State of Transition Metal Catalysts During Carbon Nanotube Growth

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We study catalyst-support and catalyst-carbon interactions during the chemical vapor deposition of single-walled carbon nanotubes by combining environmental transmission microscopy and in situ, time-resolved X-ray photoelectron spectroscopy. We present direct evidence of what constitutes catalyst functionality by comparing the behavior of Ni, Fe, Pd, and Au model catalyst films on SiO2 during preannealing in O2 and NH3 and during C2H2 decomposition. The catalyst metal surface supplies sites to dissociate the hydrocarbon precursor and then guides the formation of a carbon lattice and the liftoff of a carbon cap. The catalysts are sharply distinguished by their reactivity toward activation of the hydrocarbon precursor, following trends known from heterogeneous catalysis. For Fe and Ni, the active state of the catalyst is a crystalline metallic nanoparticle. Graphitic networks do not form on oxidized Fe. Pd forms a silicide on SiO2 under our reducing conditions. Pd (silicides) and Au nanocrystals are catalytically less efficient in terms of precursor dissociation, while the low adhesion of C on Au surfaces impedes nanotube nucleation.

1. Introduction

The extraordinary electronic, thermal, and mechanical properties of carbon nanotubes (CNTs) closely relate to their structure, which is often illustrated by rolled up graphene sheets. This, however, is not the way they actually grow. The most promising CNT growth technique, for both bulk production and localized growth on surfaces, is catalytic chemical vapor deposition (CVD), in which transition metal catalyst particles are exposed to a gaseous carbon precursor at elevated temperatures.1–3 Deterministic control of CNT growth remains difficult, in particular for single-walled CNTs (SWNTs), which still limits their widespread application. This is mainly due to an incomplete understanding of the role of the catalyst.

It has been shown that SWNT root growth occurs by the liftoff of a carbon cap,4,5 and that all carbon incorporates via the catalyst particle.6 Unlike in the arc-discharge or laser-ablation methods,7,8 in CVD a catalyst particle forms typically only one nanotube; i.e., the catalyst particle size and its deformation dictate the SWNT diameter.9,10 For surface-bound CVD, the catalyst-support interactions play a crucial role in controlling the type and shape of the resulting nanocarbon.4,13

The transport of carbon across the particle from activation to CNT incorporation sites is thereby required,14,15 which underlines how highly dependent the CNT growth process is on the catalyst structure.

However, there is still controversy for many of the suggested atomic processes during CNT growth, as one of the most basic questions is still unsettled: what is the active physical and chemical state of the catalyst during nanotube growth? Oxide,16 carbide,4,17 and metallic4 catalyst phases have all been proposed for commonly used Fe or Ni nanoparticles under comparable CVD conditions. A liquid catalyst is sometimes said to be necessary to obtain SWNTs,18 by analogy to the vapor—liquid—solid model for nanowire growth. In addition, the properties of sub-10-nm catalyst particles depend strongly on their surfaces and interfaces. Thus, in particular for SWNT growth, bulk values do not necessarily apply and effects such as melting point depression,19 solubility shifts,20,21 and higher reactivity22 have led to many speculations.

Here, we combine environmental transmission microscopy (ETEM) and in situ, time-resolved X-ray photoelectron spectroscopy (XPS) to present a systematic study of catalyst-support and catalyst-carbon interactions during SWNT growth. We emphasize that the point (ETEM) and integral (XPS) probing are both carried out at pressures up to the millibar range, which allows us to bridge the so-called “pressure gap” of UHV-only measurements and relate directly to typical CNT growth conditions.23 Our CVD conditions are chosen to restrict the secondary formation of carbon by pyrolysis, giving us access to SWNT materials and revealing the kinetic effects of the catalysts under study. We compare Ni, Fe, Pd, and Au model catalysts, which can be sharply distinguished by their reactivity toward activation of the hydrocarbon precursor and by their
carbon solubility. With the physical and chemical catalyst state characterized in detail, we are able to present direct evidence of what constitutes catalyst functionality for SWNT CVD.

