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The sorption dynamics of C_3 hydrocarbons over carbon nanotubes

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Abstract

Carbon nanotubes obtained by the catalytic vapor deposition (CVD) method were purified by various procedures to obtain samples in pure and well-defined forms. The frequency response (FR) technique was employed to determine the sorption dynamics of C_3-hydrocarbons in these samples. Two parallel sorption processes were found, characterized by different sorption capacities and time constants and were assigned to sorption on the convex and concave surfaces of the carbon tubes, respectively. Over a carbon nanotube sample at low coverage the mass transport is little influenced by the different chemical nature of the various C_3 hydrocarbons. However the dynamic sorption properties of carbon nanotube preparations were shown to be strongly affected by the absence or presence of surface functional groups on the outer and inner surfaces of the tube walls. Different rate-determining mechanisms were observed for the samples functionalized to different extents.

Keywords: FR rate-spectroscopy, sorption dynamics, carbon nanotubes, C_3 hydrocarbons

1. Introduction

Mesoporous carbon nanostructures, have received increasing attention in studies of their fundamental properties but, also, for numerous potential applications. Carbon nanotubes (CNTs) exhibit extraordinary mechanical strength and have electrical, thermal and adsorption properties which are required for these potential applications. CNTs are a unique group of mesoporous materials where the inner and outer diameters of the tubes are in the range of one to some ten nanometers and the tubes can be a few micrometers in length. Fluids can be adsorbed both within the hollow pores of the open tubes and on the external tube surfaces. However it is expected that their high aspect ratio could induce a confinement effect [1-3] on the gas or liquids trapped inside the carbon tube leading to completely different physical behavior when compared to more conventional adsorbents. When aggregates of tubes are employed it is found that the outer tube surfaces create intertubular pores which have, also, specific adsorption properties.

Since numerous applications of the CNT involve gas diffusion and sorption there is a strong interest in determining their equilibrium and dynamic adsorption properties [4-12]. Sorption over carbon tubes of faultless structure can be described by molecular dynamic or Monte Carlo type simulations [13-17]. However, the qualities of these results can, only, be judged when they are compared with experimental results using real nanotube preparations. At present only a few experimental studies have looked at the mass transport of sorbates in CNTs [8]. Although the production of carbon nanotubes is relatively simple, it is up-to now very difficult to obtain samples of good quality, containing the minimum of amorphous or graphitic microparticles. Furthermore all methods yield nanotubes with a wide distribution of lengths, helicities of the layers and diameters. Since it is important to obtain pure, homogeneous nanotube samples for accurate characterization of their physical properties and for future applications, several approaches have been developed to minimize the amount of contaminating materials. Convenient preparation and purification methods have to be developed for the large scale production of pure and, ideally uniform nanotube samples. However, it is, also, necessary to develop a quick and simple method of characterizing these preparations during the various steps of purification and modification of their surface properties.

Recently, the frequency response (FR) technique has been shown to be useful for investigating the mass transfer kinetics of gases in various adsorbents, including activated carbons [18]. An outstanding advantage of the FR method is its capability to distinguish the various molecular mobilities which may be involved. In principle, the FR method gives information about the mechanism of the rate-governing transport step and permits the determination of the dynamic parameters of the transport process [19-21]. A recent FR study compared the relationships between the structure of activated carbon and CNT samples and their equilibrium, as well as, dynamic sorption behavior [22]. These results suggested that surface functional groups on the CNT, generated by an oxidative treatment, have significant influence on the adsorption properties of the carbon tubes [23-25]. The FR technique is a macroscopic transient method. The equilibrium is perturbed and the re-equilibration process is monitored. In the FR method, unlike other transient macroscopic methods, the perturbation of the adsorption equilibrium is periodic and very small. The frequency of perturbation is an additional degree of freedom, which provides the method with the potential of distinguishing parallel processes, having different time constants which give information about the rate-controlling mechanism of the transport processes [19, 21]. Due to the formal resemblance of the FR and optical spectra, the FR method is often referred to as rate spectroscopy [19].

The aim of the present work was to determine the sorption and diffusion behaviour of C_3 hydrocarbons with different structural and chemical properties; for example, propane, propene, propyne, allene and cyclopropane in different CNT preparations. The sorption dynamics of these different molecules in a series of CNT samples can lead to a much better understanding of the differences in the nanopore diameters, structure and active surface groups.

