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Adsorption Methods of Hydrogen and Methane Storage for the Fuel Cell Application

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Abstract

Adsorption of H_2 and CH_4 was performed at a pressure of to 100 atm on the samples of catalytic filamentous carbon (CFC) and supermicroporous active carbon (SAC) with a surface area ca. 3000 m^2/g. It is shown that H_2 is better sorbed on the CFC than on the SAC, while the opposite is observed for the CH_4 adsorption. The high values of H_2 sorption on the CFC (to 25-35 mg H_2/g carbon) with a surface area of 100-300 m^2/g is explained by hydrogen intercalation between the graphite-like CFC layers. Thus, it is worthwhile investigating the possibility of hydrogen and methane storage on the carbon porous materials.

Introduction

At the moment, a huge attention is devoted to the problem of switching the vehicles to the fuel cell (**FC**) powered electric engines, which generate the electric energy by means of the electrochemical oxidation of hydrogen by oxygen from the air [1-4]. Such switching allows both to solve the environmental problems and to sharply increase the engine efficiency, which in the case of **FC** is not limited by the Carnot cycle [1]. However, the **FC** introduction is strongly slowed down by the problems of hydrogen storage or its generation from the suitable sources on board of the vehicle [2-9]. Fueling the automobile with compressed or liquid hydrogen or other gas is additionally complicated by the necessity to create the new infrastructure of fuel dispensing instead of the existing gasoline pump stations. Due to these reasons, many leaders of this direction are considering as the main source of hydrogen the liquid fuel, mostly methanol, despite the complexity of the on-board hydrogen production [2-4]. But all the carbon from the carbon-containing fuel is eventually emitted as CO_2, which decreases the environmental compatibility of such **FC**. Therefore, solving the task of on-board hydrogen storage is still important.

In 1998-1999, the Journal of Physical Chemistry has published two works of Rodriguez et al. [8,9], which attracted specific attention to the carbon fibers, obtained upon catalyzed decomposition of carbon-containing gases and their mixtures over Ni, Fe, Co and their alloys. The authors of [8] reported the exotic values of H_2 adsorption upon the exposure of such fibers to H_2 at 120 atm and 25°C. The values of *reversible desorption* when the pressure was lowered to atmospheric without any heating were reaching 1.5-2.0 g H_2/g carbon, which corresponds to the sorption of 10-12 H_2 molecules per one carbon atom. In the second communication [9], are presented somewhat more modest values of reversible sorption – up to 4 molecules H_2/atom C, which still exceeds twice the H/C atomic ratio in CH_4 and corresponds to the sorption of 0.4 g H_2/g C. But these values have not been confirmed by other authors and were subject to the strict critics [7,10-14].

The carbon fibers used in [8,9] have a long history [15,16], and were studied many times from the different viewpoints, see, for example, [17-23]. In the literature they are called graphite nanofibers (GNF) [8,9], carbon nanofibers (CNF) [10,23], vapor-grown carbon fibers (VGCF) [7], carbon nano-

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*corresponding author. E-mail: zri@catalysis.nsk.su tubes (CNT) [24] etc. But by the mechanism of formation and structure such fibers are significantly different from, for example, carbon fibers obtained from polymers or coke chemical pitch, which can also have nanosizes and be graphitized. They are even more different from the popular single-walled nanotubes (SWNT). Therefore, in order to avoid confusion, we prefer to call them *catalytic filamentous carbon* (CFC) [21,22], implying under CFC the fibers which are formed as a result of catalytic decomposition of a precursor hydrocarbon on the active face of catalyst metal nanoparticle, diffusion of the carbon through this particle and its yield on the face, which is coherent to the graphite structure [22].

