Method for Supporting Platinum on Single-Walled Carbon Nanotubes for a Selective Hydrogenation Catalyst

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We have prepared a novel material, consisting of Pt particles supported on purified single-walled carbon nanotubes (SWNTs), representing the first reported metal-loaded SWNT material. The material contains 10 wt % Pt on entangled SWNT bundles consisting of 20−100 nanotubes each. The average Pt particle size is 1−2 nm. High-resolution transmission electron microscopy (HRTEM) observations combined with electron energy-loss spectroscopy (EELS) indicate chemical bonding between Pt and the SWNT surfaces. This bonding is accomplished presumably by ion exchange on carboxylic acid sites created on the nanotube surfaces by slow wet oxidation in dilute HNO_3. In addition, a simple SWNT purification scheme requiring no filtration was developed for the preparation of this material. The purification results in a well-defined structure for the metal support useful for investigating the role of this material as a heterogeneous catalyst and the effects of metal−support interactions (MSI). Preliminary kinetics measurements of the activity of this material for the selective partial hydrogenation of 3-methyl-2-butenal (prenal) to 3-methyl-2-butenol (prenol)—a representative reaction important in the fine chemicals industry—indicates the desired catalytic selectivity above 75 °C, demonstrating a utility of this material that can be optimized in future work.

Introduction

Supported Pt-metal catalysts are extremely important commercially for heterogeneous hydrogenation reactions. An important application of supported heterogeneous Pt-metal catalysts is the selective partial hydrogenation of α,β-unsaturated aldehydes. This reaction, which follows a parallel/consecutive reaction network like that shown in Figure 1 for 3-methyl-2-butenal (prenal), has great significance in the fine chemicals industry for the synthesis of fragrances, flavorings, and some pharmaceuticals such as Vitamin A.[1] In general, the C═C bond is easier to hydrogenate than the C═O bond,[2] but the unsaturated alcohol (boxed in Figure 1) is the desired product. Thus, catalysts that activate the carbonyl function on α,β-unsaturated aldehydes and promote hydrogenation of the C═O bond are necessary.

In this work, we explore the deposition of Pt on SWNTs for use in selective hydrogenation catalysts and study the role of the well-defined support material in metal−support interactions (MSI). It is well-known that the performance of supported catalysts, namely, the activity, selectivity, and lifetime, depend strongly on the choice of support. The precise details and mechanisms of how various supports affect the catalytic performance, however, are not so well understood. The reaction shown in Figure 1 serves as a test reaction for the catalyst because it is the simplest substituted α,β-unsaturated aldehyde and also because it has been the subject of extensive previous work.[3]

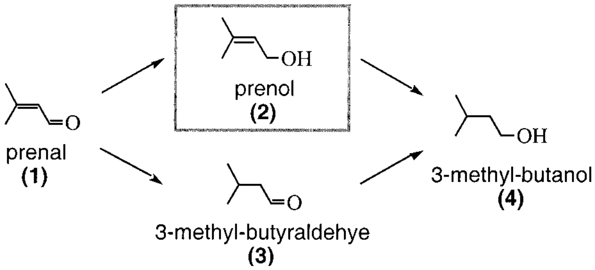

Figure 1. Parallel/consecutive reaction network of a representative α,β-unsaturated aldehyde with the desired unsaturated alcohol product indicated in the rectangle.

The inert, pristine surface of SWNTs makes a difficult substrate on which to attach metal. Physisorbed Pt can be easily removed by agitating the material in liquid (ultrasonicating), and the Pt will agglomerate into fewer larger particles as well. We chemically anchor Pt onto

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(1) Bauer, K.; Garbe, D. In *Ullman's Encyclopedia of Industrial Chemistry, Vol. A11*, 3rd ed.; Gerhartz, W., Yamamoto, Y. S., Campbell, F. T., Pfefferkorn, R., Rounsaville, J. F., Eds.; VCH: New York, 1988; p 141.

(2) Rylander, P. N. *Catalytic Hydrogenation in Organic Synthesis*; Academic Press: New York, 1979; p 72.