2. Experimentals

The catalytic chemical vapor deposition (CCVD) method was used to prepare the carbon tubes. The single-walled carbon nanotubes (SWNT) were obtained by methane carbonization over Co/MgO catalyst. A purified SWNT sample was obtained by dissolving a part of the Co/MgO using concentrated HCl solution and designated as SWCNT-59, referring to the 59-wt % carbon content of the sample. The multi-walled carbon nanotubes (MWNT) were prepared by the catalytic decomposition of acetylene over a Fe,Co/Al_2O_3 catalyst (MWCNT-47). From the MWNT-containing material the Fe,Co/Al_2O_3 was dissolved by subsequently applying NaOH and HCl solutions (MWCNT-95). Another sample was obtained by ball-milling the purified MWNT in air (MWCNT-95B) where the morphology was modified. A mixture of tube fragments, containing rather uniform, 300-400-nm length tubes and amorphous carbon debris, was obtained. In order to obtain the fragmented tubes in a pure form the amorphous carbon was oxidized to CO_2 with $KMnO_4/H_2SO_4$ solution (MWCNT-81). A part of this sample was heated up to 900 ^{o}C in argon flow to eliminate the O-containing functional groups from the surface (MWCNT-81H). The same oxidative and defunctionalizing heat treatments were carried out on the MWCNT-95 sample containing the tubes with original length resulting in MWCNT-95ox and MWCNT-95H. Preparations were characterized prior to and after the applied treatments.

Transmission electron microscopy images were taken of each sample using a Philips CM10 type microscope at 200 kV. Rh-Co grid was dipped in a glue solution and representative sample was distributed over the grid.

The sorption dynamics was studied using a batch type FR system, described by Rees *et al.* [26]. The temperature and pressure of the measurements were in the 0-70 ^{o}C and 60-600 Pa range, respectively. Under the applied conditions the hydrocarbon uptake was a small fraction of the amount corresponding to the monolayer coverage. Thus, the sorption process, characterized by the FR spectra, concerned a very small fraction of the highest energy sorption sites.

In order to avoid bed-depth effects the narrow CNT sieved fractions of the samples were distributed over a glass-wool plug, placed in the sample holder of the FR system. The samples were pre-treated *in situ* in a high vacuum at 300 ^{o}C for 1 hour. Sorption equilibrium was, then, established between the adsorbent and the sorptive hydrocarbon. A periodic, ±1% square-wave perturbation was applied to the volume of the FR chamber. The modulation frequency was changed over the range of 0.001 to 10 Hz. The in-phase (real) and the out-of-phase (imaginary) components of the response wave function were plotted as a function of the perturbation frequency to generate the FR spectrum. A resonance signal (step and peak) appears, respectively, in the components of the rate spectrum at the frequency which corresponds to the time constant of the transport process. The experimental FR spectra were fitted with characteristic FR functions, derived theoretically, assuming either rate-controlling sorption or rate-limiting diffusion [19, 21]. These functions were obtained by solving the general mathematical model of a periodically perturbed sorption system containing gas and isotropic adsorbent particles of uniform size and shape. The model includes coupled mass-transfer resistances, such as transport through an external film or surface barrier and through macro and micropores. The sorption or diffusion time constant and the sorption capacities at the equilibrium pressure are the only adjustable parameters of the best-fit characteristic function.

A valuable feature of the FR method, at least for simple systems, is the relative position of the in-phase and out-of-phase spectral components. Such positions give information about the mechanism of the process that governs the sorption rate. An asymptotical approach of the component curves at high frequencies suggests that diffusion is the slowest step among the consecutive steps of the sorption mass transport. The FR spectrum suggests that sorption is the slowest process step, when the in-phase curve intersects the out-of-phase peak at the peak maximum and at the half height of the in-phase step.

3. Results and discussion

BET measurements earlier demonstrated that on a carbon basis the surface area of the CNT in our samples depended only on the type of the nanotube, i.e., single- or multi-walled, but was virtually invariant of the carbon content of the sample and to the applied chemical and mechanical treatments [25]. These findings suggest that catalyst and carbon impurities make, only, a minor contribution to the measured surface area and that both the outer and the inner surfaces of the nanotubes are accessible to N_2 adsorption in all of the preparations. In all probability this free accessibility exist for all the probe molecules having a size similar to that of nitrogen, although barriers in different samples with various diffusional resistances are present.

