ISSN 0023-1584, Kinetics and Catalysis, 2007, Vol. 48, No. 4, pp. 599–602. © MAIK "Nauka/Interperiodica" (Russia), 2007.
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CARBON IN CATALYSIS

Carbon Adsorbents as Candidate Hydrogen Fuel Storage Media for Vehicular Applications

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Received November 10, 2006

Abstract—The prospects of carbon adsorbents as vehicular hydrogen storage media are briefly discussed.

DOI: 10.1134/S0023158407040192

A crucial aspect of the challenging problem of employing hydrogen as a nonpolluting fuel is hydrogen storage or onboard generation. There are carbon materials among the candidates for H_2 storage [1–5]. In the late 1990s, it was claimed that an adsorption capacity H_2 exceeding 60 wt % was achieved at room temperature and a hydrogen pressure of P_{H_2} = 112 atm [6, 7]. These a_{H_2} values were obtained using fibrous carbon (FC) with a graphite-like structure, which results from the decomposition of methane and other hydrocarbons on metal catalysts. The authors explained these results by the intercalation of H_2 molecules between graphite-like layers of FC. However, similar studies by other researchers demonstrated that these high a_{H_2} values are false because molecular hydrogen cannot be intercalated under the conditions indicated. The actual a_{H_2} values at both room and lower temperatures are less than 1 wt % [3, 8–10]. Our multiple attempts to reproduce the data reported in [6, 7] have been unsuccessful. Furthermore, we have not achieved any considerable enhancement of H_2 adsorption efficiency for FC materials of various origins by varying synthesis and activation conditions, by adding various intercalating agents (e.g., $FeCl_3$) or activating admixtures like Pd, or by any other means. The adsorption capacity of all systems studied does not exceed 1.0–1.5 wt %. No confirmation has also been obtained for the report by Chen et al. [11] that analogous FCs containing an alkali metal [12, 13] have a reversible adsorption capacity of 14–20 wt % at P_{H_2} = 10 atm between room temperature and 673 K.

A still more obscure issue of hydrogen storage is the applicability of single-wall carbon nanotubes (SWNTs), the closest relatives of fullerene, which also proved inefficient [2, 5]. The reversible H_2 adsorption capacity of SWNT-containing soot under near-normal conditions is 5% [14] or even 8% [15, 16] on the pure SWNT basis. This information rekindled researchers' interest in SWNTs and caused the appearance of a tremendous number of conflicting experimental and theoretical results. Some authors claimed that, at room temperature and $P_{H_2} \leq 100$ atm, the adsorption capacity of SWNT is equal to 2–6 wt %, while others reported that, even at 77 K, it does not exceed 1–2 wt % [17]. These contradictions arise from the difficulties in the isolation of the pure SWNT phase; variations in the surface area accessible to H_2; the effects of the nanotube size, shape, and packing; the way in which measurements are taken and a_{H_2} is calculated; etc.

In later experimental investigations of hydrogen adsorption on pure SWNT, it was shown that, at 298 K and P_{H_2} up to 100 atm, $a_{H_2} \leq 1$ wt % and only at 77 K can an adsorption capacity of 3–5 wt % be achieved [18–20]. Recent experimental data concerning H_2 adsorption on a number of microporous carbons, carbon fibers, and three SWNT samples of different origins [21] testify that the hydrogen adsorption capacity of purified SWNT with a maximum specific surface area of $S_{BET} = 1024$ m^2/g is 2.2 times lower than that of supermicroporous carbon with $S_{BET} \approx 2500$ m^2/g (hereafter, S_{BET} values are derived from nitrogen adsorption data obtained at 77 K). It is significant that, for all systems studied, a_{H_2} is directly proportional to S_{BET}. The constant of proportionality between a_{H_2} and S_{BET} at 77 K and $P_{H_2} \approx 40$ atm can be expressed as α_{H_2} = 9.55 ± 0.75 (μmol H_2)/m^2, and the same constant at 298 K and $P_{H_2} \approx 66$ atm is 1.15 ± 0.57 (μmol H_2)/m^2. Similar correlations between a_{H_2} and S_{BET} with similar α_{H_2} values were established in earlier studies. Data obtained by different researchers lead to the following

