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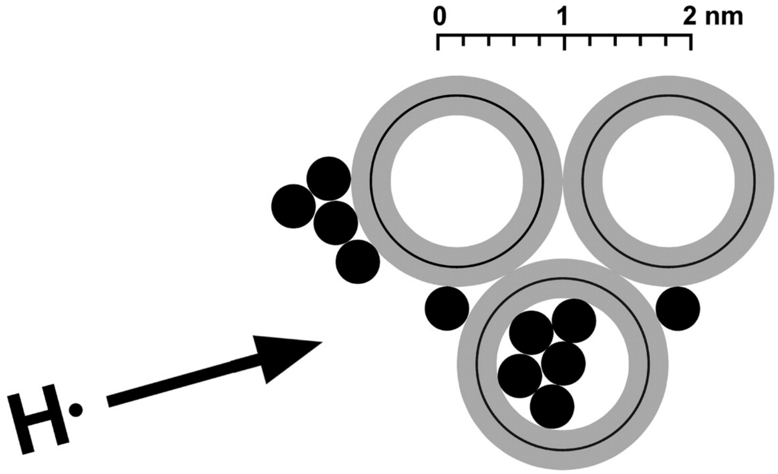

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Effects of Molecular Confinement inside Single Walled Carbon Nanotubes on Chemical Reactivity − Atomic H + 1-Heptene

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Abstract: It has been demonstrated that the confinement of physisorbed 1-heptene molecules inside of carbon single walled nanotubes (SWNTs) results in lowering of their reactivity to atomic hydrogen compared to 1-heptene molecules adsorbed on external SWNT sites.

Introduction

For a variety of molecules, the most energetically favorable adsorption site on carbon single walled nanotubes is the nanotube interior.[1−3] Such internally bound molecules may be discriminated from outside-bound molecules by several experimental methods.[4−11] In contrast to some other high area adsorption substrates (such as activated carbon), the adsorption sites on SWNTs are well defined and possess relatively narrow ranges of adsorption energies. This allows the selective population of particular nanotube adsorption sites to be accomplished by appropriately choosing the adsorption temperature. The nanotubes also have the advantage of being largely chemically inert, exposing unreactive graphite-like surfaces and binding molecules only by van der Waals forces.

Since confined molecules adsorbed in the interior are more sterically shielded than those adsorbed on external adsorption sites, it can be expected that they will be less reactive toward reactants arriving from the outside. Here we study the relative rates of reaction of interior- and exterior-adsorbed 1-heptene undergoing hydrogenation by hydrogen radicals arriving from the gas phase. Extending the results described here to reactions in solutions may potentially open up uses for carbon nanotubes as a means of controlling molecular reactivity in synthetic chemistry.

The area of supramolecular chemistry offers conceptually analogous cases of the shielding of molecules from chemical reactions. As reported by Körner et al.,[12] a nanoscopic self-assembled cylindrical capsule derived from resorcinarenes was able to enclose dibenzoyl peroxide molecules preventing a reaction with reducing agents present in the ambient solution. Nanotubes consisting of amphiphilic molecules,[13,14] zeolites,[15] as well as dendritic supramolecular assemblies[16] and ligand-created cavities[17,18] have all been studied with a view to molecular encapsulation.

Results and Discussion

Figure 1 shows the ultrahigh vacuum (UHV) apparatus used for these studies. A sample of ~13.6 Å diameter SWNTs (mass = 24 μg)[19] supported on a gold plate may be reproducibly positioned in front of a collimated and calibrated effusive beam doser for quantitative dosing of 1-heptene onto the nanotube sample.[20,21] Before the temperature programmed desorption (TPD) experiments, the SWNTs are heated in vacuum to 1073 K, a procedure which removes carbonyl and ether groups which are initially present on SWNTs.[22,23] Adsorption on SWNTs, followed by TPD, reveals that a hierarchy of adsorption sites,

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(19) The diameter of the single wall carbon nanotubes in the sample averaged 13.6 Å, with the most probable length being ~320 nm. They were prepared by laser ablation[38,39] and purified by treatment with aqueous HNO_3 and H_2SO_4.[40] Such an oxidative purification procedure causing the removal of strained end caps, as well as wall etching which leads to chemical cutting,[41] has earlier been shown to enable molecular access into the interior.[42]

