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Research

HYDROGEN SORPTION BY CARBON NANOSTRUCTURED MATERIALS

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ABSTRACT

The ability to use carbon-containing nanostructured systems for hydrogen storage has been evaluated. For considered systems, the limit of sorption capacity of hydrogen for the chemical and physical nature of the sorption, have been calculated. The results of the theoretical calculations showed the possibility and prospects for the use of hydrogen storage systems.

INTRODUCTION

The discovery of highly organized allotropic modifications of carbon, such as fullerenes, carbon nanotubes (CNT) and nanofibers (NF) made it possible to create a lot of new promising nanomaterials. The investigations in the application area have been conducting worldwide.

For the last years it was found, that materials, based on these nanostructures, have unique characteristics for absorbing gases (Hirscher et al., 2002). So the researches aimed at the studying of the sorption capacity of fullerenes, nanotubes, nanofibers and technical carbon in the relation to different gases, are relevant.

Lately it has been extensively investigating the question of the use in fuel cells, which could have accumulated hydrogen as an alternative to hydrocarbon fuel. This paper presents the results of theoretical studies of the processes of the chemical and physical adsorption of hydrogen by carbon nanostructures. The estimation of the possibility and efficiency of using these nanostructures as hydrogen sorbents are also reported.

RESULTS

Chemical Hydrogen Sorption by Carbon Nanostructures

The most common methods of numerical modeling of the electronic and atomic structure of complex systems are the methods of quantum chemistry and molecular dynamics. To use these methods most appropriate is the computer program HyperChem, which allows to use the methods of molecular dynamics and quantum chemistry.

Using the program HyperChem, it has been studied by us the process of chemical adsorption of hydrogen. The computer simulation of fullerenes, carbon nanotubes, nanofibers and the processes of hydrogen adsorption has been implemented through methods of quantum chemistry.

To determine the adsorption energy and optimization of the system's geometry, a semi-empirical method MNDO (modified neglect of diatomic overlap) has been applied. After the simulation and optimization of the geometry of the system the chemical attachment of hydrogen atoms to the atoms considered nanostructures has been studied. The coverage was defined as the ratio of the number of adsorbed atoms of hydrogen to the number atoms of the considered nanostructures:

$$\theta = \frac{N_H}{N_N}\ , \qquad (1)$$

θ, is the degree of coverage nanostructures by hydrogen; N_H, is the number of adsorbed hydrogen atoms; N_N, is the number of atoms of the considered nanostructures.

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Specific energy of the absorption was calculated by the formula (Popov et al., 2011):

$$E_{ads} = \frac{Å_{sys} - Å_N - N_H E_H}{N_H}, \quad (2)$$

E_{ads}, the specific energy of hydrogen adsorption; E_{sys}, the full energy of the system "nanostructure-adsorbate"; E_N-the full energy of the nanostructure; E_H, the energy of the single hydrogen atom; N_H, the total number of adsorbed hydrogen atoms.

Energy E_{sys} and E_N have been taken in the case of a fully optimized geometry. As the result the adsorption energy per an atom of hydrogen was obtained. If the adsorption energy is negative, then the candidate system is considered to be stable.

Then the dependence of the adsorption energy on the degree of coverage and stable conformations of the system was determined. The limit for hydrogen sorption capacity was determined from the formula:

$$\eta_H = \frac{m_H}{m_H + m_N} \cdot 100\% \quad (3)$$

η_H, the limit for hydrogen sorption capacity, wt.%; m_H, the mass of adsorbed hydrogen; m_N, the mass of free nanostructure.

The preliminary calculations showed that hydrogen atoms adsorb by vapors, as it is energetically favorable. Therefore, the cases paired adsorption of hydrogen atoms in the calculations have been considered.

The calculations were performed for a single particle of nanostructure as the quantity of adsorbed hydrogen depends on the distance between the particles, and reaches its maximum value when the influence of neighboring particles is few. In this case the adsorption of hydrogen can be regarded on a single isolated particle.

The calculated adsorption energy, depending on the degree of coverage of the fullerene molecule C_{60} by the hydrogen atoms is shown in Table 1.

The results of quantum-chemical calculation have been showed that a single molecule of C_{60} in the limit can adsorb 60 hydrogen atoms. In this case, the calculated sorption capacity was 7.7 wt. %.

Simulated single-walled carbon nanotube (SWCNT) includes 72 carbon atoms, corresponding to the three unit cells by 24 atoms along the axis. The calculation was performed for the single-walled carbon nanotube with chirality (6.6). For these SWCNTs the cases of chemical adsorption of hydrogen on the inner surface were also considered for every 6 atoms of carbon nanotubes were chemically adsorbed 1, 2 and 3 hydrogen atoms. The calculated adsorption energy, depending on the degree of coverage of SWCNT hydrogen atoms to stable conformations is shown in Table 2.

