Nanostructures with high surface area for hydrogen storage

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Abstract

The hydrogen adsorption in nanostructures with high specific surface area (SSA) has been determined at room temperature (RT) and 77 K utilizing a Sieverts'-type apparatus. Various carbon nanostructures possessing different SSA and structures showed a linear dependence between the storage capacity and the SSA. However, the uptake seems to be independent of the structure or long-range order of the materials. The maximum storage capacity of 4.5 wt.%, was obtained at 77 K for activated carbon with a BET surface area of 2560 m^2/g.

In addition the metal-organic framework MOF-5 was synthesized. These samples with a BET SSA of 576 m^2/g showed a storage capacity of 0.2 and 1.6 wt.% at RT and 77 K, respectively.

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1. Introduction

The major bottleneck for commercializing fuel-cell vehicles is onboard hydrogen storage. The presently available systems are high pressure tanks or liquefied hydrogen in cryogenic vessels, which both possess severe disadvantages. Storage in light-weight solids could be the solution to this problem. Two principle storage mechanisms are existing: (i) Adsorption of hydrogen molecules on surfaces, i.e., physisorption. (ii) Hydrogen atoms dissolved or forming chemical bonds, i.e., chemisorption. This work will focus on physisorption of new nanoscale materials with high specific surface area which is caused by weak Van der Waals forces between the adsorbate and the adsorbent. The combination of a long-range attractive term and a short-range repulsive term gives rise to a shallow minimum in the potential energy curve at a distance of approximately one molecular radius of the gas molecule (Fig. 1). This energy minimum corresponds typically to 1–10 kJ/mol. As the forces involved in the interaction between adsorbate and adsorbent are very weak, physisorption usually takes place only at low temperature [1]. There

is no energy barrier to prevent the molecule approaching the surface from entering the physisorption well. Therefore the process is non activated and fast kinetics is characteristic for physical adsorption. Materials with very high specific surface area seem to be very promising for hydrogen storage at least in systems in which cooling is not a problem [2]. Ideal candidates for hydrogen adsorption are activated and optimized carbon nanostructures which show high micropore density.

Recently, a new class of crystalline materials, which possess a very low density and high surface area, the so-called metal-organic frameworks (MOFs) have been developed and synthesized [3,4]. A whole family of MOFs have been produced by linking Zn_4O clusters with a variety of rigid organic linkers. For example in MOF-5 [4] benzenedicarboxylate groups are used to form a three dimensional cubic crystal.

In this paper we report about hydrogen storage measurements at room temperature and at 77 K for various carbon nanostructures and for MOF-5.

2. Experimental

The specific surface area (SSA), microporosity and pore size of the materials were measured recording N_2 adsorption

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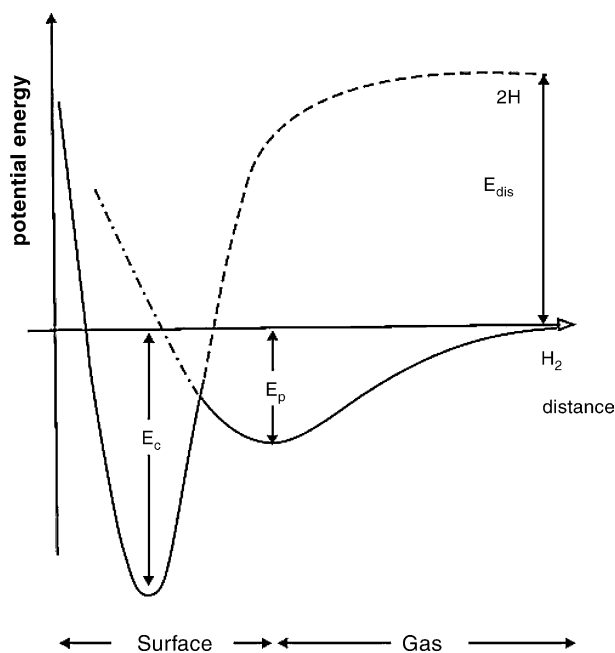 *E-mail address:* hirscher@mf.mpg.de (M. Hirscher).

