Hydrogen adsorption in different carbon nanostructures

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Abstract

Hydrogen adsorption in different carbonaceous materials with optimized structure was investigated at room temperature and 77 K. Activated carbon, amorphous carbon nanotubes, SWCNTs and porous carbon samples all show the same adsorption properties. The fast kinetics and complete reversibility of the process indicate that the interaction between hydrogen molecules and the carbon nanostructure is due to physisorption. At 77 K the adsorption isotherm of all samples can be explained with the Langmuir model, while at room temperature the storage capacity is a linear function of the pressure. The surface area and pore size of the carbon materials were characterized by N2 adsorption at 77 K and correlated to their hydrogen storage capacity. A linear relation between hydrogen uptake and specific surface area (SSA) is obtained for all samples independent of the nature of the carbon material. The best material with a SSA of 2560 m2/g shows a storage capacity of 4.5 wt% at 77 K.

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1. Introduction

Hydrogen storage is the bottleneck for the breakthrough of hydrogen as energy carrier in automotive applications. In the last years different storage technologies have been investigated [1,2] to develop a secure and cheap way to save hydrogen. By gas compression, hydrogen liquefaction, or in the form of metal hydrides, possess severe disadvantages. These drawbacks have induced the study of new storage concepts as physisorption on nanomaterials. Especially novel carbon materials, such as carbon nanotubes, activated carbon and carbon nanofibers have attracted a lot of interest, however, the values for their hydrogen storage capacity scatter over several orders of magnitude [3]. At present, the independently confirmed and repeatable storage capacities in carbon materials at room temperature are less than 1 wt% [4,5], however, higher values can be reached by lowering the temperature. The process responsible for hydrogen adsorption in carbon materials at moderate temperature is physisorption [6–10], which is based on weak van der Waals forces between adsorbate and adsorbent. At room temperature the magnitude of this interaction can be of the same order as the thermal motion energy of gas molecules on the surface, therefore only low storage capacities can be achieved [11,12]. If the system is cooled down, the interaction between the surface and the gas molecule becomes stronger than the thermal motion energy of the adsorbate, which is proportional to the temperature.

In this work, different carbon nanostructures have been characterized and investigated in view of their hydrogen adsorption capacity up to high pressures both at room temperature and at 77 K. These materials possess structures which have been optimized for the hydrogen uptake, e.g., high specific surface area and micropore density. In order to understand the nature of the adsorption process, the hydrogen storage capacity
is correlated to the structural properties of the carbon samples.

2. Experimental

2.1. Carbon nanostructures

Various carbon materials have been obtained from different suppliers worldwide for this study. Firstly, different types of carbon nanotubes (CNTs) with specific structures have been selected. Amorphous carbon nanotubes have been produced by DC arc discharge in an atmosphere of hydrogen gas at temperatures above 300 °C [13]. These nanotubes are hollow pipes with diameter ranging from 10 nm to 15 nm, and the walls show no long-range ordered structure. Single-walled carbon nanotubes (SWCNTs), which have been produced with the HiPco (High pressure CO conversion) method, have been purchased from CNI. This synthesis produces a high yield of well ordered SWCNTs with a narrow diameter distribution around 1 nm, however, still containing metal catalyst particles. Therefore, this material has been purified by either selective oxidation and subsequent HCl treatment (sample I) [14] or standard purification procedures giving 98 wt% of SWCNTs (sample II).1 Additionally, we received SWCNTs prepared by graphite arc discharge evaporation in helium atmosphere and collecting the soot from the cold walls of the reaction chamber [15]. These samples contain typically a high fraction of amorphous carbon and catalyst particles. Other samples have been produced by cracking of liquid hydrocarbons in a low voltage arc discharge or resistive heating. This method results in a mixture of MWCNTs, SWCNTs and polyhedral nanoparticles of different compositions and are called Ros 1 and Ros 3 by the producer [16]. Secondly, activated carbon samples from different suppliers have been investigated. Activated carbon I is similar to AX-21 [17], which is obtained from the reaction of coke with KOH, giving a product with a doubled specific surface area compared to regular grade porous carbon. Porous carbon samples 1 and 2 are carbon structures with ordered pores of uniform size which have been prepared by the pyrolysis of sucrose embedded in mesoporous silica [18].

