

H₂ adsorption on multiwalled carbon nanotubes at low temperatures and low pressures

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We present an experimental study on H₂ adsorption on multiwalled carbon nanotubes (MWCNTs) at low temperatures (12–30 K) and low pressures (2×10^{-5} Torr) using the temperature programmed desorption technique. Our results show that the molecular hydrogen uptake increases nearly exponentially from 6×10^{-9} wt. % at 24.5 K to 2×10^{-7} wt. % at 12.5 K and that the desorption kinetics is of the first order. Comparative measurements indicate that MWCNTs have an adsorption capacity about two orders higher than that of activated carbon (charcoal) making them a possible candidate as hydrogen cryosorber for eventual applications in accelerators and synchrotrons.

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I. INTRODUCTION

Pumping of molecular hydrogen in the Large Hadron Collider is designed by installation of cryosorbers on cryogenic elements operating at very low temperatures [1]. Among many specific requirements for the best choice of cryosorbent materials, the adsorption capacity is certainly a discriminating factor. Though many types of cryosorbers have been tested in the past [2,3], active porous carbon is still the far most important cryosorbent material due to its high specific surface area and large pore volume [4–6].

Usually, three different techniques are widely applied to study the H₂ adsorption rate, capacity, sticking and capture probability, and storage in solids: the volumetric method, which measures the pressure drop owing to hydrogen absorption after loading the specimen contained in a constant volume [7]; the gravimetric method, which measures the sample weight changes due to absorption or desorption [8,9]; and the temperature programmed desorption (TPD) technique [10]. This latest measures the hydrogen signal during desorption in high vacuum using mass spectrometry; it is highly sensitive allowing one to study samples with masses even below 1 mg and is especially suited for loading of small quantities at low pressures.

In an earliest work, Dillon *et al.* estimated the hydrogen uptake by single walled carbon nanotubes to be 5–10 wt. % for adsorption conditions of about 0.5 bar and 273 K, followed by cooling and pumping to 133 K and 10^{-6} Torr [10]. The heat of adsorption determined from the TPD measurements was close to 20 kJ/mol. Wilson *et al.* measured isotherms of H₂ and D₂ deposited on single walled, closed end carbon nanotube bundles and observed two well distinct steps corresponding to adsorption on grooves/interstitials and the graphene surface [11].

In this work we present a TPD study on H₂ adsorption on multiwalled carbon nanotubes (MWCNTs) and on charcoal at very low pressure and temperatures as a function of gas dose. We show that the molecular hydrogen uptake

decreases with the adsorption temperature and is in the order of 10^{-7} wt. %, that the desorption kinetics is of the first order, and that the desorption energy is 2.82 ± 0.16 KJ/mol. Comparative measurements indicate that MWCNTs have an adsorption capacity about two orders higher than that of activated carbon (charcoal) making them a possible candidate as hydrogen cryosorber for eventual applications in accelerators and synchrotrons.

II. EXPERIMENTAL

MWCNTs were synthesized by chemical vapor deposition using C₂H₄ and subsequently purified. As illustrated in Fig. 1, transmission electron microscopy (TEM) shows that

