



The dynamics of H₂ and N₂ sorption in carbon nanotubes

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Abstract

Single-walled and multi-walled carbon nanotubes (SWNT and MWNT) were prepared by catalytic decomposition of methane and acetylene, respectively. The resulting catalyst/carbon composites were subjected to chemical treatments to obtain samples which were enriched in nanotubes. Isotherms and frequency response (FR) spectra of N₂ and H₂ were recorded at 195 and 77 K, respectively, in the 1–800 Pa pressure range. The adsorption isotherms for N₂ were found to obey Henry's law, while the isotherms of H₂ adsorption indicated some energetic heterogeneity of the sorption sites. Stronger adsorbate–substrate interaction was detected for those samples which had been subjected to oxidative treatment. The FR measurements showed that treatment of MWNT in KMnO₄ solution changed the rate-controlling mechanism of mass transport from one of sorption to one of diffusion. Results substantiated that the surface functional groups, generated by the oxidative treatment, have significant influence on both the equilibrium and the dynamic N₂ and H₂ sorption properties of the carbon nanotubes.

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1. Introduction

Carbon nanotubes can be considered as intermediate in structure between graphite, comprising of flat carbon layers, and fullerenes, having spherical cavities. In nanotubes seamless tubes are formed from graphene carbon layers. The adsorption of molecules in nanotube materials is of fundamental interest because gas storage and separation technologies can benefit from a better understanding of the sorption properties. However, only computational studies are

available about the mass flow dynamics through carbon nanotubes [1]. In the present study, the frequency response (FR) method is used to experimentally characterize the dynamics of sorption mass transport in carbon nanotubes. This method has been used in numerous previous studies for examination of the mass transfer kinetics of sorptive gases in various sorbents [2]. In principle, the FR technique can give information about the mechanism of the rate-controlling transport step and can give also the dynamic parameters of this mass transport process. A unique advantage of the method is that it can distinguish parallel rate-limiting processes [3]. In a recent FR study, correlation was shown to exist between the structure of the activated carbon or carbon nanotube

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and its equilibrium, as well as, dynamic sorption behavior [4]. In the present work, different purification procedures were applied to recover nanotubes from preparations, obtained by catalytic methane or acetylene carbonization. The results of the FR examination suggests that both the kinetic and the equilibrium sorption properties of the samples depend on the nanotube structure and is affected, also, by the functional groups that can be present at structural imperfections and at the orifices of the tubes.

2. Experimental

Carbon nanotubes were prepared by catalytic chemical vapor deposition (CCVD) of hydrocarbons [5]. The TEM examination of the 4 wt.% carbon/Co-magnesia, obtained by catalytic methane carbonization, showed that the sample contains SWNT. With reference to the type of the nanotube and the carbon content of the sample, the sample was designated to SWNT-4. The SWNT-59 sample was obtained from the SWNT-4 by dissolving most of the catalyst using HCl solution.

The acetylene carbonization over alumina-supported Co/Fe catalyst resulted in a material containing 47 wt.% carbon. Since the carbon was present mainly in the form of multi-walled nanotubes, the sample was designated to MWNT-47. The carbon was recovered from the MWNT-47 sample by dissolving the catalyst in two steps: first using NaOH and then HCl solution. The carbon-rich product was designated as MWNT-95. Sample MWNT-95B was prepared by ball-milling the sample MWNT-95. The carbon impurity of the MWNT-95B sample, including the tube fragments formed during ball-milling, were oxidized to CO₂ by KMnO₄-H₂SO₄ solution. This treatment resulted in the MWNT-81 sample.

The nanotube samples were characterized by specific surface area (SSA) and by their equilibrium and dynamic adsorption properties. The SSA was calculated from the N₂ adsorption isotherm using the BET method. The FR method was used to study the dynamics of sorption transport. The FR method is a transient method, where the equilibrium of a gas–solid system is periodically perturbed and a response wave function is recorded. The in-phase (real) and the out-of-phase (imaginary) components of the response

wave function are plotted as a function of the perturbation frequency to get the FR spectrum. A resonance signal (peak and step) appears in the rate spectrum at the frequency that corresponds to the time constant of a transport process. In the present study a batch type FR apparatus was used that was described in detail in Ref. [6]. A $\pm 1\%$ volume modulation was applied and pressure wave response functions were recorded at different modulation frequencies. The adsorption isotherms of the gases were determined by a volumetric method.

