

Hydrogen Interaction with Carbon Nanofibers

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Abstract

Carbon nanofibers of herringbone formation were grown by chemical vapor deposition on different catalysts from a number of hydrocarbon sources. After the removal of the metal oxide particles, which are part of the catalyst system, six samples with several different ratios of Pd/C were obtained by controlled oxidation in air. The hydrogen uptake experiments performed volumetrically in a Sievert-type installation, showed that the quantity of desorbed hydrogen (for pressure intervals ranging from 1 to 100 bars) by the carbon nanostructures free of any metal catalyst particles, was between 0.04 and 0.33 % by weight. For the samples of nanofibers that contained Pd in various Pd/C ratios, palladium revealed catalytic properties and supplied atomic hydrogen at the Pd/C interface by dissociating the H₂ molecules. The results show a direct correlation between the Pd/C ratio and the quantity of hydrogen absorbed by these samples. A saturation value of about 1.5 wt. % was reached for a high ratio of about 1:1 of Pd/C. The surface area of the fibers was measured by BET and found to be 425-455 m²/g.

Introduction

Nanostructures (nanotubes, nanofibers and more recently, fullerenes or “bucky balls”) represent a great economic and scientific potential, primarily due to their mechanical and electrical properties. A new application envisioned for carbon nanostructures is reversible hydrogen storage (Dillon et al., 1997), which could be used as an energy source for electrical vehicles. To meet the U.S. Department of Energy (DOE) requirements (Tibbets et al., 2001), this type of vehicle needs a range of at least 550 kilometers (300 miles), which requires materials that can reversibly absorb large amounts of hydrogen of up to 6.5 wt %. Carbon nanostructures are considered to be materials with high potential for reversibly storing large quantities of hydrogen. A large number of experimental and theoretical publications have reported hydrogen uptake values ranging from 0.1 to 14 wt. % (Ye et al., 1999, Gupta et al., 2001, Poirier et al. 2001, Zuttel et al., 2002, Hischer et al., 2002, Browning et al., 2002). The controversy (Dagani, 2002, Cheng et al., 2001) is considered to consist in a number of factors such as: the quality of the carbon materials, the type of carbon nanostructures, the methods employed for growing these structures, and the activation method used during the hydrogen uptake measurements. Due to the variation in the hydrogen uptake values reported in literature, a more standardized method is required to produce carbon nanotubes and study their interaction with hydrogen. A careful examination (Zuttel et al., 2002) that takes into consideration the adsorption of one layer of atomic hydrogen on the surface of the carbon nanostructures gives a value of around 3.3 wt. %. If the hydrogen is considered to penetrate inside the tubes, the corresponding adsorption value varies with the diameter of the nanotubes. The model was confirmed by further studies that

showed 5.5 wt. % hydrogen physisorption at 77 K, a value that decreased to 0.6 wt. % at room temperature (Zuttel et al., 2002).

Other interesting approaches to enhance (Parila et al., 2001, Weidenkaff et al., 2002) hydrogen sorption on carbon nanotubes used hydrogen absorbing metals as a “by-pass” for hydrogen transfer to the carbon nanostructures. However, these approaches are subjected to a large number of factors that can change the surface characteristics of these metals, such as a pronounced state of oxidation or the adsorption of other gases that would not allow the hydrogen to dissociate and reach the carbon structures.

This paper presents the experimental results of hydrogen uptake on a number of carbon nanostructures grown by Chemical Vapor Deposition (CVD) using different catalyst systems. Since the Pd - hydrogen is a very well characterized system and the hydride phase equilibrium forms at relatively low pressures (below 0.11 MPa at room temperature), samples of Pd nanoparticles – carbon nanofibers mixtures were prepared using a Pd/La₂O₃ catalyst and their hydrogen uptake properties were analyzed and compared with those of the purified carbon nanotubes samples. Pd has a high potential as a by-pass transfer of hydrogen to the carbon nanostructures and to supply atomic hydrogen at the Pd-carbon interface.

