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MATERIALS SCIENCE

ADSORPTION OF HYDROGEN AND METHANE BY CARBON FOAM BASED ON CARBONIZED POLYAMIDE FIBRES

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Carbon foam based on carbonized polyamide fibres with palladium was modified. The carbon foam modified with palladium can adsorb hydrogen and methane under pressure and desorb then on heating. The possibility of using palladium-modified fibres as a solid support for reversible storage of hydrogen and methane was demonstrated.

Activity in research and experimental-design studies on use of hydrogen and methane as environmentally clean fuels and energy storage cells has increased in recent years. Large national research problems in this area are being implemented in the USA, Canada, Germany, Japan, China, and the European Union. Creation of compact and effective hydrogen and methane storehouses in which the problems of reversible storage of hydrogen and methane in solid-phase systems are solved is an important direction in implementation of these programs.

Studies on storage of hydrogen and methane are also directed toward using modified carbon materials for this purpose [1]. Nanostructures of the fullerene type, nanotubules, and nanofibres are basically to be used for hydrogen and methane storage systems. The basic research findings indicate the possibility of creating storage media from these nanostructures with a capacity of approximately 10% with respect to H_2 and CH_4. However, satisfactory results have not yet been obtained. The properties of carbon foam made from carbonized polyamide fibre material for use as a solid-phase carrier for reversible storage of hydrogen and methane are examined here.

Carbonized carbon fibres are usually prepared in two stages: carbonization [2] and activation using oxidants — O_2, CO_2, H_2O, or mixtures of them [3]. The carbonized fibres obtained in this way usually have monodisperse pore diameter distribution of 1.6-2 nm and their volume approaches 0.3-0.4 cm^3/g. Such fibres have a well-developed pore structure with a specific surface area greater than 700 m^2/g. Modification causes the formation of fibres with an even greater specific surface area of 1500-2500 m^2/g and a pore volume of 0.5-1.5 cm^3/g, primarily of micropore size. In addition, the carbonized fibres have a narrow pore size distribution in the 2-4 nm region. As a consequence, these materials have the properties of molecular sieves (ratio of separation of benzene and cyclohexane of 16:1).

The published sources that suggest the importance of using modified carbonized fibres for accumulating and storing methane [4] note that micropores play the fundamental role in adsorption of methane [4]. The optimum pore size in adsorption of methane is equal to 1.14 nm [5]. For carbonized fibres to acquire the property of adsorbing hydrogen, they probably must be additionally modified. On the other hand, the ability of palladium to occlude some gases, primarily hydrogen, in large quantities is well-known. At room temperature, 1 volume of palladium can absorb up to 950 volumes of hydrogen [6]. This is primarily determined by the high solubility and mobility of hydrogen in the face-centered cubic lattice of Pd, where the hydrogen atoms occupy octahedral positions as demonstrated by neutron diffraction for the β-phase of Pd(H) [7]. The H atom in the Pd lattice does not dissociate into proton and electron. Actually, the electron states of the H atoms are expanded under

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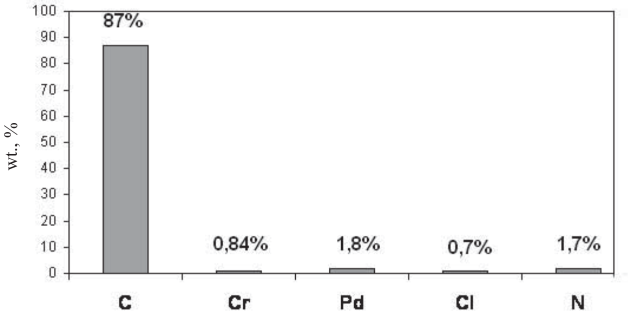

Fig. 1. Quantitative elemental IR analysis of MCF material.