The surface area and the pore dimension of the samples have been measured with quantachrome autosorp gas sorption system using nitrogen gas at 77 K and applying the multipoint BET method for the surface area, and the MP-method which is an extension of the de Boer’s t-method for the micropore volume. The different carbon nanostructures possess specific surface areas ranging from approximately 20 m²/g to 2560 m²/g, and high pore densities, see Table 1. The highest surface area is very close to the maximum theoretical surface of a double sided graphite sheet of 2630 m²/g.

2.2. Hydrogen storage measurement

The hydrogen adsorption has been measured by a manually controlled Sieverts’ apparatus, which consists of two volumes connected through a valve, i.e., sample holder and gas inlet chamber of constant volume. Owing to the design with small volumes, the apparatus can be used to investigate even small quantities of carbon material. A schematic diagram of the apparatus is shown in Fig. 1. The apparatus was previously tested for leak absence and for accuracy through calibration with the empty sample holder and with well known metal hydrides. Ultra pure hydrogen gas has been used for the experiments.

Typically the mass of the carbon samples used for hydrogen storage measurements is 100–300 mg. Prior to measurement, the samples are degassed and heated at 200 °C for approximately 2 h until a pressure of $1 \times 10^{-6}$ mbar is reached. Then the desired hydrogen pressure is introduced in the thermostated chamber and after thermal equilibrium is reached, the gas is permitted to expand in the sample holder. The measured pressure drop is caused by the gas expansion in a bigger

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1 Vajo J. Private communication.

### Table 1

Carbon nanomaterials investigated for hydrogen storage and their structural properties

<table>
<thead>
<tr>
<th>Sample (country)</th>
<th>BET SSA [m²/g]</th>
<th>Average pore diameter [Å]</th>
<th>Pore volume for pores with radius &lt;6.5 Å [cm³/g]</th>
<th>Helium density [g/cm³]</th>
</tr>
</thead>
<tbody>
<tr>
<td>Activated carbon I (Canada)</td>
<td>2564</td>
<td>11.75</td>
<td>0.75</td>
<td>2.0</td>
</tr>
<tr>
<td>Porous carbon 1 (Mexico)</td>
<td>1646</td>
<td>11.08</td>
<td>0.46</td>
<td>2.2</td>
</tr>
<tr>
<td>Activated carbon II (Germany)</td>
<td>1065</td>
<td>18.23</td>
<td>0.49</td>
<td>2.0</td>
</tr>
<tr>
<td>Purified SWCNT 1 (USA/Germany)</td>
<td>1024</td>
<td>15.37</td>
<td>0.39</td>
<td>2.0</td>
</tr>
<tr>
<td>Porous carbon II (Mexico)</td>
<td>946</td>
<td>10.60</td>
<td>0.25</td>
<td>2.1</td>
</tr>
<tr>
<td>Purified SWCNT II (USA)</td>
<td>854</td>
<td>17.09</td>
<td>0.36</td>
<td>2.1</td>
</tr>
<tr>
<td>Amorphous CNT (China)</td>
<td>369</td>
<td>14.48</td>
<td>0.13</td>
<td>2.2</td>
</tr>
<tr>
<td>SWCNTs (Russia)</td>
<td>124</td>
<td>15.52</td>
<td>0.05</td>
<td>1.7</td>
</tr>
<tr>
<td>Ros 1 (Cyprus)</td>
<td>34</td>
<td>11.46</td>
<td>0.01</td>
<td>2.1</td>
</tr>
<tr>
<td>Ros 3 (Cyprus)</td>
<td>22</td>
<td>11.32</td>
<td>0.0065</td>
<td>2.0</td>
</tr>
</tbody>
</table>
volume and hydrogen adsorption in the sample. After no more pressure change is observed, we wait for an additional 10–15 min to be sure that the thermal equilibrium is reached. After hydrogen adsorption at room temperature, the sample holder is cooled in liquid nitrogen until the new equilibrium condition is reached. In this case the decrease of the hydrogen pressure is due to the cooling of the gas and due to the enhancement of adsorption in the sample at low temperature. To evaluate the storage capacity of the carbon materials the experiment is repeated under the same conditions with a non-adsorbing blind sample (Seasand) having the same volume as the carbon material. The volume of the sample is measured volumetrically with helium gas. Each adsorption cycle is repeated at different hydrogen pressures from 2 bar to approximately 60 bar and after each adsorption the sample is heated and degassed. This means that each storage value is obtained independently from the previous step. The corrected ideal gas equation with a compressibility factor up to the second order is used to calculate the amount of adsorbed hydrogen from the pressure drop. For some samples the hydrogen storage capacity in the pressure range from 0.2 bar to 0.9 bar and at 77 K is measured gravimetrically with a Cahn microbalance. Here the mass change as a function of hydrogen pressure is recorded. The congruency of the values measured with the two different techniques is a further proof for the accuracy of our volumetric measuring system.

