Journal of SRI "Geotechnological Problems of Oil, Gas and Chemistry" of ASOIU,
Issue 2, 2025, pp. 156-161
https://doi.org/10.65294/gpogc.2026.14

Hydrogen storage with carbon nanotubes

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Abstract. Hydrogen is a promising universal energy source that can replace fossil fuels in the energy sector due to its environmentally friendly nature and diverse energy conversion capabilities. Hydrogen production technologies currently have an unlimited supply of raw materials and can be produced on an industrial scale. However, for large-scale development of hydrogen energy, a number of scientific and technological challenges must be addressed. Developing the most cost-effective and efficient methods of storing hydrogen is one of the main technological challenges in hydrogen energy. In this regard, this review discusses in detail the research being conducted to address hydrogen storage issues using hydrides, nanoporous carbon, porous nanomaterials, and composites based on them, and also analyzes the associated challenges and future prospects associated with the search for methods for its production.

Hydrogen is a highly efficient and environmentally friendly energy source. The main obstacle to stationary and mobile hydrogen use is the lack of effective storage methods. The possibility of storing hydrogen adsorbed in carbon nanotubes under various conditions has been explored.

Molecular dynamics simulations of hydrogen physical adsorption processes in carbon nanotube arrays were conducted. The interactions were described by the Lennard-Jones potential, and quantum effects were ignored. The dependences of the relative mass content and average density of hydrogen in the system on pressure and temperature were obtained. At low temperatures, the formation of a second adsorption layer was detected, leading to an increased content of stored hydrogen.

The spacing between the tubes in the array was varied to find the optimal geometry for adsorption. The relative mass content and average density of hydrogen in the system were obtained as functions of the spacing between the tubes in the bundle.

Keywords: *hydrogen storage, nanomaterials, hydride, nanotubes, adsorption, desorption.*

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Introduction. Increasing demands on the reliability of modern storage systems for efficient energy sources are driving a pressing need for materials capable of supporting a wide range of operating conditions due to the specific chemical and physical properties of such systems. Due to the depletion of energy resources, hydrogen is increasingly being considered as an ideal alternative energy source [1–3]. However, the transition to advanced hydrogen energy is impossible without the development of reliable methods for producing, transporting, and storing hydrogen in large quantities. Moreover, the main challenges in the development of hydrogen energy are concentrated in the area of storage and transportation of this type of energy source [4], while hydrogen production is, in part, a solved problem, as a sufficient number of effective, inexpensive, safe, and environmentally friendly methods have already been proposed.

There are two main groups of hydrogen storage methods: physical and chemical [5]. The former are based on physical processes, primarily compression or liquefaction. The latter involves methods in which hydrogen is stored through physical or chemical interactions with certain materials. The latter method is considered the most promising. Carbon nanotubes offer significant potential in this regard. Among the many hydrogen-sorbing materials, carbon nanotubes possess one of the highest sorption properties. This is evidenced by numerous publications in recent years.

Nearly all major research centers in developed countries are conducting intensive research in this area. Many countries have national research programs in this area. For example, the United States has a national project running until 2015 to develop systems and materials for compact hydrogen storage "onboard vehicles."

