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Hydrogen in carbon nanostructures

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Abstract

The non-dissociative hydrogen uptake for two types of carbon-based materials was explored. The maximum measured differential hydrogen uptake capacities at hydrogen pressures of 10 MPa were experimentally determined with the volumetric Sieverts method to 2.9 (300 K), and 4.1 wt% (77 K) for MWNB (multi-walled nanobarrels) and 2.6 (300 K), and 3.3 (77 K) wt% for ANPC (amorphous nanoporous carbon). The total hydrogen uptake was calculated to be 3.2 (300 K) and 6.2 (77 K) wt% for MWNB at a hydrogen pressure of 10 MPa, and 2.8 (300 K) and 4.2 (77 K), respectively, for ANPC. The adsorption energies were determined to be 7.2 and 4.2 (KJ/mol) for ANPC and MWNB, respectively, at the lowest coverage. At higher coverage (concentration), a multi-site model is required to describe the coverage dependence, consistent with large heterogeneity of the adsorption sites.

Keywords: Hydrogen; Adsorption; Carbon; Nanopouros; Uptake

1. Introduction

Substantial theoretical as well as experimental work has recently been devoted to investigations of the hydrogen uptake of carbon-based materials [1–10]. Theoretical models have been used to predict the maximum hydrogen adsorption in carbon single walled nanotubes (SWNT) and idealized Carbon slit pores [1]. The results from these simulations show that slit pores should have larger absorption capacity (~ 12), as compared to SWNT (~ 6 wt%) at 77 K. The same authors have examined the influence of the symmetry and the extension of the confinement on the hydrogen adsorption in SWNT [2]. Their simulations show that a (9,9) tube triangular array should adsorb at most ~4 and ~8 wt% at 298 and 77 K, respectively [2]. Substantially larger absorption (14 wt%) is deduced for (10,10) nanotubes by density functional calculations [3].

Reports from experimental work on the hydrogen uptake of nanostructured carbon suffer from substantial spread in the deduced hydrogen capacity. High hydrogen concentrations, (5–10 wt%, $P<0.1$ MPa, $T\approx300$ K), in carbon nanotubes has been reported by Dillon et al. [4], as well as in graphite nanofibers, 66.8 wt% at 298 K, by Chambers et al. [5]. Ye et al. [6] concluded that adsorption of hydrogen in crystalline ropes of carbon single-walled nanotubes (SWNT) exceeds 8 wt% and Orimo et al. [7] has reported that mechanical milling of high purity graphite powder under hydrogen atmosphere results in nanocrystalline graphite with a hydrogen concentration up to 7.4 wt%. Wu et al. [8] performed analysis of the hydrogen uptake of both carbon nanotubes and graphite by thermogravimetry. Their results yielded 0.25 wt% hydrogen uptake of the carbon nanotubes. Furthermore, an absence of hydrogen uptake in graphite was reported, which also is in strong contrast to other reports on similar materials [4,7]

Another approach, which has been explored to enhance the hydrogen uptake, is the introduction of alkali metals in carbon-based materials. Chen et al. [9] have recently explored the influence of alkali metal (Li and K) doping on the hydrogen uptake of CNT (carbon nanotubes). Large uptake was inferred at moderate temperatures and ambient pressures, 20 wt% for Li-doped at 653 K and 14 wt% for K-doped CNT. No measurements of the absorbed–desorbed species were reported.

Large discrepancies are evident on the reported uptake of hydrogen in carbon-based materials. The reason for this can be considered to be two-fold, experimental errors and/or limited characterization of the materials of interest. One of the biggest obstacles for classical thermodynamic investigations is the amount of available materials (sample size). Often researchers are working with extremely small

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amounts of materials, which does limit the accuracy of the measurements. Furthermore, purity is essential in this context. Minute amount of impurities can significantly alter the experimental results, and the presence of water at any temperature can give rise to large experimental artefacts.