In the Boreskov Institute of Catalysis were conducted the detailed studies of molecular and supramolecular structure (texture) of CFC, obtained via the methane decomposition over Ni and Ni-Cu catalysts at 823-848 K, see, for example, [21,22,25,26]. It was shown, that the graphite planes (graphenes) stacking arrangement near the surface of studied CFC is substantially different from their stacking in the bulk of filament, because graphenes on the surface tend to be parallel to the filament axis. According to the data of high resolution transmission electron microscopy (HRTEM) and scanning tunnelling microscopy (STM) [21,22], the surface of CFC having the herringbone bulk structure (further – type **I**) is covered by the steps and terraces formed from the graphenes. In its turn, the surface of CFC having the plateled bulk structure (further – type **II**) is covered by the curved “closed layers” or “caps”. It is interesting to note, that the filamentss with herringbone bulk structure, formed over the Ni catalysts, have the “fish-skin”-like coverage, while CFC with plateled bulk structure and characteristic macroscopic octopus morphology, obtained over the Ni-Cu catalysts, are covered by the numerous “suckers” [22]. Such surface structure of the filaments is governed not by the special conditions of their synthesis, but by the general thermodynamic tendency to minimize the surface energy. Indeed, according to Abramson [27] the surface enthalpy of the open edge planes is almost 40 times higher in comparison with that of the basal plane of graphite (*ca.* 6.1 and 0.155 Jm^{-2}, respectively [27]). Such screening of the open edge planes occurs spontaneously and is confirmed by the numerical calculations using the molecular dynamics methods [28].

This is the reason why the surface structure of the filaments must be different from their bulk structure and tentatively (as it was shown experimentally) only a small part of the filament external surface could be represented by the open graphene edges. According to [22], the surface not covered by graphenes constitutes only 2÷7% of the total external surface of the filaments. This part of the surface can be envisaged as a deck of playing cards with non-aligned edges. The spaces between the next-neighbor graphene layers with different length are forming the slit-like micropores, which have the uniform size *ca.* 0.34 nm. This size was experimentally measured by the new gas-chromatographic molecular probe method, using the halogenated benzene derivatives as the molecular probes [26]. The total volume of such micropores is extremely small, its measurements by means of the adsorption of nitrogen at 77 K or of benzene and heptane at 298 K give the values of about ~0.01 ml/g or $2 \div 6 \bullet 10^{-5}$ ml/m^2 of the external surface of filaments of the type **I** or **II** [22]. According to the secondary ion mass spectrometry (SIMS) data, the depth of defect zone, corresponding to the length of micropores, expanded for 1÷2 nm into the bulk of filaments [25]. At the same time, the external surface of filaments, calculated after the filling of micropores, reaches ~100 m^2/g for the type **I** and ~300 m^2/g for the type **II** [22].

Rodriguez et al. [8,9] explain the anomalously high values of H_2 sorption in such filaments by its intercalation in the molecular form between the graphene layers, which are held together by the weak van der Waals bonds. In the authors opinion, that the key moment of such intercalation is in the fact, that “kinetic” diameter of the hydrogen molecule (0.289 nm) has a value slightly smaller than that of the interlayer spacing in graphite and turbostrate graphite-like materials (0.335÷0.350 nm). The authors suppose, that as a result of nonrigidity such system can expand to accommodate hydrogen in multilayer configuration [8]. However, though the size of intercalated component is important, it is by far not the determining parameter of intercalation [29,30]. The most important is electron exchange between the “guest” (intercalate) and “host” (carbon), where carbon can be both the donor and the acceptor of electrons [29]. Thus, for example, the large complex PtF_6^- is intercalated easily enough (in this case, graphite is the acceptor), and the relatively large cations of cesium and rubidium are intercalated substantially easier than the small ions of lithium and sodium with lower electronegativity [29]. In the graphite/hydrogen system, the difference in electronegativities is small, and therefore the possibility of hydrogen intercalation into the graphite and graphite-like systems is under discussion. Still, the defective structure and the mosaic pattern of carbon filaments allow to make various assumptions, though the possibility of *multilayer* intercalation of hydrogen seems to be even more doubtful.

