentagons) [13] and over bonds between carbon atoms [10, 14]. This is probably due to the specificity of both the surface curvature and electronic structure of such objects. Therefore, it is reasonable to expect that the interaction of carbon nanostructures containing seven-membered rings (heptagons) in addition to hexagons with transition-element atoms will be different from the interaction of graphene and carbon nanotubes with the same atoms. This interaction will possibly be more efficient for the formation of the uniform metal coating. In particular, analogs of fullerenes with a negative surface curvature (Buckygym) [15, 16] are such carbon objects.

In this paper, we report on the results of the quantum-chemical simulation of the interaction of small carbon clusters containing hexagons and pentagons,

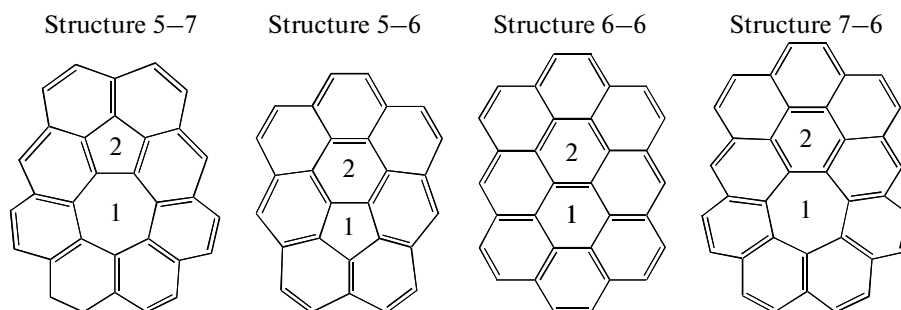


Fig. 1. Structural formulas of objects under study. Digits mark sequential positions of metal atoms.

hexagons and heptagons, and heptagons and pentagons with scandium and titanium atoms. The aim was to calculate the interaction energies in these objects, potential barriers for hops of metal atoms between neighboring carbon rings, and kinetic parameters of these hops. The main goal is to determine the potential efficiency of using carbon nanostructures containing alternating five- and six-membered rings, as well as seven- and six-membered rings, for the sorption of transition metal atoms without their aggregation on the surface.

## 2. OBJECTS AND METHODS OF INVESTIGATION

We studied four small carbon clusters. Their structure can be described as follows. A pair of adjoint carbon rings serves as the key part, where a pair is formed by two hexagons (6–6 structure) in the first case, by a pentagon and a hexagon (5–6 structure) in the second case, by a heptagon and a hexagon (7–6 structure) in the third case, and by a pentagon and a heptagon (5–7 structure) in the fourth case (Fig. 1). The last pair is a Stone–Wales topological defect of the graphene structure [17]. Scandium (Sc) and titanium (Ti) atoms were individually located over both the first and second rings, and the transition of each of these atoms between this pair of rings was considered. The choice of this arrangement of metal atoms is caused by previous study [12], where it was shown that the binding of Sc and Ti atoms over the centers of hexagons is energetically preferable than carbon–carbon bonds. Since the main aim is to study carbon surfaces and we dealt with their cluster models, each of the indicated ring pairs was additionally surrounded by one layer of carbon atoms in order to take into account the effect of neighboring atoms on the key part with which the interaction of scandium and titanium atoms was considered. The unsaturated chemical bonds of carbon atoms of this layer were terminated by hydrogen atoms.

The geometric and electronic structures of the indicated objects in equilibrium and transition states were simulated in the quantum chemical Vienna ab initio simulation package (VASP) [18–20] in the local

density functional formalism [21, 22] with ultrasoft Vanderbilt pseudopotentials [23] and the PW91 exchange–correlation potential [24]. The wavefunction was expanded in the plane wave basis with a cutoff energy of 286 eV. Since only cluster models were studied, only the  $\Gamma$  point of the first Brillouin zone was used in calculations.

The used software package is developed to simulate periodic structures when a unit cell with given translation vectors is considered as an object. Since molecular clusters are considered in this work, periodic conditions should be excluded in order to avoid the interaction between objects from neighboring cells. To this end, the clusters under study were placed at the center of cubic supercells with a translation vector of 15 Å. The intermolecular interaction at these distances can be neglected and only individual molecules are simulated.

The binding energies  $E_b$  of scandium and titanium atoms with carbon clusters were calculated by the formula

$$E_b = E_{\text{surf}} + E_{\text{Me}} - E_{\text{surf-Me}},$$

where  $E_{\text{surf}}$ ,  $E_{\text{Me}}$ , and  $E_{\text{surf-Me}}$  are the calculated total energy of the carbon cluster in the equilibrium state without metal, the energy of the metal atom, and the energy of the cluster with the metal atom on the surface, respectively.