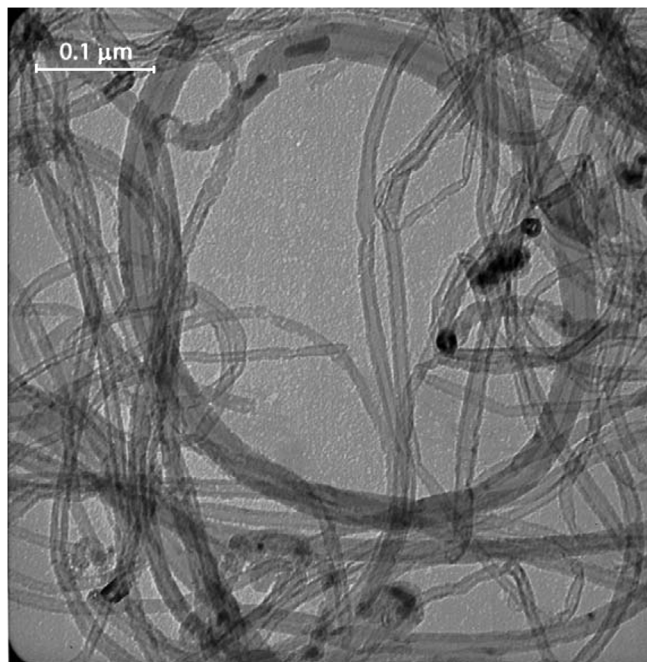


FIG. 1. Transmission electron micrograph of multiwalled carbon nanotube sample used in this study.

our MWCNT sample was made of individual nanotubes with an outer (inner) diameter of 10–15 (3–6) nm and that many of them were open ended. Microporosity measurements yielded a specific surface of 174 m²/g. 10 mg of MWCNTs were dispersed in orthodichlorobenzene and sonicated in a glass container. The sample then was deposited directly onto the copper head (6 cm²) of a cold finger with closed He cycling and dried. A quite uniform thin film was obtained and its adhesion to the copper surface remained stable during all the measurements.

The experiments were conducted in a UHV chamber (base pressure in the low 10⁻⁹ Torr range) evacuated with a dry turbo pump. H₂ gas (purity of 99.999%) was introduced in the chamber through a precision leak valve while keeping the sample at a desired adsorption temperature T_{ad} and a fixed pressure of 2×10^{-5} Torr (measured at room temperature and corrected for the ion gauge sensitivity factor) for a chosen time interval, then the gas was pumped out. The sample temperature was monitored with a Au/0.7%Fe-chromel thermocouple. Thermal desorption was achieved by heating the head of the cold finger with a linear ramp and the desorbed H₂ was measured with a

quadruple mass analyzer. No appreciable contamination gas signals were detected neither in the adsorption nor in the desorption processes. Complete reversibility of charging and discharging cycles was routinely verified and a total reproducibility was observed.

The vacuum system pumping speed was calibrated by admitting a known quantity of hydrogen into the chamber at desired quadruple reading pressures and monitoring the time needed for evacuation. A linear dependence on the pressure was observed. The desorption rate was obtained by multiplying the detected hydrogen partial pressure (the integral intensity of a quadruple mass spectrum centered at $m = 2$ a.u. composed of some 50 data points) by the system pumping speed and the total amount of desorbed hydrogen then could be evaluated from the integration of the desorption rate-time curves with an estimated error of about 20%.

The density of MWCNTs should be close to 2 g cm⁻² once deposited on the cold finger in a compact form (not measured). For small quantities of our samples (up to

