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The Sorption Dynamics of C_3 Hydrocarbons over Carbon Nanotubes

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1. Introduction

Since some of the possible applications of carbon nanotubes involve gas diffusion and sorption, the equilibrium and the dynamic adsorption properties of these materials have been intensively studied. The sorption over carbon tubes can be easily described by theoretical methods, such as, molecular dynamics and/or Monte Carlo simulations [1]. The results obtained, however, have to be tested against experimental results determined for real nanotube preparations. 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 [2]. An outstanding advantage of the FR method is its capability to distinguish different molecular mobilities which may be present in the system. 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 [3]. The aim of the present work was to learn more about the sorption and diffusion of C_3 hydrocarbons, such as propane, propene, propyne, allene and cyclopropane in different carbon nanotube preparations by taking advantage of the unique potentials of the FR technique.

2. Experimental

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 part of the Co/MgO using concentrated HCl solution. The multi-walled carbon nanotubes (MWNT) were prepared by the catalytic decomposition of acetylene over a Fe,Co/Al_2O_3 catalyst. From the MWNT-containing material the Fe,Co/Al_2O_3 was dissolved by subsequently applying NaOH and HCl solutions. Another sample was obtained by ball-milling the purified MWNT in air. 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 pure form the amorphous carbon was oxidized to CO_2 with $KMnO_4$/H_2SO_4 solution. Preparations were characterized prior to and after the applied treatments.

The sorption dynamics were studied using a batch type FR system, described by Rees *et al*. [4]. The temperature and pressure of the measurements were 273 K and 133 Pa, respectively. Under the applied conditions the hydrocarbon uptake was only a small fraction of the amount corresponding to monolayer coverage. Thus, the sorption process, characterized by the FR spectra, concerned only a very small fraction of the highest energy sorption sites.

3. Results and discussion

The surface area of the carbon in the 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. These findings suggest that catalyst and the carbon impurities introduced only a minor contribution to the measured surface area. Moreover, both the outer and the inner surfaces of the nanotubes are accessible for N_2 adsorption in all of the studied preparations.

The rate spectra, recorded under identical conditions for the SWNT and MWNT samples were similar except for the signal intensities. The intensities reflected the sorption capacities of the samples, having different surface areas, as well as the different sorption capacities for the different hydrocarbons containing three carbon atoms. Results suggested two parallel sorption processes with distinctly different time constants. These processes were assigned to sorption on the convex and concave surfaces of the carbon tubes. The adsorbing areas are consistent with the surface areas of the outside and inside of the tubes. However the energetics of these surfaces are quite different. The FR measurements showed that treatments in oxidative medium changed the rate-controlling mechanism of the mass transport from one of sorption to one of diffusion. Results substantiated that the surface functional groups generated have significant influence on diffusional resistances of the different samples. Also the strength of the adsorbate-surface interactions changes depending on the chemical bonds present in these C_3 hydrocarbons resulting in different coverage. The diffusivities were little different for the various isomers, supporting the conclusion that Knudsen type diffusion prevailed.

4. Conclusion

It can be concluded that various nanotubes samples, represent distinctly different resistances to sorption mass transport. The results suggest that, at low sorption coverage, the dynamic sorption properties of the nanotubes are strongly affected by the structural defects and the oxygen-containing functional groups, generated mainly during the purification procedures. The FR rate "spectroscopy" proved to be an effective method to characterize the dynamics of sorption in carbon nanotubes.

References

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