The geometric structure of the transition state of objects under study upon hops of scandium and titanium atoms on the surface from one carbon ring to another was determined by the nudged elastic band method [25]. To determine the rate constants ( $k$ ) of these hops, vibrational spectra were calculated. The frequencies of vibrations of metal atoms on surfaces were determined from the numerically obtained dynamic displacement matrices of these atoms and atoms of the corresponding carbon cluster that are closest to the former atoms. In transition state theory,  $k$  values were calculated by the formula

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

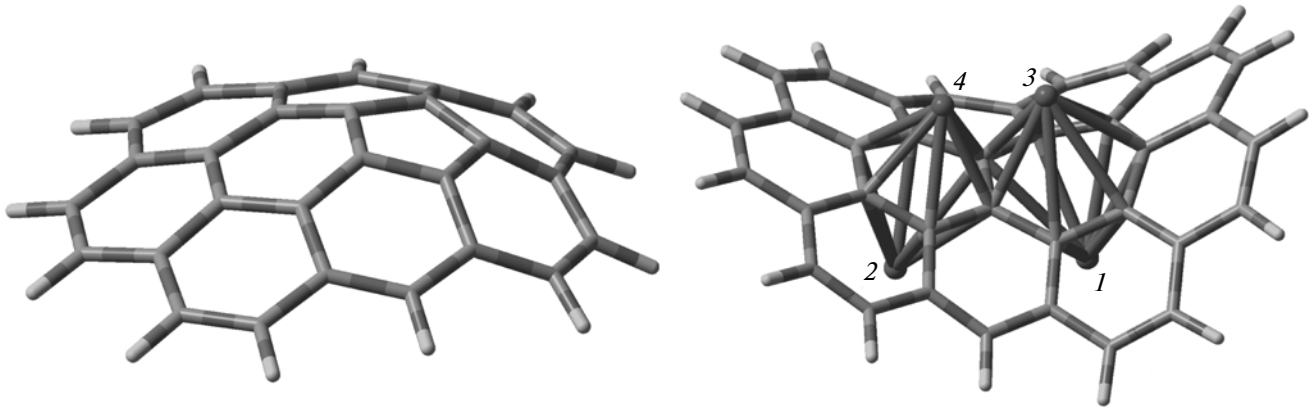


Fig. 2. Optimized (left panel) 5–6 and (right panel) 7–6 structures with the indication of the positions of metal atoms.

where

$$A = \frac{k_B T}{h} \frac{\prod_{i=1}^{3N-7} [1 - \exp(h\nu_i^\# / k_B T)]}{\prod_{i=1}^{3N-6} [1 - \exp(h\nu_i / k_B T)]}.$$

Here,  $T$  is the temperature and  $\nu_i$  and  $\nu_i^\#$  are the vibration frequencies calculated for the objects under study in the equilibrium and transition states, respectively. The activation energy  $E_a$  of hops of metal atoms from the equilibrium states to transition states was determined as the difference between the following total energies of these states including the zero-point energy of the system in these states:

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

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

where  $n$  is the vibrational quantum number. The approximation ( $n = 0$ ) used in the final expressions is justified by the preliminary calculation result based on the Gibbs distribution, which indicated that the population of excited vibrational levels does not exceed 3% even at a temperature of 600 K.

### 3. RESULTS AND DISCUSSION

In the process of simulation of the geometric structure of objects under study in the equilibrium state without metal atoms, the 6–6 and 5–7 structures remain flat, whereas the surfaces of the 5–6 and 7–6 structures acquire a positive Gaussian curvature (such as in the case of fullerenes) (left panel in Fig. 2) and a negative Gaussian curvature, respectively. This fact was taken into account when choosing the positions of metal atoms over the corresponding carbon rings. In

the case of the 6–6 and 5–7 structures, both sides of each cluster are identical; for this reason, any of them can be chosen. In the 5–6 structure, scandium and titanium atoms were placed over the convex side, similar to the interaction with fullerenes. In the 7–6 structure, we considered both cases of the location of metal atoms on both sides (Fig. 2, right panel). As compared to Fig. 1, there are two new positions, 3 and 4, similar to positions 1 and 2 on the opposite side of the cluster. In the last case, two sides were considered because the interactions of metal atoms with both sides of the carbon surface are possible in a three-dimensional periodic structure with the negative surface curvature. It is noteworthy that we additionally simulated the 5–6 structure, where metal atoms were located on the concave side of the surface (similar to the inner surface of fullerenes). Irrespectively of the initial position of a scandium or titanium atom (over a pentagon or a hexagon), the geometry optimization leads to a structure in which a metal atom is located over a carbon–carbon bond between both rings under consideration. In this case,  $E_b = 1.05$  and  $1.09$  eV for scandium and titanium, respectively. The resulting structure will not be considered below, because the aim of this work is to study the migration of metal atoms between adjacent rings, which is not observed in this structure.