(3) (a) Pradier, C. M.; Berthier, Y.; Cordier, G.; Oudar, J. In *Catalyst Deactivation 1991*; Bartholomew, C. H., Butt, J. B., Eds.; Elsevier: New York, 1991; p 505. (b) Pradier, C. M.; Birchem, T.; Berthier, Y.; Cordier, G. *Catal. Lett.* **1994**, *29*, 371; (c) Birchem, T.; Pradier, C. M.; Berthier, Y.; Cordier, G. *J. Catal.* **1994**, *146*, 503; **1996**, *161*, 68. (d) Delbecq, F.; Sautet, P. *J. Catal.* **1995**, *152*, 217.

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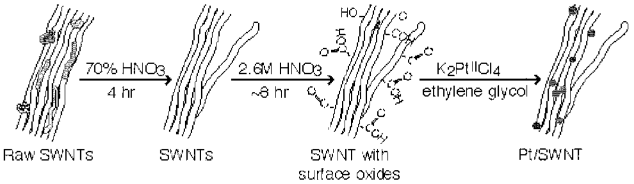

Figure 2. Schematic of catalyst preparation, showing purification by concentrated HNO_3, followed by surface oxidation in dilute HNO_3 and then Pt loading by an ion exchange reaction with surface acid groups using a Pt precursor salt in a reducing medium (ethylene glycol).

the surfaces of the SWNTs using a two-step process of wet oxidation followed by ion exchange reaction with a Pt precursor salt. A prior step of strong wet oxidation is used to purify the raw SWNT material without the use of filtration.

This paper describes the first reported metal-loaded SWNT material and the first time SWNTs have been used as a catalyst support. The material consists of 10 wt % loading of Pt, with an average Pt particle size of 1−2 nm. Each bundle of hexagonally packed SWNT contains on average 20−100 nanotubes. Preliminary kinetics experiments reveal the desired activity to produce the unsaturated alcohol (prenol) above 75 °C in the test reaction of Figure 1.

In a previous work, organometallic reactions involving the carboxylic and carbonyl groups present on the surfaces of multiwalled carbon nanotubes (MWNTs) after oxidation (see below) were used to deposit particles of U, Y, and Ag.[4] In another work, particles of Au, Pt, and Ag were deposited on MWNTs by refluxing metal precursors in HNO_3.[5]

Deposition of metal onto SWNTs using these techniques is significantly more difficult because of the greater inertness, smaller size, and higher curvature of SWNTs vs MWNTs. A very carefully controlled slow oxidation step is required, as described in more detail below. These same characteristics of SWNTs make them interesting candidate supports for heterogeneous catalysts. The structure of SWNTs is nearly perfect, even after surface oxidation, while MWNTs contain a significant concentration of structural defects in their walls. The small size, in conjunction with the high surface curvature, translates to a higher surface area-to-volume ratio and also promotes the deposition of smaller Pt particles (1−2 nm and smaller). The high curvature also significantly distorts the π-bonding of the graphene network, leading to interesting electronic properties of SWNT surfaces in terms of d-band modification. A study of the catalytic properties of Ru physisorbed on MWNTs showed an unexplained increase in selectivity for a liquid-phase reaction of the type shown in Figure 1.[6] However, the metal loading in this case was only 0.2 wt % Ru and the particles were 3−7 nm in diameter. Physical adsorption of Ru onto MWNTs is possible probably because of the large number of surface defects on MWNTs, but as mentioned above, physical adsorption of Pt onto SWNTs does not work.

Experimental Section

Catalyst Preparation. The three steps of the catalyst preparation procedure are illustrated in Figure 2. The first step is a strong oxidation in nitric acid to purify the nanotubes. This is followed by a weak oxidation to create anchor sites (surface oxides) for the Pt. Finally, Pt is attached to the surface-oxidized SWNTs by reduction of $K_2Pt^{II}Cl_4$ in ethylene glycol, likely achieving ion exchange with the hydrogen atom on carboxylic acid sites on the surfaces of the SWNTs. Using highly purified SWNTs provides a well-defined support material to allow more direct study of metal−support interactions and also prevents self-poisoning of the catalyst. The purification procedure is based on previous work,[7] modified to eliminate the need for filtration. The metal deposition procedure is partly adapted from previous works on MWNTs.[4,5] However, certain of our developments of the procedure are crucial to obtaining any Pt loading on SWNTs. For example, the conditions (acid concentration and reaction time) of the first two steps are critical because fast and slow oxidations are performed successively. The first step removes amorphous carbonaceous impurities, which tend to poison the catalyst surface;[8] the slow second step oxidizes the surfaces of the SWNTs and controls very sensitively the ultimate degree of

