

Effect of carbon nanotubes' crystal structure on adsorption kinetics of small molecules

An experimental study utilizing ultra-high vacuum thermal analysis techniques

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Abstract The effect of carbon nanotubes' (CNT) crystal structure on chemical reactivity has been studied in much detail in the liquid phase using CNT suspension. This type of information is pertinent for developing CNT separation strategies. However, few experimental studies are available providing data for gas–CNT interactions utilizing ultra-high vacuum (UHV) surface science techniques. Structure–activity relationships (SAR) for gas–surface interactions are important for sensor designs and heterogeneous catalysis exploring, for example, CNT's potential as a support for fuel cell catalysts. We report on UHV kinetics experiments with single-wall metallic, semiconducting, and mixed CNTs in order to provide the experimental basis to correlate CNT's crystal structure and chemical activity. Thermal desorption spectroscopy (TDS), a simple temperature ramping technique, has been used to determine the binding energies of a number of probe molecules including alkanes, alcohols, thiophene, benzene, and water on CNTs at UHV conditions. TDS allows for the identification of adsorption sites of probe molecules in CNT bundles, using gold foil or silica as a support for the drop-and-dry technique. A weak and probe molecule dependent SAR is present for adsorption inside the CNTs but not for the population of external sites by the probe molecules. The experimental data are in part consistent with current theoretical predictions by other groups. In addition, the effect of different solvents (methanol, SDS, and NMP) and cleaning procedures will briefly be discussed using results of spectroscopic (Auger electron spectroscopy) and kinetic techniques. Furthermore, molecular beam scattering techniques were utilized to characterize the adsorption

dynamics, i.e., the gas-to-surface energy transfer processes of alkanes on CNTs. For example, opening the CNT tube ends by high temperature annealing, increases the so-called initial adsorption probability, that is, the probability for adsorption in the limit of zero surface concentration (coverage). This result directly illustrates the effect of large surface areas of CNTs, using internal and external surfaces, for gas adsorption.

Keywords TDS · Kinetics · CNTs · SAR

Introduction

In this invited contribution to the NATAS (North American Thermal Analysis Society) conference proceedings, I am briefly summarizing the projects of my group on single-wall carbon nanotubes (CNTs), conducted at ultra-high vacuum (UHV) conditions, utilizing typical surface science measuring techniques such as thermal desorption spectroscopy ((TDS), a thermal analysis technique), Auger electron spectroscopy (AES) [1], and molecular beam scattering [2]. We characterized the adsorption kinetics of alkanes [2, 3], alcohols [1, 4, 5], benzene [3, 6], water [6], and thiophene [7] on CNTs as well as the adsorption dynamics of *n*-butane and iso-butane on thin-supported CNT films [2]. The supports (silica [8, 9]) and highly oriented pyrolytic graphite (HOPG) [10] have been considered separately.

For most of the projects, HiPco (high pressure CO disproportionation (HiPco) [11], from Carbon Nanotechnologies Inc) CNT powders have been used as the starting material. Later on, we compared the adsorption kinetics of a few probe molecules on HiPco, CoMoCAT (from South West Nanotechnologies (<http://www.swnano.com/tech/products.php>)), and metallic-enriched CNTs, nanofabricated in Sun's group

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at Clemson University, in order to correlate CNT's crystal structure and chemical activity [6]. In addition, for the first time, molecular beam scattering data have been collected on CNTs in collaboration with Turro's group at Columbia University [2]. Surface science studies from other groups, conducted at UHV conditions, have been reviewed recently in [12]. The first UHV surface science studies on CNTs have, to the best of my knowledge, been published by the Yates and the Smalley group [13], which triggered my interest in this topic. In the meanwhile, we performed similar surface chemistry experiments on inorganic nanotubes (NT) such as TiO_2 NTs [14–16] and WS_2 NTs [17] together with the materials science and synthetic inorganic groups of P. Schmuki (Nuernberg-Erlangen University) and R. Tenne (Weizmann Institute of Science), respectively. Due to the high aspect ratio (NT height-to-width ratio) of WS_2 NT confinement effects, very similar to what was already known for CNTs were present also for the inorganic WS_2 NT. In contrast, the TiO_2 NTs synthesized by the anodization technique, behaved like porous thin films rather than NTs. This conference proceeding contribution considers only CNTs.