Given in the literature data on the H_2 sorption on CFC at the ambient temperature are rather controversial, which can be caused by the structural features of CFC, methods of the sample pre-treatment, and also incorrect measurements due to the existence of small leakage, mistakes in the calculation of reversible sorption values, etc. Such controversies also remain upon the studies of CFC, obtained and pre-treated in the regimes, recommended by Rodriguez et al. [8,9]. For instance, according to Gupta and Strivastava, the CFC prepared from ethylene at ~600°C over the Cu/Ni catalysts have the hydrogen storage capacity of 10÷15 wt.% at the pressure of ~90 atm [31] (however, it should be noted that these CFC could contain a rather significant amount of Ni, which was used as a catalyst; therefore part of the sorption can be assigned to the formation of hydride NiH_3). On the other hand, according to Poirier et al. [14], the CFC produced from acetylene or ethylene over the Ni or Cu/Ni catalysts at the same hydrogen pressure demonstrated the storage capacity of only ~0.7 wt.%. It is remarkable, that upon the same hydrogen pressure of 10.5 MPa the identical capacity was shown by supermicroporous AX-21 [14]. The latter one has the surface area *ca.* 3000 m^2/g and possesses, in the opinion of Dubinin [32], a very highly developed micropore volume (~1.5 ml/g). The CFC with the same hydrogen storage capacity had the surface area value of *ca.* 290 m^2/g and, apparently, was the analogue of CFC, studied in [22], which were obtained over the Cu/Ni catalysts of the same composition and had the identical value of surface area. But in this case the huge difference in the specific adsorption values, referred to the surface area, can be regarded as a proof of intercalation effect in CFC, studied in [14].

The objective of this work is to examine the presence of hydrogen intercalation in CFC at the ambient temperature and increased pressures. In order to do this, we had previously conducted comparative studies of the hydrogen adsorption at the ambient temperature on some samples of CFC with different textural characteristics, synthesized in the Boreskov Institute of Catalysis. The same conditions were used to study the sorption of hydrogen on a number of microporous carbon sorbents with the amorphous structure, synthesized from the oil coke in the Institute of Carbon and Carbon Chemistry. The choice of the latter ones as a reference materials is conditioned by the fact, that all of them are obtained from the same precursor, have the amorphous structure with the texture varied in a wide range, and the samples with the maximum value of surface area (~3000 m^2/g) are the analogues of AX-21 (Amoco) or AX-31M (Anderson Development Co.) [33], which have been thoroughly studied in many works, for example, [14, 32-36]. As an additional reference in the same conditions was studied the adsorption of methane, which is also considered as a potentially perspective type of fuel for the hydrogen generation [2,3], and its sorption has been investigated in many works [32-38].

Experimental

The extensive series of CFC samples were prepared via the decomposition of methane, ethylene, divinyl and hydrogen mixtures over the selected supported metal catalysts at the temperatures between 500 and 600°C. Further are discussed the results, obtained using the typical representatives of this series, which illustrate the diversity of properties of the obtained CFC. The composition of metal component of the catalysts employed is given in the name of each sample. The catalyst composition, hydrocarbons used as the CFC precursors and the synthesis temperature are listed in Table 1, which also includes the main textural characteristics of CFC. The procedures of catalyst preparation and characteristics of the CFC are described more thoroughly in the previous publications [20-22].

The microporous carbons for the reference series were prepared from the oil coke using the different regimes of thermochemical activation. Their synthesis and properties will be described in more detail in a separate communication.

The standard textural characteristics of all the carbon materials were determined by the nitrogen adsorption isotherms at 77 K, which have been measured using the instrument ASAP-2400 Micrometrics. These characteristics included the values of surface area A_{BET}, the volume of micropores $\mathbf{V_{\mu}}$, the total area of meso- and macropores $\mathbf{A_{\alpha}}$ remaining after the filling of micropores, the total volume of micro- and mesopores (with characteristic sizes up to ~100 nm) $\mathbf{V_{\Sigma}}$. The A_{BET} was determined by the

Table 1

Conditions of synthesis of the typical CFC and their main textural characteristics

No	Conditions of CFC synthesis			CFC textural characteristics		
	Catalyst	Hydrocarbon	T, °C	A_{BET}, m^2/g	V_Σ, cm^3/g	V_μ, cm^3/g
1	70 wt.% Ni + 30 wt.% Cu	ethylene	600	243.6	0.19	0.041
2	82 wt.% Ni + 8 wt.% Cu/Al_2O_3	methane	550	203.9	0.55	0.012
3	85 wt.% Fe/Al_2O_3	methane	625	103.1	0.44	0.005
4	90 wt.% Ni/MgO	methane	550	88.4	0.15	0.006
5	Fe:Ni:Cu = 12:7:1	ethylene	600	133.7	0.15	0.026
6	Ni -100-1	divinyl	550	139	-	0.002
7	Ni -100-2	divinyl	550	366	-	0.010
8	Ni -100-3	divinyl	500	250	-	-

standard procedure [39] for the BET method. The $\mathbf{V_\mu}$ and $\mathbf{A_\alpha}$ were calculated using the comparative method [36] (modification of the more known α_S-method by Sing [39]), the related calculations routine is considered in detail in [41]. The $\mathbf{V_\Sigma}$ was determined by the limiting value of nitrogen adsorption at the relative pressure of $P/P_0 = 0.98$ [39].

