

*Rapid communication***Hydrogen storage using physisorption – materials demands**

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**Abstract.** A survey is presented of the storage capacities of a large number of different adsorbents for hydrogen at 77 K and 1 bar. Results are evaluated to examine the feasibility and perspectives of transportable and reversible storage systems based on physisorption of hydrogen on adsorbents. It is concluded that microporous adsorbents, e.g. zeolites and activated carbons, display appreciable sorption capacities. Based on their micropore volume ( $\sim 1$  ml/g) carbon-based sorbents display the largest adsorption, viz. 238 ml (STP)/g, at the prevailing conditions. Optimization of sorbent and adsorption conditions is expected to lead to adsorption of  $\sim 560$  ml (STP)/g, close to targets set for mobile applications.

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In the last two decades there has been an increasing interest in the development of (transportable) reversible systems for hydrogen storage with a high capacity, which is critical to the large-scale application of hydrogen fuel cells, in particular for mobile applications [1]. Up to now focus has mostly been on liquid-hydrogen and metal-hydride systems, which both have low energy efficiencies [2]. A higher energy efficiency is attainable with systems in which hydrogen is concentrated by physical adsorption above 70 K using a suitable adsorbent [3–5]. Such an adsorbent should be safe, light and cheap and of course have a high adsorption capacity. In order to obtain a suitable driving range for automotive applications the United States Department of Energy (DOE) target has been set to 6.5 wt %, which equals 720 ml (STP)/g<sub>adsorbent</sub>. Schwarz and co-workers [6–8] studied the applicability of molecularly engineered activated carbons and came up with promising results. Much excitement has arisen on recent reports on the use of carbon nanofibers [9] and carbon nanotubes [10, 11], but because of further research [12] the 'exciting' results have become questionable.

In this paper we present a survey of the storage capacity for hydrogen at 77 K and 1 bar of a large number of different types of adsorbents – silicas, aluminas, zeolites, graphite, activated carbons and carbon nanofibers – in a wide range of specific surface areas and of different textures, in order to give further direction to our research on the development of a suitable storage system.

**1 Experimental**

A large number of carbonaceous (see Table 1) and silica-alumina-based (see Table 2) sorbents were all characterized using N<sub>2</sub> physisorption at 77 K and up to a pressure of 1 bar. The sorbents were chosen to represent a large variation in surface areas and (micropore) volumes. Both non-porous materials, such as aerosil and graphites, and microporous sorbents, such as activated carbons and zeolites, were selected. First we provide a brief description of the samples selected with the sample numbers between brackets. Activated carbons are highly micro- and mesoporous carbon materials. They have been steamed or chemically activated. Steam-activated carbons (7, 8, 11, 12, 14–19) have been prepared from raw materials (e.g. peat, lignite, coal) and carbonized and reacted with steam at 1000 °C. In this way some of the carbon atoms are removed by gasification, which yields a very porous structure. Chemically activated carbons (20) are produced by mixing an activation chemical (usually phosphoric acid) with a young carbonaceous material (usually sawdust), and carbonizing the resultant mixture at 500 °C. The resulting very porous carbon structure is filled with activation agent, which is removed from carbon by washing [15]. Activated carbon fibers (5, 6, 12) have been prepared by controlled pyrolysis of various structures, e.g. the synthetic polymer polyacrylonitrile (PAN) or coal-tar pitch [16]. These fibers are subsequently subjected to activation as described for the activated carbons. Activated graphite (3, 9) is synthetic graphite that has been activated in the same way as described for the activated carbons. Carbon nanofibers (2, 4, 10, 21) have been catalytically synthesized. They consist of conical (fishbone, 2, 4, 10) or tubular (parallel, 21) graphite planes [17]. Zeo-

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**Table 1.** Texture analysis and hydrogen-adsorption capacities at 77 K and 1 bar for carbonaceous materials