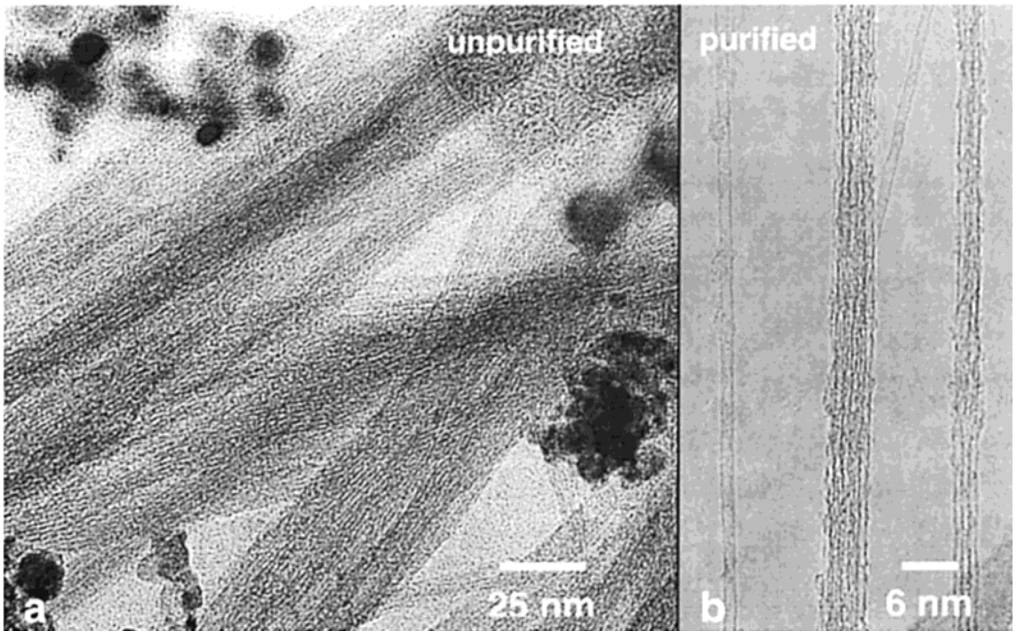

Figure 3. (a) Unpurified SWNT material consists of bundles of hundreds of nanotubes as well as carbonaceous and metal impurities. (b) The purified material contains much smaller bundles and very little impurities.

