Hydrogen adsorption on carbon materials

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Abstract

Studies are focused on the hydrogen adsorption on carbon materials at ambient temperature. The hydrogen adsorption from the gas phase was measured by isothermal gravimetric analysis, using a microbalance at hydrogen pressures up to 125 bar at 23°C. In this work, the hydrogen adsorption reached values of approximately 1.5 wt.% at ambient temperature and 125 bar. © 1999 Elsevier Science S.A. All rights reserved.

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1. Introduction

Hydrogen adsorption on carbon materials has been known for many years. The adsorption amount for activated carbon reaches values of approximately 0.5 wt.% hydrogen at ambient temperature and 60 bar pressure. Under cryogenic conditions, this amount increases up to approximately 5 wt.% at 60 bar pressure [1–3]. For nanostructured carbon materials, theoretical considerations allow for a maximum hydrogen absorption of 8 wt.% at ambient temperature [10].

New results at North Eastern University in Boston (US) of Rodriguez [4], Rodriguez and Baker [5], Baker [6], and Chambers et al. [7] promise a hydrogen storage capacity of 20 lH_2 (STP) per gram of highly orientated carbon nanofiber, which would result in a storage capacity of approximately 60 wt.% hydrogen.

The aim of this work is to verify these findings. Therefore, different carbon samples (fibrous materials and activated carbon) available from several laboratories were investigated by isothermal gravimetric analysis. The hydrogen adsorbed from the gas phase was measured with an ultramicrobalance at 23°C. Gravimetric data are compared with Brunauer–Emmet–Teller (BET)-specific surface area.

2. Experimental

A ''Sartorius Supermicro S3D-P'' balance was used. A schematic drawing of the apparatus is shown in Fig. 1. The balance chamber can be pressurized up to 150 bar. The mass resolution is 0.1 μg. The reference crucible (R) was loaded with quartz and the sample crucible (S) with the carbon material. Buoyancy was corrected numerically. The helium adsorption was measured to analyze the sample volume, assuming that no helium is adsorbed on the carbon material. Before starting the high-pressure experiment, the sample chamber was rinsed with the gas (H_2, He) to be adsorbed. The chamber was evacuated with an oil pump until pressure and mass were stable for 30 min. After evacuation, the samples were measured in one ad-

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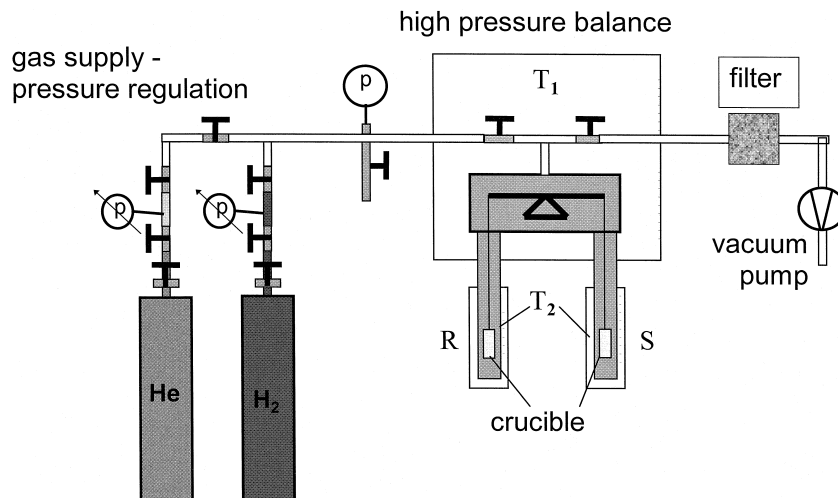Internet: http://www.zsw.uni-ulm.de.

Fig. 1. Schematic experimental set-up of the gravimetric hydrogen adsorption analysis.

sorption–desorption cycle with a maximum pressure of 125 bar.

The hydrogen adsorption amount (Δm, wt.%) is calculated by the mass increase divided by the sample plus adsorbed hydrogen mass.

The investigated samples are divided in two types of carbon material. The activated carbon samples are high porous materials with an amorphous structure. The fibrous material typically was synthesized from the gas phase on fine catalyst particles. The structure of this carbon material is fibrous and consists of graphitic layers.