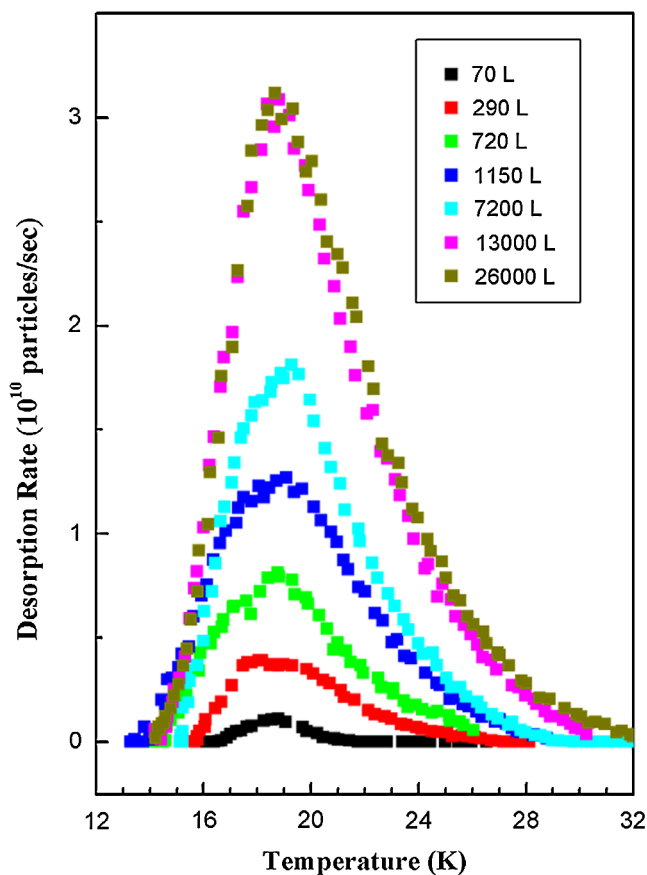


FIG. 2. (Color) Temperature programmed desorption traces of molecular hydrogen adsorbed at $T_{ad} = 15$ K and $P_{ad} = 2 \times 10^{-5}$ Torr. The dose is expressed in Langmuir (1 L = 10^6 Torr sec).

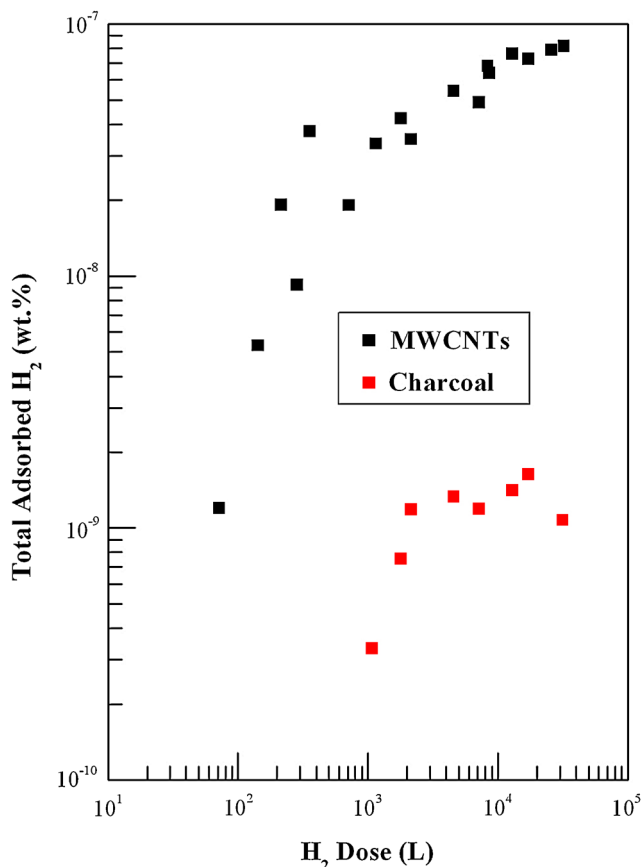


FIG. 3. (Color) Molecular hydrogen adsorbed on MWCNTs as a function of H₂ dose for adsorption temperature of $T_{ad} = 15$ K. Also shown are the results for a charcoal sample. The active surfaces are 174 m²/g and 23 m²/g for MWCNTs and charcoal, respectively.

10 mg on a surface of 6 cm²), we found the sorption capacity is proportional to the sample mass.

III. RESULTS AND DISCUSSIONS

In Fig. 2 we illustrate some representative H₂ TPD traces taken at a constant adsorption temperature of $T_{\text{ad}} = 15$ K and varying exposure time. The H₂ dose Φ was expressed in units of Langmuir (1 L = 10⁻⁶ Torr sec) and the sample heating rate was fixed at $\beta = 5$ K/min. These spectra are substantially narrower than those previously reported in literature for H₂ dosing at higher temperatures and pressures [10,12]. These TPD traces are quite similar to each other and the spectrum maxima remain unchanged as the hydrogen adsorption increases clearly indicating a first order desorption mechanism.