Some parameters of supermicroporous carbons obtained from rice husk

Activation temperature, °C	Specific surface area, m^2/g		Pore volume, cm^3/g			H_2 adsorption at 77 K and 40 atm		CH_4 adsorption at 273 K and 60 atm
	S_{BET}	S_α	V_μ	V_S	V_μ/V_S, %	a_{H_2}, wt %	α_{H_2}, μmol/m^2	
700	3170	490	1.74	2.26	77	5.8	9.1	33.8
750	3450	180	1.68	2.01	83	5.7	8.2	26.7
800	3364	260	1.87	2.18	86	6.29	9.3	32.5
850	3170	110	1.45	1.77	82	5.46	8.5	25.5
900	3210	33	1.48	2.97	50	6.21	9.6	40.8
AX-21	2800	120	1.20	1.60	75	5.10	9.1	17.2

Note: S_{BET} is the total specific surface area, S_α is the specific surface of the mesopores after the micropores are filled, V_μ is the micropore volume, and V_S is the total pore volume, all derived from 77-K nitrogen adsorption isotherms.

α_{H_2} values (μmol H_2)/m^2: 8.3 (78 K, P_{H_2} = 40 atm) [22], 7.5 (77 K, P_{H_2} ≈ 1 atm) [23], and 1.6 (300 K, P_{H_2} = 60 atm) [24]. For crude (S_{BET} = 262 m^2/g) and purified (S_{BET} = 552 m^2/g) SWNT samples under H_2 pressure, α_{H_2} at 77 and 298 K is ~12.5 and 0.9 (μmol H_2)/m^2, respectively.

Although the physical meaning of S_{BET} as applied to microporous systems is uncertain [25–27], it seems quite appropriate to use this quantity in the formal comparison of different materials. From the above-mentioned correlations, it follows that SWNTs have no fundamental advantages over microporous carbons, which possess a larger specific surface area. Efficient hydrogen adsorption on all carbon adsorbents is possible only at low temperatures.

The largest S_{BET} and, accordingly, a_{H_2} values are observed for supermicroporous carbons of the AX–21 type (which are essentially the same as AX–31 and Maxsorb). They are produced by chemical activation of petroleum coke or coconut shell [28] in an KOH melt at 700–800 K in an inert atmosphere followed by washing and thermal treatment (table).

Using a similar chemical activation method, we have synthesized a number of carbon adsorbents similar to AX-21 from different carbonaceous precursors. The parameters of the microporous carbons that are the most efficient H_2 and CH_4 adsorbents are listed in the table. These carbons were obtained by chemical activation of rice husk charcoal at 700–900°C followed by washing out all natural and activating mineral components (their adsorption properties are considered in [26]). It is clear from the table that the carbons obtained are somewhat superior to AX–21 in their texture parameters.

Hydrogen adsorption was measured for 1- to 3-g samples between 77 and 273 K at pressures up to 100 atm using a static volumetric procedure. CH_4 adsorption was measured at 273 K for the same samples. The 77-K H_2 and 273-K CH_4 adsorption isotherms for the samples listed in the table are shown in Fig. 1. These isotherms, like the adsorption data in the table, are presented in terms of excess adsorption, which is defined as the difference between the total amount of adsorbate in the measurement ampule and the amount of adsorbate in the free space.

The equilibrium adsorption of H_2 at 273 K in all cases does not exceed 1 wt % at P_{H_2} = 60 atm, and α_{H_2} ≈ 1.2 (μmol H_2)/m^2. More efficient adsorption suitable for H_2 storage is observed only at lower temperatures. At 77 K, the excess adsorption limit is reached at P_{H_2} ≈ 40 atm. In order to desorb ~90% of the adsorbed H_2, it is necessary to decrease pressure to ~0.1 atm or to warm up the sample to 150–200 K at P_{H_2} ≈ 1.0 atm. The ratio of the specific adsorption of H_2 at 77 K to S_{BET} is close to the earlier reported values of α_{H_2} (μmol H_2)/m^2.

Thus, H_2 adsorption on known carbon materials is effective only at low temperatures. The storage of H_2 as adsorbate on AX–31 at 150 K is competitive with the storage of compressed hydrogen at 200 atm and 300 K [29]. Some authors believe that the temperature should be lowered to 100 K [4], so a low temperature is required for this hydrogen storage method in any case. This conclusion is likely true for the other systems intended for storage of physically adsorbed H_2, including zeolite-like and other microporous adsorbents, which also adsorb H_2 efficiently at cryogenic temperatures only [4, 30]. The factor determining storage efficiency is not the nature of the adsorbent, but the weakness of the intermolecular interaction of dihydrogen. This brings about the question of how promising this low-temperature storage technology is.