3. Results and discussion

Similar adsorption isotherms have been obtained for all investigated carbon nanostructures. Furthermore, they show a complete reversibility of the hydrogen uptake. After each adsorption cycle at a given pressure the hydrogen is removed from the sample and the measurement is repeated for a different pressure. The hydrogen storage capacity is independent of the number of adsorption cycles which proves that hydrogen is stored reversibly in these carbon materials. If hydrogen gas was expanded in the sample holder, the equilibrium pressure is reached within a few seconds. During waiting for 10–15 min no further pressure change is observed, indicating that thermal equilibrium is reached. These fast kinetics are characteristic for physisorption.

Fig. 2 shows the hydrogen adsorption isotherms of activated carbon I and of purified SWCNTs II at 77 K and at room temperature. Even though the two materials possess a completely different nanostructure, the shape of the isotherms is very similar. This shape is
characteristic for all investigated carbon materials. At 298 K the hydrogen uptake is a linear function of the pressure, which can be explained with Henry’s law. At room temperature no saturation occurs in the investigated pressure range and the adsorbed hydrogen layer on the carbon surface is very diluted.

At low temperature the isotherms can be fitted with a Langmuir-type equation (type I isotherm) indicating that saturation takes place with a hydrogen monolayer formation, as usual for microporous surfaces. In fact, the pore dimensions limit the hydrogen adsorption to one molecular layer in structures with micropores [19,20].

Additionally, an average value of the adsorption enthalpy at 77 K can be estimated by applying the Langmuir equation [21–23]:

$$\theta = \frac{1}{1 + \exp \left( \frac{-\varepsilon}{kT} \right)}$$

where $\varepsilon$ is the adsorption potential of the solid, $k$ the Boltzmann constant, $T$ the temperature, $\theta$ the fractional coverage, and $\mu$ the chemical potential of a hydrogen molecule in the gas. The chemical potential as a function of the hydrogen pressure is calculated using the tabulated values of the enthalpy and the entropy at 77 K [24]. This evaluation yields an average adsorption enthalpy of $-(56 \pm 10)$ meV for activated carbon I, which is with a storage capacity of about 4.5 wt% at 77 K, the best material analyzed. This adsorption potential has to be considered as an approximate value since any dependence between the adsorption potential and coverage has been neglected. Nevertheless, the low value clearly indicates that hydrogen is physically adsorbed in this carbonaceous nanoporous material. Chemisorption of hydrogen would require more than ten times higher enthalpy of adsorption [25,26].