No.	Material	PV (ml/g)	$S_{\text{BET}}$ ( $\text{m}^2/\text{g}$ )	$S_{\text{t}}$ ( $\text{m}^2/\text{g}$ )	MPV (ml/g)	$\text{H}_2$ total (ml (STP)/g)	$\text{H}_2$ meso (ml (STP)/g)	$\text{H}_2$ micro (ml (STP)/g)
1	Synthetic graphite	0.04	7	7	0.00	0	0	0
2	Large-diameter CNF	0.10	49	26	0.01	6	2	4
3	Activated graphite 100	0.26	119	85	0.02	14	6	8
4	Medium-diameter CNF1	0.28	120	120	0.00	12	11	1
5	ACF 400	0.40	883	12	0.34	143	1	142
6	ACF 1200	0.42	899	7	0.37	184	1	183
7	AC Norit 990721	0.43	988	17	0.43	142	2	140
8	AC Norit ROZ 3	0.50	287	84	0.05	36	6	28
9	Activated graphite 300	0.51	287	183	0.05	36	16	19
10	Medium-diameter CNF2	0.55	65	65	0.00	7	7	0
11	AC Norit SX 2	0.60	841	194	0.27	150	17	133
12	ACF 500	0.61	988	173	0.40	142	15	127
13	AC Norit UOK A	0.65	1195	110	0.47	188	10	178
14	AC Norit SX 1	0.67	922	206	0.31	168	18	150
15	AC Norit SX 1G AIR	0.68	1030	180	0.36	171	16	155
16	AC Norit GSX	0.78	933	302	0.26	161	27	134
17	AC Norit SX plus	0.79	1051	238	0.35	165	21	144
18	AC Norit SX 1 G	0.83	1176	229	0.40	187	20	167
19	AC Norit 990293	1.03	2029	78	0.92	238	7	231
20	AC Norit Darco KB	1.39	1462	610	0.42	146	54	92
21	Hyperion CNF	2.75	238	238	0.00	22	22	0

**Table 2.** Texture analysis and hydrogen-adsorption capacities at 77 K and 1 bar for silica and alumina

No.	Material	PV (ml/g)	$S_{\text{BET}}$ ( $\text{m}^2/\text{g}$ )	$S_{\text{t}}$ ( $\text{m}^2/\text{g}$ )	MPV (ml/g)	$\text{H}_2$ total (ml (STP)/g)	$\text{H}_2$ meso (ml (STP)/g)	$\text{H}_2$ micro (ml (STP)/g)
22	$\text{SiO}_2$ 90	0.23	79	64	0.01	4	4	0
23	Zeolite L	0.25	344	26	0.12	59	1	58
24	Zeolite ZSM5	0.28	431	43	0.16	80	2	78
25	Zeolite ferrierite	0.32	344	41	0.12	65	2	63
26	$\text{SiO}_2$ D051 A	0.48	172	172	0.00	9	9	0
27	$\text{SiO}_2$ 1614 E	0.51	97	97	0.00	9	9	0
28	$\text{SiO}_2$ Caboxil M5	0.59	185	183	0.00	11	11	0
29	S980G	0.60	67	67	0.00	5	5	0
30	$\text{SiO}_2$ Aerosil 200	0.66	167	167	0.00	0	0	0
31	$\text{SiO}_2$ Becker AD 050	0.74	330	330	0.00	18	18	0
32	$\text{SiO}_2$ -60-1	0.75	61	52	0.00	3	3	0
33	$\text{Al}_2\text{O}_3$ preshaped	0.80	233	233	0.00	7	7	0
34	$\text{SiO}_2$ 380	0.87	322	273	0.03	27	15	12
35	MCM-41	1.04	1017	1017	0.00	65	65	0
36	S970SH	1.08	290	268	0.01	28	15	13

lites are highly crystalline, microporous materials, consisting of silica and alumina. Zeolite L (23) consists of unidimensional 12-ring pores, with 0.9 nm diameter. Ferrierite (25) is a two-dimensional pore network, consisting of pseudo-spherical cages with 8 ring openings ( $0.35 \times 0.48$  nm) and interconnecting 10-ring pores ( $0.42 \times 0.55$  nm). ZSM-5 (24) consists of tridimensional interconnecting 10-ring pores of dimensions  $0.51 \times 0.55$  nm [18]. The silicas and aluminas (22, 26–34, 36) are all commercially available inert catalyst supports selected for their lack of microporosity. MCM-41 (35) is an all-silica material, consisting of highly regular, 3-nm-diameter channels [19, 20].

From the  $\text{N}_2$  physisorption data, obtained with a Micromeritics ASAP 2400 apparatus, the BET surface area, total pore volume (PV), micropore volume and t-surface were derived. All pore volumes are expressed in ml/g; the micropore volume (MPV) is defined as the pore volume of the pores  $< 2$  nm. The BET surface area ( $S_{\text{BET}}$ ) is the surface area of

the sorbent according to the model formulated by Brunauer et al. [13] for planar surfaces ( $\text{m}^2/\text{g}$ ). The equation is formulated to assess multilayer adsorption of small inert molecules on substrates. The t-surface area ( $S_{\text{t}}$ ,  $\text{m}^2/\text{g}$ ) is derived from the t-plot and is the mesoporous ( $> 2$  nm) surface area of the sorbent, i.e. the amount of surface area excluding the micropores [14].