Experimental

Materials

In order to obtain samples which can be analyzed by means of surface science techniques, typically the so-called drop-and-dry technique is employed. Here, a sonicated and centrifuged research grade CNT suspension with SDS (sodium dodecyl sulfate) or NMP (*n*-methyl pyrrolidone), for example, is the starting material. Depending on the solvent, the sonication is eventually breaking and debundling the CNTs. The centrifugation is removing amorphous carbon and impurities such as catalyst particles. The supernatant is then used. A film of CNTs on supports, such as silica or gold foil, is formed (Fig. 1) by wetting the support repeatedly with a drop of the CNT suspensions which is allowed to dry at ambient pressure. This sample is then transferred into a UHV chamber and cleaned by high temperature annealing/flashing, which is believed to remove most of the solvent residuals. Side effects of this UHV cleaning procedure and the effect of the thicknesses of the CNT films are discussed in [1]. For example, solvent and probe molecule specific artifacts were evident. Metal supports allow for fabricating cleaner samples due to greater flashing temperatures. Silica-supported samples were not stable for flashing temperatures above 600 K, i.e., the CNTs appear to desorb. Thick CNT films either generate readsorption effects in UHV TDS experiments and/or are strongly affected by bundle formation of the CNTs, see

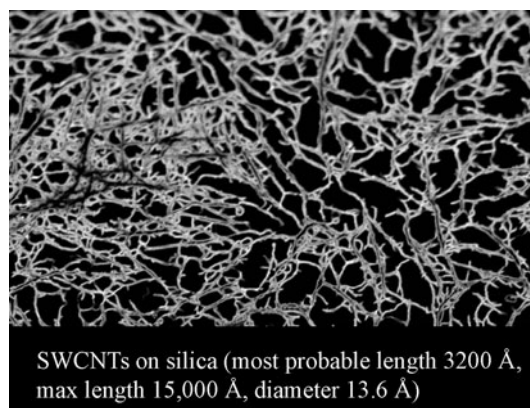


Fig. 1 Scanning electron microscopy image of a silica supported HiPco carbon nanotube sample (thin CNT films are easier to image)

[3] for details. Whether large bundles indeed affect the adsorption kinetics of probe molecules need to be further investigated. The data shown here are obtained from thin CNT films where SEM (scanning electron microscopy) images indicate at most two loosely stacked layers of CNTs, e.g. the support is still evident in SEM images. However, the total surface area of the CNTs exceeds by at least a factor of 10 the support area which suppresses any possibly occurring support effects in kinetics and dynamics data. A thin CNT layer consists of internal, external, and groove sites (Fig. 2). Typically clean samples, as judged by AES and TDS, can be obtained using metal supports, SDS, and flashing temperatures of at least 1200 K, as noted by others before. A thermal analysis technique such as TDS appears more sensitive to judge the cleanliness of the samples than a spectroscopic technique such as AES as detailed in [1]. The main source of impurities and artifacts in UHV surface science studies appears to be solvent related and not caused by the research grade CNT powders.

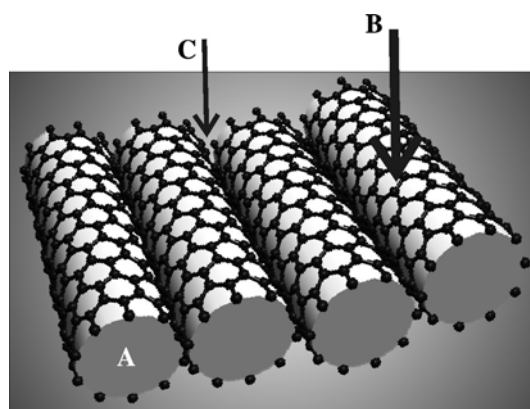


Fig. 2 Possible adsorption sites on supported carbon nanotubes bundles can be identified using a surface science thermal analysis technique such as thermal desorption spectroscopy. **A** Interior, **B** exterior, **C** groove sites

For example, we also used methanol as a solvent which results in perfectly clean samples since methanol evaporates without leaving behind any impurities in contrast to SDS. However, in this case the CNTs form large bundles which result again possibly in artifacts [3]. Thus, the cleaning of CNT samples for UHV studies remains a challenge and an experimental hassle. Despite differences in the cleanliness, whether a metal or semiconductor was used as the support had no effect on kinetics data.

