Acetylene Sorption Dynamics in Carbon Nanotubes

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Single-walled and multi-walled carbon nanotubes (SWNT and MWNT, resp.) were prepared by applying the catalytic chemical vapor deposition (CCVD) technique. Different nanotube samples were obtained from the as-synthesized carbon/catalyst composites by treatments applied to remove the catalyst and the amorphous carbon. The dynamic and equilibrium adsorption properties of the samples were compared. Acetylene was used as an adsorptive probe. The sorption mass-transport properties have been characterized by applying the frequency response (FR) technique. Results reflected that the surface functional groups, generated by an oxidative treatment, have significant influence on both the static and the dynamic acetylene sorption properties of the carbon nanotube materials. The rate of acetylene mass transport was governed by the rate of sorption in all the samples, except in MWNT after oxidative treatment, where the intracrystalline diffusion in the nanotubes was the rate-controlling process.

Introduction. – Carbon nanotubes (NT) offer a number of potential technological advantages and have become the subject of much applied research. The benefits expected from their application in electronic devices and composite materials, as catalyst support and as sorbents for gas storage, stimulates intensive research to understand and control the structure and related properties of these materials.

Although gas diffusion is involved in many of the expected uses, computational molecular-dynamics and/or Monte Carlo studies have been used mainly to follow diffusion in various ideal carbon nanotubes [1]. Only in a few experimental studies, mass transport within carbon nanotubes has been considered, *e.g.*, methane mobility in single-walled nanotubes (SWNT) by quasi-elastic neutron scattering [2]. Experimental studies of gas adsorption and transport frequently involve many uncertainties in establishing the precise nature of the adsorbent material. Furthermore, pore topology and pore-size distribution may generate a variety of possible transport mechanisms. Under these circumstances, it is important to study adsorbent behavior by sensitive macroscopic experimental techniques. Recently, the frequency response (FR) method has been shown to be useful for the characterization of the mass-transfer kinetics in various sorbents, which include activated carbons [3–5]. In principle, the method can be used to determine the mechanism of the rate-governing transport step and the dynamic parameters of the transport process [6][7].

In the present work, various purification procedures were applied to recover nanotubes from preparations obtained by catalytic methane and acetylene carbonization. The aim of this study was to learn more about the adsorption and diffusion of acetylene as the probe molecule, which is an important source of carbon in multi-walled nanotubes (MWNT) preparations, by the unique potential of the FR method. It is expected that these studies will stimulate further investigations of the mass transport dynamics of various gases in carbon nanotubes, which will help to characterize and generate the production of high-quality homogeneous carbon-nanotube products for various practical uses.

Experimental. – Nanotubes were prepared applying the catalytic chemical vapor deposition (CCVD) method. The MWNT-47 sample was produced by the decomposition of acetylene over a Fe,Co/Al_2O_3 catalyst at 700°, while SWNT-4 was produced from CH_4 at 1080° using Co/MgO as the catalyst. The number in the sample designation gives the C content in mass percentages. The carbon/catalyst composites were studied in their as-synthesized form and after various chemical treatments. In the SWNT-59 preparation, only the removal of the catalyst by dissolution twice in HCl soln. was involved because a large fraction of the SW material was lost in each treatment. In the case of MWNT, the carbon was recovered by dissolving the catalyst in two steps: first in 10M NaOH soln. refluxed two times, and then in cold HCl soln. (MWNT-95). Ball milling [8] was carried out to obtain shorter tubes with a narrow tube-length distribution and small carbon fragments (MWNT-95B). This step was followed by the removal of the amorphous carbon by-product and nanotube fragments by oxidation in 1M H_2SO_4/0.3M $KMnO_4$ soln., resulting in a MWNT-81, which had an increased catalyst residue concentration because of carbon loss.

The acetylene probe (*BOC Gases*, UK) was of 98.5% purity and was further purified by applying the freeze-pump-thaw procedure before use.

Transmission electron microscopic (TEM) images of the samples were taken up with a *Philips CM10* type microscope.

Adsorption isotherms of nitrogen and acetylene were determined at − 196° and at 0°, resp., with an all-glass, volumetric system equipped with a *Barocel 571A* pressure transducer. The adsorbent was activated under high vacuum at 300° for 3 h.