The adsorption of hydrogen and methane was measured in the statical volumetric high pressure setup, the scheme of which is shown in Fig. 1. The setup is made of stainless steel and includes electric solenoid high pressure valves, the ampoule-adsorber for the sample with volume of $\mathbf{V_0}$, reference volume $\mathbf{V_R}$ between the valves 1 and 2, electric pressure gauge; it is connected with the cylinders containing helium and hydrogen or methane, vacuum pump, the line of atmospheric air admission, and also with the system of measurement of the amount of gas evolving during the desorption.

The volume of ampoule $\mathbf{V_0}$, reference volume $\mathbf{V_R}$

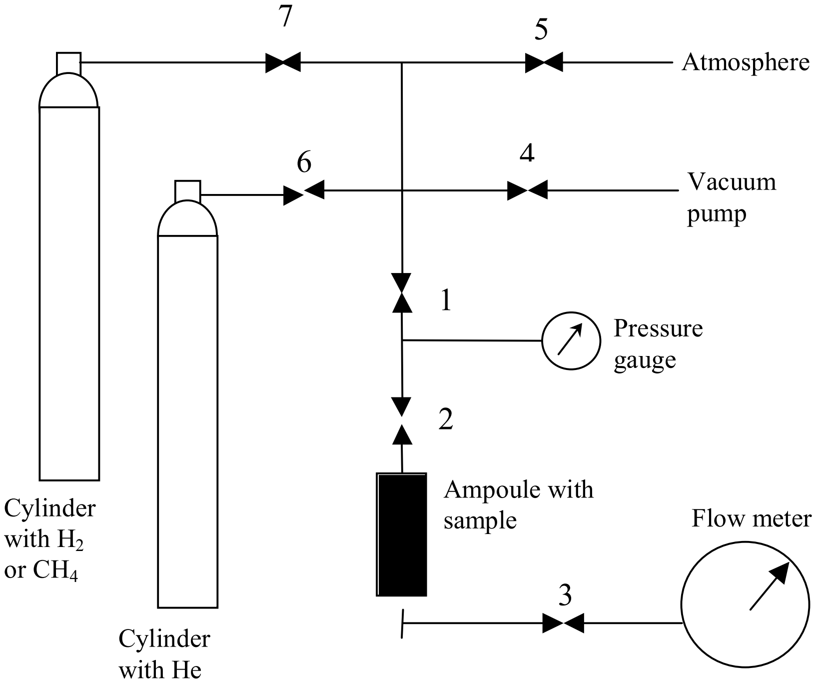

Fig. 1. Scheme of the laboratory setup for the measurement of hydrogen and methane sorption at the pressures up to 100-200 atm.

and the free volume of ampoule $\mathbf{V_{0A}}$, remaining after the loading of sample, were determined via the calibration by He, which was considered as a non-sorbing gas. Two ampoules were used, with the $\mathbf{V_0}$ volumes of 6.15 cm^3 and 15.10 cm^3, respectively, and $\mathbf{V_R}$ = 18.57 cm^3. In order to measure the sorption of hydrogen or methane, the system was first evacuated, then a dose of adsorbate at the pressure of $\mathbf{P_1}$ was introduced into the reference volume $\mathbf{V_R}$, after which the valve 1 was opened and the equilibrium pressure $\mathbf{P_2}$ was established within 0.5-3 hours. The moment of equilibrium pressure establishment was registered by the termination of pressure change by more than 1% within 0.5 hour. The equilibrium value of sorption $\mathbf{a_e}$ at the pressure $\mathbf{P_2}$ was calculated from the balance equation

$$\mathbf{P_1V_R/RT = P_2(V_R + V_{0A})/RT + a_e m} \quad (1)$$

where **R** – universal gas constant, **T** – absolute temperature, **m** – adsorbent loading. Activation (pretreatment) of the samples was conducted at 300°C under vacuum in a separate unit, after which the sample was weighted and loaded into the ampoule. The measurements were performed in the $\mathbf{P_1}$ pressure range up to 100÷120 atm using either the regime of stepwise $\mathbf{P_1}$ values increase, or the desorption by means of lowering the pressure to atmospheric and measuring the amount of evolved gas.