The total molecular hydrogen content, as determined from the integral of the desorbed H₂ TPD trace curves, is plotted in Fig. 3 as a function of Φ for $T_{\text{ad}} = 15$ K. It is interesting to note that it increases linearly with Φ at low doses and saturates at about 8×10^{-8} wt.% for $\Phi \geq 10^4$ L. The saturation at a very low value and the relatively narrow line shape would suggest that hydrogen adsorbs only on a limited number of sites.

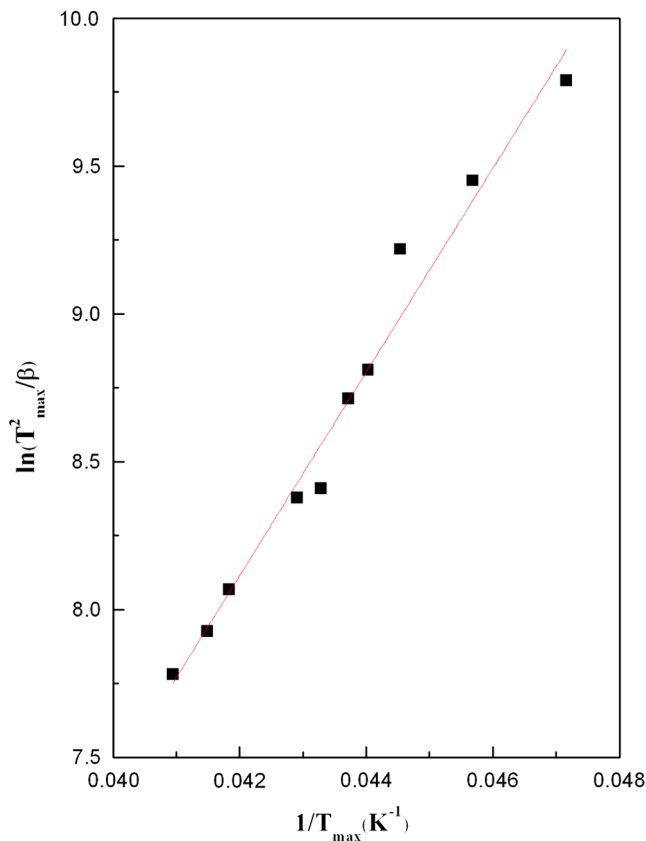


FIG. 4. (Color) Plot of $\ln(T_{\text{max}}^2/\beta)$ versus T_{max}^{-1} for a series of TPD spectra taken at fixed $T_{\text{ad}} = 19$ K, $\Phi = 2160$ L, and varying heating rate β . T_{max} is the temperature corresponding to the desorption rate maximum.

To gain some information on the hydrogen binding energy we varied the sample heating rate β for constant $\Phi = 2100$ L and $T_{\text{ad}} = 19$ K. In Fig. 4 we plot $\ln(T_{\text{max}}^2/\beta)$ versus T_{max}^{-1} , where T_{max} is the temperature corresponding to the desorption rate maximum. The slope of the linear fit yields a desorption energy of $E_{\text{des}} = 340 \pm 20$ K (or $E_{\text{des}} = 2.82 \pm 0.16$ kJ/mol).

It is interesting to note that, though there is a large body of experimental studies on hydrogen adsorption on carbon nanotubes because of its potential application as a storage material, very few measurements were undertaken below 77 K [11,13]. To the best of our knowledge, no experimental data are available in literature for adsorption at very low pressures. The binding energy value found in this study is lower than that for H₂ on graphite (480 K) [14] in accord with the isothermal adsorption measurements reported by Wilson *et al.* (3.3 kJ/mol) [11]. This suggests that hydrogen molecules mostly adsorb on the outer surfaces and the reduction in binding energy value is generally attributed to the surface curvature [11,15–17].

