RESULTS OF THEORETICAL AND EXPERIMENTAL INVESTIGATIONS OF HYDROGEN ADSORPTION CAPACITY BY CARBON NANOSTRUCTURES

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Introduction

Published data of the adsorption efficiency for the same carbon substances are often contradictory [1-3]. The discrepancies may be related to differences in the structure of objects studied by various researchers. In this paper we present results of experimental investigations of physical hydrogen adsorption by different carbon-based materials obtained in carbon-helium plasma at atmospheric pressure. These results are at good correlation with our theoretical calculations.

Results and discussion

We developed installation for the hydrogen adsorption measurements. In this installation we can carry out investigation at the temperature from 77K to 773K and pressure up to $1.5{\cdot}10^7$ Pa.

Hydrogen adsorption was investigated on the following samples: termolisis residual (T), fullerene-containing soot caught from outlet gas of reactor (S1), fullerene-contained soot taken from the walls of reactor (S2), fullerene mixture (F). All samples were obtained in the reactor for fullerene synthesis described in detail in [4–5]. Also we investigate hydrogen adsorption on graphitized Al_2O_3 sorbent (A), which was obtained by original plasma method [6].

Each sample was heated to 773K in a vacuum of 10^{-2} Pa created by roughing (mechanical) and oil-diffusion pumps via a liquid-nitrogen trap. Then the pumping stage was disconnected and the chamber was filled by hydrogen at a pressure of 10^7 Pa. The hydrogen pressure was maintained constant, while the sample was cooled up to 77K and kept under these conditions for 20 min. In order to desorb the stored hydrogen, the sample was gradually heated. Maximum value of temperatures were different (it depended on sample stability). The amount of evolved hydrogen was measured during heating.

The temperature dependence of the mass of hydrogen desorbed from various samples is presented in the fig. 1. As can one see, the amounts of evolved hydrogen in all cases are increased with the sample temperature. The maximum yield (0.92 weight %) was observed for the sample caught from outlet gas of reactor. As our investigations showed this substance contains about 9% of fullerenes and more than 40% of singe-wall carbon nanotubes (SWCNT).

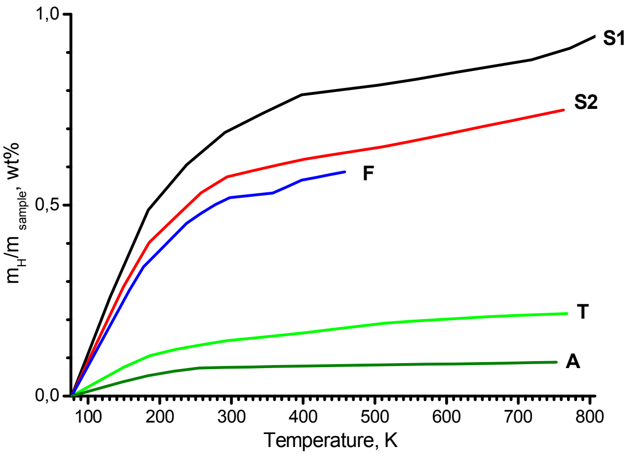

Fig. 1. Temperature dependence of hydrogen content evolved from the samples

We propose here a new method for theoretical modeling of the hydrogen adsorption at nanostructure surfaces. This method in full measure took into account temperature and quantum effects. At that interactions of adsorbable particles include the weak van-der-Waals interaction which may be important for light molecules. This method is high effective and may be applied for systems which include many atoms at any temperature. At the heart of this method there is solution of the Schrödinger equation for the adsorbable particle which is moved under the influence of surrounding molecules and atoms of nanostructure walls.

By this method it was calculated thermodynamics of the hydrogen adsorbed inside or outside single wall carbon nanotubes (SWCNT) (10, 10) (diameter D=13.56 A) and (20,20) (D=27.13 A) of standard notation.

It was calculated dependences of the free energy F and the Gibbs thermodynamic potential H from the external pressure P and the temperature T.

From these data dependence of the adsorbed hydrogen content $m(P,T)$ was calculated also. It should be noted that dependence $m(P,T)$ with taking into consideration of quantum effects has been calculated for the first time.

The results of our calculations have demonstrated that adsorbed hydrogen density at SWNT surfaces may be changed stepwise, in other words undergo phase transition series. At that the hydrogen density is increased at pressure increased or temperature decreased.

Also it was established that hydrogen adsorption value outside SWCNT is less than that inside. It is influence of weakening of the H_2 molecule effective attraction by the atoms of SWCNT surface (Fig. 2). At SWCNT diameter increased the adsorption value is decreased because of weakening of the effective attraction too.

According to our calculations the total hydrogen adsorption value outside and inside of SWCNT does not exceed 3% (wt.) at pressures till $5*10^7$ Pa.

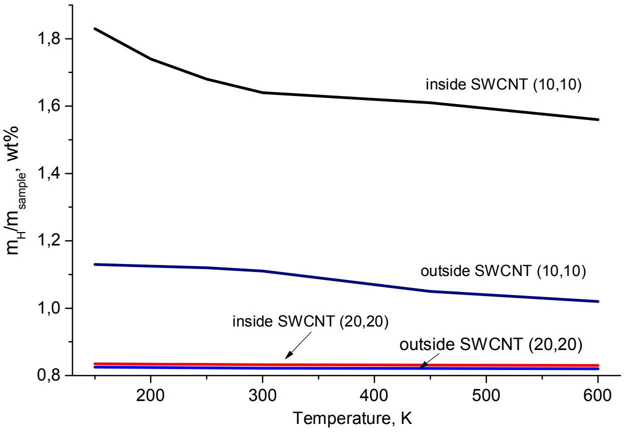

Fig. 2. Calculated temperature dependence of adsorbed at SWCNT surface hydrogen content at pressure 10^7 Pa

Moreover, we investigated the possibility of hydrogen chemical adsorption at SWCNT surfaces because of H_2 molecule dissociation. With help of ab-initio calculations we established that energy of H_2 molecule thermal dissociation is changed very slightly and stay ~6 eV at the molecule is approached to surfaces of SWCNT or fullerene. So the possibility of hydrogen chemical absorption at SWCNT surfaces is negligible without catalyst action.

Conclusions

The results of our both theoretical and experimental investigations allow one to draw the conclusion that effective storage of hydrogen at SWCNT or fullerene surfaces can not be reached with help of physical adsorption mechanism only. It is necessary to turn energies to investigations of the hydrogen chemical adsorption and search of effective catalysts.

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