Methodology for the Hydrogen Uptake Measurements

Determination of the hydrogen absorption/desorption values was done volumetrically in a Sievert-type installation shown in Fig.1, which was used to determine the P-c-T isotherms. This technique was used successfully for a number of years to study the hydrogen

absorption/desorption properties of different metals and alloys (Biris et al., 1976, Lupu et al., 1999). To eliminate the problem of measuring small pressure variations due to the hydrogen adsorption (in small quantities of samples at high hydrogen pressures 100 bar), as well as to obtain a good desorption, an absorption equilibrium was established over a 24 hour time interval. Subsequently, the amount of desorbed hydrogen was measured by opening the reactor's valve, allowing the gas to expand in the entire installation's volume, reaching a final equilibrium pressure (1 to 6 bars) measured accurately with a high precision manometer. Special precautions were taken through the use of small volume reactors (~2 ml). Blank measurements without any sample in the reactor were performed for control purposes. The installation was rigorously and repeatedly checked for hydrogen leakage during the measurements. The valves used in this setup are a special design that were built and patented at the National Institute for Research and Development of Isotopic and Molecular Technologies (NIRDIMT). The valves were checked for hydrogen leakage and found to be less than 0.0001 MPa during a 100 hour time interval. Ultrapure hydrogen (purity of 99.9999 %) desorbed from a hydride reservoir was used as the source gas, and sample activation/degassing was accomplished under vacuum for 4-5 hours at temperatures ranging from 350 to 550 °C.

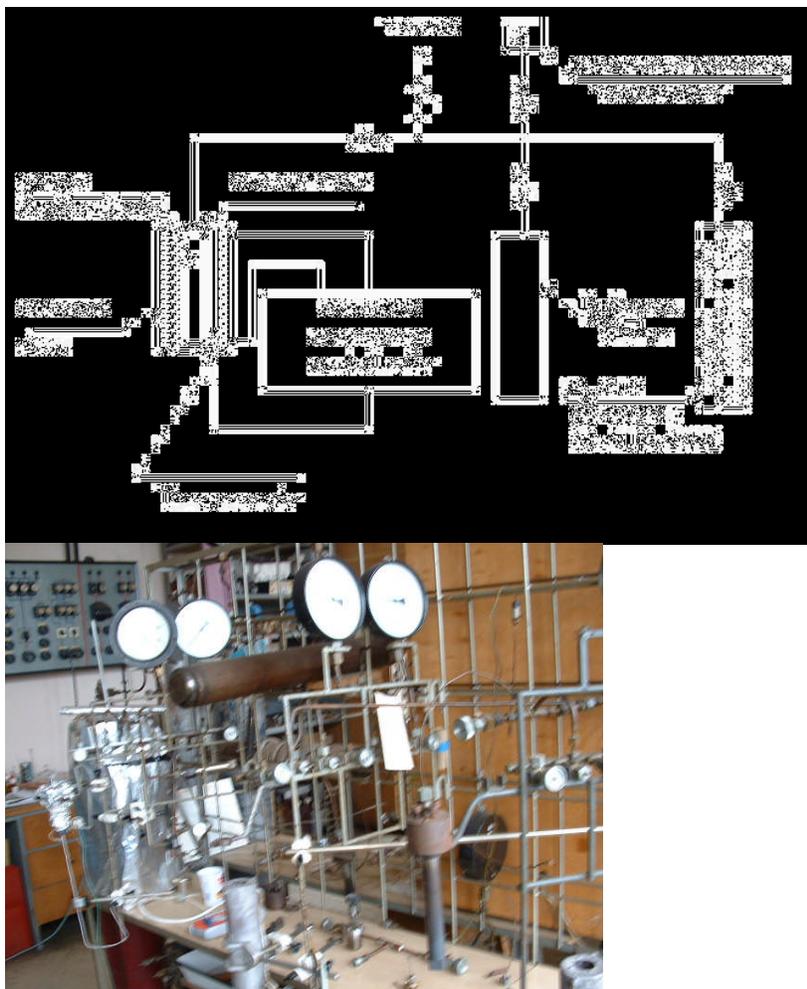


Fig. 1. The Sievert-type installation used to volumetrically measure the hydrogen absorption and desorption uptake