This site assignment is in accord with the TEM observation that our sample was essentially made of individual nanotubes (Fig. 1). On the other hand, adsorption on inner walls would imply a much stronger bonding [11,18] and

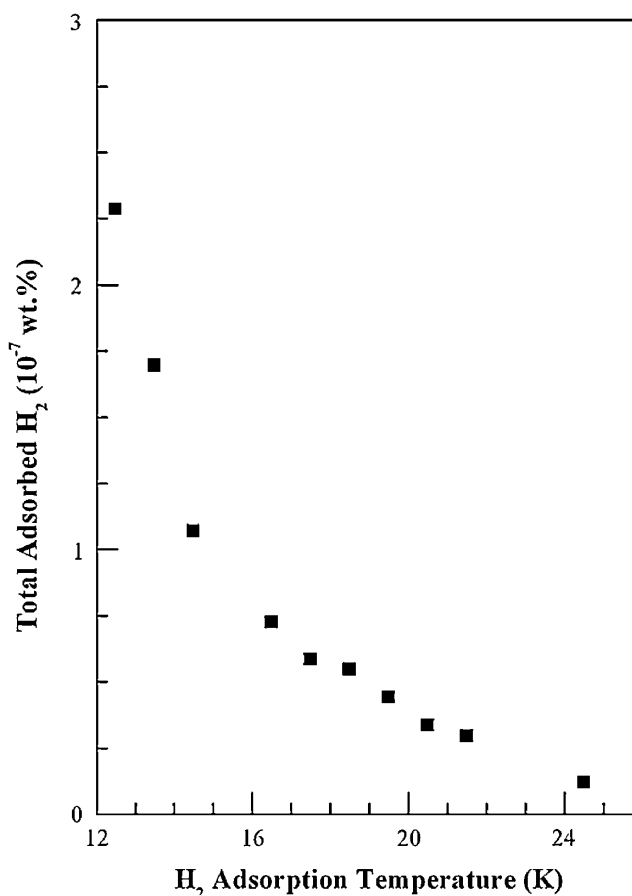


FIG. 5. Saturated molecular hydrogen content adsorbed on MWCNTs as a function of adsorption temperature of T_{ad} .

diffusion into those open ended nanotubes. Quasielastic neutron scattering measurements performed by Narehood *et al.* also indicated the absence of H₂ mobility in SWNTs at temperatures below 30 K [19].

For comparison, in Fig. 3 we also present the total H₂ adsorption amount of 10 mg activated charcoal powders (specific surface area 23 m²/g) under exactly the same experimental conditions. It exhibits very similar characteristics as that of MWCNTs but is about two orders smaller.

Finally, in Fig. 5 we illustrate the saturated total amount of adsorbed hydrogen as a function of adsorption temperature T_{ad} . As expected, the total hydrogen adsorption capacity decreases with the cryosorber temperature. For $T_{ad} \geq 27$ K, no H₂ adsorption is observed.

Our results contrast sharply with those reported for hydrogen storage measurements at higher temperatures and pressures and strongly indicate that under high vacuum conditions, hydrogen does not adsorb on the nanotube surface beyond the sublimation temperature and the diffusion is essentially inhibited, as already confirmed by previous works. We mention that the testing measurements on carbon nanofibers actually used in the LHC were also taken at higher pressures and the so determined sorption capacity can be much higher than the real values in UHV conditions [5,6]. More quantitative works are currently being undertaken to determine the realistic possibility of using nanotubes as cryosorbers in UHV systems.

IV. CONCLUSIONS

In conclusion, we presented first experimental measurements of molecular hydrogen adsorption on MWCNTs at low pressures (10^{-5} Torr) and low temperatures (12–30 K). We showed that the adsorption capacity decreases sharply with temperature and is in the order of 10^{-7} wt. % at 12 K. This figure is about two orders higher than that obtained for commercial active carbon, making MWCNTs a potential candidate as cryosorbent materials for accelerators.

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