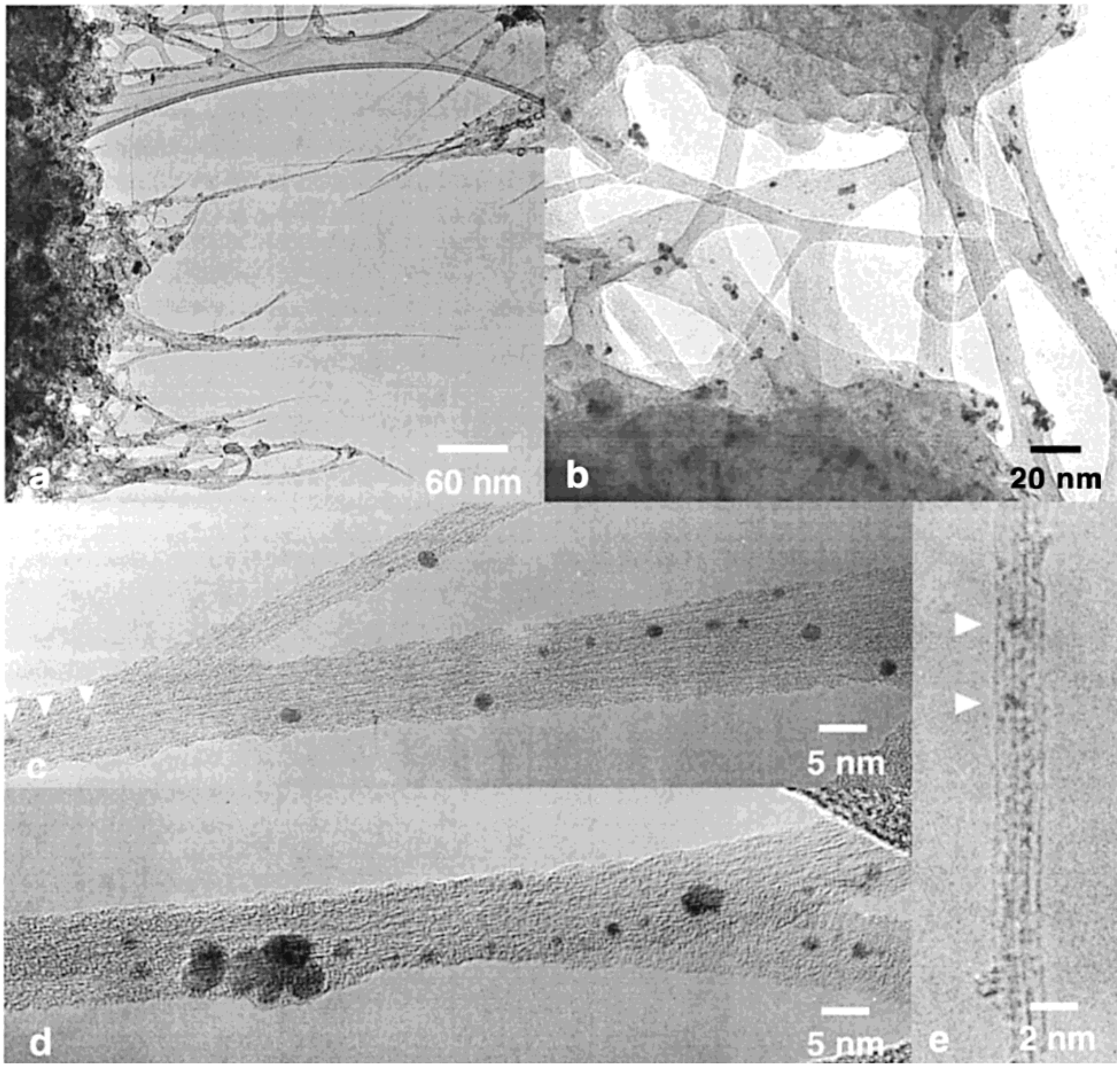

Figure 4. (a),(b) The final catalyst material consists of micron-sized clumps of entangled SWNTs covered with Pt particles. (c) A high magnification view of a single bundle showing typical loading and Pt particle sizes. (d) An example of a broad distribution of particle sizes on a single bundle. (e) The smallest particles are <1 nm, shown here attached at the interface between two SWNTs bundled together.

metal loading and dispersion.[9] The purification step also etches away some of the outer SWNTs in the bundles, so this step must be well controlled to avoid excessive mass loss.

AP-grade SWNTs (Carbolex, Lexington, KY) produced by the arc-discharge method is the raw material. Purification is performed by a 4-h reflux in 70% HNO_3 at 120 °C, using a volume of acid (in mL) approximately equal to half the mass (in mg) of the raw SWNTs. Prior to heating, the reaction mixture is ultrasonicated for 30 s using a Branson 450 Sonifier at 17−20% power to disperse the solids. This first oxidation step results in 70−80% weight loss, with mostly the carbonaceous impurities being removed. Following reflux, the reaction mixture is allowed to cool to room temperature and then is centrifuged in round-bottom tubes for 15 min at 5000 rpm. The wet solids are washed twice with deionized water (DI H_2O) and once by dilute nitric acid (∼10:1 by volume DI H_2O:70% HNO_3) by ultrasonicating the wash suspension for 5−10 s, centrifuging, and decanting. This sequence of washes accompanied by ultrasonication and centrifugation is the key to eliminating filtration from the procedure. Without filtration, ≈2 days of labor are saved and as much as 60% mass loss is avoided. The resulting purified SWNT solids are dried in an oven at 60 °C.

Surface oxidation is accomplished with ∼2.6 M HNO_3 refluxed for 8 h. After the mixture is cooled, centrifuged (15 min @ 5000 rpm), decanted, and dried at 60 °C, an additional 25% weight loss is observed. Previous XPS studies of oxidized MWNTs reveals that the surfaces become covered with carboxylic (−COOH), carbonyl (−C=O), and hydroxyl (−COH) groups in the approximate proportions of 4:2:1, respectively.[4,10] A similar surface alteration occurs with SWNTs, although the concentration of surface oxides is much lower and the walls are left essentially intact.[7] EELS study of the material also reveals the presence of surface oxides all over the SWNTs (see below). The slow, controlled oxidation step resulting in surface oxides is critical for obtaining any loading of Pt onto the SWNTs.