It is seemingly possible to equip filling stations (FS) with relatively cheap refrigerating plants used in air liquefaction and to fit vehicles with adsorbers with a multilayer vacuum insulation capable of maintaining low

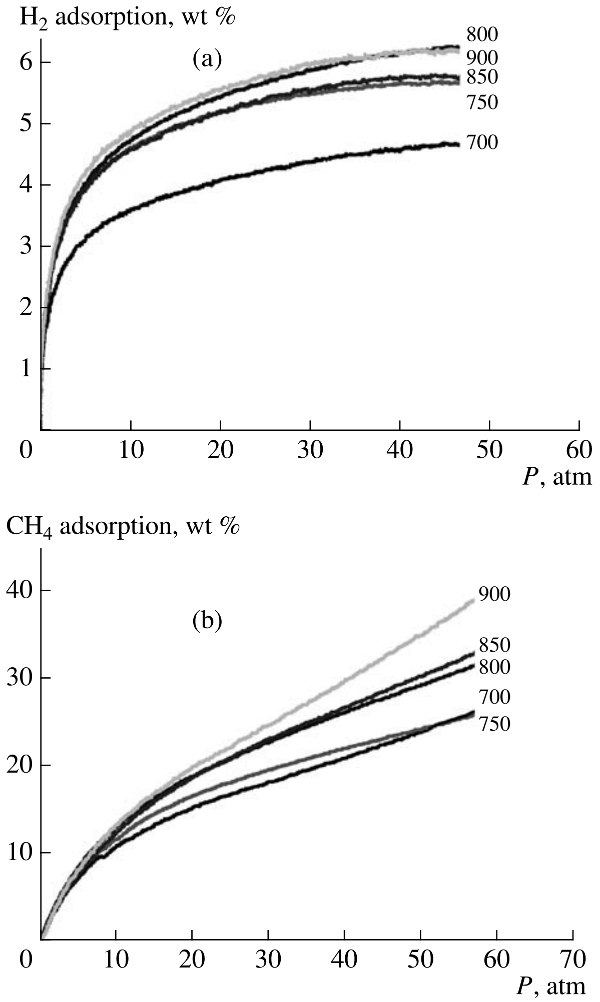

Fig. 1. Adsorption isotherms for (a) hydrogen at 77 K and (b) methane at 273 K on the microporous carbons listed in the table. The numbers at the curves are activation temperatures, °C.

temperatures. The weight and dimensions of this storage equipment can be similar to those of the equipment used in metal hydride or compressed (~200-atm) hydrogen storage. The method based on physical adsorption is advantageous from the standpoint of safety in emergency situations.

Nevertheless, low-temperature storage is always time-limited, which is unacceptable for commercial application in motor transport. Apparently, this fundamental drawback will not be crucial if a low temperature is used only in hydrogen delivery from a gas plant to an FS by motor transport. It is obvious that the transportation of liquid hydrogen is more efficient. The minimum power input L per unit cold Q in hydrogen cooling from the initial temperature T_0 to the final temperature T is determined by the reverse Carnot cycle equation

$$L/Q = (T_0 - T)/T = (T_0/T) - 1.$$

Theoretically, cooling to 77 K instead of 20 K allows one to reduce this minimum power input by a factor of ~5 (and to a much greater extent in practice). Therefore, there is a potential niche in hydrogen power engineering for carbon adsorbents with a highly developed surface.

A more probable application of carbon adsorbents is the storage of CH_4 or natural gas, which is adsorbable at room temperature (table, Fig. 1b). For this reason, researchers' attention in recent years has been focused on CH_4 adsorption on carbon materials at room temperature. The immediate task in this area is to create adsorbents capable of adsorbing more than 150 (l CH_4/l adsorbent) [31].

ACKNOWLEDGMENTS

The authors thank P.P. Kuznetsov, T.Ya. Efimenko, and P.M. Eletskii for their assistance in experiments.

This work was supported by the Russian Foundation for Basic Research, project nos. 04-03-32578 and 06-03-32268a.

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