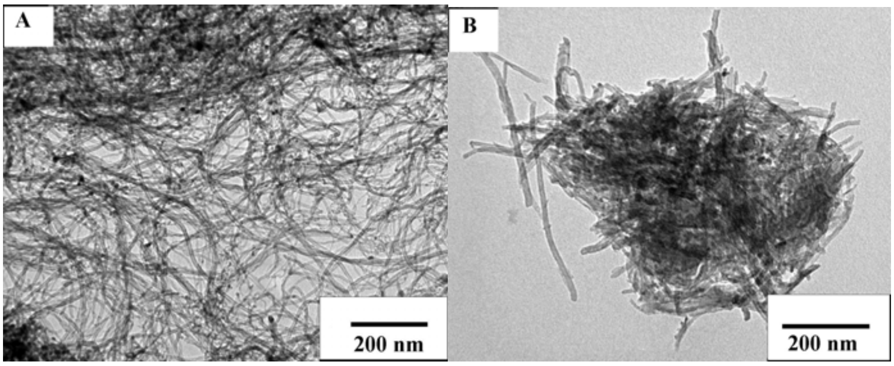

Fig.1. TEM micrographs of (A) MWCNT-95 and (B) MWCNT-95B samples

TEM images of MWCNT-95 and MWCNT-95B, the morphologically most different samples are shown in Fig. 1. The average length of the nanotubes in MWCNT-95 was found to be over 2-3 μm. The almost completely removal of the catalyst residues can be observed. These tubes had a fluffy structure with a wide distribution of intertubular mesopores and macropores. The micrograph of the MWCNT-95B sample shows that after a 100-hour ball-milling the average length of the tubes decreased from 2-3 μm to 3-400 nm while the basic nanotube structure remained unchanged. This feature is very important in investigations where the inner cavities of the tubes are involved. During and after ball-milling the originally loose and fluffy CNT sample becomes more and more compact upon mechanical and chemical treatments. The change results in the development of mesopores among the tubes with sizes smaller than about 50 nm [25]. The chemical treatments affect the volume and the size distribution of intertubular mesopores, but have little or no effect on the size distribution of the smaller, intratubular nanopores.

The FR spectra for propyne sorption or diffusion, shown in Fig. 2, demonstrate the changes which can be observed on applying the FR technique on the various samples. From each spectrum of the MWCNT samples recorded on the smallest sieve fractions at 0 °C (Fig. 2 A-E) two parallel sorption processes could be resolved. The resonance signals suggest that sorption processes on the convex and concave surfaces of the carbon tubes are involved. The process generating the low frequency response with a larger time constant is, most probably, related to the intertubular diffusion on sorption sites or sorption on the convex outer surface of the nanotubes. The process with a smaller time constant is associated with transport through the intratubular nanopores or sorption on the inner tube surfaces. In MWCNT-95 and -95B (purified and ball-milled) samples (Fig. 2 A and B) the ad/desorption processes are the rate-controlling process on both, the inner or the outer walls of tubes. The adsorption areas are comparable in size to the surface