2. Experimental Section

Thin catalyst films (99.9% purity) are evaporated onto thermally oxidized Si(100) wafer (200 nm SiO2), perforated SiO2 membranes (SPI supplies) or onto 2000 mesh Cu TEM grids (Agar Scientific) coated with SiO2 nanopowder (Degussa Aerosil Ox50) and a ∼30 nm sputtered SiO2 layer. The evaporation rate is <1 Å/s at <10^{-6} mbar base pressure. The film thickness is monitored in situ by a quartz crystal thickness monitor and calibrated ex situ by spectroscopic ellipsometry. The samples are transferred in air. We use a modified Tecnai F20 ETEM, operated at 200 or 120 kV, equipped with a differential pumping system and a Gatan imaging filter. Video sequences can be recorded with 15 frames/s time resolution at a specified information limit of 0.14 nm. The electron dose is representative of that typically implemented for high-resolution imaging, and the electron beam was never focused onto the specimen in order to minimize the effects of electron-beam-induced damage and modification of the specimen. Temperatures refer to the differentially pumped stages of the lens system of the electron microscope (SEM, FEI Nova 600, LEO 1530VP, FEI SEM), HRTEM (JEOL JEM 4000EX, 400 kV; Tecnai F20, 200 kV), and Raman spectroscopy (Jobin Yvon LabRam, Renishaw 1000 Raman spectrometer, 514, 633, and 785 nm excitation).

3. Results

For thin film based catalysts, the overall CVD growth process can be viewed as a two-step process: (1) restructuring the film into catalytically active nanoparticles during a pretreatment step and (2) introduction of carbon feedstock and SWNT growth. The step of catalyst formation by metal film dewetting on the supporting oxide is equivalent to the calcination step in conventional heterogeneous catalysis. This step produces the active, metastable catalyst form, usually by oxidizing a precursor to a defective oxide that is then carefully activated into the final catalyst form. This procedure is also followed here, by a combination of an oxidation and reduction step. The highly potent ammonia was chosen as reducing agent, to minimize the thermal load on the nanoparticles.

Step 2 was carried out by direct exposure of the reduced metal nanoparticles to the feed atmosphere. In situ observation allows discrimination of carbon adsorption, activation, and nanotube formation. It will be seen that the different catalyst systems perform differently in the two catalytic processes of carbon activation and nanocarbon nucleation.

3.1. Catalyst Activation. Figure 1a shows a series of XPS Ni 2p CORE level spectra recorded during the in situ vacuum annealing of a ∼0.13 nm thick Ni film on SiO2, i.e., stage 1. We use a 200 nm SiO2 support layer to inhibit metal diffusion into the Si and thus to prevent the formation of buried silicides. Background correction is performed by using a Shirley background. The spectra are fitted following the Levenberg–Marquardt algorithm to minimize the χ^2. Peak shapes are modeled by using asymmetric Doniach–Sunjic functions convoluted with Gaussian profiles. The accuracy of the fitted peak positions is ∼0.05 eV. CVD recipes are calibrated and repeated ex situ in a diffusion-pumped (base pressure <10^{-6} mbar) stainless steel CVD reactor. The SWNT yield is thereby similar. For comparison, ex situ CVD is also carried out in a 2 in. diameter atmospheric pressure quartz tube furnace. In the tube furnace, samples are heated in Ar up to a growth temperature of ∼900 °C, followed by a 10 min pretreatment in 200 sccm H2 and growth in 100/500 sccm H2/CH4 for 15 min. The samples are characterized ex situ by field emission gun scanning electron microscopy (SEM, FEI Nova 600, LEO 1530VP, FEI SEM), HRTEM (JEOL JEM 4000EX, 400 kV; Tecnai F20, 200 kV), and Raman spectroscopy (Jobin Yvon LabRam, Renishaw 1000 Raman spectrometer, 514, 633, and 785 nm excitation).
The Ni is initially oxidized due to air exposure during specimen transfer. We observe a peak at 856.3 eV, corresponding to a Ni$^{3+}$ oxidation state. This high binding energy Ni 2p$_{3/2}$ peak most likely arises from OH groups adsorbed on disordered NiO. As water is removed, O$^{2-}$ species are formed together with Ni vacancies. Annealing at over 100 °C reduces the Ni$^{3+}$ concentration (Figure 1a). The reduction might be facilitated by reaction with adsorbed carbon. At about 460 °C, the metallic Ni peak at 852.6 eV dominates the spectrum.