Measuring techniques

Since the audience at NATAS conferences is interdisciplinary and, therefore, naturally diverse, I may briefly outline the main measuring techniques used in our studies.

TDS is a standard surface science kinetics (thermal analysis) technique, allowing for the determination of the binding energies of gas-phase species on a surface. In addition, different adsorption sites can often be identified (Fig. 2), such as adsorption on defect or pristine sites of single crystal surfaces which differ distinctly by their binding energies for some systems [18]. In a TDS experiment, the gas-phase species are dosed onto the surface at low temperatures which initially prevents desorption of the adsorbates back into the gas-phase. The amount of dosed species is given in Langmuir (L) units, 1 L equals a gas exposure of 1 s at 1×10^{-6} mbar. After the adsorption step, the surface temperature is linearly ramped and simultaneously the pressure in the vacuum chamber recorded using a mass spectrometer. Pressure versus time (temperature) curves reveal kinetics information in a simple way. For example, the higher the peak temperature of the TDS trace, the greater the binding energy. Pre-

exponential factors can be determined as well by TDS, but these are more commonly assumed or obtained in data fitting procedures. Similar sample ramping techniques are used in many diverse areas such as thermal gravimetry or differential thermal analysis. The main difference of a TDS experiment to other thermal analysis techniques is the use of an ultra-high (ultra clean) vacuum environment.

In addition, adsorption transients (pressure vs. exposure time) have been recorded using the so-called King and Wells [19] technique. In doing so, information about gas-to-surface energy transfer mechanisms is available which is commonly obtained by analyzing initial adsorption probabilities, S_0 . S_0 is the reactivity of a gas-phase species toward adsorption on the surface in the limit of zero surface

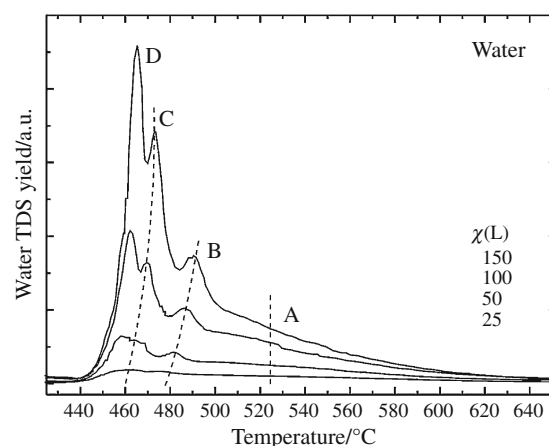
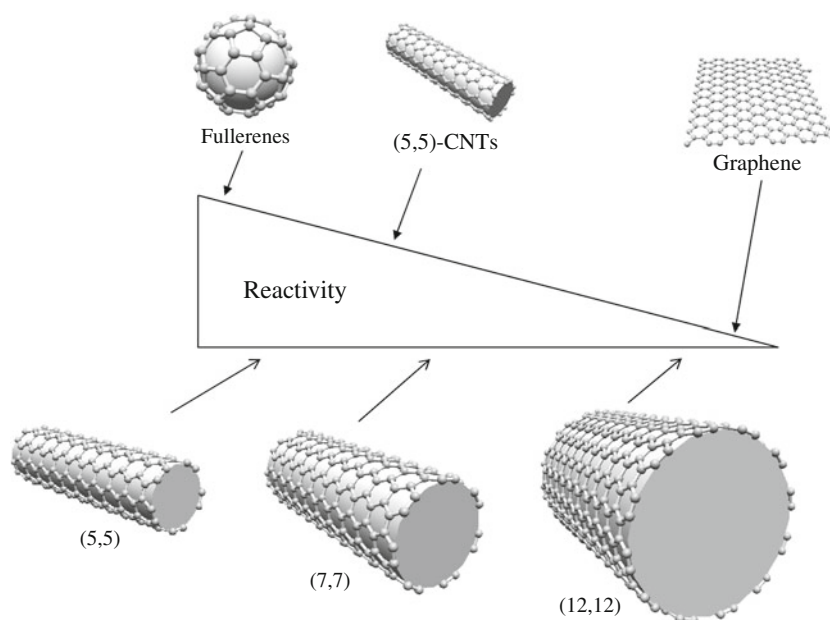