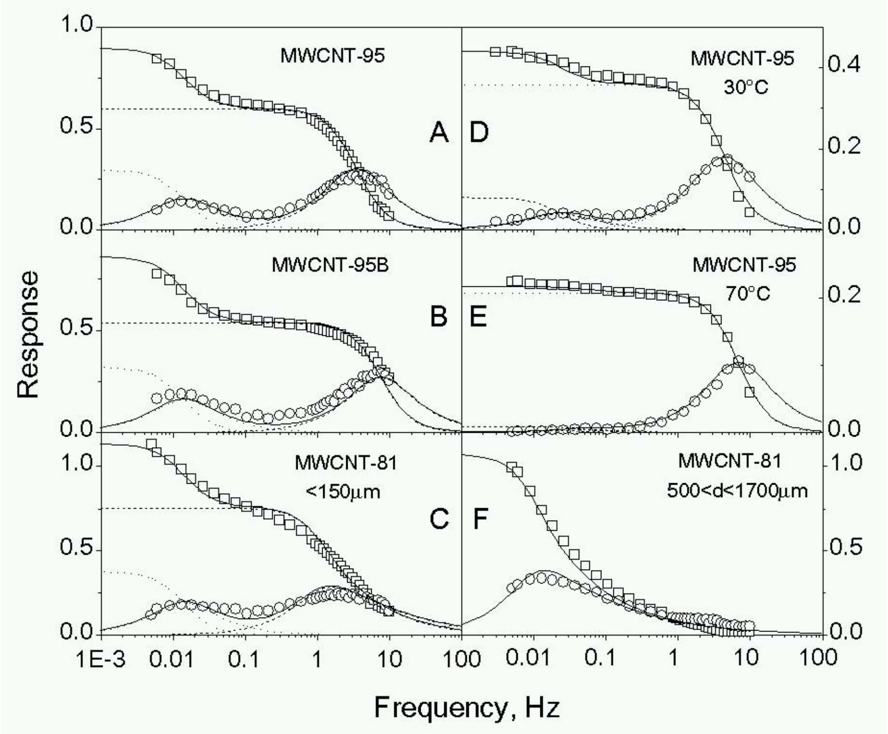

Fig. 2. FR spectra of propyne sorption on MWCNTs at 0 °C and 133 Pa. Each measurement was made on 200 mg CNT. Symbols correspond to the in-phase (□) and out-of-phase (○) components of the experimentally determined response functions. Full lines are the best-fit characteristic functions.

outside and inside the tubes. The energetic character of the adsorption sites are, however, quite different resulting in different coverages and FR signal intensities. The position of the low frequency peak reflecting sorption on the outer surface of the tubes does not change following ball-milling and tube shortening. The high frequency peak, on the other hand, moves significantly to higher frequencies because of the carbon tube shortening reflecting the shorter diffusional paths through the CNTs. This observation indicates that in this latter case the dominant sorption process is coupled with intratubular mass transport through the carbon tubes and is, thus, sensitive to the tube length. When propyne/MWCNT-95 FR spectra were compared at increasing temperatures signals moved to higher frequencies reflecting weaker sorption interactions and/or higher diffusivities (see Fig. 2 A, D and E).

Upon ball milling in air, oxygen-containing functional groups can be generated at locations where the tubes fracture. The treatment of MWCNT-95B sample in oxidizing solution further increased the surface concentration of the oxygen-containing functional groups (OH, COOH, CO, etc.), at tube ends and at defects on the tube walls. The presence of polar functional groups hinders the molecular motion and contributes to an increased diffusion resistance in the intratubular nanopores of the MWCNT-81 sample. Due to the increased diffusion resistance in the nanopores diffusion becomes the rate-controlling mechanism of the sorption process of C_3 hydrocarbons (see in Fig. 2 C and F). The theoretical analysis of the FR measurement suggested that the relative curve position is characteristic of the rate-controlling diffusion process. However, the rate-controlling transport resistance cannot be assigned only on the basis of the FR results to the transport in the macro, meso or micropores of the sample. The diffusion time constant (r^2/D) depends on the diffusivity (D) and the length of the diffusion path (r). Fig. 2 F shows that in the case of the ball-milled and oxidized MWCNT-81 sample the high frequency signal moves to lower frequencies for the larger particle size fractions i.e., the diffusion time constant depends on the sieve fractions. The CNT tubes must be of about the same length in the different fractions. Thus, in the larger aggregates the rate-controlling diffusion proceeds most probably in the macro or mesopores. The single low-frequency resonance signal obtained for the sieve fraction, containing particles between 500 - 1700 μm suggests that, for this sample, the rate-governing intertubular transport is rate-determining. The effect of particle size on the FR spectrum was similar for all hydrocarbon sorptives investigated over all temperatures in the case of the most dense, more compacted MWCNT-81 sample. This kind of macropore diffusional resistance appears by formation of larger and denser aggregates and can be eliminated by decreasing the aggregate size.

Fig. 2 and 3 suggest that the mechanism of the C_3 hydrocarbon sorption is sensitive to the presence of surface functional groups. Different mechanisms of transport prevail in the carbon tubes prior to and after oxidative and thermal treatment of the tubes. The adsorption-desorption step was the rate-controlling step of sorption on purified or ball-milled MWCNT (95 or 95B), while diffusion controlled the rate of transport following an oxidative treatment MWCNT (95ox or 81). The higher concentrations of oxygen-containing functional groups on the surface posed a higher resistance to diffusion mass transport. As a result diffusion became the rate-governing step. An example for the effect of carbon functionalization on the transport mechanism of cyclopropane is shown by the