3. Results and discussion

Fig. 2 shows the increase of the hydrogen adsorption rate vs. hydrogen pressure. The samples, mpe_9, NORIT

and zsw_1, are activated carbons. The measured maximal hydrogen adsorption amount of these samples is shown in Table 1. The adsorption isotherms measured follow approximately the characteristic plot of Langmuir adsorption. The calculation of the experimental data as a Langmuir isotherm results in a maximal adsorption amount (Table 1) [8]. The measured and calculated data are similar. In accordance with these results, we assume that a hydrogen monolayer covers the activated carbon samples at 120 bar. Because of the Langmuir characteristics of the experimental data and the similar values of the calculated maximal adsorption rate, we suppose that only physisorption takes place. This can explain the correlation of increasing hydrogen adsorption with the increasing specific surface area for the activated carbon samples, as shown in Fig. 3. Simulation results of physisorption of hydrogen on microporous carbon confirm these results [9].
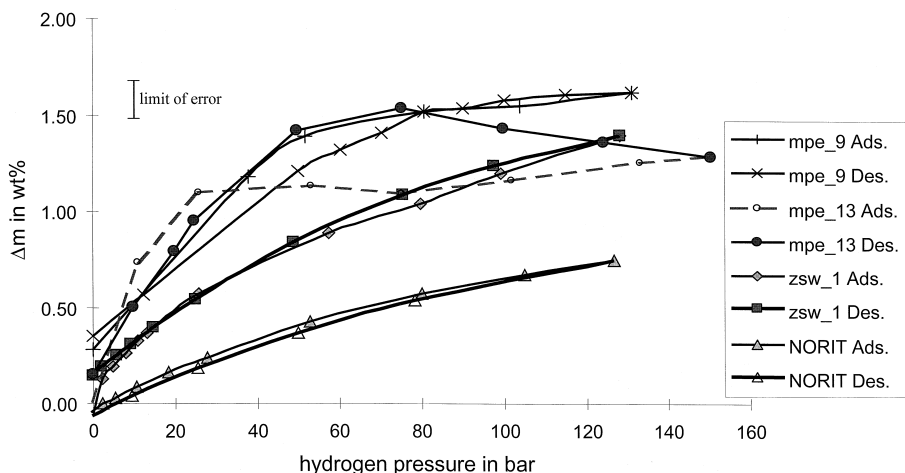

Fig. 2. Hydrogen adsorption vs. hydrogen pressure at 23°C.

Table 1

Sample	Maximal adsorption data (wt.%, measured)	Maximal adsorption data (wt.%, calculated)
NORIT	0.75	1.0
zsw_1	1.4	1.6
mpe_9	1.6	1.6

The sample, mpe_13, a catalytically vapor–grown nanofiber, shows a unique behavior (Figs. 2 and 3). The increase of the hydrogen adsorption amount with rising pressure does not fit the Langmuir isotherm. For low pressures, there is a rapid mass increase leveling off at approximately 20 bar. The sample adsorbs H_2 (≈ 1.2 wt.%) despite its low specific surface area (Fig. 3). The sample consists of solid fibers (ϕ 10 μm, length 250 μm) (Fig. 4). Its surface is covered by a small amount of a fibrous material (ϕ 100 nm, length 1 μm), looking similar to a carbon fleece. It can be suspected that the H_2 adsorption takes place mainly in the finely structured material. Taking this suspicion into account, the storage capacity will be higher than 1.2 wt.% measured for this sample. But so far, only first-cycle experiments have been carried out. However, changes of sample morphology under hydrogen pressure cannot be excluded.