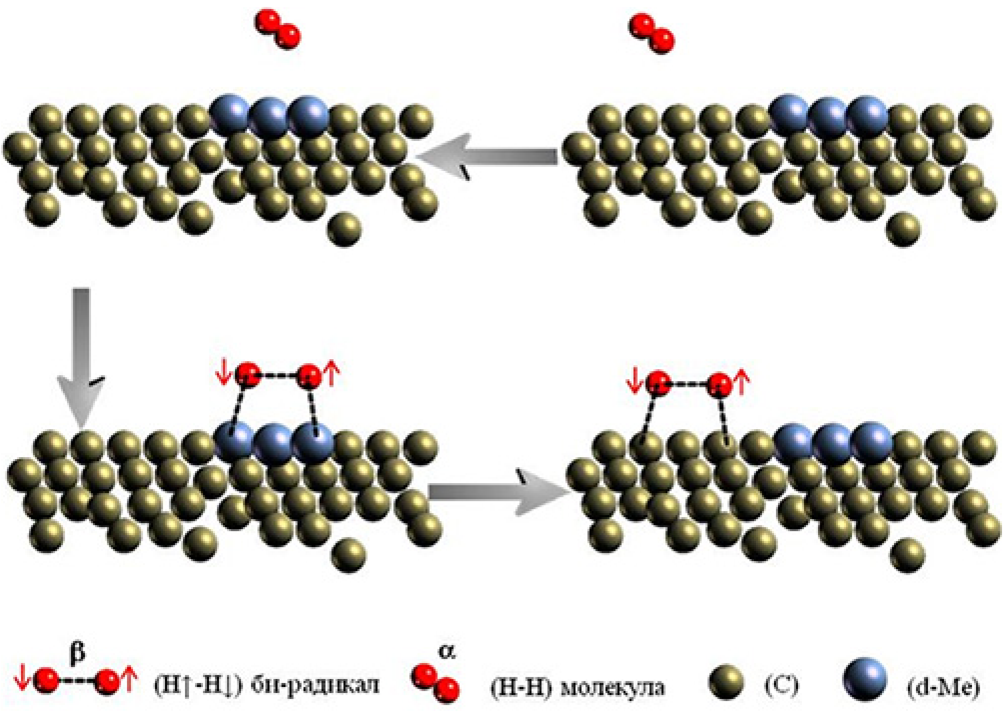
This ability of nanotubes is of great practical importance, as it opens up the possibility of safe storage of hydrogen for its further use as an environmentally friendly fuel.

Since their initial production, nanocarbon nanotubes have remained the subject of ongoing scientific research in various fields of knowledge, including hydrogen energy [6 – 9]. However, real experiments on this topic require complex and high-precision equipment. Moreover, in addition to significant material resources, time is also required. Therefore, although the number of experimental studies conducted in laboratories around the world is steadily increasing, they do not contribute to the creation of a comprehensive picture of the understanding of this issue. A solution to this problem cannot be achieved solely through the development of practical work. This situation can be rectified by taking into account not only applied work, but also thorough theoretical studies that reveal fundamental aspects and contribute to an understanding of the nature of such processes under study, i.e., the uncovering of the mechanism. To implement such theoretical studies, computer modeling is used, which, as an alternative research method and based on the methods and approaches of quantum chemistry, quantum mechanics, as well as the mathematical apparatus and numerical methods for describing and calculating the properties of chemical compounds, allows for virtually any experiment to be conducted at the atomic level. At the same time, such preliminary work on studying the possibility of using carbon nanotubes as a storage medium for hydrogen allows, in combination with experimental work, to evaluate the possibility of the existence of effective nanotubular hydrogen batteries.

Published scientific literature on the results of experiments and theories on hydrogen sorption by carbon nanotubes reveals a contradictory picture.