Hydrogen uptake of carbon-based materials can be divided into two possible paths, non-dissociative and dissociative uptake. In the first case there are no other processes than pore filling, adsorption on the solids surface and diffusion, whereas in the latter case dissociation of the adsorbing molecule is also present. At low temperatures, non-dissociative processes are expected to dominate the uptake. At elevated temperatures, the importance of the dissociative reaction path will increase in importance, especially for alkali-doped materials.

In the current work we discuss the non-dissociative uptake of hydrogen in of amorphous nanoporous carbon (ANPC) and multi-walled nanobarrels (MWNB). The hydrogen uptake was determined by measuring adsorption and desorption isotherms, and isobars on samples of amorphous nanoporous carbon (ANPC) and multi-walled nanobarrels (MWNB). Furthermore we discuss some possible pitfalls in measuring the hydrogen uptake of C based materials.

2. Models and methods

Adsorption is a process where molecules, from a gas phase or from a solution, forms a condensed layer on a solid or liquid surface either dissociatively or non-dissociatively. The simplest approach for describing gas adsorption on surfaces is the idealized theory of Langmuir. The basic assumptions of the Langmuir theory are the following: The surface is homogeneous, adsorption on surface is localized and each site can adsorb only one molecule [11–13]. The theory is based on kinetic principles, i.e. the rate of adsorption is equal to the rate of desorption. Discussion on the kinetic theory of gases can for example be found in [11–13]. Other commonly used isotherms in the literature, concerning adsorption on microporous solids are the Sips, Toth, Unilan, Volmer, Fowler–Guggenheim, DR, DA and BET isotherms [11,12].

To include heterogeneity of the adsorption sites requires some modification of the Langmuir model, as for example in the Sips isotherm,

$$C_{\mu} = C_{\mu s} \frac{(b(T)P)^{1/n}}{(1 + b(T)P)^{1/n}} \tag{1}$$

where the difference compared to the Langmuir isotherm is the heterogeneity parameter, n. C_{μ} is the amount adsorbed in mole per unit mass, $C_{\mu s}$ the maximum adsorbed concentration corresponding to monolayer coverage, b is the Langmuir affinity constant and P is the pressure.

The hydrogen uptakes of porous solids are not solely due to the adsorption on surfaces and therefore, when discussing adsorption energies, one also has to take into account the mechanism of pore filling. According to Do [11], the uptake process depends on the diameter of the pores. Up to a diameter of 10 Å, the uptake is almost exclusively due to pore filling. For pores with diameter of 10–1000 Å, this process dominates up to a threshold pressure where the formation of a monolayer takes over.

There are several different techniques available to determine the total amount of hydrogen adsorbed in a volume spanned by a porous carbon material. To achieve accurate and reliable results one has to consider some specific problems connected to adsorption analysis. The carbon material and the hydrogen gas must be as clean as possible since other species adsorbed can block (or 're-place') the uptake of hydrogen. Even minute amount of impurities can cause severe problems. At a partial pressure of 10^{-4} Pa, one monolayer of molecules is striking the adsorbent surface per second and if these components have a high sticking coefficient, all available adsorption sites will rapidly be occupied [13]. Using pure hydrogen gas and large sample quantities can decrease the relative amount of impurities, and species desorbing from the walls of the system can be minimized by using properly out-gassed ultra-high vacuum (UHV) systems. The problems concerning the vacuum conditions are extremely severe when working with small sample quantities. However by extensively out-gassing the whole system including the carbon sample at elevated temperatures, water and other adsorbed gases in the system can almost be eliminated.

Important to define, for all experimental techniques, is which reference the uptake is compared to, vacuum, gas phase or ambient conditions. If the gas phase is used as a reference, a differential hydrogen uptake is achieved, i.e. the difference between the hydrogen uptake of a volume without carbon compared to the uptake of a volume spanned by a carbon host. When calculating the total uptake of a material, using the Sievert approach, the volume spanned by the sample is an essential parameter. The density of nanoporous materials is not easily defined, hence the weighting of the sample will give an uncertain volume contribution in the calculations. This uncertainty is avoided when using the differential uptake. Only with vacuum as the reference the results will describe the total uptake of the investigated material.