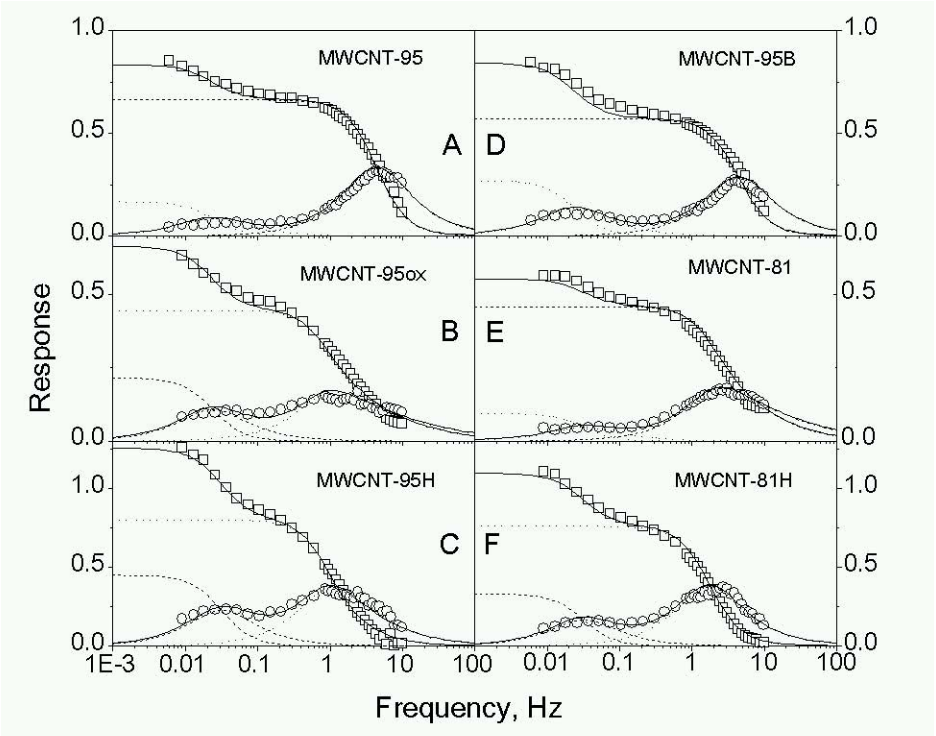

Fig. 3. FR sorption rate spectra for the sorption of cyclopropane, recorded at 0 °C and 133 Pa using 200 mg of <150- μm size particles. Sample MWCNT-81 was obtained from MWCNT-95B by oxidative treatment. The MWCNT-81H was prepared from the MWCNT-81 by thermal treatment at 900 °C in argon. The same procedure was applied with the carbon nanotubes having the original length.

middle FR spectra in Fig. 3 B and E. In an inert atmosphere at elevated temperatures surface groups decompose producing water, carbon monoxide and carbon dioxide. The diffusion barrier, posed by the functional groups, is, thus, removed. This is shown by the FR spectrum of the heat-treated MWCNT-95H and -81H samples (Fig. 3 C and F). The in-phase and out-of-phase components of FR response functions intersect suggesting that the rate controlling diffusion resistance has been removed by the high-temperature treatment and adsorption-desorption becomes again the rate-governing process. However, it should be noted, that the resonance signal now appears at lower frequency than in the spectrum of the parent MWCNT-95 and -95B samples, indicating that the sample is not the same as before the treatments. The removal of O-containing group from the carbon nanotube surface leaves defects which can introduce new sites for sorption.

