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Desorption kinetic detection of different adsorption sites on opened carbon single walled nanotubes: The adsorption of *n*-nonane and CCl_4

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Abstract

We show that thermal desorption kinetics clearly resolve adsorbates bound in different sites on single walled carbon nanotube bundles. The molecules *n*-C_9H_{20} and CCl_4 were compared and it was found that the nanotube internal sites exhibited the highest desorption temperature, whereas external groove sites exhibited the next highest desorption temperature for both molecules. When *n*-C_9H_{20} and CCl_4 coadsorb, the more strongly bound *n*-C_9H_{20} quantitatively displaces CCl_4 from internal sites to groove sites. Molecular shape governs the capacity of the different sites for the two molecules.

1. Introduction

The nature of adsorption sites in and on carbon nanotubes, and how the adsorptive properties of the material can be enhanced by its modification, has been addressed in a number of studies [1–12, and references therein]. The interest in adsorption on nanotubes stems partly from their relative uniformity as compared to such widely used materials as activated carbons, and the fact that the curvature of the nanotube walls results in high binding energy for molecules bound on internal adsorption sites, and in groove sites between adjacent nanotubes [10,13].

Previous studies in this laboratory [14,15] showed that etching with O_3 can open both end cap and wall entry ports in closed nanotubes permitting adsorption into the nanotube interior. Vibrational spectroscopy experiments with the simultaneous adsorption of two molecules showed that a more polarizable Xe molecule displaces CF_4 from the interior of the nanotubes [11].

In this Letter we present an investigation of the adsorptive properties of opened single walled carbon nanotubes (o-SWNTs) by temperature programmed desorption (TPD) of two dissimilar molecules, CCl_4 and *n*-C_9H_{20}. Previously we have shown that TPD is a useful analytical method to observe adsorption in o-SWNTs [9,16]. While CCl_4 is a compact almost spherical molecule, *n*-nonane is a long chain alkane that is approximately twice as long as the diameter of a CCl_4 molecule. This difference in molecular shapes leads to interesting configurational effects in the external linear groove sites in SWNT bundles.

2. Experimental

The single walled carbon nanotubes were produced by R.E. Smalley and collaborators [17,18] using the pulsed laser vaporization technique. The average diameter of the nanotubes was 1.3 nm. Purification by

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HNO_3/H_2SO_4 treatment was employed to remove catalyst particles and graphitic impurities. The purification step also results in chemical cutting of the nanotubes, giving o-SWNTs with a most probable length of 320 nm [19].

The sample consisting of approximately 36 μg of nanotubes was deposited onto a 0.5-mm thick gold support plate from a suspension in dimethyl formamide. The gold plate measuring 10×14 mm is part of a sample holder assembly allowing precise and reproducible heating and cooling of the sample as well as translation inside the vacuum system. Heating is accomplished by passing current through two tungsten wires supporting the gold plate. Prior to adsorption the sample is cooled to 100 K (or 120 K, in the case of n-C_9H_{20}) via thermal contact with a liquid nitrogen-filled tube which acts to support the sample holder. Temperature is measured by a type K thermocouple attached to the Au support plate.

An identical gold plate containing no nanotubes was used as a blank reference to monitor the desorption from the gold itself compared to desorption from the nanotubes. Non-multilayer adsorption on the Au support plate was found to be less than 1% of that observed on the SWNT samples.

Before adsorption experiments the sample and reference plate were annealed at 1073 K to decompose oxygen-containing functional groups that might be present on the nanotubes. Such groups had earlier been shown to prevent transport of the molecules into the interior of the nanotubes [20]. The annealing step also serves to remove adsorbed background gas molecules such as water that might have accumulated on the nanotube material left for extended periods of time in vacuum.

Experiments were performed in an ultrahigh vacuum (UHV) chamber with a base pressure of 2×10^{-10} Torr. A collimated molecular beam doser with a limiting pinhole conductance [21,22] was used to deliver the adsorbates to the surface. The delivery rate at the sample surface was 9.6×10^{12} molecules $Torr^{-1}$ s^{-1} cm^{-2} for n-C_9H_{20} and 8.8×10^{12} molecules $Torr^{-1}$ s^{-1} cm^{-2} for CCl_4. The limiting doser conductance was absolutely calibrated with CCl_4 and Xe using careful measurements of the rate of depletion of a standard volume[1].

After dosing, the sample is positioned in front of a shielded quadrupole mass spectrometer (QMS) and the temperature is linearly ramped at a rate of 2.0 K s^{-1}, leading to the desorption of the adsorbate molecules. A shield encloses the mass spectrometer source used to detect desorbing molecules through an aperture (3 mm in diameter) which is reproducibly positioned ~1 mm from the nanotube deposit on the Au support plate. The end cap of the QMS was biased to −100 V to prevent stray electrons from the ionization source from reaching the sample.

The apparatus and procedure for automated exposure to adsorbate and for acquiring the TPD data automatically and with high reproducibility are described elsewhere [23].

3. Results

Two types of experiments were carried out. One group of experiments involved probing the desorption kinetics of individual adsorbates as a function of exposure to the gas of interest, while the other focused on coadsorption of n-C_9H_{20} and CCl_4 to observe displacement effects.

Temperature programmed desorption spectra obtained for increasing exposures of both n-C_9H_{20} and CCl_4 are given in Figs. 1 and 2, respectively. Here, only one adsorbate is dosed onto the SWNTs.

Four overlapping spectral peaks (labeled with letters A to D) can be seen in the nonane desorption spectra, indicating the presence of four accessible environments for adsorbed n-nonane molecules, each desorption process having different characteristic desorption temperatures. As is often the case, at low exposures only the sites with high desorption temperatures are occupied. At higher exposures a sequence of desorption peaks at monotonically decreasing temperatures is observed.

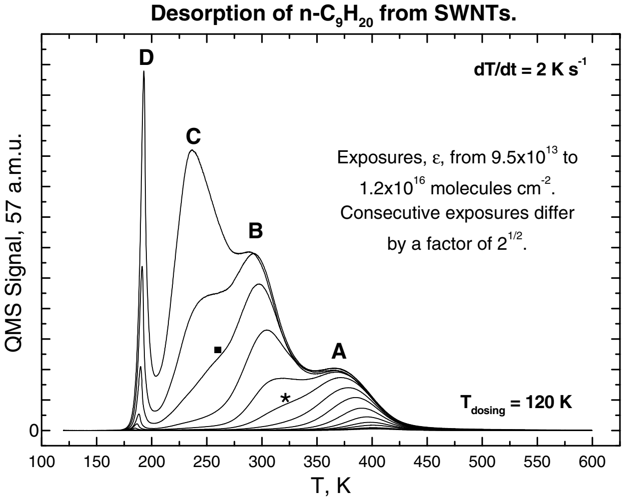

Fig. 1. Desorption of n-nonane from nanotubes for a range of exposures. Four resolved spectral features are evident, labeled A, B, C and D. The ∗- and ■-labeled traces correspond approximately to the completion of filling of sites which contribute respectively to the A and B desorption processes.

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[1] The CCl_4 and Xe conductance values were found to scale inversely with the square root of the molecular weight, as predicted by the effusion equation, to within ~1% accuracy. The doser conductance for n-C_9H_{20} could not be measured directly due to interfering effects of gas adsorption on doser system walls, as the dosing pressure was close to the saturation pressure of n-C_9H_{20}. The n-C_9H_{20} value was calculated from the CCl_4 value using the inverse square root of mass law.