3. Experimental details

3.1. Synthesis of the nanotube-like and amorphous carbon material

The nanoporous carbon materials used was prepared using a reaction of halogen gas with SiC and Al_4C_3 at elevated temperatures. Through the etching reaction the Si and Al atoms are removed from the lattice, resulting in a carbon matrix with high initial density of vacancies and dangling bonds. The overall process follows the general reaction $MC_a(s)+2a\cdot X_2(g)\rightarrow a\cdot C(s)+MX_{4a}(g)$ (MC_a, $a=1$ for a 4-valent metal) without any noticeable change in volume or shape of the grains. This gives a high volume content of nanoporosity in the obtained carbon material [14]. For further details about the synthesis and characterization of these materials see [14,15].

3.2. Adsorption and desorption isotherms

The adsorption and desorption isotherms were measured with a Sieverts apparatus, schematically illustrated in Fig. 1, equipped with an roughing pump (Alcatel Pascal 200S SD), turbo molecular pump (Varian V250), pressure transducer (MKS Baratron 870B), quadropole mass spectrometer (Leda Mass Ltd) and a temperature reading unit (Eurotherm 2408 with a type K thermocouple).

Prior to the measurements the experimental set-up including the sample holder containing the carbon powder was out-gassed for 12 h at 200°C, i.e. all measurements were performed under UHV conditions (base pressure in the range of 10^{-9} mbar). The out-gassing during baking, as well as at some stages of the desorption process, were monitored by residual gas analysis. Typically the partial pressure of H_2O was in the 10^{-10} mbar range.

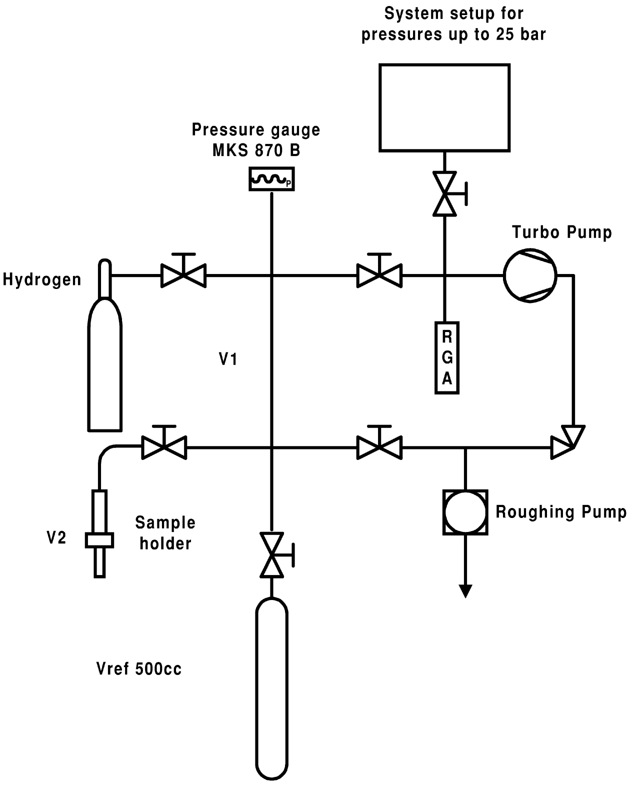

Fig. 1. Schematic illustration of the experimental system set-up used for measuring the hydrogen uptake.

The differential hydrogen uptake was determined from the measured amount of hydrogen in the volume V_2 (the sample holder), with and without the carbon material. The total hydrogen uptake can be obtained by assuming some density of the carbon material, i.e. the density obtained from the N_2-adsorption method, and compensating for the volume of carbon spanned in V_2 corresponding to this density. Hence, some uncertainties in the determined total uptake are expected, depending on the uncertainties related to the density of the material.