The  $\text{H}_2$ -adsorption measurements were performed with a Micromeritics ASAP 2010 at 77 K in the pressure range 0–1 bar. From adsorption–desorption experiments it is evident that reversible physisorption exclusively takes place with all samples.

## 2 Results and discussion

The results of the  $\text{N}_2$  and  $\text{H}_2$  physisorption measurements are shown in Tables 1 and 2. In these tables CNF is used to des-

ignite carbon nanofibers, ACF is used for activated carbon fibers and AC for activated carbon.

In a first approach the total amounts of hydrogen taken up per gram of adsorbent at 77 K and 1 bar are correlated with  $S_{\text{BET}}$ . From Fig. 1 it can be concluded that this correlation is not very straightforward. Nevertheless it is clear that with the mesoporous silicas and aluminas a low  $\text{H}_2$  capacity is found, even with the MCM-41 sample (35) exhibiting a  $S_{\text{BET}}$  of  $1017 \text{ m}^2/\text{g}$ . Only with the zeolites (23–25) is an enhanced capacity measured, obviously because of their microporous texture. This also holds for the mainly microporous carbon samples (5–7, 11–18), although a high microporosity does not always give rise to a corresponding increase of the  $\text{H}_2$  capacity as is demonstrated with samples 6 (activated-carbon fiber) and 20 (activated carbon).

The above results suggest that a better correlation is to be expected between the micropore volumes and the respective adsorption capacities for  $\text{H}_2$ . Here it is important to realize that hydrogen does not exclusively adsorb in the micropores but also on the surface of the mesopores. Therefore, to find the actual  $\text{H}_2$  uptake in the micropores we have corrected the total  $\text{H}_2$  uptakes for the amounts adsorbed on the mesopore surface area. We calculated the contribution by the mesopores using the correlation which exists, as shown in Fig. 2, between the adsorbed volumes and the t-surfaces of

the various non-microporous silica (27, 31), alumina (29) and carbon samples (4, 10, 21, all carbon nanofibers). Obviously hydrogen has a preference for carbon surfaces: the oxidic surfaces take up  $0.06 \text{ ml (STP)/m}^2$  at 1 bar, the carbon surfaces  $0.09 \text{ ml (STP)/m}^2$ . Using the above correlations and the t-surface areas as derived from the  $\text{N}_2$ -physisorption measurements the surface coverage of  $\text{H}_2$  at 1 bar can be calculated, if the average area occupied by one  $\text{H}_2$  molecule ( $a_{\text{M}}$ ) is known. Following the approach of Emmett and Brunauer [21], we estimated  $a_{\text{M}}$  to be  $0.14 \text{ nm}^2$ . With this a monolayer capacity for  $\text{H}_2$  can be calculated as  $7 \times 10^{18} \text{ molecules/m}^2$ . Thus, for the oxidic surfaces we arrive at a coverage of 22%, while with the carbon surfaces a coverage of 34% is attained at 1 bar.

In Fig. 3 the micropore volumes of various microporous silica (34), alumina (36) and zeolite (23–25) samples are plotted against the t-surface corrected hydrogen uptakes. In Fig. 4 this is done for the microporous carbon samples. A good correlation is found with the oxidic samples (Fig. 3). The scatter of the data points at low hydrogen uptakes is due to the relatively large error in the calculated micropore volumes. Based on the derived linear correlation the  $\text{H}_2$  uptake per ml of micropore volume amounts to  $490 \text{ ml (STP)/g}$ . The apparent density of  $\text{H}_2$  inside the zeolite micropores amounts to  $0.044 \text{ g/ml}$ , that is 63% of the density of liquid hydrogen