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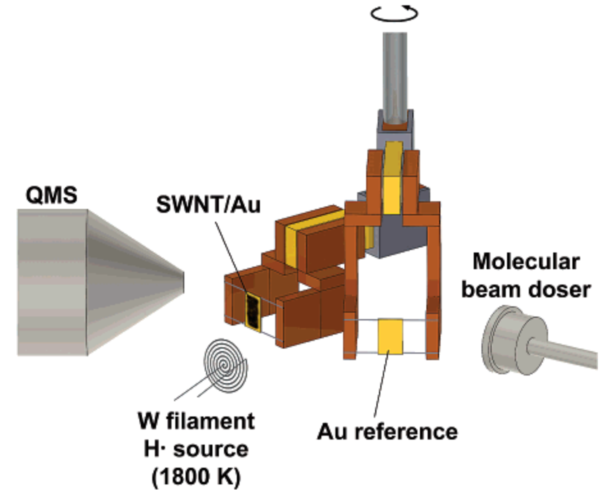

Figure 1. UHV apparatus for study of the adsorption and desorption of molecules on single walled carbon nanotubes, and for reactivity studies with atomic H, made from H_2 (g) using a heated W filament. A blank gold plate serves as a reference.

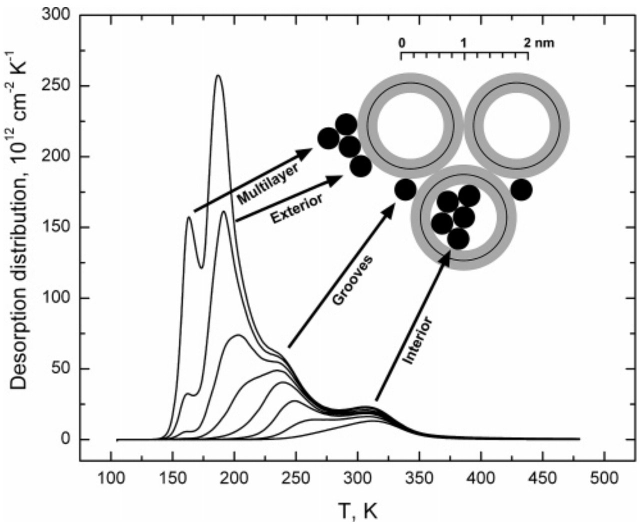

Figure 2. Temperature programmed desorption of 1-heptene from single walled carbon nanotubes for increasing initial coverages. The adsorption site locations corresponding to each desorption process are indicated on the schematic of a nanotube bundle,[24,25] where the SWNT diameter and the end-on van der Waals diameter of the 1-heptene molecules are drawn approximately to scale.

having different binding energies, is present.[24,25] Four sequential desorption processes are observed as the temperature is raised, as shown in Figure 2 for adsorbed 1-heptene. Increasing coverage leads to thermal desorption processes occurring at progressively lower temperatures as sites with lower adsorption energies become occupied.

The highest temperature process corresponds to desorption from the nanotube interior, with the maximum rate of desorption at about 315 K. The next highest temperature process, with a rate maximum at about 230 K, corresponds to 1-heptene adsorbed in the exterior groove sites which exist between nanotubes held together in bundles by van der Waals forces.[26] The third from highest state corresponds to 1-heptene bound to the convex exterior SWNT wall sites,[2] and the lowest temperature state corresponds to multilayer 1-heptene which forms on all exterior surfaces. The latter can be easily identified by the characteristic zero-order desorption kinetics that produces overlapping leading edges as the multilayer coverage is increased (not shown). Previous experiments have shown that this sequence of desorption states is observed for a number of hydrocarbons (linear and branched)[25] as well as for non-hydrocarbon molecules such as CCl_4.[24] In the case of hydrocarbons, the saturated occupation of the interior sites is controlled by the volume occupied by the adsorbing molecule, whereas the occupation of the groove sites is governed by the molecule's length,[25] as would be expected for a one-dimensional adsorption site. Control experiments from the clean gold reference were also carried out, to verify that all effects reported are due to 1-heptene adsorbed on the SWNTs.

