Hydrogenization of fullerene as a method of storage of hydrogen

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Abstract. In the present work the method of catalytic hydrogenation of fullerenes is considered. To determine the optimal regime for the hydrogenation of fullerenes at a hydrogen pressure of 12 MPa and a temperature in the range of 200-600°C, the mass of fullerite C60 was equal to 0.501 g. During the conducting of this experiment, it was found that the system reached its maximum interaction speed at 2150 minutes, which corresponded to temperature of 433°C. As a result, the temperature, at which the rate of interaction of hydrogen with the fullerene molecule is maximized, was defined and the given value of temperature is in the range of 425-455°C, where the total hydrogen content is about 8.2% by weight.

1. Introduction
The search for an ecologically clean and highly efficient cheap energy carrier, an easily accessible and almost inexhaustible source of energy has long ago and firmly taken the leading place in the list of problems affecting the future of not only further development but also the existence of all mankind. One of the promising ways of obtaining thermal energy is the use of hydrogen produced from water using environmentally friendly primary energy sources. Hydrogen is an ideal fuel with a high calorific value and a non-hazardous combustion product - water vapor [1].

2. Methods
Storage of hydrogen is one of the intermediate links in the life cycle of hydrogen from its production to consumption. The development of the most economical and efficient ways of storing hydrogen is one of the main technological problems of hydrogen energy.

To store hydrogen various types of hydrogen batteries are suggested - hydrogen sources, in which at room temperature hydrogen atoms are in a bound state with a sorbent material, either chemically or in an encapsulated form. As the temperature rises, such bonds of hydrogen with the sorbent are destroyed, thereby releasing hydrogen atoms. Today due to their low specific density and large specific surface area carbon nanomaterials are used to store hydrogen. For example, activated carbon [2], graphene [3-4], multi-walled and single-walled carbon nanotubes [5-6], fullerenes [7-8], etc. Thus, the study of hydrogen-sorption characteristics of fullerene is very relevant.
It is known that fullerene can exist as a gas (at temperatures of 450°C and above) or a solid. Under normal conditions fullerene is in the form of a solid, which is called fullerite. Hydrogenation of solid fullerene can be carried out by various methods such as direct non-catalytic hydrogenation [9], catalytic hydrogenation in toluene solution [5], radical hydrogenation with the C2H5I promoter [10] and many other methods presented in [11-14].

To carry out work on the hydrogenation of fullerene samples a method was developed based on the determination of the hydrogen-sorption characteristics of the samples at different pressures and temperatures. Typically, the hydrogen sorption capacity is measured by a volumetric method in installations of the Sievert type. This known method is sufficiently accurate, if we work with samples of hydrogen sorbing materials having a strictly defined density. Otherwise, especially if the specific density is low, the value of uncertainty in the density can give a very large contribution to the error in determining the hydrogen sorption capacity.

The structure of the experimental setup consists of a stainless tube (reaction chamber), stove, systems of evacuation and puffing working gas of hydrogen through a special purification filter [15]. This installation is intended primarily for studying the hydrogen-sorption characteristics of carbon materials and composites on their basis with low specific density using volumetric method in the pressure range from 0.01 to 30 MPa H₂ and at the boiling point of liquid nitrogen and when heated to a temperature of about 1000°C.

**Figure 1.** Schematic diagram of the experimental setup for the measurement of hydrogen sorption [15]: 1 - refueling port; 2 - manometers; 3 - a hydrogen valve; 4 - cylinder with compressed hydrogen of technical purity; 5 - metal hydride accumulator compressor with a capacity of 220 liters of hydrogen; 6 - experimental reactor; 7 - thermostat; 8 - the main line of discharge into the atmosphere; 9 - vacuum system; 10 - low pressure collector; 11 - buffer capacity of 50 cm³; 12 - buffer capacity of 300 cm³.
3. Results and discussion

In this paper hydrogen-sorption characteristics of fullerene are studied by a non-catalytic method at the Sievert type installation. The essence of the experimental procedure is as follows: if the hydrogen capacity of the sample is known in advance, for example, the sample is not hydrogenated and it is located in a closed volume filled with hydrogen with certain parameters, then the percentage of hydrogen in the sample can be determined from the changes in the parameters of the gas phase and comparison with the initial values.

The sorption capacity for hydrogen was determined by the following formula [15]:

\[ a = \frac{\Delta n}{m} + \frac{P}{Z RT \rho}, \]

where \( Z = Z (P, T) \) is the compressibility factor for gaseous hydrogen, \( R \) is the gas constant, \( \Delta n = n_0 - n \) is the difference, and \( \rho \) is the specific density.

In the process of studying hydrogen-sorption characteristics of fullerenes experimental work on hydrogenation was carried out. The experiment was carried out in two stages: the first - preliminary annealing. The second is the hydrogenation of fullerite.

Experimental work on hydrogenation was carried out to obtain hydrofullerite. It is known that in direct non-catalytic hydrogenation hydrofullerites \( C_{60}H_{18} \) are obtained at known hydrogen pressure parameters of 50-85 MPa and temperatures in the range of 300-350°C. Such high pressures of the working gas (hydrogen) lead to the polymerization of fullerene molecules, the destruction of their frames and the hydrogenation of the formed fragments (it was shown by analyzing mass spectrometry and dehydrogenation of products obtained under these conditions). Thus, in order to avoid the polymerization and destruction of fullerene molecules, a necessary condition is a reduction in the pressure of the working gas, and with it, therefore, an increase in the synthesis temperature to create hydrogenation conditions. For these purposes, an experiment was performed at the catalytic hydrogenation of fullerene molecules in a toluene solution at hydrogen pressures of 12 MPa. As a result, it was found that the samples of hydrofullerene are not destroyed. Based on these considerations, the working pressure in subsequent experiments of non-catalytic method was the hydrogen pressure of 12 MPa.