Fig. 1. Potential energy curve for chemisorbed and physisorbed hydrogen as a function of the distance from the adsobent's surface. The minima of the two curves correspond to the equilibrium distance for physically and chemically adorbed hydrogen, respectively.

isotherms at 77 K. Powder X-ray diffraction and SEM images were used to characterize the crystalline samples.

Hydrogen adsorption was measured by a manually controlled Sieverts' apparatus, which consisted 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 could be used to investigate even small quantities of carbon material. Prior to the hydrogen uptake the samples were heated under vacuum at 473 K in order to remove moisture and adsorbed gases from the surface. Volumetric hydrogen adsorption measurements were performed both at room temperature (RT) introducing the sample holder and the gas inlet chamber in a water bath and at 77 K in liquid nitrogen. Each adsorption cycle at RT and 77 K was repeated for different hydrogen pressures from 1 bar to approximately 70 bar and after each adsorption the sample was evacuated and degassed. This means that each storage value was obtained independently from the previous step.

3. Results and discussion

3.1. Carbon nanostructures

Various carbon materials possessing different microstructure were obtained from suppliers worldwide, comprising purified and unpurified single-walled carbon nanotubes (SWCNTs), amorphous nanotubes, activated carbon, porous carbon with uniform pore dimensions and mixtures of MWCNTs and SWCNTs [5]. These carbon nanostructures pos-

sessed specific surface areas ranging from approximately 22 to 2560 m^2/g, and a high pore density. The highest surface area was very close to the maximum theoretical surface of a double sided graphite sheet of 2630 m^2/g. All investigated materials showed complete reversibility of the hydrogen uptake and very fast adsorption kinetics. In addition the shape of adsorption isotherms was similar for all investigated carbon nanostructures. At 298 K the hydrogen uptake is a linear function of pressure and shows no saturation. This can be explained with Henry's law which is valid for a diluted layer adsorbed on the surface. In contrast the low temperature isotherm shows a saturation and can be fitted to a Langmuir type equation, which indicates a monolayer formation of hydrogen typical for microporous surfaces. The hydrogen uptake of the different carbon nanostructures is plotted versus their specific surface area in Fig. 2.

Both at room temperature and at 77 K an almost linear relation between the storage capacity and the specific surface area is obtained for all materials investigated. The slope is determined to be of 0.23×10^{-3} and 1.91×10^{-3} wt.% $g\,m^{-2}$ for room temperature and 77 K, respectively, and the highest storage capacities obtained are 0.5 and 4.5 wt.%, respectively. Similar results of a linear relation between hydrogen uptake and specific surface area of carbon materials have been obtained by Nijkamp et al. [6] at a pressure of 1 bar and 77 K. Furthermore, the structure of the carbon nanomaterials, e.g. long-range order or curvature of the graphene sheets does not seem to have any influence on the storage capacity. This result is supported by inelastic neutron scattering measurements reported by Schimmel et al. [7,8].
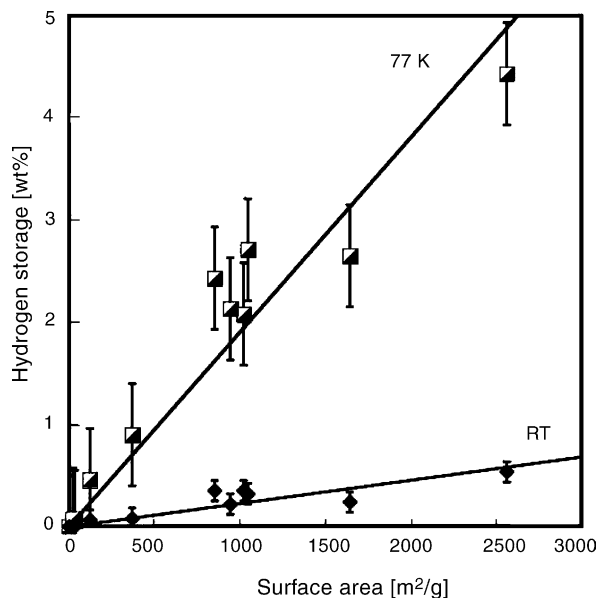