3. Results and discussion

The surface area was related to the carbon content of the sample. The SSA of the carbon (SSAC) was found to be different for the SWNT samples (SSAC = 700–800 m²/g) and for the MWCT samples (SSAC = 200–250 m²/g), but was virtually invariant to the carbon content and to the applied chemical/and mechanical treatment of the sample. These results suggest that the surface of the catalyst and the carbon impurities make minor contributions to the measured surface. Moreover, both the outer and the inner surfaces of the nanotubes are accessible for nitrogen adsorption in all of the studied preparations.

Isotherms and FR spectra of N₂ adsorption are shown in Fig. 1. The amount of N₂ adsorbed was proportional to the pressure, demonstrating the energetic homogeneity of the of N₂ adsorption sites (Fig. 1A). Under the FR conditions (196 K, 133 Pa) the N₂ uptake was about a 10⁻³ fraction of the amount of N₂ adsorbed in a monolayer. This low coverage was perturbed by a $\pm 1\%$ pressure modulation. Consequently, the sorption process characterized by the FR spectra (Fig. 1B–D), concerns a very small fraction of the highest energy sorption sites. The FR intensity must correspond to the sorption capacity related with the perturbed process. Accordingly, the FR intensities were found to parallel the slopes of the isotherms (Fig. 1). A unique potential of the FR method is that it can provide, at least for simple systems, information about the rate-controlling mechanism of the sorption mass transport [7]. If the in-phase and out-of-phase component curves of the FR spectrum intersect at the maximum of the peak and the half height of the step then sorption can be substantiated as the slowest

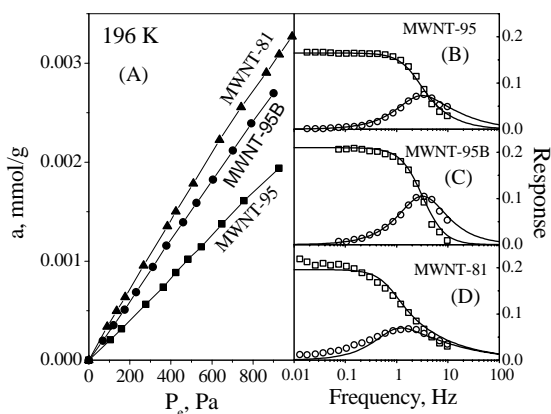


Fig. 1. (A) Isotherms and (B–D) FR spectra of nitrogen sorption over MWNT samples at 196 K. Samples were pretreated by 1-h evacuation at 573 K. The FR spectra were recorded at 133 Pa using about 500 mg of 500–150 μm size nanotube particles. Symbols correspond to in-phase (\square) and out-of-phase (\circ) components of the experimentally determined response functions. Full lines represent the best-fit characteristic curves.

process step (Fig. 1B and C). The asymptotical approach of the component curves at the high frequency side suggests that the rate of diffusion governs the transport rate (Fig. 1D). Similar spectra were recorded for sample MWNT-47, MWNT-95 and MWNT-95B. A remarkable finding of this work is that the oxidative treatment induced a significant change in the equilibrium and the dynamic adsorption properties of the sample. The strength of N_2 adsorption increased (Fig. 1A) and the rate of sorption mass transport decreased (Fig. 1B–D). The FR spectrum of the MWNT-81 sample, shown in Fig. 1D, suggests that the diffusion to the sorption sites was the rate-controlling step of the process. The diffusivity was found to be independent of the N_2 pressure in the range of 100–800 Pa, suggesting that Knudsen type diffusion prevails. A previous study correlated the strength of N_2 adsorption with the curvature of the adsorbing graphene layers [8]. The different sorption properties of our MWNT samples can hardly be related to similar structural variances. It seems more probable that the samples differ in the concentration of the oxygen-containing functional groups, such as, COOH, OH, and C=O. The polar functional groups can increase the adsorption capacity by enhancing the solid–fluid potential. It was shown previously that ball-milling in air and/or treatment in oxidizing agents, such as,