Hydrogen (≥99.9996% purity) was introduced into the system, with the valve to V_2 closed, to pressures ranging from 0.1 to 10 MPa. Thereafter the carbon material, with mass of 2.0214 g for ANPC and 0.4717 g for MWNB, was exposed to hydrogen by opening the valve to V_2. When pressure equilibrium was reached, typically after less then 10 min, the sample holder was cooled to 77 K with LN (liquid nitrogen). When new pressure equilibrium was established at 77 K the cooling was stopped. The sample holder was thereafter slowly heated to room temperature by the ambient air, the valve to V_2 closed and hydrogen introduced to a new pressure in V_1+V_{ref}. This procedure was repeated cumulatively up to a maximum pressure of approximately 10 MPa. The experiments were also performed non-cumulatively in order to verify the obtained results.

4. Results and discussion

Using SiC as precursor in the carbon synthesis results in an amorphous nanoporous carbon structure (ANPC) with pores of typically 10 Å in size while the Al_4C_3 results in a structure of inter-grown nanotube-like aggregates, nanobarrels (MWNB). These barrels typically have five to 10 walls, distanced by 0.34 nm, with an inner diameter of 5–27 nm and outer diameter of 6–30 nm. The length is in the range of 6–50 nm and each barrel is covalently interconnected to neighboring barrels, forming amorphous networks of barrels aggregated in larger particles [15]. HRTEM images of the samples are illustrated in Fig. 2 (ANPC) and Fig. 3 (MWNB). The density of the ANPC sample is 2.2 g/cm^3 and the specific surface is 1000 m^2/g while MWNB sample has a density of 0.75 g/cm^3 and a specific surface area of 600 m^2/g [14].

Isotherms at three different temperatures (300, 195 and 77 K) were plotted for the ANPC (Fig. 4) and MWNB (Fig. 5) samples and the differential and total hydrogen uptake calculated for selected pressures (see Table 1). These isotherms were well described, for both samples, by the Sips isotherm with *n*-values of ~3.6 for MWNB and ~4.5 for ANPC, indicating a strong degree of heterogeneity at moderate and high concentrations.

At hydrogen pressures of 10 MPa the maximum differential uptake was determined to 2.9 (300 K) and 4.1 wt% (77 K) for MWNB and 2.6 and 3.3 wt%, respectively,

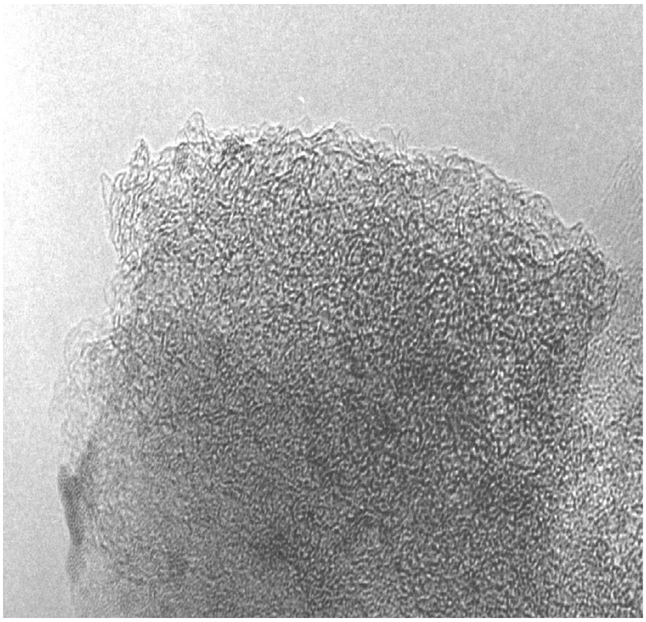

Fig. 2. HRTEM image of the ANPC sample.