Some researchers point to the impossibility of achieving high hydrogen sorption capacity in carbon nanotubes under normal conditions. This appears to be true, given that they rely on classical considerations regarding the formation of bonds between hydrogen and the nanocarbon surface, i.e., through intermolecular van der Waals interactions (physical adsorption) and chemical covalent bonds (chemical adsorption). Moreover, in the first case, the hydrogen capacity of nanotubular carbon does not exceed 1–2 wt.% under normal conditions, while in the second case, it is 7.7 wt.%—the known calculated value of the theoretical limit (however, this does not ensure process reversibility, since a covalent bond is realized). Nevertheless, existing theoretical studies have demonstrated the possibility of achieving high-capacity hydrogen storage in carbon nanotubes. However, it is important to note that these values are only realized at cryogenic temperatures (~77 K). In this regard, it is appropriate to consider the results of several studies. For example, in [10], under conditions of a temperature of 77 K and a pressure of 5 MPa, a model calculation yielded a hydrogen mass concentration of ω = 5 wt.% for a nanotube system, while for a single nanotube this value was 10.5 wt.%. In their next work [11], the authors searched for the best structure of a nanotube system that would provide good sorption capacity. A significant influence of the distance between nanotubes on the amount of adsorbed hydrogen was indicated. The hydrogen capacity reaches its maximum value under the condition of a small influence of neighboring nanotubes, when hydrogen adsorption can be considered as for the case of an individual isolated nanotube. Optimization of the spatial structure of a nanotube system at a temperature of 77 K and a pressure of 5 MPa led to a value of ω = 10 wt.%. In the study [12] the amount of hydrogen at temperature T = 77 K and hydrogen pressure P_{H2} = 10 MPa reached the value ω = 9.6 wt.%, whereas at temperature T = 300 K and hydrogen pressure P_{H2} = 10 MPa this value was only 1.4 wt.%. The authors of the work [13] when modeling the interaction of hydrogen with a system of nanotubes at temperature 77 K and pressure 15 MPa obtained the value of capacity ω = 6.88 wt.%. In the work [14] also shown unoptimistic results of hydrogen adsorption (less than 1 wt.%). However, others are of the opinion that it is possible to achieve a high value of hydrogen capacity above 7.7 wt.%. In this case, they note [15 – 16] that the required values of the interaction energy of hydrogen with carbon nanostructures (20–40 kJ/mol) are an order of magnitude higher than the bond rupture energies characteristic of physical adsorption and an order of magnitude lower than the bond rupture energies characteristic of chemical adsorption. There are no new theoretical concepts regarding this type of interaction in the works. In this regard, in a number of works [17–19] Yu . S. Nechaev speaks of the possibility of creating a hydrogen superadsorbent based on nanocarbon structures only if not only practical work in this area is developed, but also due attention is paid to the development and formation of fundamental knowledge about the nature and characteristics of the interaction of hydrogen with carbon nanostructures.

One promising way to increase hydrogen adsorption capacity is to use hydrogen spillover, a process in which an active particle adsorbed at one site migrates to a neighboring site that does not itself adsorb such particles under normal conditions. For a hydrogen nanotubular battery system, spillover can be represented as a schematic diagram.



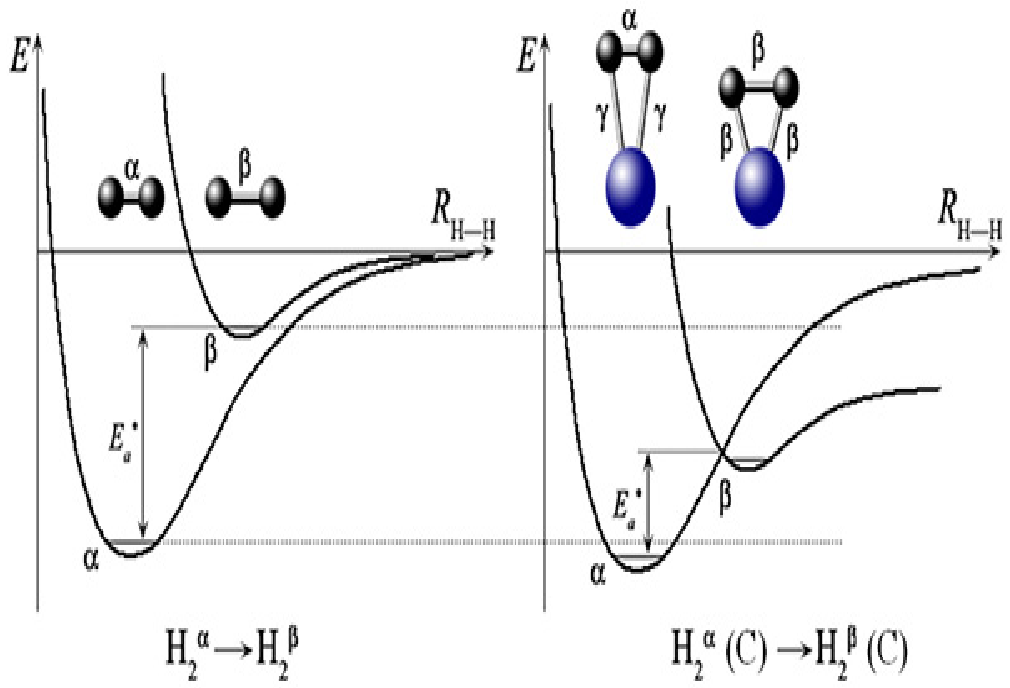
The mechanism of activation of hydrogen molecules in the active center of catalysis and spillover of hydrogen biradicals onto the carbon surface