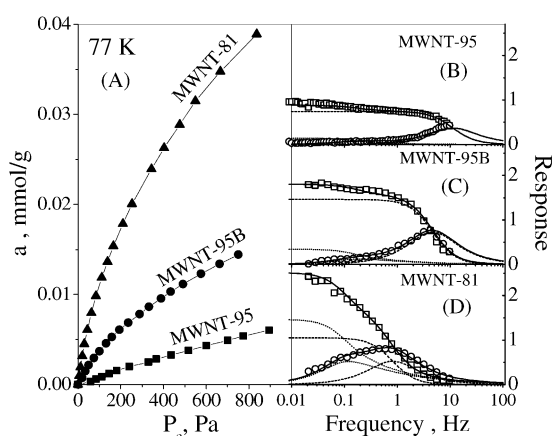


Fig. 2. (A) Isotherms and (B–D) FR spectra of hydrogen sorption over MWNT samples at 77 K. See the legend of Fig. 1 for details. The dotted lines give the FR spectra, resolved for parallel processes.

HNO_3 or KMnO_4 solutions introduce oxygen-containing functional groups, which terminate the ends of the fractured tubes and link to imperfections on the tube walls [9,10]. The sorption site functional groups, forming domains at the orifices of the nanotubes, are suggested to be responsible for the increased diffusion resistance of the oxidized MWNT-81 sample.

At 195 K and 133 Pa H_2 pressure the sorption capacity was too low to record the FR spectra of sorption. Isotherms and FR spectra of H_2 adsorption, determined at 77 K are shown in Fig. 2. Above the pressure of the FR experiment the isotherms start to deviate from the Henry's law (Fig. 2A). The single FR resonance obtained for the MWNT-95 can be assigned to a mass transport process governed by the rate of sorption (Fig. 2B). The presence of the oxygen-containing functional groups seems to be detected more sensitively by the H_2 sorption than by the N_2 sorption measurements. The appearance of the weak resonance signal at lower frequency can be attributed to the presence of functional groups, introduced during the ball-milling procedure (Fig. 2C). With increasing extent of the oxidation the intensity of the low-frequency resonance increased. FR resonance signals of two parallel processes could be resolved: into a slower diffusion and a faster sorption process (Fig. 2D). The parallel sorption processes, having different rate-controlling mechanisms, demonstrate that the sample

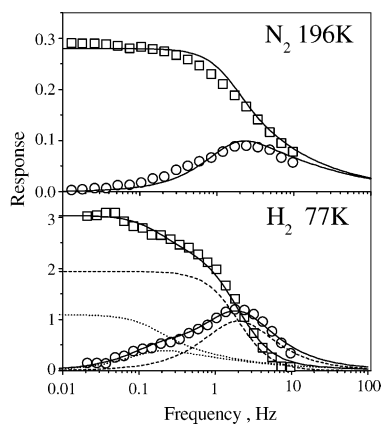


Fig. 3. FR spectra of N_2 and H_2 sorption over the SWNT-59 sample. See the legends of Figs. 1 and 2 for details.

comprises of two groups of nanotubes that are functionalised to distinctly different extents.

The FR spectra, characterizing the dynamics of N_2 and H_2 sorption over the SWNT-59 sample, was very much similar to those obtained for the MWNT-81 sample (cf. Figs. 1D, 2D and 3), suggesting that functional groups play a decisive role in determining the interaction of the adatoms and SWNT surface.

4. Conclusions

Oxygen-containing functional groups are generated on the carbon nanotubes during ball-milling the

nanotubes in air and/or during the procedure of chemical purification. At low adsorption coverage the equilibrium and dynamic sorption properties of the nanotubes are strongly affected by the surface functional groups.

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