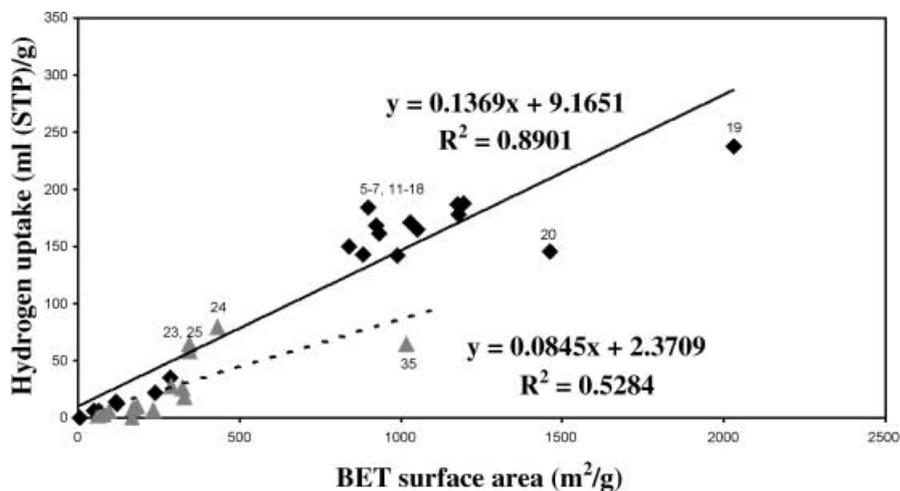


Fig. 1. Hydrogen adsorption versus BET surface area at 77 K and 1 bar for carbon (◆), silica and alumina (▲)

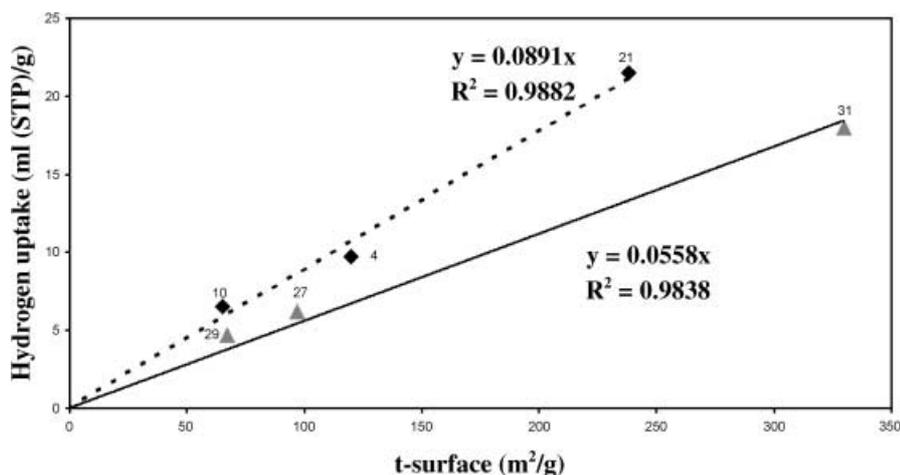


Fig. 2. Hydrogen adsorption versus t-surface at 77 K and 1 bar for carbon (◆), silica and alumina (▲)

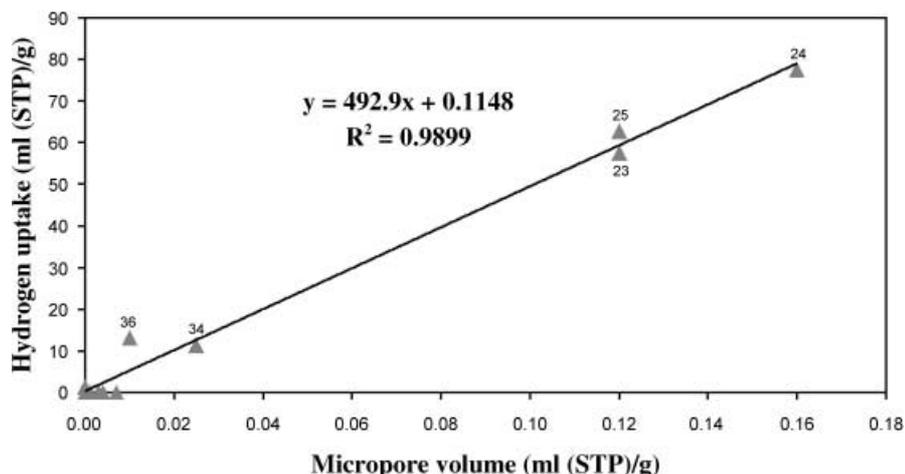


Fig. 3. t-surface corrected hydrogen adsorption versus micropore volume at 77 K and 1 bar for silica and alumina