Hydrogen uptake values measured or calculated in volumetric experiments (Sievert-type installations and gravimetric) require the exact density of the sample be known. The reported values (Browning et al., 2002, Johansson et al., 2002) for the density of the carbon nanostructures are in a broad interval ranging from 0.7 to 2.2 g/cm³. Small density values, if used, could be responsible for unrealistically high hydrogen uptake values previously reported in

the literature. The volume of a sample can be measured using an inert gas like helium. This method is suitable for tubes with clogged ends, when neither helium nor hydrogen can penetrate inside. Parallel density measurement experiments were performed on the carbon nanostructures generated according to the procedure already described. The first measurement used a Sievert-type installation and the second involved measurements of the sample floating effect in a Sartorius microbalance. Both methods provided similar density values, ranging from 2 to 2.25 g/cm³.

Synthesis of Carbon Nanostructures and Their Corresponding Hydrogen Uptake Values

Carbon nanostructures were synthesized using CVD on Ni/Cu catalysts (Lupu et al., 2002). This method was reported to produce carbon nanostructures with high hydrogen uptake (Ye et al., 1999, Gupta et al., 2001, Poirier et al. 2001, Zuttel et al., 2002, Hischer et al., 2002, Browning et al., 2002). The catalysts were prepared using a co-precipitation technique, starting from elemental solutions mixed in required mole ratios. After precipitation, the precipitate was washed, filtered, dried, and calcinated. The activation of the catalysts was achieved *in situ* inside a reactor in a hydrogen stream at high temperature. These conditions favor the formation of metal particles with diameters in the range of a few dozen nanometers and avoid sintering. After the catalyst was activated, the hydrocarbon or the mixture of gases containing the hydrocarbon was introduced to allow catalytic decomposition to occur. The reaction conditions are represented in Table 1. The nanofibers grown on the Ni:Cu (97.5% Ni:2.5% Cu) catalyst are shown in Fig. 2. An analysis of Fig. 2 shows that under these conditions, nanotubes were generated with exterior diameters ranging from 50 to 100 nm.

Table 1. The type of hydrocarbon and catalysts as well as the reaction conditions used to generate carbon nanostructures

Catalyst	Hydrocarbon	Conditions of reactions (temp.-pressure-flow)	Efficiency (mg C /mg Cat.)
Ni(1.3m ² /g)/Cu(3.8m ² /g) (95%/5%)	Acetylene : Hydrogen (2:1)	650 °C – 0.4 bar static	0.65
Ni(1.3m ² /g)/Cu(3.8m ² /g) (97.5%Ni:2.5%Cu)	Ethylene : Hydrogen (4:1)	600 °C – 0.2 bar static	0.5
Ni /Cu co-precipitate (97.5%Ni:2.5%Cu)	Ethylene : Hydrogen (4:1)	600 °C – 0.2 bar static	0.6

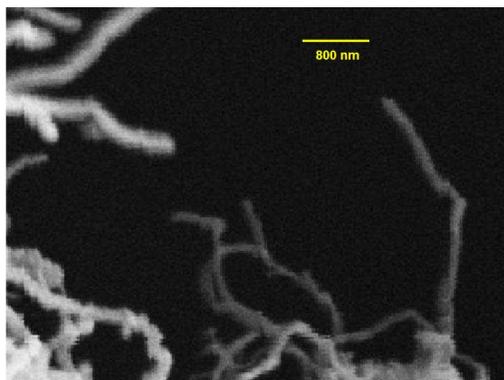


Fig. 2. SEM picture of carbon nanofibers obtained by using a Ni:Cu (97.5% Ni:2.5% Cu) catalyst, which was obtained by co-precipitation.