The hydrogen uptake of the different carbon nanostructures at 77 K is correlated to their specific surface area (Fig. 3). An almost linear relation between the storage capacity, evaluated from the saturation value of the Langmuir fit, and the specific surface area is obtained for all materials investigated. In contrast, the storage capacity seems to be independent of the nature of the carbon nanomaterial, as long-range order or curvature of the graphene sheets. In accordance, similar findings by inelastic neutron scattering investigations have been reported in Refs. [8,9].

An upper limit of the hydrogen adsorbed in a monolayer can be estimated by assuming the density of the liquid adsorbate [10]. Accordingly, the maximum hydrogen storage capacity per specific surface area of carbon can be theoretically calculated to $2.28 \times 10^{-3}$ mass% m⁻² g⁻¹.

The experimental results yield a slope of $1.91 \times 10^{-3}$ mass% m⁻² g⁻¹, which is smaller than the theoretical value, because at 77 K the density of the monolayer is smaller than the density of liquid hydrogen. The measured value corresponds to an occupancy of one hydrogen molecule per 17.5 Å² of carbon surface. Assuming a closely packed distribution of hydrogen molecules on the surface of the adsorbent, this occupancy corresponds to a reticular distance of 4.5 Å between hydrogen molecules on the carbon surface. Further considering the area of a carbon hexagon of the graphene sheet (5.2 Å²), approximately six hydrogen molecules would occupy the area of 20 carbon hexagons.

On the other hand, under the assumption that the closely packed hydrogen monolayer has an intermolecular distance equal to that of liquid hydrogen (4.1 Å), the experimental value at 77 K corresponds to a surface coverage of 84%.

Similar results of a linear relation between hydrogen uptake and specific surface area of carbon materials have been obtained by Nijkamp et al. [27] with a slope of $1.5 \times 10^{-3}$ mass% m⁻² g⁻¹ at a pressure of 1 bar and 77 K.

Theoretical calculations [28,12] indicate, that hydrogen adsorption is favoured in small micropores. Therefore, the hydrogen adsorption capacity is correlated to the pore volume of pores possessing diameter less than 1.3 nm (Fig. 4). The linear relation between the pore volume and the storage capacity demonstrates that carbon materials ideal for hydrogen storage should possess a high microporosity with a small pore dimension.

Fig. 5 shows that at room temperature as well the storage capacity of the carbon samples at a pressure of 65 bar depends almost linearly to their surface area. In this case the slope of the curve is only $0.23 \times 10^{-3}$ mass% m⁻² g⁻¹, which corresponds to a surface coverage of only 10% assuming the density of the liquid adsorbate. Similar low hydrogen storage capacities at
RT have been found by NMR investigations in SWCNTs [29–31].

4. Conclusion

Different carbon materials have been investigated with optimized structures for hydrogen adsorption. The fast kinetics and complete reversibility give clear evidence that the process responsible for hydrogen adsorption in carbon nanostructures is physisorption. The amount of hydrogen physisorbed depends almost linearly on the specific surface area, both at low temperature and at room temperature, and is independent of the type of carbon nanostructure. Therefore the hydrogen adsorption process is based on the local interaction between the hydrogen molecule and the surface, however, independent of long-range order, curvature or ordered arrays of the graphene sheets. As a consequence promising materials for hydrogen adsorption are nanostructures with high surface area and micropore density.

While at room temperature the highest measured storage value is less than 1 wt% even at high hydrogen pressure, at 77 K it is possible to store up to 4.5 wt% of hydrogen. Among all investigated materials activated carbon with high grade of porosity is the best carbon nanostructure for hydrogen adsorption. Owing to the fast adsorption and desorption kinetics and the reversibility, physisorption is a very promising concept for hydrogen storage at moderate conditions. Future investigations should concentrate on new materials with surface area, even higher than activated carbon, in order to achieve successful storage capacities not only at low temperature but also at ambient conditions.

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References