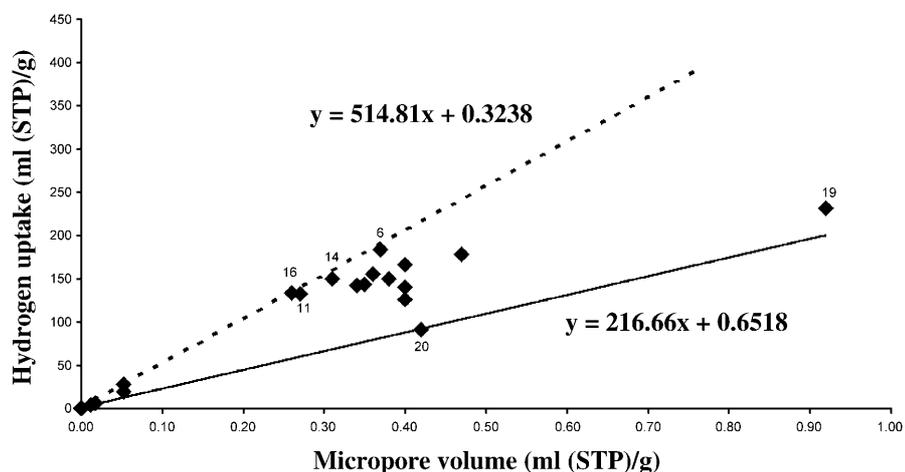


Fig. 4. t-surface corrected hydrogen adsorption versus micropore volume at 77 K and 1 bar for carbon

(0.07 g/ml). For carbon-based sorbents a large scatter between the data for the  $H_2$  uptake and the micropore volume is observed (Fig. 4). A lower limit for the correlation is given mainly by samples 19 and 20. The lower line shown in Fig. 4 relates to an  $H_2$  uptake of 220 ml (STP)/ml or an  $H_2$  density of 0.020 g/ml (28% of liquid  $H_2$ ). The upper limit (samples 6, 11, 14 and 16) gives 515 ml (STP)/ml or an  $H_2$  density of 0.046 g/ml (66% of liquid  $H_2$ ). For microporous carbons the details of the pores (size and shape) apparently affect the specific  $H_2$  uptake to a large extent.

In comparing microporous oxides (zeolites) and carbons (activated carbons) it turns out that similar hydrogen densities (0.04–0.05 ml/g) are observed at 77 K and 1 bar. For mesoporous surfaces (Fig. 2) carbon interacts somewhat more strongly with  $H_2$  than oxides do. For micropores this difference vanishes, probably due to the different shape of the micropores for activated carbons (slits) and zeolites (cylinders). The main advantage of carbon over oxides resides with the range of micropore volumes that can realistically be achieved. Zeolites with a micropore volume of say 0.5 ml/g or above are unlikely, whereas with activated carbon 1 ml/g is common practice. The details of the pore size and shape are very important with the latter, though.

The importance of the size of pores in hydrogen uptake can be illustrated further with the hydrogen-adsorption capacities of MCM-41. This oxidic material has very regular, 3-nm-diameter pores, which makes it a completely mesoporous

material. It adsorbs 65 ml (STP)/g, which is a 12% higher uptake than other mesoporous oxides (see Fig. 2). This shows that the hydrogen in the mesopores of MCM-41 is slightly more stabilized than by other oxidic mesoporous surfaces. It is however not stabilized as much as  $H_2$  in the micropores of zeolites (see Fig. 3).

The density of  $H_2$  in the micropores of carbon at the prevailing conditions (77 K, 1 bar) ranges from 0.02–0.05 g/ml, that is 30%–70% of the density of liquid  $H_2$ . With the current type of carbon sorbents and sorption conditions a maximum uptake of 238 ml (STP)/g has been observed, amply below the DOE target of 720 ml (STP)/g for mobile applications. If we can realize a micropore volume of 1 ml/g, with a  $H_2$  density of 0.05 g/ml, the uptake rises to 560 ml (STP)/g, much closer to the DOE target. By optimization of both sorbent and sorption conditions ( $P$ ,  $T$ ) the  $H_2$  density might approach that of liquid  $H_2$ , giving rise to an uptake of 780 ml (STP)/g.

### 3 Conclusions

Our results demonstrate that a large storage capacity for hydrogen by physisorption under the chosen conditions is only obtained with adsorbents containing a large volume of micropores with a suitable diameter. Although with zeolite-like materials the chance to find an optimal pore diameter seems realistic, their unavoidably limited micropore volume makes

their applicability less likely. With carbonaceous adsorbents (e.g. activated carbons) a more optimistic perspective can be offered. Their intrinsic interaction with hydrogen seems to be slightly stronger than that with oxidic adsorbents, their micropore volume can probably be increased to a value above 1 ml/g, while by increasing the storage pressure or by tuning the pore diameter the storage capacity can be raised to the targets set for mobile applications. Because of the various sizes and shapes of the micropores in activated carbon it is as yet impossible to comment on the optimum pore size and shape. Future research will be focussed on a more precise identification of the optimal pore diameter and on the development of experimental procedures to provide carbon materials with a high volume of these suitable pores.

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