Their corresponding hydrogen desorption values are shown in Table 2 and range from 0.04 to 0.33 wt. % hydrogen. They are much smaller compared with the high values of 10 – 14 wt. % reported by some authors for graphite nanostructures obtained from similar conditions on Ni:Cu catalysts and ethylene as hydrocarbon. The results presented in this paper are in a good agreement with the values of 0.4 to 0.7 wt. % hydrogen at pressures of 100 bar reported by Poirier et al., 2001 for nanostructures prepared on similar catalysts. The second desorption is generally only 60 to 70 % of the initial one.

Table 2. The amount of desorbed hydrogen for carbon nanostructures generated from different hydrocarbons and catalysts

Hydrocarbon//Catalyst	Hydrogen desorbed (wt. %) [Pressure range (bar)] *
Acetylene:H ₂ (2:1) // Ni(1.3 m ² /g)/Cu(5%)(1.3 m ² /g)	0.33 [100 – 1.3]
Ethylene :H ₂ (4:1) // Ni(1.3 m ² /g)/Cu(3.8 m ² /g) (97.5%Ni:2.5%Cu) (mixture)	0.04 [100 – 4.4]
Ethylene:H ₂ (4:1) //Ni(1.3m ² /g)/ Cu(3.8m ² /g)(97.5%Ni:2.5%Cu) (co-precipitate)	0.04 [100 – 4.4]
	0.08 [100 – 6]
	0.1 [100 – 6]

In a separate experiment, carbon nanofibers were grown by using a Pd/La₂O₃ catalyst and a mixture of ethylene/hydrogen gas as a carbon source in the CVD process. The nanofibers obtained were herringbone-like with exterior diameters ranging from 10 to 100 nm and several μm long, as seen in Fig. 3. The surface area of the fibers was measured by BET and found to be 425-455 m²/g.

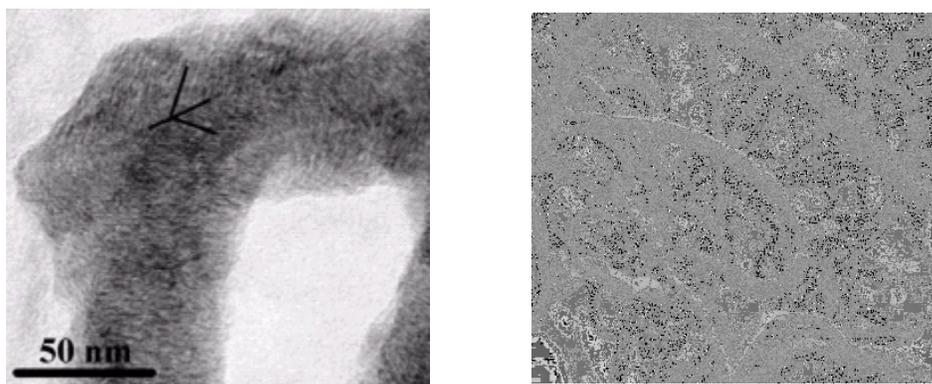


Fig. 3. TEM and SEM pictures of carbon nanofibers obtained from ethylene-hydrogen mixtures on a Pd/La₂O₃ catalyst. TEM picture shows the herringbone-like structure of the fibers with an angle between the fringes and the fiber axis of about 45°.

