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Thermoanalytical investigations of hydrogen adsorption on carbon materials

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Abstract

The hydrogen adsorption on carbon nanofibers of different origin was investigated by thermogravimetric measurements at temperatures between −10 and 25 °C and pressures up to 140 bar. The applied gravimetric apparatus yields a distinctly higher precision, compared to volumetric and calorimetric methods. All investigated carbon nanofibers show a hydrogen uptake below 0.3 wt.% independently from sample pretreatment.

Keywords: Carbon nanofibers; Hydrogen adsorption

1. Introduction

The future-oriented hydrogen technology is the motivation to the intensive search for suitable hydrogen storage materials for mobile applications. In this context, the information about extreme hydrogen storage capacities of carbon nanostructures of about 60 wt.% released an avalanche of research activities concerning this topic [1]. However, the several research teams report contradictory results until now [2,3]. Carbon nanotubes were suggested as the most suitable storage structures [4,5]. Nevertheless, their storage capacities do not exceed the limit of 1 wt.% hydrogen. The present work reports about thermogravimetric and calorimetric investigations of hydrogen adsorption on carbon nanofibers of different origin and with different pretreatment.

2. Experimental

The central part of the gravimetric array is a modified Sartorius Supermicro S3D-P balance (Fig. 1). There are two thermostated regions in the balance, the weighing cell with a constant temperature of usually 40 °C and the suspended chambers with a temperature adjustable between −40 and 500 °C. Cooling is realized by double jacketed vessels connected with a thermostate and heating by electrical twin furnaces. The balance chamber can be pressurized up to 150 bar (at 25 °C). The material of the used crucibles is alumina. The balance has a resolution limit of 0.1 μg, a relative error of ±0.25% and a stability of ±2.5 μg in 24 h. According to this, a resolution of 0.01 wt.% in hydrogen uptake can be achieved if about 5–10 mg of sample were used. A correction of the measured value with the buoyancy of the sample, the reference substance and the weighting system is necessary. The buoyancy of the system was estimated by measurement with blank crucibles under identical conditions.

Experimental procedure: The sample and an equal mass of reference substance (NaCl with a density similar to the carbon material) were loaded into the crucibles. In the case of pretreatment of the sample by heating in an argon flow, the balance chamber was rinsed with argon (99.9999%) and subsequently a constant gas flow of argon was adjusted during the heating. Before starting of the adsorption experiment, the balance chamber was rinsed with dried hydrogen (99.9999%) and evacuated until the pressure and the mass signal were stable. The hydrogen adsorption was measured under isothermal conditions (predominantly at 25 °C) in steps of 40 bar up to a maximum pressure of about 140 bar. The amount of adsorbed hydrogen in weight percent was calculated by the corrected mass increase. The isothermal calorimetric measurements were realized in a heat flow calorimeter DSC 111 (Setaram) with hydrogen pressures up to 100 bar.

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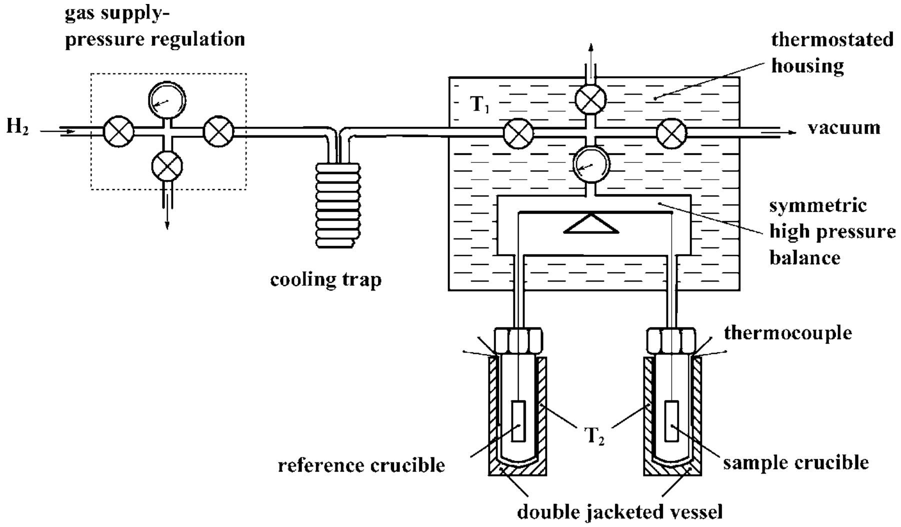

Fig. 1. Schematic experimental setup of the gravimetric hydrogen adsorption analysis.

3. Results and discussion

The accuracy of the gravimetric apparatus was tested by measurements of activated carbons and some binary and ternary metal hydrides. Fig. 2 shows four adsorption isotherms at 25 and −10 °C of an activated carbon with an extreme large surface of 3000 m^2/g and proves the good reproducibility of the method. The pressure dependence of the adsorbed hydrogen amounts can be well described by the Langmuir isotherm for physical adsorption. At 140 bar and 25 °C, a maximum adsorption of 0.7 wt.% for activated carbon was found. The molar enthalpy of adsorption is reflected by the temperature dependence of the adsorption isotherms and decreases with increasing occupation degree of surface. Its order of magnitude is of about 8 kJ/mol. These facts provide evidence for a pure physical adsorption process where the adsorption capacity is proportional to the sample surface.