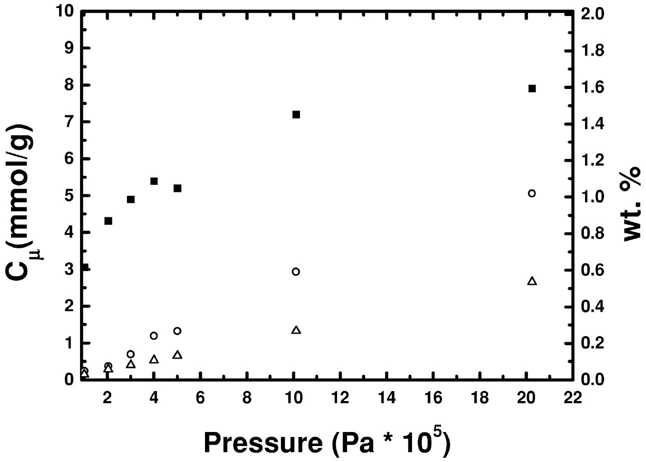

Fig. 4. The hydrogen uptake as a function of applied hydrogen pressure for ANPC. The triangles (△) are representing 300 K, circles (○) 195 K, and filled squares (■) 77 K.

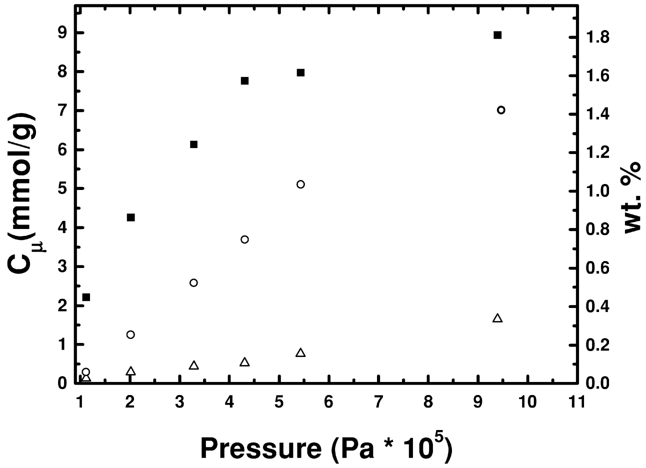

Fig. 5. The hydrogen uptake as a function of applied hydrogen pressure for MWNB. The triangles (△) are representing 300 K, circles (○) 195 K, and filled squares (■) 77 K.

for ANPC. The total uptake calculated to 3.2 (300 K) and 6.2 (77 K) wt% for MWNB and 2.8 (300 K) and 4.2 (77 K), respectively, for ANPC.

The MWNB sample has larger differential uptake as compared to the ANPC sample although the surface area, as determined by nitrogen adsorption, is smaller. This indicates that the as-determined-specific surface area is underestimated. Naively this could be understood as size-limited adsorption, the diffusion of nitrogen into interstices being hindered by its size (0.374 nm [16]), which is larger than the distance between the tube walls of the multi-wall structure (0.34 nm). Hydrogen has a molecular diameter of 0.275 nm [17] and diffusion of hydrogen could therefore be possible into the interstices, not accessible to the nitrogen gas.

The isosteric heat of adsorption was calculated for low coverage, using the Clausius–Clapeyron relation [11]:

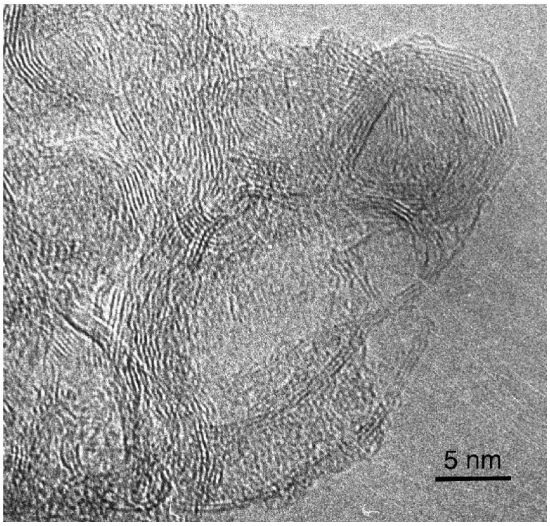

Fig. 3. HRTEM image of the MWNB sample.