We have selected an aggressive chemical reaction to study the effects of molecular confinement of 1-heptene on the reaction rate. The reaction of atomic H with the terminal double bond in alkenes is nearly nonactivated.[27,28] The reaction occurs readily on condensed alkene films even below 100 K, preferentially producing secondary alkyl free radicals.[29] The free radicals then undergo disproportionation by abstracting a hydrogen atom from a neighbor radical species,[30,31] producing the alkane and regenerating the alkene, as shown in eqs 1 and 2 for the case of 1-heptene.

$$C_5H_{11}CH{=}CH_2 + \dot{H} \Rightarrow C_5H_{11}\dot{C}H{-}CH_3 \qquad (1)$$

$$2C_5H_{11}\dot{C}H{-}CH_3 \Rightarrow C_5H_{11}CH_2{-}CH_3 + C_5H_{11}CH{=}CH_2 \qquad (2)$$

Thus, the production of heptane from 1-heptene may be used to monitor the reactivity of atomic hydrogen with the 1-heptene and to measure the relative reactivity of interior-bound 1-heptene compared to exterior-bound 1-heptene.

For the comparison to be carried out between the reactivities of the interior- and exterior-bound 1-heptene, selective population of the adsorption sites in question must be accomplished. In the experiments described here, exclusive population of the nanotube interior was achieved by choosing the SWNT temperature to be 270 K during 1-heptene dosing. At this temperature only the interior sites were capable of retaining the adsorbate. Alternatively, when the 1-heptene adsorption temperature is set at 215 K, both the nanotube interior sites and the exterior groove sites become populated. Following such controlled adsorption, the SWNT samples containing 1-heptene were then subjected to atomic H irradiation at 150 K.

Figure 3 shows a sequence of TPD measurements of the relative desorption rates (proportional to the amplitude of the mass spectrometer signal in a fast-pumped vacuum system as used here[32]) as increasing irradiation by atomic H occurs, for the case when both interior and groove sites are filled with 1-heptene. The atomic H is produced by a W filament at 1800 K which operates in 4.4×10^{-5} Torr (using a relative ion gauge sensitivity factor of 0.46 compared to N_2) of continuously

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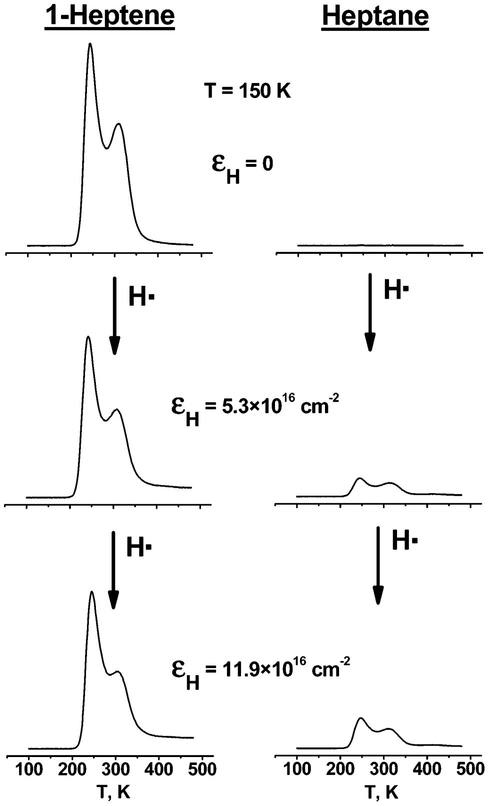

Figure 3. Series of experiments in which an identical coverage of 1-heptene, present in the interior sites and on external groove sites, is irradiated with atomic H for varying exposures, ϵ_H. The consumption of 1-heptene ($m/e = 98$ amu) and the production of heptane ($m/e = 100$ amu) is observed. Corrections have been made for the mass spectrometer sensitivity for the two molecules, so that the relative molecular population of 1-heptene and heptane may be measured from the area of the TPD spectra shown. To compare the hydrogenation rates, an identical series of experiments was also conducted for the SWNT sample with 1-heptene adsorbed only in the interior sites (corresponding to the high-temperature peak in the figure). $dT/dt = 2$ K s^{-1}.