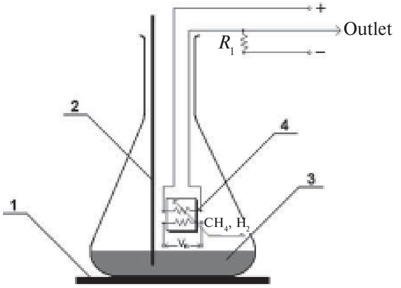

Fig.2

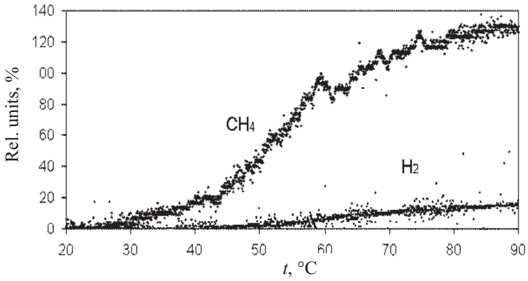

Fig.3

Fig. 2. Diagram of the experiment on adsorption of hydrogen and methane by MCF material: 1) heater; 2) thermocouple; 3) material tested; 4) SnO_2-based TGS 2610 sensor.

Fig. 3. Results of the experiment on sorption of H_2 and CH_4 by MCF material: CH_4 — methane desorption curve; H_2 — hydrogen desorption curve.

the effect of the field of the surrounding Pd atoms and the electrons are collectivized due to an exchange reaction with the electrons in the *d*-zone of Pd, where the density of the states near the Fermi level is very high. The H atoms in octahedral positions can thus be represented as protons shielded by electrons, and the shielding charge only occupies part of the expanded states in the 4*d* zone and the delocalized states in the 5*s* zone of the lattice of the matrix. We hypothesized that if palladium atoms were injected in the structure of the pores in carbon foam material, then hydrogen would be adsorbed by a mechanism similar to dissolution of hydrogen in metallic palladium. In this case, all of the absorbed hydrogen can easily be removed in heating the material to 100°C.

Fabric made from polyamide fibre (GOST 22693—98) based on poly-ε-caproamide $[—NH—(CH_2)_5—CO—]_n$ with a molecular weight of 15,000-25,000 and melting point of 225°C was selected for modifying the carbon foam fibres by injecting palladium atoms into their structure. The diameter of the fibres in the threads in the fabric was approximately 20 µm. The highly recommended technology for production of carbonized fibres in two states was used [8]. In the first stage, in heating in air, oxidative degradation takes place, where crosslinks are simultaneously formed between the macromolecules (crosslinking). Formation of crosslinks was used to raise the melting point. In the second stage, in slow heating of the sample in an inert medium to a temperature of approximately 1000°C, carbonization takes place.

However, some specific properties of polyamide fibres must be considered [9]. Amines and carboxyls are usually the terminal groups in polyamides. Adsorption of hydrochloric acid increases with a decrease in the pH of the medium, attaining the maximum at pH 2.2-2.6. This corresponds to the time of neutralization of the amine groups. For this reason, palladium acetate, $Pd(CH_3COO)_2$, which is readily soluble in hydrochloric acid, was selected for fabricating the modified carbonized fibre (MCF) material.

A solution with pH = 2.4 consisting of 88.72 wt. % distilled water, 5.82% concentrated HCl, 4.95% $Pd(CH_3COO)_2$ with a minimum mass fraction of Pd of 46.5%, and 0.51% $Cr(NO_3)_3 \cdot 9H_2O$ was prepared. The last compound was used here, as in

[10], for catalysis of dehydration, redox processes, and crosslinking of the polymer. The polyamide fabric was steeped in the solution for three days. Swelling of the polymer was monitored by weighing it. The concentration of the solution was chosen to exclude adhesion of the fibres. The material obtained was washed in a stream of tap water and placed in a programmable thermostat with forced air ventilation.

Oxidative degradation of the polymer included two stages. In the initial stage, the material was slowly heated from room temperature to 175°C at the rate of 1°/min and the material was then held at this temperature for 2 more days. After cooling, the material initially became brittle, but after 2-3 days, it acquired elasticity due to the uniform redistribution of stresses inside the polymer.

The material was carbonized in a programmable thermostat with a forced nitrogen current to create an inert medium and remove reaction products. The sample was heated from room temperature to 800°C at the rate of 50°/h. At the end of the process, the sample was cooled naturally to room temperature.