Fig. 3 Thermal desorption spectroscopy data of water adsorption on supported CNTs, as a function of water exposure, χ , given in Langmuir. **A** Internal, **B** groove, and **C** external adsorption sites. **D** condensation peak

Fig. 4 In case of strongly interacting probe molecules, theoretically predicted is an increase in binding energies of probe molecules with increasing curvature (see this figure). The opposite holds true for weakly interacting adsorbates. The CNT images have been generated with a software tool available from <http://www.jcrystal.com/>



concentration (coverage). For example, if initially 30% of the impinging gas-phase species adsorbs on the surface, S_0 equals 0.3. Integrating the adsorption transients allows for the determination of the total surface concentration (coverage) and the coverage dependent adsorption probability. Using a supersonic molecular beam allows for varying of the impact energy, E_i , of the gas-phase species and reduces the background pressure, for example. Different adsorption mechanisms such as a direct or precursor-mediated process (here particles are trapped in a weakly bond state before adsorption) result in different functional forms of $S_0(E_i)$ curves. A thermal analysis of S_0 data, i.e., collecting S_0 as a function of surface temperature, allows for the determination of reaction activation energies.

Adsorption kinetics

An example of a set of TDS data is shown in Fig. 3. Here, water has been used as the probe molecule. With increasing exposure, χ , four peaks grow in the order of their binding energy, starting with the highest desorption temperature (binding energy) feature. Very similar TDS curves have been seen by Yates and our group for various probe molecules including alkanes, alcohols, and benzene [12]. (However, NO and Xe do not generate multiple TDS peaks.) Most prior studies about water adsorption on CNTs focused on determining the structure of water in CNTs, as reviewed in [12]; kinetics parameters were not available. Following the proposal of Yates et al. (see for e.g. [13]), we assign the TDS peaks to adsorption on internal (A), external (C), and groove (B) sites of water molecules on the CNT surfaces (see Fig. 2). The low temperature peak indicates the condensation of water and is, therefore, adsorption site and sample unspecific. It can be used to calibrate the temperature reading. Tables including binding energies of various gas-phase species on CNTs can be found in [6, 12]

A large number of theoretical studies are available where the effect of CNT's crystal structure on the binding energy of probe molecules has been studied. Unfortunately, theoretical studies often consider rather exotic systems which can hardly be studied experimentally. Anyway in a nutshell, the predictions are as briefly summarized by the following: for strongly interacting adsorbates, small diameter CNTs are catalytically more active than large diameter CNTs (Fig. 4), and for weakly interacting probes, the opposite trend is theoretically predicted. (Only calculations for the outer surface of the CNTs appear to be available.) Thus, the reactivity scales with the curvature of the carbonaceous systems. This effect is basically related to the misalignment of the Pi orbitals in a curved system with respect to the bond forming orbitals of adsorbates. For a