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(4) Ebbesen, T. W.; Hiura, H.; Bisher, M. E.; Treacy, M. M. J.; Shreeve-Keyer, J. L.; Haushalter, R. C. *Adv. Mater.* **1996**, *8*, 155.

(5) Shatishkumar, B.; Vogl, E. M.; Govindaraj, A.; Rao, C. N. R. *J. Phys. D.: Appl. Phys.* **1996**, *29*, 3173.

(6) Planeix, J. M.; Coustel, N.; Coq, B.; Brotons, V.; Kumbhar, P. S.; Dutartre, R.; Geneste, P.; Bernier, P.; Ajayan, P. M. *J. Am. Chem. Soc.* **1994**, *116*, 7935.

Finally, an 8-h reflux with K_2PtCl_4 in dilute ethylene glycol (3:2 by volume ethylene glycol:DI H_2O) at 120−130 °C deposits Pt particles onto the SWNTs. Approximately 1.5 mg of K_2PtCl_4 and 20 mL of diluted ethylene glycol are added per 10 mg of SWNTs. The final product (Pt-loaded SWNT bundles) is cooled, centrifuged, washed with DI water made slightly acidic with a few drops of HCl (a nonoxidizing acid to destabilize the suspension), centrifuged again, and then dried at 60 °C. Typical metal loading of the final material is ∼10 wt % Pt.

Transmission electron microscopy (TEM) samples were prepared by suspending the powder in acetone and dropping onto holey C-coated Cu grids. TEM was performed using a Philips CM200 field-emission gun TEM, operated at 200 kV. An attached Gatan GIF200 postcolumn energy filter was used to acquire EELS spectra. EELS spectra were recorded in diffraction mode to obtain sufficient brightness of the electron beam. Additionally, a small condenser aperture is inserted to ensure a nearly parallel beam striking the sample, while a 2 mm entrance aperture to the GIF gives maximum energy resolution. Also, the objective aperture is taken out to eliminate diffraction effects from its edges. When local EELS spectra were taken, electron beam spot sizes of 1−5 nm were used.

Kinetics Measurements. Preliminary kinetics measurements were performed in the gas phase using a heated continuous-flow glass U-tube reactor, with on-line gas chromatography for effluent analysis (8 ft × $^1/_8$ in. copper column packed with HayeSep R 80/100 @ 85 °C).[9] Before the reactor was packed, the dried catalyst was crushed to a fine powder. Experiments were done from room temperature up to 110 °C, at 1 atm total pressure, using ∼20 mg of catalyst, with a contact time of ∼0.02 (mol of reactants)/(g of catalyst)/(min). The partial pressure of prenal ranged from 0.001 to 0.02 Torr, while H_2 ranged from 400 to 700 Torr. Helium was used as both the diluent and carrier gas.

Results and Discussion

Figure 3 shows TEM micrographs of the SWNT material before and after purification. The unpurified material shown in (a) consists of bundles of SWNT containing hundreds of nanotubes each and also carbonaceous impurities both on the surfaces of bundles and agglomerated in the bulk. Large diameter (∼10 nm) metal impurities (Co and Ni) are also present from the SWNT synthesis. The purification process, both through oxidation and ultrasonication, thins the bundles and disentangles many nanotubes, increasing the surface area-to-volume ratio. About half of the original metal impurities (∼1−2 wt %) remain, but otherwise the purified material is very clean.

The second, slow oxidation step is critical to obtaining material with good Pt loading and dispersion. If this step is omitted, no metal is found to deposit on the surfaces of the SWNTs, underscoring the importance of surface oxides. Although the purification step also involves wet oxidation, the reaction with concentrated nitric acid is too fast to control. As soon as a defect (surface oxide) is formed on a SWNT, a large portion of the nanotube is subsequently etched away due to its extremely small size and high curvature. This leads to thinning of the SWNT bundles, but no surface oxide formation. The slow oxidation accomplished with dilute nitric acid can be stopped after surface oxides are formed but before significant nanotube degradation occurs. To obtain a sufficient concentration and the desired dispersion of surface oxides, the reaction needs to be overrun somewhat and so an additional mass loss occurs as a small number of outer nanotubes are etched from the bundles. The concentration of HNO_3 used in this step, and the reaction time, need to be optimized to maximize metal loading (i.e., surface oxide formation) while minimizing bulk damage to the nanotubes and mass loss.