All the measurements were conducted upon the maximum filling of ampoule volume by the adsorbent in the form of powder or fraction of 2÷3 mm, which corresponded to the loadings of several grams.

Results and Discussion

Summary of the main results of studying the reference microporous samples of active carbon is presented in Table 2: here are given the main textural characteristics and the sorption values of hydrogen (pressure 70-90 atm) and methane (pressure 30-40 atm) at the ambient temperature.

The surface area of studied reference samples was varied in the range of 400÷3400 m^2/g, the micropore volume – in the range of 0.2÷1.12 cm^3/g. Among them most interesting are the samples with surface area over 3000 m^2/g, for which the area of mesopores, remaining after the micropores are filled, constituted 5-7% of the total surface area, and 60÷70% of the total pore volume belonged to the micropores. Presented rough estimate of the average micropore size as $\mathbf{H = 2V_\mu/\Delta A}$, where $\mathbf{\Delta A = A_{BET} - A_\alpha}$, gives the values of **H** ~0.70÷0.75 nm. Evaluation using the DR equations of the theory of micropore volume filling [42-44] gives the values of **H** ~1.0÷1.1 nm.

The values of total surface area and volume of micropores for the samples AC-1, AC-2 and AC-3 are very close to those values, which are usually given in literature for the supermicroporous AX-21 (same as Amoco PX-21, later known as Anderson AX-21 and now made by Kansai under license from Amoco and marketed as Maxsorb [33]). Cook et al. [33] have recently made the survey of works, where this unique adsorbent is used for the methane storage. According to this survey, the typical value of total surface area, measured in different works, is ~2800÷3200 m^2/g, and the micropore volume ~1.1÷1.2 cm^3/g. Therefore, one can expect, that porous structure of the samples with surface area above 3000 m^2/g, presented in Table 2, is similar to the structure of AX-21. This is also confirmed by the close values of hydrogen and methane sorption on these samples and AX-21. For instance, according to the survey [33],

Table 2

Results of study of the reference microporous samples of active carbon

Sample	Surface area, m^2/g		Micropore size H*, nm	Pore volume, cm^3/g		Adsorption, mg/g	
	BET method, A_{BET}	Mesopores, A_α		Micropores, V_μ	Total, V_Σ	H_2	CH_4
AC-1	3195.7	168.1	0.74	1.12	1.62	6.0	158
AC-2	3349.3	256.4	0.71	1.10	1.84	8.0	107
AC-3	3100.6	143.7	0.73	1.08	1.55	6.6	128
AC-4	864.0	132.6	1.07	0.39	0.44	5.4	6.0
AC-5	1404.2	238.7	1.11	0.65	0.81	4.5	7.8
AC-6	449.7	13.3	0.96	0.21	0.23	7.0	5.2

* The size of micropores **H** was evaluated using the relationship $\mathbf{H = 2V_\mu/\Delta}$A where $\mathbf{\Delta A = A_{BET} - A_\alpha}$, which corresponds to the slit shape pores [39].

the data of different authors show, that the values of CH_4 sorption at 3.4 MPa and 298 K vary in the range of 130÷160 mg/g, which matches well the data listed in Table 2. According to [14], in the conditions studied by us AX-21 sorbs ~7 mg H_2/g, and the similar values are obtained if the data are extrapolated [34]. These values are also corresponding to those listed in Table 2. In the whole, these results confirm the substantial reliability of the measurement methods used by us.

Now let us consider the results of hydrogen sorption study in the same conditions on the CFC samples. In this case, the sorption of methane did not exceed 1-2 mg/g, that is it was close to the measurement accuracy, and therefore these data are not shown. Summary of the main results of hydrogen adsorption measurements is presented in Table 3.

