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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