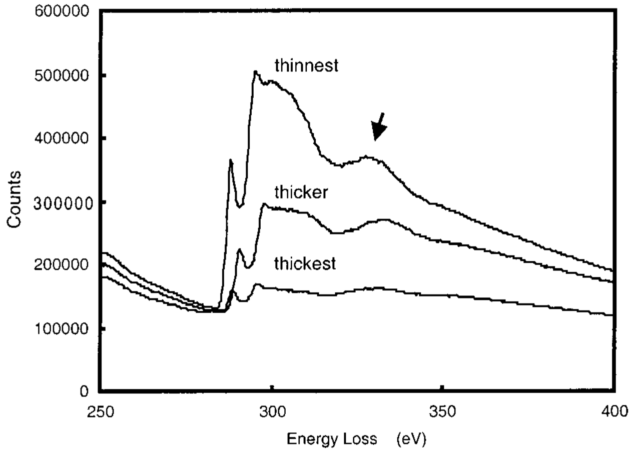

Figure 5. Series of carbon−K edge EELS spectra taken from regions with varying thickness. The relative intensity of the hump at ∼330 eV increases with the number of Pt particles sampled. The spectra are not background-subtracted and are scaled vertically to fit on one set of axes.

The final material contains 10 wt % loading of Pt on bundles of on average 20−100 SWNTs. The particles range in diameter from <1 to 10 nm, but the average size is 1−2 nm. HRTEM images of the catalyst are shown in Figure 4. Most of the SWNT bundles are entangled into micron-sized clumps, with individual bundles protruding from the edges, as seen in Figure 4a. Figure 4b shows a higher magnification view of a region where individual bundles are visible. A high magnification view of a single bundle is shown in Figure 4c, where the typical loading of 1 Pt particle per tens of nm^2 is seen as well as the typical range of particle sizes. A broader distribution of particle sizes found less commonly in samples is shown in Figure 4d. Pt particles are never observed on isolated SWNTs, but bundles containing as few as two nanotubes have been observed with Pt attached. As shown in Figure 4e, the particles in this case are attached at the interface between the two nanotubes. These observations, together with EELS data that show unreacted oxides covering the SWNT surfaces (see below), suggest that each Pt particle might be attached to at least two closely spaced oxide sites. We also note the very tiny diameters (<1 nm) of the particles in Figure 4e and those indicated by arrows in Figure 4c.

Core-loss EELS spectra for C and Pt were taken from various areas of the samples, for both large areas and focused areas of a few nm^2. No difference was found between Pt−M_5,M_4 core-loss spectra (∼2122, 2202 eV) from regions of the material with deposited Pt vs free Pt particles. However, the Pt edges do not exhibit fine structure, and at such high energies, the edge positions are only accurate to within ±7 eV, obscuring any

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(7) Dujardin, E.; Ebbesen, T. W.; Krishnan, A.; Treacy, M. M. J. *Adv. Mater.* **1998**, *10*, 611.

(8) Freifelder, M. *Practical Catalytic Hydrogenation: Techniques and Applications*; Wiley-Interscience: New York, 1971; pp 1−83, 282−312.

(9) Lordi, V. Senior Thesis, Princeton University, Princeton, NJ, 1999.

(10) Dai, L.; Griesser, H. J.; Mau, A. W. H. *J. Phys. Chem. B* **1997**, *101*, 9548.