From Table 3 it can be seen, that on the different samples H_2 sorption varies in a wide range – from 3-6 mg/g to 35 mg/g. The obtained limiting values of H_2 sorption are much lower than those presented in the works of Rodriguez et al. [8,9] and Gupta et al. [31], but are much higher than obtained in the works [7,10-14]. Note that these results disprove the opinion of Tibbetts et al. about the impossibility of achieving the values of adsorption over 10 mg/g on the carbon materials without deep cooling [7]. Our measurements of H_2 sorption on CFC and AC, employed as the references, are conducted in the identical conditions. The data for references are in good agreement with the results of other authors, which supports the reliability of results obtained for CFC.
From the comparison of data in Tables 2 and 3 it follows, that adsorption of H_2 on the samples CFC 1,5,6,7, which have the surface area in the range of 130-360 m^2/g, is 3-5 times greater than on the samples of supermicroporous active carbon AC, which have the surface area over 3000 m^2/g (see Table 2). This effect can not be explained by the adsorption in the micropores of CFC, the volume of which is negligibly small. We assume, that here the only possible explanation is associated with the intercalation effect.

Dresselhaus et al. [45,46] carried out solely geometrical estimates of the limiting hydrogen sorption on the surface of graphite basal face. We will use the similar approach in order to calculate the limiting intercalation capabilities of molecular hydrogen. According to the modern concepts of the structure of intercalated graphite compounds [29], the intercalate **G** ("guest") is located precisely in the "hollows" between the carbon atoms of the neighboring layers, that is in the centers of opposite hexagons C_6 with vertexes at the carbon atoms. This provides maximum interaction between the intercalate and carbon, but requires the displacement of graphene layers with the transition from sequence **ABABAB** to **AGAGA**. Fig. 2 gives the examples of some configurations, which can be formed in the basal plane. The densiest structure of the **GC$_2$** type is shown, where one "guest" molecule accounts for the two carbon atoms (Fig. 2 b,c), as well as the loose structure of the **GC$_6$** type, where one "guest" molecule accounts for the six carbon atoms (Fig. 2 d,e). Also the structures of **GC$_3$**, **GC$_4$**, etc. types are possible [29]. The type of structure formed depends on the geometric relationships between the sizes of H_2 molecule and hexagon, and the interactions of **GG** and **AGA** types.

Into the hexagon with the edge size of 0.1415 nm,

Table 3

Adsorption of hydrogen at the ambient temperature and pressure of 70-90 atm

No	Sample	H_2 adsorption, mg/g	H_2 desorption, mg/g
1	CFC (70 wt.% Ni + 30 wt.% Cu)	20.0	20.0
2	CFC (82 wt.% Ni + 8 wt.% Cu/Al_2O_3)	2.1	-
3	CFC (85 wt.% Fe/Al_2O_3)	8.0	-
4	CFC (90 wt.% Ni/MgO)	2.7	2.7
5	CFC (Fe12Ni7Cu1)	24.5	24.5
6	CFC (Ni-100-1)	26.1	-
7	CFC (Ni-100-2)	35.4	27.5
8	CFC (Ni-100-3)	4.3	4.3