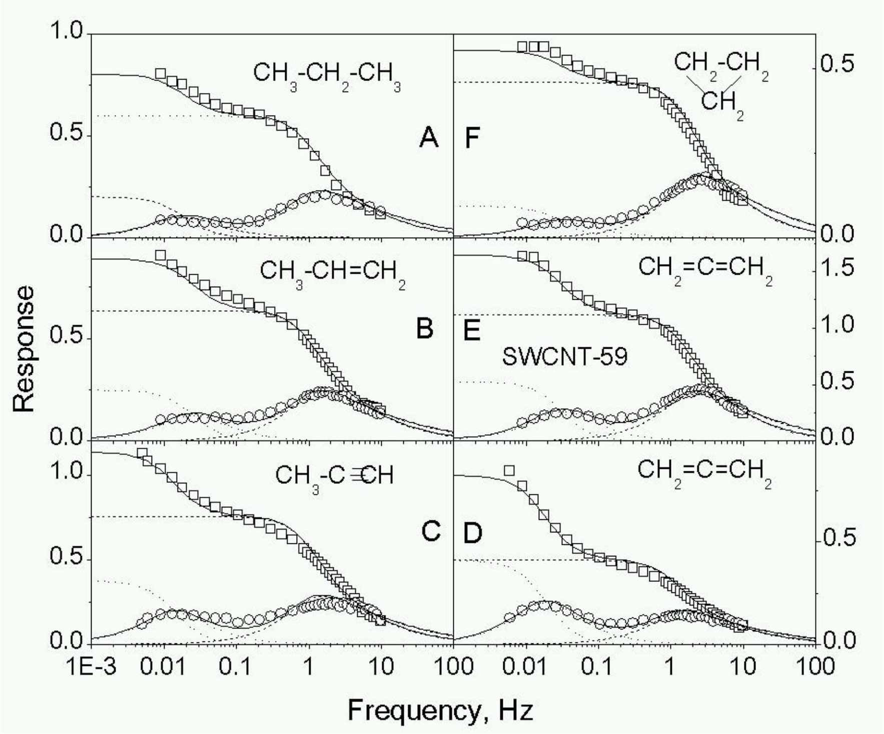

Fig. 4. FR rate spectra for the sorption of various C_3 hydrocarbons, recorded at 0 °C and 133 Pa using 200 mg of <150- μm size particles on sample MWCNT-81 and SWCNT-59.

Fig. 4 demonstrate that on MWCNT-81 and SWCNT-59 samples at low coverage mass transport is only slightly affected by the different chemical nature of the various C_3 hydrocarbons. For all probe molecules and CNT preparations results suggest that two parallel sorption processes with distinctly different time constants are present. These processes were assigned to sorption on the convex and concave surfaces of the carbon tubes. The FR measurements showed that oxidative treatments changed the rate-controlling mechanism of mass transport inside the carbon nanotubes from one of sorption to one of diffusion (see the high frequency signals in Fig. 4). Also the strength of the adsorbate-surface interactions changes depending on the chemical nature molecules of similar size resulting in different coverages. The FR signal intensities reflected these different sorption capacities for the different hydrocarbons containing three C atoms. The intensity ratios of the two components in the FR spectra significantly depend on the structure of the probe molecules. The coverage of the convex, outer surface of the carbon nanotubes compared with the concave walls increases on going from none to one and, then, two double bonds or on the introduction of a triple bond. The shortest C_3 hydrocarbon; i.e. cyclopropane, is less preferred on the outer walls.

Allene FR spectra are compared in Fig. 4 D and E, on singlewall and multiwall CNTs. The significantly different ratios of the two spectral components reflect the different character of two different carbon nanotube structures. FR seems to be very powerful technique for characterization such complex gas-solid systems.

However, the rates and the mechanism of mass transport of the different C_3 hydrocarbons are quite similar on a given CNT sample. The diffusivities through nanopores of oxidative treated MWCNT-81 were little different for the isomers and were found to be invariant of the hydrocarbon pressure in the range of 60-600 Pa substantiating that Knudsen type diffusion prevailed. The behavior of cyclopropane, however, seems to be different giving a resonance at significantly higher frequencies. The faster diffusion of this molecule must arise from its shorter length and more spherical shape.

Since the sorption dynamics behavior of chemically, quite different, hydrocarbon probes of similar molecular mass is quite similar we can conclude that the application of the FR technique for quality control of CNT product samples is not dependent on specific properties of the probe molecule. All of the hydrocarbons used in this study seem to be suitable as probe molecules for FR rate-spectroscopy. However, propane, as the chemically less reactive species would seem to be the preferred probe.

3. Conclusion

FR rate “spectroscopy” has been shown to be an effective method to characterize the dynamics of sorption in carbon nanotubes.

Various nanotube samples showed distinctly different resistances to sorption mass transport. Two parallel sorption processes can be distinguished and assigned. These two processes characterized by different sorption capacities and time constants were assigned to sorption on the convex outer and concave inner surfaces of the carbon tubes, respectively. The results suggest that, at low sorption coverage, the dynamic sorption properties of the nanotubes are strongly affected by structural defects and by the presence of oxygen-containing functional groups on both kind of surfaces, generated mainly during the purification of the nanotubes. Hydrocarbon probes which are smaller by one order of magnitude compared to the size of the mesopores inside the carbon nanotube sorbents showed quite similar behaviour.

Propane seems to be the best probe for the fast dynamical characterization of CNT products by the FR technique.

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