The reduction of Ni oxide leads to a physical dewetting of the Ni catalyst from the SiO$_2$ support, as seen in the ETEM image sequence of Figure 1b. This is consistent with the weak metal–support interaction seen previously for Ni catalysts on silica supports. The as-formed Ni nanoparticles coarsen with increasing temperatures and process time. This reflects the higher surface free energies of metal facets compared to the oxide support, and also the low adhesion energy of Ni. The lattice fringes and faceting in Figure 2a, c show that Ni remains crystalline.

For most nanocrystals, only one set of lattice fringes is visible, so it is difficult to assign the chemical state of the catalyst based only on lattice spacings. The 0.20 nm reflection is consistent with metallic fcc Ni(111), but also with Ni$_2$O$_3$(200) and Ni$_3$C(311). In addition, the lattice spacings of nanocrystals are affected by finite size, rapid thickness variations, and orientation changes. Here, a combination of environmental electron microscopy with in situ XPS allows a clear assignment of metal/carbon structures and core-level signatures. For pretreatment in an oxygen-depleted atmosphere and as CNT growth is typically carried out in a reducing atmosphere, Figure 1 already excludes Ni oxide as an active catalyst phase during CNT growth.

We carried out a systematic comparison of Ni, Au, Fe, and Pd catalysts using the following procedure, during which XPS spectra were continuously recorded. As-loaded, nominally 0.25 nm thick films on SiO$_2$ are heated up in vacuum to ~500 °C, exposed to ~10$^{-3}$–0.5 mbar O$_2$, followed by ~0.5–0.8 mbar NH$_3$, and then exposed once or twice to ~1–5 × 10$^{-3}$ mbar C$_2$H$_2$. We first expose the samples to oxygen, in order to reduce the C 1s signal due to adventitious carbon absorption during sample transfer in air, and hence to create a low background for controlled acetylene exposures. We then expose to ammonia to compare the catalysts in their metallic state. Due to its higher affinity to oxygen, we find that Fe does not fully reduce by annealing in vacuum or in H$_2$ pressure below 4 mbar. On the other hand, Fe can be completely reduced by NH$_3$, with the subsequent formation of hydroxyl groups and water desorption. For comparison, we probe the catalytic activity of Fe oxide by deliberate oxidation before the hydrocarbon exposure. As a “baseline”, we measured empty SiO$_2$ with the same procedures and found only a negligible increase in a C 1s signal at ~284.6 eV, which we attribute to amorphous carbon (a-C). Such a-C deposition on the substrate is commonly reported in particular for hot-wall CVD at higher temperatures and high hydrocarbon partial pressures. Here, our cold-wall CVD conditions do not result in C$_2$H$_2$ autopyrolysis, and all measured C 1s signatures can be attributed to selective carbon interactions at the catalyst.

Figures 3–7 summarize the carbon and metal core-level lines before, during, and after exposure of the catalyst nanoparticles to C$_2$H$_2$. Consider first the spectra before growth starts. After the cleaning and reducing cycle, the metal core levels show support interactions. The Ni 2p$_{3/2}$ lines in Figure 3b show contributions of 3+ and 2+ oxidation states, with small intensities at binding energies of 856.3 and 854.1 eV, respectively. For Ni, this relates to the appearance of a small Si 2p peak at 99.8 eV in addition to the main Si$^{4+}$ peak of SiO$_2$ at 103.9 eV, i.e., a weak silicidation at the interface. For Fe, we measure contributions of 3+ and 2+ oxidation states at 711.2 and 709.5 eV, respectively (Figure 4b). In the absence of measurable Si reduction, we attribute the Fe$^{3+}$ and Fe$^{2+}$ contributions to interface bonding to oxygen of the substrate.

The Pd 3d$_{5/2}$ region shows a broad peak at around 336 eV (Figure 6). We assign this to silicide formation with a range of stoichiometries present and a weak metallic Pd peak at ~335 eV. This is consistent with the observation of a Si 2p peak at 99.9 eV, which is much higher in intensity than for Ni.

A direct redox reaction between a metal and its silica support is thermodynamically predicted only for metals with electronegativities less than 1.5 on the Pauling scale. This behavior pattern can be related to the oxide free energy of formation per O atom, which increases (negatively) as the metal work function decreases, i.e., the more electropositive the metal. Fe, the most electropositive metal studied here, shows a very weak oxidation signature, without reducing SiO$_2$. In comparison, we find stronger Fe oxide signatures, i.e., interfacial bonding, for Al$_2$O$_3$-supported Fe, and we can show that this results in a narrower Fe particle size distribution during the pretreatment compared to Fe on SiO$_2$, and hence this enhances the nucleation of CNT forests. Thus the interaction strength at the metal/oxide interface determines the metal wetting.