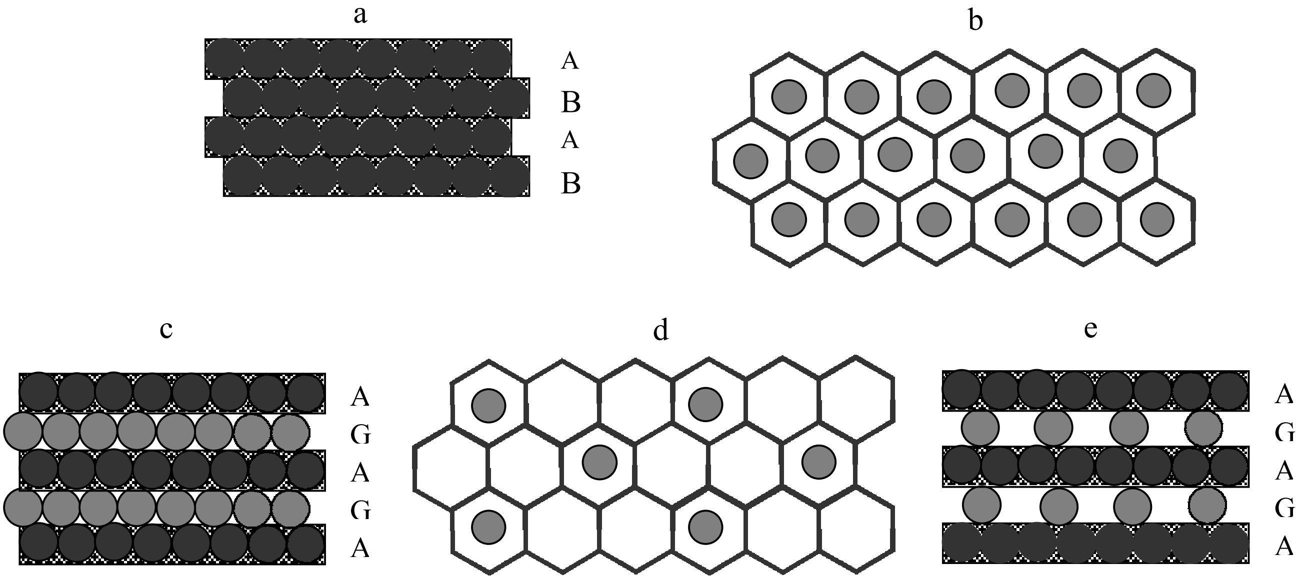

Fig. 2. Models of the molecular hydrogen placement upon intercalation: **a** – initial graphite structure, **b** and **c** – intercalated structure of the **GC$_2$** type, **d** and **e** – intercalated structure of the **GC$_6$** type; **b** and **d** – view in the basal plane, **c** and **e** – view in the direction normal to the basal plane.

equal to the distance between carbon atoms in graphene, can be inscribed the circle with the diameter 0.245 nm. In the calculations of Dresselhaus et al. [45,46] is used the "kinetic" diameter of H_2, equal 0.29 nm. This size corresponds to the Lennard-Jones diameter, which value, according to the different estimates, can vary in the range of 0.291-0.287 nm [47,48]. Such model molecule does not fit into the hexagon C_6 and allows to obtain only the loose packing of the **GC$_6$** type (see Fig. 2 d,e) with the calculated sorption capacity of 28 mg H_2/g C. Exactly this sorption value is given in [45,46]. In addition, the authors of [45,46] evaluated the maximal sorption of H_2 for the situation, when the placement of hydrogen molecules on the surface of graphite basal planes is not correlated with the location of carbon atoms. For the random dense packing of the molecular hydrogen with effective diameter of 0.29 nm, the maximal sorption value obtained was 42.7 mg H_2/g C.

However, in reality the hydrogen molecule is not a sphere, but a *configuration of two spheres*. The minimum and maximum van der Waals dimensions of this molecule are, respectively, 0.24 and 0.31 nm [47-50], and according to [51] its characteristic van der Waals diameter is 0.240 nm. Packing of the molecules with diameter of 0.24 nm allows formation of the **GC$_2$** type structure, shown in Fig. 2 b,c, to which corresponds the atomic ratio H/C (which also is the limiting sorption value) of 83.9 mg/g. This value exceeds, for example, the stoichiometric capacity of MgH_2 and looks substantial for the usage of such carbon sorbents in the systems of hydrogen storage for the **FC** powered vehicle engines [52].

Therefore, the experimental values of hydrogen sorption on CFC, obtained in the present work, are within the margins admissible if the intercalation exists. Upon all the other conditions being the same, the extent of usage of the limiting intercalation capabilities should significantly depend on the features of molecular and supramolecular structure of the particular carbon material. These features determine the key, in our opinion, intercalation conditions: lability and electronic properties. The importance of individual electronic properties is caused by the fact, that intercalation is associated with electron exchange interaction between the "guest" and the "host" (see [29,52] for more details). The lability of structure, providing the structural transformations necessary for intercalation, is determined, in its turn, by the extent of binding the neighboring graphenes via the covalent bond bridges, by the sizes and packing defectiveness of graphene aggregates [52]. Exactly these features can explain the difference in sorption properties of the studied CFC of different origin.

In order to explain the anomalously high values of hydrogen sorption, which are reported in the works [8,9,31], from our viewpoint it is necessary to admit the possibility of existence of multilayer intercalation of hydrogen – these problems are discussed in more detail in [52]. But, in any case, intercalation of hydrogen into CFC at the ambient temperature and increased pressures requires more systematic studies, which are already started in the Boreskov Institute of Catalysis.

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