The batch type FR system, described by *Rees* and *Shen* [9], was used to study the acetylene transport dynamics at 0° in the 60 – 600 Pa pressure range. About 400 mg of sample was distributed in the FR sorption bulb in a plug of glass wool. The sample was treated *in situ* under a high vacuum at 300° for *ca.* 3 h, cooled to the temp. of the FR measurement, and equilibrated with acetylene at a selected pressure. Then, the volume of the FR chamber was modulated by $\pm 1\%$ over frequencies between 0.01 and 10 Hz. A response pressure wave was recorded at each modulation frequency. The in-phase (real) and the out-of-phase (imaginary) components of the response wave function are plotted as a function of perturbation frequency to get the FR spectrum. When the characteristic time of modulation is close to that of the rate-determining mass transport time constant in the sorbent particles, resonance occurs. A resonance signal (peak and step) appears in the rate spectrum at the frequency that corresponds to the time constant of the rate-controlling transport process. The experimental FR spectra were compared with characteristic FR functions, derived theoretically [6][7], assuming either rate-controlling sorption or rate-limiting diffusion. The sorption or diffusion time constant can be obtained as the only adjustable parameter of the best-fit characteristic function.

Results and Discussion. – After 100 h of ball milling, the MWNT samples were homogeneous, all nanotubes were broken, and no long nanotubes remained. The TEM pictures (see *Fig. 1*) demonstrate a great change considering the length of nanotubes; however, the ordered carbon structure is not damaged, and the tubes have open tips. The last observation is important for the applications that will take advantage of the confinement effect in the nanotube cavity such as gas storing and separation. For the untreated nanotubes or after short ball-milling times, only the length of the smaller tubes (those shorter than 10 μm) can be measured from the TEM images, since the longer tubes form balls and do not fit in a single TEM picture. As a consequence, only the short tube lengths can be determined by this method, *i.e.*, the size necessary to be measured for calculation of transport-diffusion constants by using the mass-transport-time constants obtained in FR rate spectra. Grinding of the nanotube samples in ball

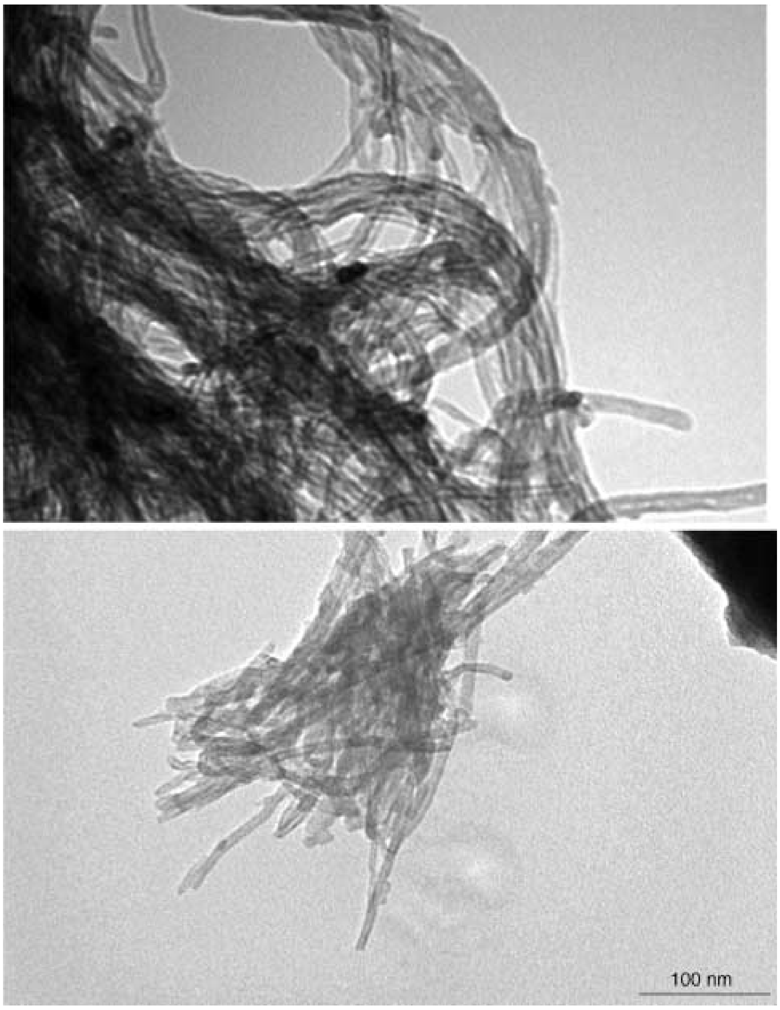

Fig. 1. *TEM Images of multi-wall carbon nanotubes before* (MWNT-47) *and after* (MWNT-95B) *100 h of ball milling*

mills produces nanotubes with a narrow tube length distribution and well-defined diffusion-path length.

Nitrogen-adsorption isotherms recorded at $-196°$ are shown for the various carbon-nanotube samples in *Fig. 2*. The Type-II adsorption isotherms suggest that nitrogen molecules physisorbed in the meso- and macropores. A similar adsorption isotherm was measured for a MWNT sample by *Kaneko* and co-workers, who suggested that the adsorption isotherm could be resolved into two-component isotherms, corresponding to the adsorption over the inner and outer surfaces of tubes [10]. The uptake was found to be much lower for MWNT samples, reflecting the structural difference between SWNT and MWNT carbons, moreover it was proportional with the C content of the samples. The nitrogen-adsorption capacity after ball milling, breaking the long carbon tubes, decreased a little, indicating formation of a small portion of amorphous carbon. The ground nanotube samples before (MWNT-95B) and after (MWNT-81) oxidative treatment gave practically the same isotherms expressing unchanged accessibility of the inner and outer surfaces of nanotubes and a negligible uptake of the removable carbon impurities.