flowing H_2[33]. The rate of bombardment by atomic hydrogen at the sample position is estimated to be ~2×10^{13} H atoms cm^{-2} s^{-1}. The sample temperature is automatically controlled by resistive heating of the Au support plate to maintain a constant temperature of 150 K during irradiation.[34]

As 1-heptene is consumed, heptane is produced. Since hydrocarbon molecule migration between different sites occurs readily when the temperature is increased during the TPD measurement, the distribution between the groove sites and the interior for the two molecules will not reflect the relative rates of hydrogenation in the two sites. Thus, it is only the amount of heptane produced that is of interest in this experiment, not the distribution between the groove sites and the interior.

When the 1-heptene is exclusively contained in the interior sites of the SWNTs, a lower rate of reaction is observed, compared to experiments in which both interior and groove sites are occupied, as shown in Figure 4.

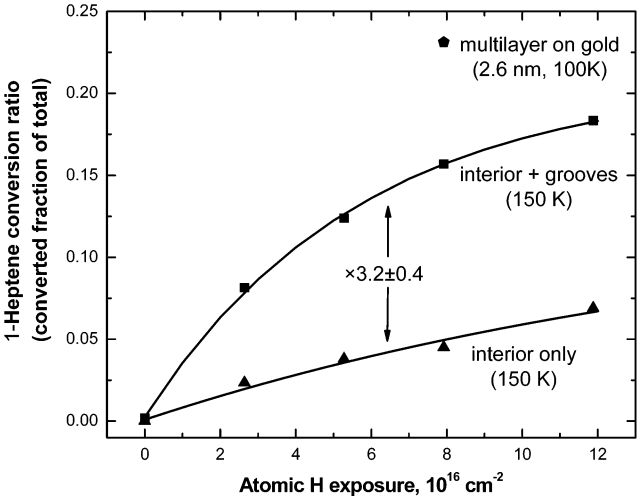

Figure 4. Fraction of 1-heptene converted to heptane by atomic H, using SWNTs containing 1-heptene in interior sites, compared to experiments involving the occupancy of interior and external groove sites.

Figure 4 shows that the reactivity of molecules exclusively in interior sites is a factor of 3.2 ± 0.4 lower than that found for nanotubes exposing 1-heptene in both interior and exterior groove sites. The single point shown in Figure 4, corresponding to a study of multilayer 1-heptene reactivity with atomic H on the Au reference surface, shows that the conversion ratio for the reaction is even higher for the unconfined 1-heptene multilayer.

These results show that confinement of a reactant molecule inside a single wall nanotube results in a substantial reduction of its reactivity with an aggressive gas-phase reactant. The observation of ***some*** reactivity for the confined molecules is probably due to the chemical opening of the tubes needed for molecular adsorption into the interior.[7,22,35] These openings provide the pathways for the H radicals to access the interior-adsorbed molecules.

It is known that the nanotubes can themselves react with atomic H.[36,37] Indeed, after exposures to H comparable to those in the experiments described above, but without any 1-heptene adsorbed on the SWNTs, we find that chemisorbed hydrogen was present on the SWNT sample. When the SWNTs were heated to 800 K, H_2 as well as hydrocarbons with between 1 and 5 carbon atoms in the chain were evolved. We could not discount the possibility that the small amount of the hydrocarbons seen was due to the cracking of the residual background of *n*-heptene (which should ideally be zero) on the tungsten filament during hydrogenation. Therefore we only used these measurements to put an upper limit on the amount of carbon lost during hydrogenation. Using the mass spectra of the evolved

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hydrocarbons and the experimentally measured QMS sensitivities toward hydrocarbons with different chain lengths, we estimated this upper limit at 0.07% of the total number of carbon atoms in the SWNTs, meaning that nanotube hydrogenation can be neglected under these conditions. This amount of carbon was also about 2 orders of magnitude smaller than the amount of carbon in the adsorbed 1-heptene molecules.

Conclusions

It was found that nanotube walls prevent atomic H species from entering and undergoing reaction with the double bonds of confined alkene molecules. This observation suggests a new use for nanotubes in which molecular confinement is used to control the chemical reactivity of a molecule.

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