Fig. 2. Hydrogen storage capacity of various carbon nanostructures versus the specific surface area at RT and at 77 K. The slope of the curves are 0.23×10^{-3} and 1.91×10^{-3} wt.% $g\,m^{-2}$, respectively.
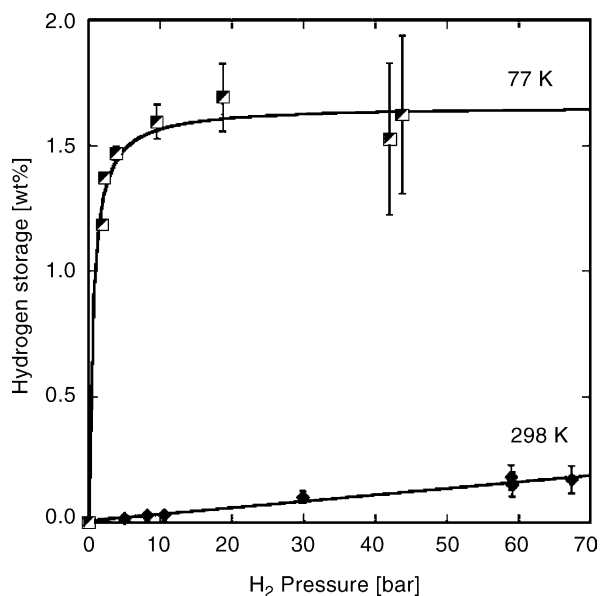
Fig. 3. Hydrogen adsorption isotherms for MOF-5 at room temperature and 77 K. At RT the storage capacity is a linear function of the hydrogen pressure. At low temperature the isotherm is fitted with a Langmuir-type equation.

3.2. Metal-organic frameworks

Crystalline metal-organic framework consisting of Zn_xO subunits and benzenedicarboxylate as organic linkers were synthesized following ref. [9]. The X-ray diffraction pattern of the white solid were congruent with a Le Bail profile matching based on a Fm-3m structure according to ref. [4] showing that the product was MOF-5 with a lattice parameter of 25.80 Å [10]. N_2 adsorption measurements at 77 K of our MOF-5 sample yield a BET specific surface area (SSA) of $572 \, m^2/g$ and Langmuir SSA of $1014 \, m^2/g$, about three times lower than the value of $2900 \, m^2/g$ estimated by the group of Yaghi in ref. [4,11] and $3362 \, m^2/g$ in ref. [12]. Fig. 3 shows the pressure dependence of the hydrogen storage capacity for MOF-5 both at RT and at 77 K. The kinetics of the adsorption process was very fast which is characteristic for physisorption. For room temperature our measurements show an adsorption capacity of MOF-5, less than 0.2 wt.% at pressures up to 67 bar. This value is considerably lower than the RT storage capacity reported by Rosi et al. [11]. These authors found at 20 bar a twenty times higher storage capacity which cannot be solely explained by the three times higher SSA of their sample. At 77 K the adsorption isotherm for MOF-5 has a Langmuir isotherm profile with a saturation value of 1.6 wt.% reached already at pressures above 10 bar (Fig. 1). Our values at low temperature are consistent with the newest results of Yaghi's group [12] obtained at lower pressures.

4. Conclusions

All investigated different carbon nanostructures with various SSA show a similar fast kinetics and high reversibility for hydrogen adsorption which is typical for physisorption. The amount of hydrogen physisorbed depends almost linearly on the specific surface area of the carbon material both at low temperature and at room temperature and is independent from the type of nanostructure investigated, e.g., long-range order, curvature or ordered arrays of the graphene sheets.

Furthermore, we synthesized crystals of metal-organic framework MOF-5 with a Langmuir surface area of $1014 \, m^2/g$. At RT we observed a hydrogen storage capacity of only 0.2 wt.% which is far lower than previously reported [11]. At 77 K the H_2 uptake followed over a wide range a Langmuir profile with a saturation value of 1.6 wt.%. These values correspond to 6.1 hydrogen molecules per formula unit and are characteristic for hydrogen adsorption exclusively in the micro pores of the metal-organic crystal.

Together these findings indicate that nanostructures with high SSA and micro pore density are very promising materials for hydrogen storage at low temperature which, e.g., may be used for cryogenic storage systems in long-term satellite missions.

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