The correlation of the specific surface area and the hydrogen adsorption amount in Fig. 3 shows the expected increase of the hydrogen adsorption rate with an increasing BET surface for activated carbon samples. The solid line is a fit of all measurements data. It is apparent that the nanofiber samples, mpe_13 and mpe_14, do not fit into this characteristic. The matching hydrogen adsorption plot confirms the similar morphology of these two samples already observed by electron microscopy. The unexpected behavior can be explained by the assumption that during
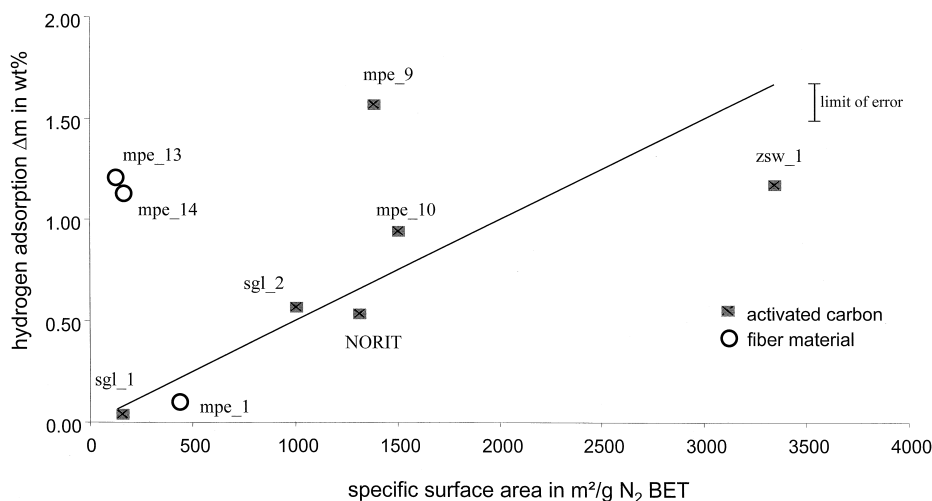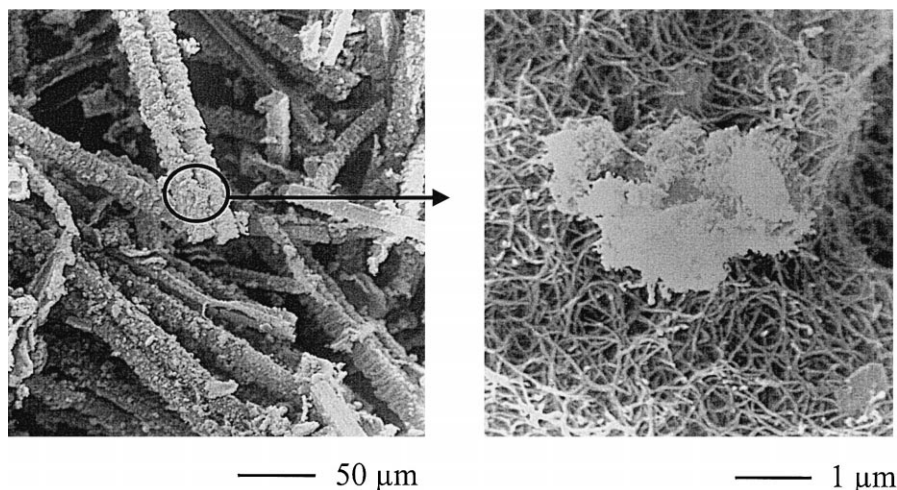

Fig. 3. Hydrogen adsorption vs. specific surface area.

—— 50 μm   —— 1 μm

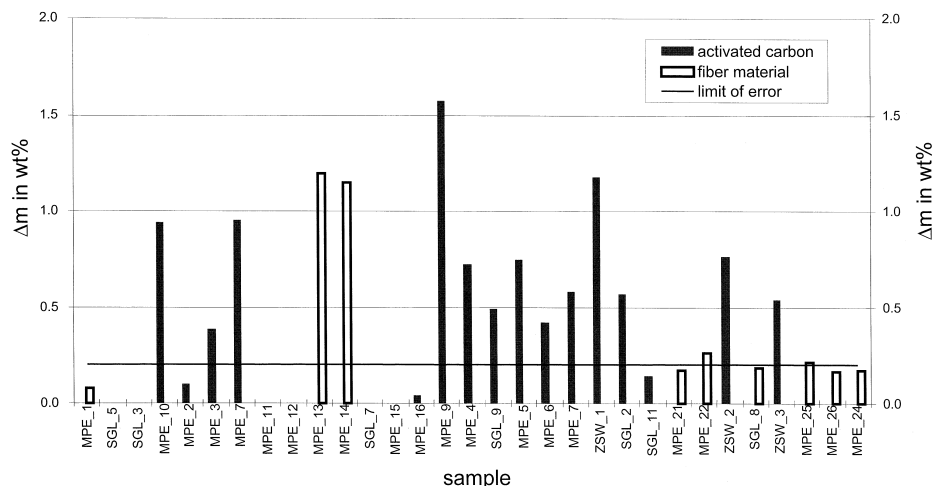Fig. 4. Electron micrographs; magnification 200 $\times$ and 10,000 $\times$.

Fig. 5. Hydrogen adsorption at 100 bar and 23°C for different samples.

BET surface determination, the nitrogen condensation does not reach the same surface area like hydrogen does. For this reason, there must be a high content of a nanostructured material in this sample. But this results have to be confirmed by nanostructure analysis, e.g., by TEM.

4. Conclusions

A great variety of different carbon structures was investigated (Fig. 5). The large adsorption numbers published [6,7] could not be confirmed. The measured hydrogen adsorption rate has a maximum of 1.6 wt.% in activated carbon. This value is in accordance with physisorption calculations. However, samples of a dual microstructure do have an unusual behavior in hydrogen atmosphere which most probably can be attributed to their nanostructure. Further research is in progress.

Acknowledgements

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