To determine the optimal mode for carrying out the hydrogenation reaction of a fullerene molecule at a hydrogen pressure of 12 MPa, a 75-hour experiment was carried out. In the course of this experiment, the temperature, at which the rate of interaction of hydrogen with the fullerene molecule was maximized, was determined. To carry out the experiment we used a sample of fullerite \( C_{60} \) with a mass of 0.501 g. The reactor was evacuated for one hour to remove impurities from the fullerite. After that, hydrogen was fed from the metal hydride storage to the reactor up to the pressure of 12.5 MPa and held for 4 hours. Then, the temperature in the reactor was raised to 200°C (at a speed of 1 degree per minute). The pressure in the reactor increased by 0.3 MPa (reaching 12.8 MPa). This can be explained by the decomposition of solvates formed during the crystallization of fullerite. To stabilize the baro-temperature regime the sample was held for another 4 hours (\( T=200^\circ\text{C}, P=12.8 \text{ MPa} \)). At 480th minute the temperature rise in the reactor was continued from 200 to 600°C at a rate of 0.125 degrees per minute.

In the course of this experiment it was found that the system reached its maximum interaction speed at 2150th minute, which corresponded to a temperature of 433°C (Figure 2).
Figure 2. Dependence of the pressure change in the reactor with a temperature change at a rate of 0.125 degrees per min. (1 - curve of pressure change in the reactor, 2 - curve of temperature change in the reactor).

This corresponds to a change in temperature from 425 to 455 °C. With a further increase in temperature the rate of interaction began to decrease.

In this experiment holding of the sample for 10 hours at P=12 MPa and a temperature of 200°C resulted in a change in the sample mass by 0.6% by weight. The total amount of hydrogen absorbed by the sample during the experiment was fixed at 8.2 wt.% of H (Figure 3).

Figure 3. Experimental curve of the interaction of gaseous hydrogen with fullerite. The arrow indicates the fraction of fullerized hydrogen (H_f).

Another experiment showed that preliminary annealing of fullerite in a vacuum at 350°C leads to a more intense interaction of it with hydrogen gas. A rapid (within 3 hours) temperature rise to 550°C at a hydrogen pressure of 12.5 MPa leads to saturation of the sample with hydrogen to 7.3% by weight of H during this period.

Experiments have shown that hydrogen absorbed by fullerite after depressurization gradually spontaneously desorbs under normal conditions. Such hydrogen mobility can mean that the process of
chemisorption of hydrogen by all fullerene molecules of C₆₀ will proceed uniformly with the formation of energetically equivalent molecules, or at least fullerene molecules having an equal number of hydrogen atoms throughout the lattice volume. In this case the topochemistry of the hydride formation reaction will correspond to the volume formation of the hydride.

Based on the conducted experiments, it can be concluded that the hydrogenation of a fullerene molecule is an energy-controlled process, in which the temperature of the system determines the number of hydrogen atoms on the shell of the fullerene molecule. This conclusion is of great importance for the further study of the fullerene-hydrogen system and, especially, for its application.

As already mentioned above, carbon nanomaterials such as activated carbon, carbon nanofibres, graphene, multi-walled and single-walled carbon nanotubes, fullerenes, etc. are used to create the capacity of the hydrogen storage due to its low specific density and large specific surface area.

Activated carbon (ACs) is synthesized by carbonization of organic precursors followed by an activation step using, for example, annealing in an oxidizing atmosphere or chemical treatment. Such results of the synthesis procedure in materials with a very high specific surface area up to 3300 m²/g, which have excellent properties of hydrogen adsorption at 77 K. ACs is capable of adsorbing about 6.0 wt% of H₂ at a pressure of 40 bar at 77 K [16]. As for carbon nanotubes, were first discovered in 1991 by Professor Iijima [17] and after attracted much attention as a promising material for hydrogen storage applications. Before the adsorption of hydrogen, the measurements of nanotubes are usually subjected to some processing to make the inner part accessible for penetration of the gas and to increase the available surface area, in CNT there is basically a specific surface area in the range of 600-2600 m² / g [18]. At the temperature of liquid nitrogen CNT capable of adsorbing up to 8.0 wt.% of H₂ [19]. Nevertheless, at room temperature hydrogen the capacity of CNTs for storage of H₂ is less than 1mass% at pressures up to 100bar [20-21]. Considering various modifications of carbon nanostructures, it is necessary to focus on fullerenes and their hydrides, since they have unique adsorption properties and during our experiment it was recorded that the amount of hydrogen absorbed by the sample reached 8.2% by weight of H₂, which exceeds the ability to adsorb in the above works.

Thus, during the conducting of the experimental work on the hydrogenation of fullerite, hydrofullerenes with various hydrogen contents were experimentally obtained. The optimal hydrogenation regime of C₆₀, leading to complete hydrogenation of the fullerene C₆₀ molecule, was determined. It was also found that the optimum conditions for the hydrogenation of fullerite C₆₀ are P=12 MPa and T=425–455°C.

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