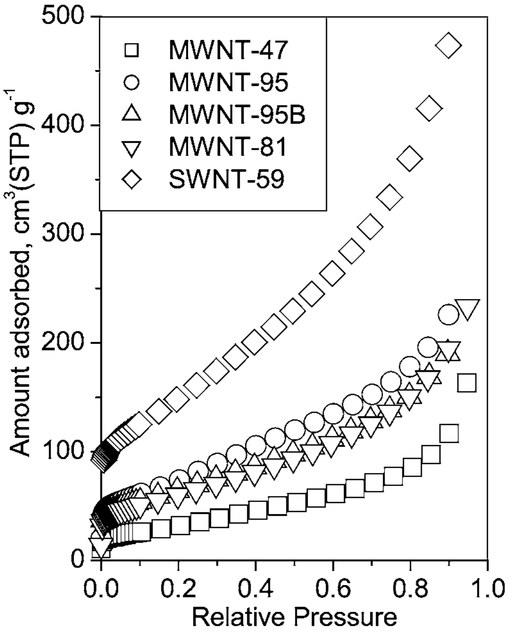

Fig. 2. *Isotherms for the adsorption of nitrogen at −196° determined over the SWNT and different MWNT carbon samples*

The specific surface area (SSA) was calculated from the nitrogen-adsorption isotherm by the BET method and equated to the C content of the sample. The SSA of the two nanotube types was found to be different, *i.e.*, 700–800 m^2/g for SWNT and 200–250 m^2/g for MWNT samples. These values were invariant to the C content, and to the applied chemical and mechanical treatments. These findings suggest that the surface of catalyst and the carbon impurities have minor contribution to the measured surface areas. Moreover, both the outer and the inner surfaces of the nanotubes are accessible for nitrogen in all preparations studied.

Isotherms and FR rate spectra of acetylene sorption over carbon-nanotube samples are shown in *Fig. 3*. The FR intensities must correspond to the sorption capacity of the perturbed process [6]. Accordingly, the FR intensities were found to parallel the slopes of the isotherms (*Fig. 3*). Acetylene isotherms are shown only for the MWNT samples. At the equilibrium pressure of the FR experiment, the isotherms deviate from *Henry*'s law being sensitive to the energetic inhomogeneity of the acetylene adsorption sites. Under the FR conditions (0°, 133 Pa), acetylene uptake was *ca.* 10^{-3} of a monolayer. This low coverage was perturbed by a ±1% volume modulation. Consequently, the

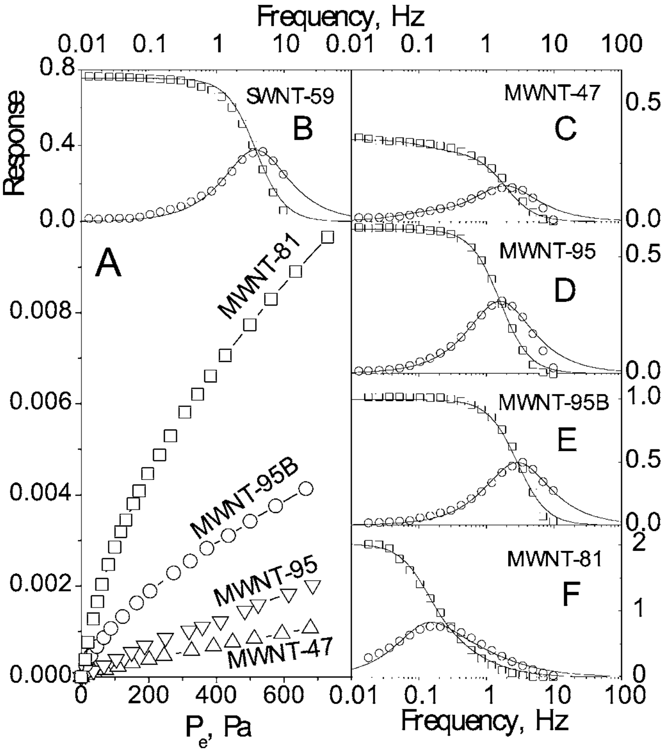

Fig. 3. *Isotherms* (*A*) *and FR spectra of acetylene sorption* (*B – F*) *over carbon samples at 0°*. The FR spectra were recorded at 133 Pa with *ca.* 400 mg of 150 – 500-μm nanotube particles. Symbols correspond to the in-phase (□) and out-of-phase (○) components of the experimental response wave functions. Full lines represent the best-fit characteristic curves.

sorption process characterized by the FR spectra involves only the highest-energy sorption sites, which can be defects and functional groups (*e.g.*, OH, C=O, and COOH) on the nanotube crystals. It seems more probable (see *Fig. 3*) that the samples differ in the concentration of the O-containing functional groups, which can increase the adsorption capacity by enhancing the solid-fluid potential. Previously [8][11], it was shown that ball-milling in air and/or treatment in oxidizing agents introduce O-containing functional groups, which terminate the ends of the fractured nanotubes and link to imperfections on the tube walls.