The lanthanum oxide was removed by washing the nanofibers in HCl and finally they were rinsed with distilled water over a porous sintered ceramic plate and dried at 120 °C. For the dissolution of Pd some of the samples were washed in HNO₃ for 20 hours and rinsed with distilled water. In order to be able to study the influence of the Pd content on the H uptake measurements, the nanofibers were carefully oxidized in air for various time intervals (30-90

min) at 520 °C. This process allows a control of the Pd/C ratio due to partial oxidation of carbon and was proved to generate the agglomeration of Pd nanoparticles on the surface of the carbon nanofibers. The Pd nanoparticles on the surface of the nanofibers have a catalytic effect on the oxidation process and lower the oxidation temperature. The Pd loading rate at each stage was well monitored by careful gravimetric measurements. A batch of nanofibers was completely oxidized and the resulting metallic Pd was exposed to hydrogen at 10 MPa. The absorbed value of 0.74 wt. %, along with the buoyancy effect, were the two correlations that were considered for each hydrogen uptake measurement of the Pd loaded carbon nanofibers batches. The hydrogen uptake values for carbon were calculated after subtracting the contributions given by the metallic Pd and the buoyancy from the overall weight change.

The hydrogen uptake experimental results show saturation at 1.5 wt. % of the hydrogen adsorbed on the carbon nanofibers' surface, with a direct correlation between the amount of adsorbed hydrogen and the Pd/C ratio (Fig.4). Basically, an increase in the amount of metallic Pd corresponds to a higher hydrogen adsorption value on the carbon nanofibers. This result can be explained by the catalytic properties of the Pd particles that dissociate H₂ into atomic H. Another explanation is the possible charge transfer between Pd and C, given the work function difference between palladium (5.1-5.6 eV) and carbon nanofibers (4.9-5.05 eV) (Michaelsson, 1977, Shiraishi and Ata, 2001, Buzatu et al., 2004). The relationship between the H uptake values by the C nanofibers and the Pd/C ratio shows that the atomic H that is generated by Pd diffused on the C surface, but not at very large distances. The H uptake values vary with the contact surface area between the Pd nanoparticles and the C nanofibers (Lupu et al., 2004).

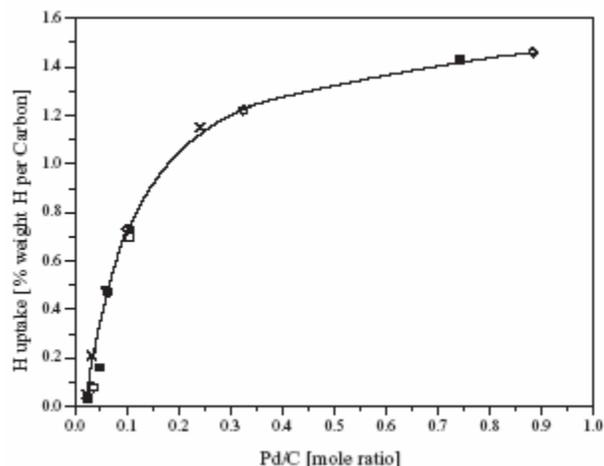


Fig. 4. The hydrogen uptake variation with the Pd/C ratio

Conclusions

Carbon nanostructures were obtained by the CVD method with different characteristics. Nanofibers with outside diameters varying from 50 to 100 nm were obtained on a Ni:Cu catalyst and their hydrogen desorption capacities were determined volumetrically for hydrogen pressures from 1-6 to 100 bar. The results ranged from 0.04 to 0.33 wt. % of hydrogen. These values were found to be in good correlation with some previously reported results, but did not confirm the high values reported by other research groups. Experiments in progress show that higher uptake values up to 1.5 % H can be obtained with the herringbone type carbon nanofibers (prepared on Pd/La₂O₃ catalyst) by increasing the Pd/C ratio. These experiments provide information regarding hydrogen – carbon nanostructure interaction, and possible enhanced H uptake catalyzed by metals that can supply atomic hydrogen. A direct correlation was found between the quantity of hydrogen adsorbed on the carbon nanofibers and the ratio Pd/C, suggesting that Pd

could play an important catalytic role. The Pd nanoparticles help the dissociation of H₂ into atomic hydrogen which then diffuses on the surface of the nanofibers, but not for large distances. The higher the Pd/C ratio, the higher the contact surface area between Pd and C. This area therefore is a measure of the amount of H adsorbed on the carbon surface.

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