Table 1
Differential and total hydrogen uptake (wt%) from the isotherms at 300, 195 and 77 K and a hydrogen pressure of 2 MPa for ANPC and 1 MPa for MWNB

Type	300 K	195 K	77 K
ANPC	0.50[a]	1.00[a]	1.60[a]
	0.54[b]	1.10[b]	2.00[b]
MWNB	0.40[a]	1.40[a]	1.80[a]
	0.44[b]	1.55[b]	2.72[b]

[a] Measured differential hydrogen uptake.

[b] Calculated total hydrogen uptake.

Table 2
The isosteric heats of adsorption for ANPC and MWNB

μ wt%	ΔH_{ad} for ANPC (KJ/mol)	ΔH_{ad} for MWNB (KJ/mol)
1.1(1)	7.2	4.2
1.3(1)	5.6	4.2
1.5(1)	4.8	4.2
2.0(2)	4.4	4.2
2.2(2)	2.2	4.0

$$\frac{\Delta H_{ad}}{R} = \left(\frac{\partial \ln P}{\partial(1/T)}\right)_{\mu} \qquad (2)$$

The pressure range in the isotherms, used when calculating the isosteric heat of adsorption, was chosen to be 0.1–2.0 MPa and the adsorbed densities (μ) 1.1(1), 1.3(1), 1.5(1), 1.7(2), 2.0(2) and 2.2(2) wt% for the fitting of data to the Clausius–Clapeyron relation. Table 2 is a compilation of the results from the determination of the isosteric heat of adsorption for both samples, at intermediate concentrations. Large differences in ΔH_{ad} is observed for ANPC while MWNB has fairly constant ΔH_{ad} due to the larger heterogeneity of ANPC.

The isosteric heat of adsorption of hydrogen on super-activated carbon was determined to be 5–6 KJ/mol, at adsorbed densities of 1.1–2.2 wt% (corresponds to 5–10 mmol/g), by Bénard and Chahine [18]. The results obtained in the current work are thus in the same range as obtained for super-activated carbon. Moreover, a maximum hydrogen uptake of 5.8 wt% was inferred at 77 K and a hydrogen pressure of 35 bar, which is comparable to the results presented here.

5. Conclusions

We have measured some adsorption and desorption isotherms by the volumetric Sieverts method and also determined the adsorption energies for hydrogen in two nanostructured carbon samples synthesized from SiC (ANPC) and Al_4C_3 (MWNB). The uptake process is considered to be non-dissociative (non-activated adsorption) since no hysteresis is present in the uptake–release process.

The maximum total hydrogen uptake at 77 K and 10 MPa hydrogen pressure was determined to be 4.2 and 6.2 wt% for ANPC and MWNB, respectively. At higher temperatures the uptake is smaller, which is expected for non-activated adsorption. These results are quantitatively in line with previous experimental work on different commercial types of activated carbon [18].

The measured adsorption isotherms were compared with the adsorption models of Langmuir and Sips. The adsorption isotherms were better described by Sips isotherms, which indicates the existence of heterogeneous adsorption sites. The results from fitting the experimental data by Sips isotherms, indicates a strong degree of heterogeneity, with n-values of ~3.6 for MWNB and ~4.5 for ANPC. At higher coverage, multisite model is required to describe the coverage dependence.

The results from the calculations of the isosteric heat of adsorption are consistent with fairly constant adsorption energies at lowest coverage for both samples. However, at intermediate concentrations large differences in ΔH_{ad} are observed for ANPC although almost constant for MWNB. The lower value of n for MWNB indicates a larger range of adsorption sites with similar adsorption energies as compared to the ANPC. The lower degree heterogeneity results in more uniform adsorption energies. This is qualitatively in line with the inferred structure of the materials, i.e. distribution in the channel size, where the investigated materials have a range of sites that have similar adsorption energies.

Acknowledgements

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