The pretreatment has a strong influence on the adsorption behavior of surfaces. The heating under vacuum effects a cleaning of the surface. Some authors found evidences to a strong influence of the thermic pretreatment on the storage capacity of carbon materials. Therefore, the hydrogen adsorption of samples with and without pretreatment were investigated. According to the instructions in the literature, pretreatment was divided in two steps [1]. First, heating at 925 °C in an argon flow in a vertical quartz reactor, second, heating at 190 °C for approximately 8 h in an argon flow or under vacuum.

The hydrogen adsorption of 15 different carbon nanofibers with and without thermic pretreatment was investigated. Fig. 3 shows a typical adsorption isotherm at 25 °C with an extremely low hydrogen uptake of about 0.04 wt.% at 140 bar. This graph demonstrates the excellent resolution of the gravimetric array. The maximum hydrogen adsorption obtained for the samples of carbon nanofibers ranged

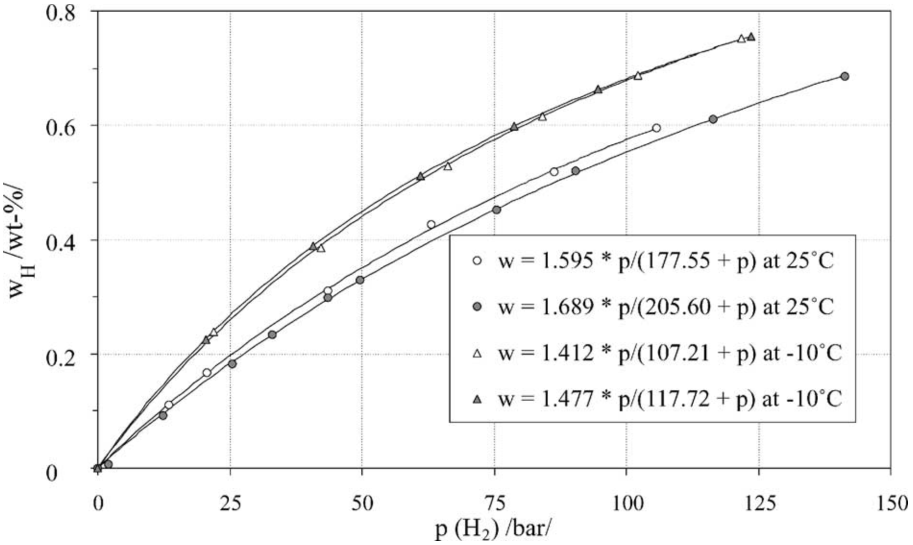

Fig. 2. Hydrogen adsorption isotherms of an activated carbon.

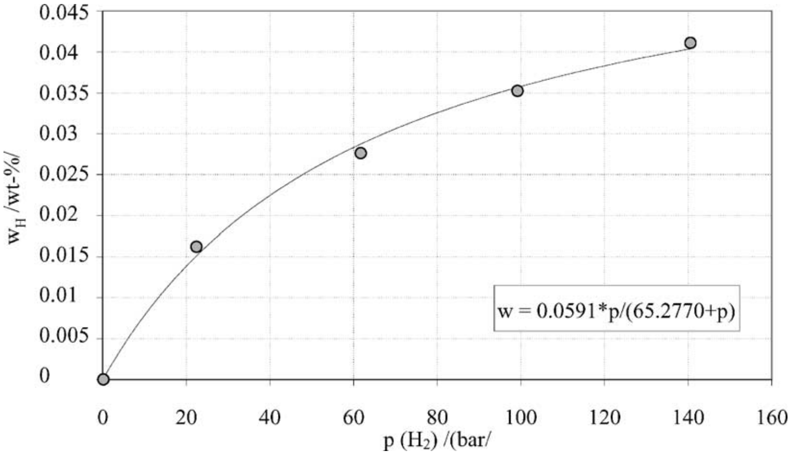

Fig. 3. Hydrogen adsorption isotherm of a carbon nanofiber sample at 25 °C.

between 0.01 and 0.3 wt.% at 140 bar, independently of their pretreatment.

In the beginning of the investigations, a rapid and large weight increase of about 7 wt.% of the sample was obtained, followed by a slow decrease over the next days. This surprising effect was checked by comparisonal measurements with helium and deuterium instead of argon and hydrogen and was identified as an artefact of the gas change from argon to hydrogen. If the argon is not removed quantitatively, a large hydrogen adsorption is pretended by the different diffusion rates of hydrogen and argon in the porous material (law of Graham). Hydrogen diffuses into the solid material rapidly and prevents the desorption of argon. The following adsorption experiments were carried out by careful removing of argon traces before hydrogen was allowed to contact the sample. After the elimination of this artefact, all samples did not show a mass increase of more than 0.3 wt.% during the experiment.

4. Conclusions

The hydrogen storage capacity of the investigated carbon nanofibers of 0.3 wt.% at 140 bar and 25 °C is smaller than that of the activated carbon with about 0.7 wt.%. Hirscher et al. [6] found likewise a very small hydrogen adsorption for several carbon nanomaterials. The evaluation of the gravimetric and calorimetric measurements points to pure physical adsorption only. No indications of other mechanisms for the hydrogen bonding could be found. However, the adsorbed amounts of hydrogen are too small to obtain the adsorption enthalpy quantitatively. These results do not favor a technical application of carbon nanomaterials for hydrogen storage.

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