An outstanding advantage of the FR method is that it can provide, at least for simple systems, information about the rate-limiting mechanism of the sorption mass transport. In this study, the intersection of in-phase and out-of-phase characteristic curves mostly occured at the maximum of the out-of-phase curve and exactly at half of the maximum of the in-phase curve (*Fig. 3*, *B – E*). The theoretical analysis of the FR measurement has shown that this kind of characteristic response curve can indicate that the rate of adsorption is the rate-controlling step. The asymptotical approach of the component curves at high frequencies indicates that one of the rates of diffusion among the series of sorption-process steps governs the transport rate. Between these limiting cases, mixed diffusion/adsorption can be rate-controlling. Then, the point of intersection of the two component curves depends on the ratio of the adsorption rate and diffusion rate in the mesopores, inside the carbon nanotubes (see *Fig. 3,F*) [6][7]. The low value of this ratio can mean also that the equilibrium at the pore mouth is only slowly attained as a consequence of strong surface barriers. The significant accumulation of barriers at the pore mouths of carbon nanotubes is a consequence of the oxidative purification step. Catalyst particles or catalyst residues at the growing open ends of the tubes before and after their imperfect dissolution and, also, small carbon fragments at the tube apertures after ball milling can hinder access to the tube inside. All these defects were expected to decrease after dissolution and oxidative treatments. The dissolution of the catalyst residue was hardly effecting the molecular transport (*cf. Fig. 3,C* and *D*). After ball milling, *i.e.*, creating much shorter tubes with shorter diffusional path lengths and two open ends, the FR signal moves a little to higher frequencies, indicating a faster process with a smaller time constant. However, after oxidative treatment, the spectrum (*Fig. 3,F*) demonstrates a mechanism change with creation of a low-frequency diffusional-type signal reflecting a much slower rate-controlling process.

In carbon nanotubes, the ratio of the external and inner surfaces is proportional to the ratio of the tube diameters. The areas of these energetically different, concave and convex surfaces are comparable in extent. However, in every case, the acetylene FR spectra can be fitted only with a single process, which means that the sorption seems to be dependent on the available inner surface under the experimental conditions. At low coverages of the graphitic surface with the probe, as determined at low pressures and high temperatures, sorption is mainly inside the tubes where the sorption interaction is energetically stronger. This sorption process increases incrementally because the slope of isotherms and the intensity of FR signals increase in parallel from *C* to *F* in *Fig. 3*. The different equilibrium and dynamic properties of our MWNT samples cannot be explained from structural variances, *i.e.*, with surface barriers at pore mouths. It seems more probable that the samples differ in the concentration of the O-containing functional groups, such as OH, C=O, and COOH, which can be created during ball milling at the tube ends and other imperfections on the tube walls under oxidative conditions. The higher number of polar functional groups increases the adsorption capacity at low coverage and is responsible for the increased diffusional resistance in the tubes of the oxidized MWNT-81 sample in spite of the fact that the specific surface area is unchanged. At higher temperatures, above 80°, where diffusion can be much faster, a mechanism change can be observed again in consequence of a large decrease in ratio of adsorption to diffusion rates.

The SWNT structure has little resistance to the purification agents, to mechanochemical and to oxidative treatments. Consequently, less pure samples that do not exhibit diffusion control can be obtained (see *Fig. 3,B*).

According to the TEM image, the average length (l) of the carbon tubes in the MWNT-81 samples is *ca.* 0.25 μm, while the average inner diameter is 4 nm. Assuming that $l/2$ is the characteristic mean distance of the transport and the resonance frequency has a time constant of *ca.* 10 s, the transport diffusivity of acetylene will be *ca.* 2×10^{-13} m^2/s.

We need now to produce carbon nanotubes with a more homogeneous morphology although it must be remembered that, under purification, a considerable fraction of the nanotubes are destroyed. The first step to extend our knowledge of nanotube-gas-sorption dynamics is to collect data on various nanotube samples with the powerful FR technique. Use of FR rate spectroscopy offers a promising new approach for studying the mobilities of adsorptives within carbon nanotubes, and these experimental results can stimulate improvements in the synthesis, purification, and modification techniques.

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