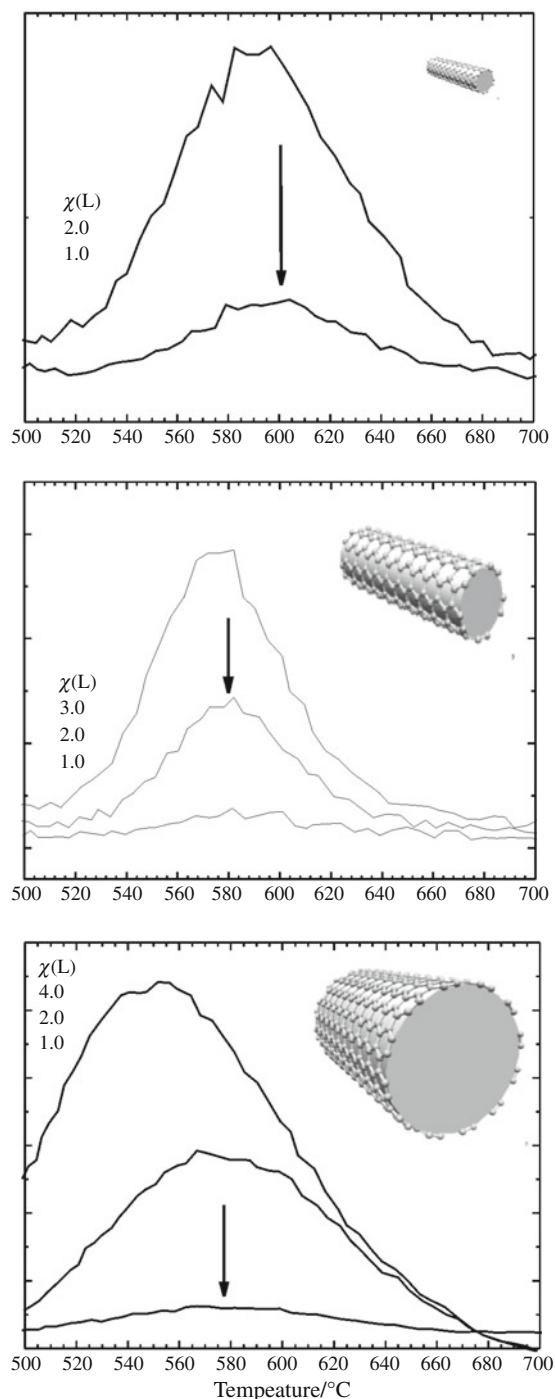


Fig. 5 Benzene TDS data. Top to bottom CoMoCAT, HiPco, and metallic CNTs. The diameter of the CNTs increases from top to bottom from 0.7 to 1.4 nm

planar system such as HOPG, the PI orbitals are perpendicular to the surface plane. See [12] for a detailed literature survey. Unfortunately, in most cases no experimental data were available to verify or deny the predictions.

An example of TDS data which can in principle close this information gap is depicted in Fig. 5. Shown are

benzene TDS curves for very small exposures where only the internal adsorption sites are populated. Slightly larger binding energies (TDS peak positions) are seen for metallic and large diameter CNTs as compared with mostly semi-conducting smaller diameter CoMoCAT CNTs. In addition, desorption temperatures as large as 300 K were present. On the other hand, no trends were evident for adsorption of benzene on external and groove sites. In this case, the binding energies are comparable with benzene's binding energy on HOPG, which is consistent with DFT (density functional theory) predictions. Unfortunately, DFT calculations for internal adsorption sites are not available at

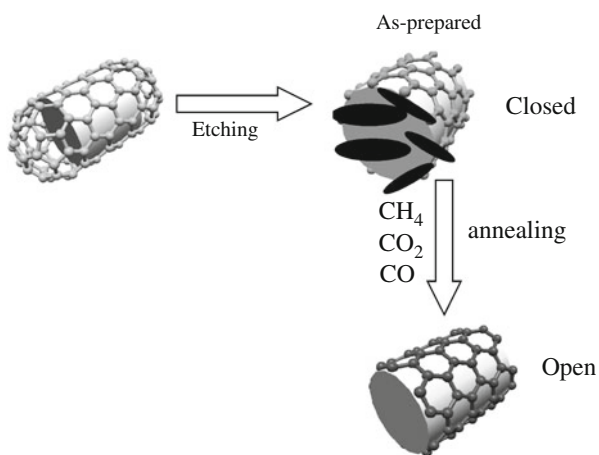
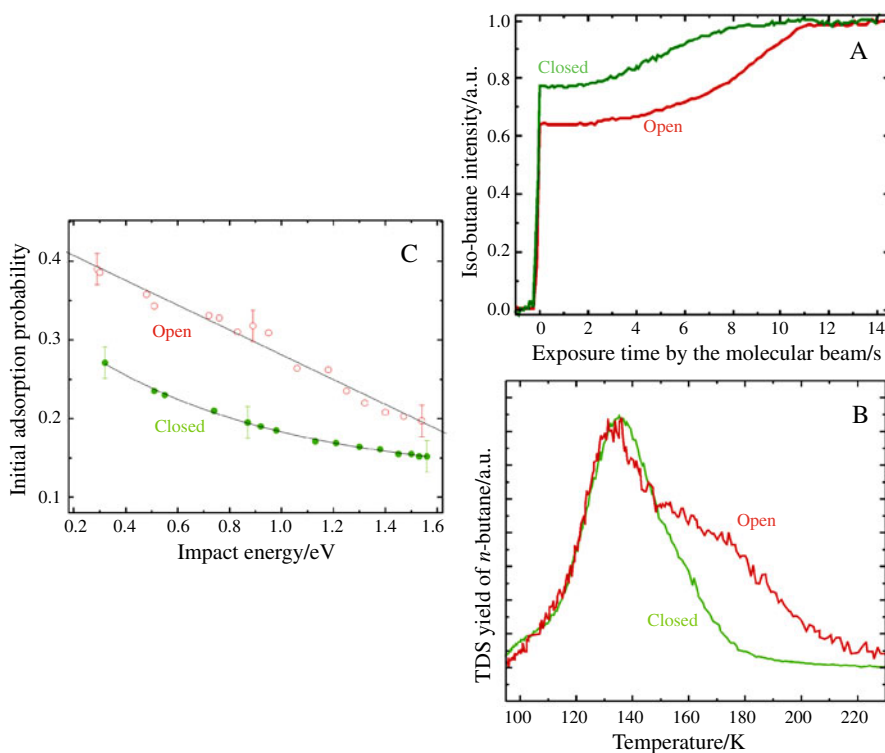