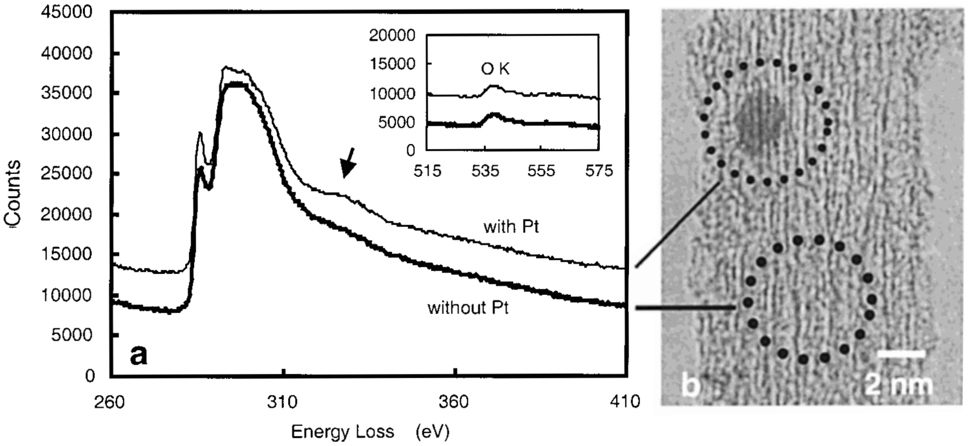

Figure 6. (a) C−K EELS spectra taken from 5-nm areas on a SWNT bundle around a Pt particle and in a clean region show an anomalous shoulder at ~330 eV when Pt is present. Sampling areas are indicated in (b). In general, the intensity of the shoulder is proportional to the number of Pt particles sampled. Inset: O−K spectra showing oxygen present in both cases.

chemical shift that may be present. Also, the number of Pt atoms interacting with the SWNT surface is very small, resulting in an extremely weak signal.

On the other hand, a hump or shoulder at ~330 eV in the C−K core-loss spectrum (~284 eV) appears where Pt is attached to the SWNTs. The relative intensity of the hump is proportional to the number of Pt particles in the sampling region, as shown in Figure 5, where thicker regions contain more Pt particles. The shoulder is present, even when sampling only one Pt particle on a single bundle with a focused beam, as shown in Figure 6. This difference in the C−K spectrum indicates a special interaction between the Pt and the nearby C. The persistence of this feature when only a single Pt particle on a single bundle is probed rules out the possibility that it is caused by a phonon vibration of the nanotube lattice. The feature may arise from a resonance of the "C−Pt" bond because Pt is 16 times heavier than C (and 12 times heavier than O).

The inset of Figure 6a shows the O−K core-loss spectra (~532 eV) for the same sampling regions used to acquire the C−K spectra, indicating the presence of surface oxides (many unreacted) all over the nanotubes, even where no Pt is present.

Preliminary kinetics experiments using our material as a catalyst for the test reaction in Figure 1 indicate the desired activity to produce unsaturated alcohol above 75 °C. The activity and selectivity could not be reliably determined quantitatively in these experiments, but the desired catalytic activity of our material has been demonstrated. No unsaturated alcohol was detected in the effluent at similar temperatures with no catalyst present. Typical reaction temperatures in the literature for this reaction catalyzed by Pt range from 60 to 100 °C.[3]

Conclusions

A simple, effective SWNT purification scheme utilizing oxidation with concentrated HNO_3 followed by centrifugation and washing and employing ultrasonication to disperse and mix the suspensions was developed. Our method requires no filtration and saves up to 2 days labor and 60% mass loss over previously published methods. Slow oxidation of the purified SWNTs in dilute HNO_3 is a critical step in preparing the nanotube surfaces for metal deposition by creating surface oxides without overly damaging the SWNT walls. These surface oxides, mostly carboxylic acid functions, act as anchors for Pt particles deposited on the nanotubes, presumably through an ion exchange reaction in a reducing agent. The conditions of the slow, dilute HNO_3 oxidation need to be carefully controlled to maximize surface oxide formation while minimizing bulk damage to the SWNTs.

We have produced material consisting of 10 wt % Pt on SWNTs with metal particle sizes averaging 1−2 nm. This material has been shown to possess the desired catalytic activity for the partial hydrogenation of an α,β-unsaturated aldehyde, and further optimization could yield a useful catalyst. This material represents the first reported metal-loaded SWNT material.

Evidence suggests that our material contains Pt chemically bonded to the surfaces of SWNTs. We imagine these bonds to be in the form of −COO−Pt, although further study is necessary to confirm this hypothesis. Pt does not adhere to SWNTs that have not been surface oxidized because there are no acid sites at which ion exchange with H can occur. Anomalous EELS C−K core-loss spectra have been recorded from the SWNTs in regions containing Pt particles, even when only a single Pt particle on a single SWNT bundle is probed. Also, because particles are only observed on bundles of at least two SWNTs (at their interface) and because O−K EELS indicates many unreacted surface oxides, each Pt particle is probably bonded to at least two closely spaced carboxylic acid sites on the SWNT surface. Further understanding of the interaction of the Pt atoms with the SWNT carbon lattice would provide indispensable new knowledge toward understanding the role of MSI in catalytic function.

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