Table 1. The energy of hydrogen adsorption by fullerenes.

The Degree of coverage	The Adsorption energy, eV	The Degree of coverage	The Adsorption energy, eV
0.033	-2.453	0.567	-2.695
0.100	-2.520	0.633	-2.614
0.167	-2.840	0.700	-2.574
0.233	-2.642	0.767	-2.548
0.3	-2.641	0.833	-2.552
0.367	-2.748	0.900	-2.604
0.433	-2.667	0.967	-2.614
0.500	-2.704	1.000	-2.658

Table 2. The energy of hydrogen adsorption of SWCNT.

External adsorption		Internal adsorption	
The Degree of coverage	The Adsorption energy, eV	The Degree of coverage	The Adsorption energy, eV
0.083	-3.349	0.167	-0.228
0.250	-3.236	0.333	-1.335
0.417	-3.976	0.500	-0.871
0.583	-2.635		
0.750	-2.870		
0.917	-2.829		
1.000	-2.807		

For external adsorption maximum sorption capacity was amounted to 7.7 wt.%, for internal adsorption - 4 wt.%. To calculate the sorption capacity of the graphene layer of nanofiber, the layer consisting of 30 carbon atoms has been selected.

The calculated adsorption energy, depending on the degree of covering layer nanofiber by hydrogen atoms, is shown in Table 3. From the results of the calculation it has been founded, that the graphene layer can adsorb over 36 hydrogen atoms, thus the maximum adsorption capacity is 9.1 wt.%.

Table 3. The energy of hydrogen adsorption by nanofiber.

The Degree of coverage	The Adsorption energy, eV	The Degree of coverage	The Adsorption energy, eV
0.067	-4.795	0.667	-4.166
0.133	-4.763	0.733	-3.986
0.200	-4.757	0.800	-3.849
0.267	-4.781	0.867	-3.637
0.333	-4.893	0.933	-3.598
0.400	-5.058	1.000	-3.534
0.467	-5.142	1.067	-3.507
0.533	-4.754	1.133	-3.485
0.600	-4.310	1.200	-3.453

Calculation of Physical Hydrogen Sorption by Carbon Nanostructures

With the help of HyperChem software package the process of physical adsorption of hydrogen for carbon nanostructures by molecular dynamics using the Amber 94 force field was calculated.

For the C_{60} fullerene molecule the value of the sorption capacity for hydrogen at a temperature of 80 K and a hydrogen pressure of 0.1 MPa, 1 MPa and 10 MPa was 0.9 wt.%, 2.7 wt.% And 7 wt.%, respectively; and at T=300 K and a pressure of 10 MPa-3.3 wt.%.

In the case of SWNT (6.6) consisting of 72 carbon atoms, the value of the sorption capacity for hydrogen at a temperature of 80 K and a hydrogen pressure of 0.1 MPa, 1 MPa and 10 MPa, respectively, was 0.2 wt.%, 1.1 wt.% and 5.3 wt.%. At T=300 K and a pressure of 10 MPa sorption capacity of hydrogens equal to 2.3 wt.%.

For HB graphene layer nanofiber consisting of 30 carbon atoms, the value of the sorption capacity for hydrogen at a temperature of 80 K and a hydrogen pressure of 0.1 MPa, 1 MPa and 10 MPa was 1 wt.%, 3.2 wt.% And 9 wt.% ; and at a temperature of 300 K and a hydrogen pressure of 10 MPa - 4.7 wt.%.

From these data, it is clear that the increase in pressure increases the sorption capacity. At the same time, the temperature rise on the contrary lead so a drop in the value of the weight percentage sorption capacity by hydrogen.

The evaluation of sorption capacity of the technical carbon in view of that its layers structure is irregular, was performed according to the model proposed in "Science of Fullerenes and Carbon Nanotubes" (Dresselhaus et al., 1996). Having a model that hydrogen is a liquid and the sorption caused by the penetration it in pore volume of the sorbent and filling all empty space.

Maximum of sorption capacity is determined by the formula:

$$\eta_H = \frac{\rho_H}{\rho_H + \rho_t} \cdot 100\% \quad (4)$$

ρ_H = 70.8 kg / m^3 - the density of liquid hydrogen; $\rho_{t,}$ the mass density of the sample.

Furthermore, the calculation of the sorption capacity of the technical carbon was carried out under the assumption, that it is appropriate for transportation in a granular state. In this case, the density of technical carbon is 300-600 kg/m^3, as a result of the maximum adsorption capacity of hydrogen, according to the formula (4) is in the range of 19.1-10.6 wt.% respectively.

CONCLUSION

Thus, the results of the theoretical calculations showed the possibility and prospects for the use of hydrogen storage systems, and in particular of technical carbon and nanofibers and having according to information, received the greatest values of sorption capacity for hydrogen.

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