HYDROGEN ADSORPTION ON CARBON NANOPOROUS MATERIALS

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Introduction

It is known that the majority of methods used for preparation of carbon materials is based on chemical reactions of decomposition of solid (resins), liquid (pitches) or gaseous (hydrocarbons) carbon-containing substances. In contrast to these methods for carbon preparation carbides can be used to run the process by the following replacement reaction:

$$MeC + \frac{n}{2}Cl_2 \rightarrow MeCl_n + C$$

Such reactions are thermodynamically and kinetically admissible for the absolute majority of covalent and metal-like carbides and can be run at 300-1000°C. The most important feature of the reaction (1) is constant composition and structure of the taken initial components and also its irreversibility, which provides practically 100% yield by carbon.

The reaction of chlorination (1) provides a total removal of the carbide-forming element out of the carbide composition. In this case, the crystal sub-lattice of the carbides is rearranged to form a new carbon structure, which contains a lot of open nanopores with narrow width distribution. The results by porosimetry have shown that porosity of NPC is divided into two groups: pore size of < 2-4 nm (nanopores) and pores greater than 50 nm (macropores) (Fig.1). The volume content of nanopores in NPC can be calculated from the mass balance by carbon. The results are in good correlation with experimental data.

It is important to note that during the preparation of NPC there is no change in its shape or sizes and a prepared carbon material has high strength, which is determined by a carbon skeleton formed in it.

An important feature of the considered method is possibility to prepare hydrogen-less carbon substances. This makes the method principally distinguishing from other production methods of carbon, for example from hydrocarbons, sinters, resins using which hydrogen always remains in the structure of final material.

In the study NPC activity for hydrogen sorption has been investigated. As samples NPC produced from different carbide products such as particles, fibers, bodies have been used.

Experiment

Hydrogen sorption has been studied at pressure up to 10 MPa ant temperature 220-300K use an apparatus presented on fig.1. Sample volume is 2-6 cm^3.

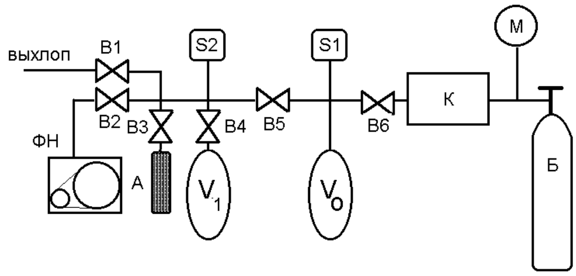

Fig.1. Apparatus for sorption tests.
B1–B6 – valves, S1 and S2 – pressure gauges, M–manometer, Б–hydrogen gas vessel, A–sample ampoule,V0–dosing vessel, V1–volume measure, ФН– vacuum pump, К–pressure pump

Hydrogen adsorption isotherms, hydrogen density in sample volume and sorption excesses have been determine. Sorption excesses have been calculated as:

$$\Gamma m = (C - D)/ M$$

where: C – a hydrogen mass in sample volume, D – a hydrogen mass in high pressure condition in NPC pores, M – sample mass.

Results and discussion

Experimental results are presented on fig 2-4. One can see that studied materials have almost the same sorption activity (sorption excess – 0.4-1 mass.% at pressure 10 MPa). A high rate of adsorption should be noted.

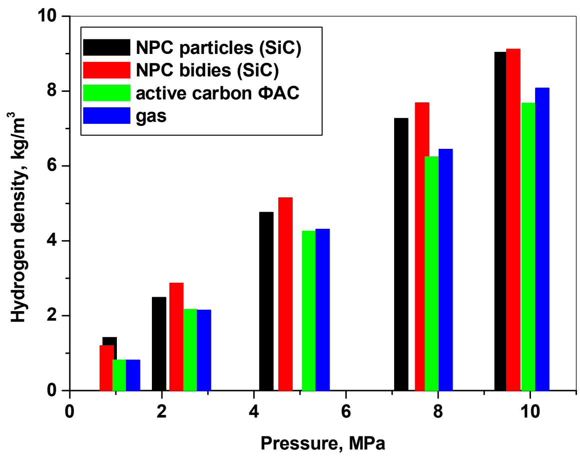

Fig.2. Hydrogen density in empty volume and in NPC volume.

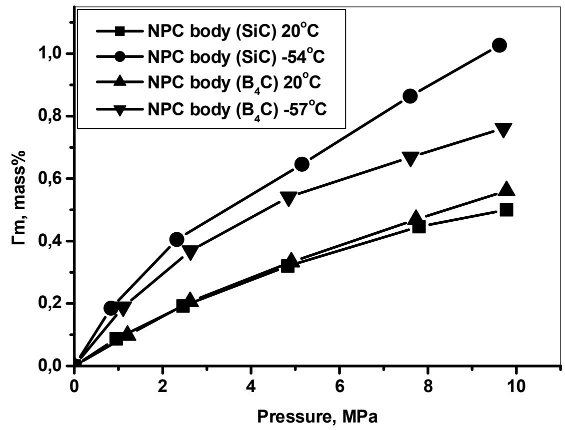

Fig.4. Hydrogen sorption excesses for NPC.

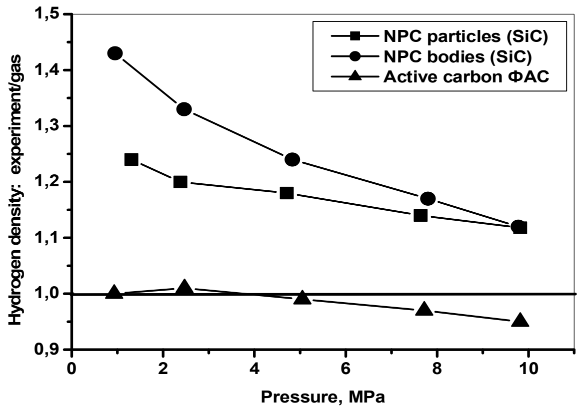

Рис.3. Degree of hydrogen density increase in a volume filed by NPC.

Base on nanopore volume on NPC a density in napores at different pressures have been calculated (table). It is 2-2.5 times less than that of gas at the same conditions (at 300K). At low temperatures (225K) The mention ratio increases up to 3-3,5. At pressure 10 MPa hydrogen densities in nanopores are greater than 35 kg/m^3. It is more than critical density of hydrogen (31 kg/m^3).

Table. Hydrogen densities in NPC nanopores.

Material	t, °C	P, MPa	Hydrogen density (gas), kg/m^3	Hydrogen density in nanopores, kg/m^3	Ratio ρ_{nano}/ρ_{gas}
Particles from SiC (HT 1000°C)	21	1,30	1,14	3,05	2,6
	22	9,83	8,06	19,0	2,4
Particles from SiC (HT 1500°C)	22	1,99	1,73	4,00	2,3
	22	9,77	8,02	16,3	2,0
Bodies from B_4C (HT 1000°C)	19	4,91	4,22	8,61	2,0
	-57	4,85	5,61	12,7	2,3
Bodies from SiC (HT 1000°C)	18	9,78	8,14	20,2	2,5
	-54	9,62	10,53	35,4	3,4

Conclusion

Nanoporous carbon materials are more active than active carbons in hydrogen sorption processes Hydrogen density in NPC nanopores is 2-3 times higher than density in gaseous hydrogen in the same p-T conditions. Unfortunately, NPC adsorption characteristics are far from request for applicable hydrogen storage materials.