Fig. 6 Opening CNT entry ports for UHV annealing

Fig. 7 Molecular beam scattering and TDS data, see discussion



present. However, DFT appears to predict generally the opposite trend for probe molecules such as benzene which physisorb on CNTs. In this case, larger diameter CNTs should be more reactive, which is clearly not the case for adsorption on internal sites. Although the effects seen experimentally are close to the uncertainties of a TDS experiment, difficulties of DFT calculations with physisorption interactions are well known.

Adsorption dynamics

Finally, I would like to summarize briefly the results of molecular beam scattering experiments which basically indicate the effect of the large surface area of CNTs. This is one of the key advantages of CNTs when used as supports in catalysis.

As described in the “[Experimental](#)” section, the starting material consists mostly of open-end CNTs (due to sonication) but with solvent residuals attached to the CNT surfaces (Fig. 6). Desorbing solvent residuals particularly from the entry ports of the CNTs require large flashing/annealing temperatures. However, this allows for comparing closed-end and open-end CNTs simply by controlling the annealing temperature.

Figure 7A shows TDS data for samples which are nearly clean and those where the CNT ends were still blocked with solvent residuals. That this is indeed correct, is apparent from the appearance of the A peak in the TDS

data after flashing the samples to greater temperatures. Here, *n*-butane was used as the probe. If the A TDS peak is present, most of the CNTs must be open ended. If only the B and C TDS peaks are evident, the external walls of the CNTs must be reasonably clean, but the tube ends are still blocked. Similar experiments have been reported first by Yates group using TDS. Now, one can use this trick to study the effect of opening the CNT entry ports on the adsorption dynamics of, e.g., *n*-butane. This is shown in Fig. 7B.

Figure 7B depicts adsorption transients for open-ended and close-ended CNTs. Most striking, the area above the transient and below the saturation level increases by about 50% when opening the tube ends. Thus, the alkane coverage increases by 50%, as expected when all CNT ends are indeed clean after flashing the sample to just the right temperature. The inner and outer surfaces should have about the same area. In addition, the height of the initial step in the transient decreases when opening the CNT tube ends. Thus, the initial adsorption probability, S_0 , increases.

Figure 7C shows a more detailed analysis of the impact energy dependence of S_0 for *n*-butane. Indeed, open-ended CNTs have larger S_0 values, i.e., a larger initial reactivity toward the adsorption of *n*-butane. This is certainly expected since S_0 is basically the ratio of exposed molecules to adsorbed molecules. Therefore, increasing the number of possible adsorption sites while opening the tube ends increases S_0 . This effect is opposite to the well-known site-blocking effect in catalysis by catalyst poisoning.

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