The results of the calculation of the binding energy  $E_b$  of scandium and titanium atoms with carbon clusters (shown in table) indicate that the strongest bindings of metal atoms are with five- and seven-membered carbon rings. In this case,  $E_a$  of transition states is in any case higher for the transition of the metal atom from pentagon or heptagon (from positions 1 and 3), rather than from hexagon (from positions 2 and 4). This indicates that compounds in which scandium or titanium atoms are located over five- and seven-membered carbon rings are more stable. In the 5–7 structure, the activation energy  $E_a$  of the transition of a scandium or titanium atom from a heptagon to a pentagon is higher than that in the opposite direction. The binding energy  $E_b$  of the metal atom with the

Values of energies  $E_a$ ,  $E_b$ , and hops  $k$  of scandium and titanium atoms on the surfaces of the objects under study

Structure	Metal atom position	$E_b$ , eV		$E_a$ , eV		$k$ , s <sup>-1</sup>	
		Sc	Ti	Sc	Ti	Sc	Ti
5–6	1	1.61	1.69	0.42	0.34	$8.34 \times 10^5$	$6.61 \times 10^{11}$
	2	1.25	1.64	0.06	0.28	$3.56 \times 10^{10}$	$3.65 \times 10^{11}$
5–7	1	2.27	2.45	0.44	0.69	$1.72 \times 10^5$	$1.41 \times 10^1$
	2	1.95	1.90	0.12	0.14	$9.78 \times 10^9$	$6.80 \times 10^9$
6–6	1	0.93	1.44	0.03	0.46	$1.27 \times 10^8$	$4.43 \times 10^5$
	2	0.93	1.44	0.03	0.46	$1.27 \times 10^8$	$4.43 \times 10^5$
7–6	1	1.92	2.00	0.51	0.52	$9.20 \times 10^3$	$9.67 \times 10^3$
	2	1.47	1.71	0.05	0.24	$4.98 \times 10^{11}$	$5.15 \times 10^8$
	3	1.97	2.22	0.88	0.93	$1.87 \times 10^{-2}$	$1.15 \times 10^{-2}$
	4	1.36	1.72	0.27	0.42	$9.61 \times 10^6$	$5.16 \times 10^5$

heptagon is higher than that with the pentagon. The situation with the 5–6 and 7–6 structures is similar. Comparison shows that the binding energy of Ti in the 5–6 structure is about 0.2–0.3 eV higher than the results reported in [10] for fullerene C<sub>60</sub>. This is primarily because the titanium atom in [10] was located over the carbon–carbon bond and this position is apparently most energetically favorable, because the curvature of the surface of fullerene is larger than that of the 5–6 structure. Thus, the curvature of the carbon surface affects the choice of the most favorable localization of the metal atom, which was obtained optimizing geometry when scandium and titanium atoms were located on the concave side of the 5–6 structure and were attached to the structure over the carbon–carbon bond between the adjoint rings under consideration.

Comparison shows that the binding energy of the metal atoms with the six-membered ring in the 5–6 and 7–6 structures is higher than that in the 6–6 structure because the change of a hexagon to a pentagon or heptagon is accompanied by the distortion of the carbon surface. This distortion leads to the violation of the conjugation of the electronic  $\pi$  system; as a result, the reactive capability of these structures increases. Thus, the feature of the curvature of the carbon surface affects the strength of binding of scandium and titanium atoms, but taking into account that the binding energy of these atoms with the five- and seven-membered rings is higher, it is noteworthy that this is not the only factor. The features of the geometric and electronic structures of the pentagon and heptagon probably constitute an additional factor.

Concerning kinetic aspects, the  $k$  value for the 1–2 and 3–4 transitions is five to eight orders of magnitude lower than that in the opposite direction (see table) except for the transition of the titanium atom in the 5–6 structure, where the constants almost the same in both cases. Therefore, the scandium and titanium atoms interacting with the carbon surface containing

five- and seven-membered rings are preferably bound with these rings than with six-membered rings. This is because the diffusion of scandium and titanium atoms on the surface under identical thermodynamic conditions in the 1–2 and 3–4 directions is more probable than in the 2–1 and 4–3 directions. The  $k$  value for the transition of the metal atom from the heptagon to the pentagon in the 5–7 structure is four to eight orders larger than that in the opposite direction. Thus, in the presence of a Stone–Wales defect on the carbon surface, diffusion of transition metal atoms preferably occurs from five-membered rings to seven-membered rings rather than in the opposite direction.

#### 4. CONCLUSIONS

The performed quantum-chemical calculations confirm that the interaction of transition metal atoms with the carbon surface containing five- and seven-membered carbon rings is stronger than that with the surface containing only six-membered rings. An increase in the binding energy of metal atoms is due to the curvature of the carbon surface and, probably, to the features of the geometric and electronic structures of five- and seven-membered rings. The interaction of scandium and titanium with these rings is stronger than that with six-membered rings; for this reason, it should be expected that the aggregation of metal atoms located over seven-membered rings will not occur in these structures similar to fullerenes with the negative curvature of the surface. This will make it possible to exclude the dissociation of hydrogen molecules because they will interact with individual transition-element atoms, which lead to the formation of the aforementioned Kubas complexes.

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