Five series of experiments were conducted. As control weighing of the samples showed, after the stage of oxidative degradation, the weight of the material was 73.82% and after carbonization, 26.23% of the initial weight. Quantitative elemental IR analysis of the material obtained was also conducted (Fig. 1), which showed that the samples retained a fibrous structure.

In measuring adsorption of hydrogen and methane, the material obtained was divided into two parts, one used in the experiments with hydrogen and the other with methane. The material was first placed in an autoclave and held at H_2 or CH_4 pressure at 1225.8 kPa for 1 h at room temperature. The autoclave was first blown through with a current of the tested gas. The material was then placed in a flask with a thermocouple and a SnO_2-based TGS 2610 oxide-semiconductor sensor from Figaro (Fig. 2).

The parameters of the electrical circuit connecting the sensor were selected so that its sensitivity would range from 500 to 5000 ppm. The sample was heated from room temperature to 100°C at the rate of 20°/min, monitoring the readings of the thermocouple and sensor with a PCS500 two-channel oscillograph from Velleman Instruments and a computer. The curves of methane and hydrogen desorption by the material tested were obtained in this way.

As the results of the experiment show (Fig. 3), the MCF material obtained in this experiment can adsorb both hydrogen and methane. The curve for CH_4 shows desorption of methane as a result of heating the tested material, and the H_2 curve shows desorption of hydrogen.

Since carbonized fibre materials are rich in micropores, CH_4 was adsorbed in the material similar to processes in molecular sieves. However, the mechanism of adsorption of H_2 had a different character. Both metallic palladium absorbs a small amount of hydrogen, which is a linear function of the square root of its pressure and which increases with an increase in the temperature [11], and in our experiments, an important part of hydrogen is occluded in the submicroscopic pores in the carbon form containing palladium atoms. This corresponds to an endothermic process of absorption when a Pd_2H system is formed. As in the case of metallic hydrogen, vacancies in the 4*d* band in palladium is occupied by electrons from H atoms [12]. Heating the sample of carbon foam modified with palladium indicates the similarity of adsorption in the material obtained and adsorption in metallic palladium. A smaller part of the hydrogen diffuses in the pores of the carbon foam and remains there until desorption.

It is thus possible to use modified carbon foam based on carbonized polyamide fibres as a solid-phase support for reversible storage of hydrogen and methane. This technology could be promising for creating methane and hydrogen storage systems in the form of gas condensate which have sufficient capacity at relatively low pressure.

REFERENCES

1. S. Korobtsev, *Byull. Atomn. Energ.*, No. 7, 18-23 (2006).
2. T. V. Komarova, *Carbon Fibres: Text of Lectures* [in Russian], RKhTU D. I. Mendeleev, Moscow (1994), p. 42.
3. K. L. Foster, R. G. Fuerman, et al., *Chem. Mater.*, **4**, 1068 (1992).
4. J. Alcaniz-Monge, M. A. de la Casa-Lillo, et al., *Carbon*, **35**, 291-297 (1997).
5. K. R. Matranga, F. L. Myers, and E. D. Glandt, *Chem. Eng. Sci.*, **47**, 1596 (1992).
6. I. V. Petryanov-Sokolov, V. V. Stantso, and M. B. Chernenko, *Popular Library of Chemical Elements. Book One. Hydrogen — Palladium* [in Russian], Nauka, Moscow (1983), p. 566.
7. T. B. Flanagan, *Engelhard Ind. Tech. Bull.*, **7**, 9 (1966).
8. A. V. Tovmash, V. N. Polevov, et al., *Khim. Volokna*, No. 3, 29-32 (2005).

9. V. V. Korshak and T. M. Frunze, *Synthetic Heterochain Polyamides* [in Russian], Goskhimizdat, Moscow (1962), p. 245.
10. T. Druzhinina, D. F. Volkov, et al., *Khim. Tverd. Topl.*, No. 4, 79-88 (2003).
11. N. A. Galaktionova, *Hydrogen in Metals* [in Russian], Metallurgiya, Moscow (1967).
12. G. Heard, *Introduction to the Chemistry of Hydrides* [Russian translation], Moscow (1955).