The first stage involves the interaction of a hydrogen molecule with transition metal atoms, which results in the activation of the hydrogen molecule and its transition to an activated state, as demonstrated in [20]. The "new" form of hydrogen then interacts quite readily with nanocarbon. This is possible because the energy barrier is significantly reduced in this case compared to the interaction of an unactivated hydrogen molecule with nanocarbon.

If a metal particle (catalyst) serving as a source of atomic hydrogen (adsorbate) is deposited on a low-capacity carrier, the capacity can be increased by using an intermediate receptor with high capacity. The spillover that occurs in this manner is called a secondary spillover. This phenomenon is discussed in detail in [21]. In this case, *the secondary spillover* (transfer from a high-capacity receptor to a low-capacity one) is preceded by a typical *primary spillover* —transfer from the metal to the high-capacity receptor.

The role of the spillover mechanism in the interaction of hydrogen with carbon nanotubes is considered in [22 – 26].

Another method for increasing the sorption capacity of carbon nanostructures is their activation, for example, chemically [27] or through mechanosynthesis, as reported in [28]. A study to increase the sorption capacity of carbon nanotubes for hydrogen was conducted in [29] with the simultaneous use of microwave plasma activation of nanotubes and catalysts. As a result, a capacity value of ω = 4.5 wt.% was obtained, which, as the authors indicate, is three times higher than the result in the absence of a catalyst.



The mechanism of activation of hydrogen molecules in the active center of catalysis.

Ultimately, reversible hydrogen accumulation at room temperature exceeding 6% by weight is considered acceptable. Quantum chemistry and molecular dynamics methods have demonstrated the presence of only two known mechanisms for hydrogen accumulation: physical molecular and chemical atomic sorption of hydrogen on the nanotube surface. These studies demonstrated that both physical and chemical hydrogen adsorption on the CNT surface are unsuitable for producing effective hydrogen accumulators. However, these mechanisms of equilibrium hydrogen sorption do not explain the achievement of effective reversible hydrogen sorption in CNTs in a number of experimental studies.

The above problem is solved using the idea that the achievement of reversible accumulation of over 6 wt.% hydrogen in single-wall carbon nanotubes at room temperature is due to the fact that in the nonequilibrium process of CNT sorption it is not H—H molecules or H atoms that take part, but nonequilibrium activated biradicals $H_{\uparrow}$—$H_{\downarrow}$ hydrogen.

In theoretical studies [20 , 30–31], it was shown that intermediate forms of hydrogen biradicals arise in the active centers of transition metal catalysts. Interaction with the *sd* -electron subsystem of transition metal atoms in the active center disrupts the spin symmetry of the electronic state of the free hydrogen molecule, transferring it to the activated state of the biradical. For example, the spin-singlet hydrogen molecule H_2 upon such activation passes into a nonequilibrium state of the biradical, which is not eigenstate for the spin operator $\boldsymbol{S}^2$. Due to this, the biradical is not described within the framework of standard calculation methods of quantum chemistry of free molecules and remains unaccounted for in these calculations. In the present work, the development of this approach consists in the fact that as a result of the transport of hydrogen biradicals from the active catalytic centers to the carbon matrix, their conservation occurs. The latter is a consequence of the emergence of spin-forbidden reactions in nonequilibrium activated biradicals upon interaction with carbon, preventing their deactivation into hydrogen molecules or decomposition into atomic hydrogen. As a result, the system of activated biradicals on the surface of carbon nanotubes, due to contact exchange interactions with the walls and with each other, manages to transition to nonequilibrium stationary states of hydrogen "superadsorbate" with "anomalous" values (20–40 kJ/mol) of hydrogen sorption energy by nanocarbon.

Conflict of interest.

The authors declare that they have no conflict of interest in relation to this research.

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