It has been suggested that metal δ+ species at the SiO$_2$ interface can alter the interface free energy, so that it is thermodynamically possible for silicides to form by a direct reaction between the metal and SiO$_2$. In the presence of hydrogen, silicides can form by a different mechanism. The thermodynamic driving force is the formation of water. The observed Pd silicide formation can thus be due to annealing in NH$_3$, which illustrates the influence of CVD conditions at stage 1. It should be noted that we observe a small N 1s peak at 399.2 eV, which may correspond to adsorbed NH$_3$, for Ni and Pd but not for Au. For Fe we measure a small N 1s peak at 398.6 eV and a minor peak at 396.6 eV. Whereas the former can be assigned to the adsorption of nitrous species, the latter might indicate a stronger interaction and Fe–N bonding.

The Au 4f$_{7/2}$ region shows a metallic component at 84.05 eV (Figure 7). The initial additional component at 84.5 eV can be interpreted as a size effect, due to the pinning of Au atoms at defects on the amorphous oxide. We do not observe Si reduction for Au. As-evaporated sub-2-nm thick Au readily forms nanometer-sized islands (Figure 2b), which remain crystalline on annealing (Figure 2d). However, as for other metals, these islands are prone to coarsening during prolonged
The phase contrast observed for Au and Ni can be consistently assigned to metallic (111) fringes (Figure 2c, d). Our data, however, clearly emphasizes the need to analyze metal–support interactions prior to interpreting the interactions with C2H2 at stage 2 of the CVD process.

3.2. Catalyst–Carbon Interactions. For Ni and Fe, the introduction of C2H2 leads to the growth of lateral nanotube networks, as shown by the SEM images (Figures 3a, 4a). The Raman radial breathing mode (RBM) signatures and structured G bands combined with low D peak intensities (Figures 3a and 4a and Supporting Information) indicate the abundance of SWNTs. This is consistent with our HRTEM (Figure 8) and ex situ results. Besides multiwalled carbon nanotube and fibrous carbon nucleation, we expect the SWNT growth to give a clear contribution to the convolved XPS signatures. The SWNT diameters can be extracted from the radial breathing mode wavenumbers.42 The nanotube diameters are in the range of 1.2–2.1 nm for Ni catalysts and 0.8–1.7 nm for Fe. Note that the peak intensities do not reflect absolute SWNT abundances due to the strongly resonant character of Raman scattering. SEM analysis suggests a higher degree of bundling for Fe-catalyzed SWNTs, which might reflect their smaller average diameter and/or a higher nucleation density.

The evolution of C 1s and Ni/Fe 2p3/2 core-level spectra during C2H2 exposure gives an interesting comparison. For Ni, the initial carbon contamination gives a C 1s peak at ∼284.6 eV (Figure 3b). Within 50 s of C2H2 exposure, a C 1s peak centered at 284.3 eV appears, together with a small subsidiary peak at ∼285.8 eV, which then shifts to 285.55 eV (see Supporting Information). The main C 1s peak saturates within ∼3 min of C2H2 exposure. The Ni 2p3/2 peak energies remain unchanged, with their intensities decreasing for increasing carbon coverage (Figure 3b).

In the case of Fe, a C 1s peak at 284.65 eV and a subsidiary peak at ∼285.8 eV arise during the initial C2H2 exposure (Figure 4b). Only after ∼6.5 min growth time, the main C 1s peak energy shifts to 284.45 eV, with the minor peak at 285.4 eV. The C 1s line does not saturate completely within 20 min deposition time. Compared to Ni (Figure 3b), the minor C 1s peak at higher binding energies has a clearly higher intensity and the main C 1s peak a smaller fwhm. The Fe 2p3/2 lines remain at 707.3, 709.5, and 711.2 eV, with their intensities decreasing (Figure 4b). Deliberately oxidized Fe is not reduced by C2H2 for our CVD conditions (Figure 5). Furthermore, we find that oxidized Fe does not catalyze CNT growth. During C2H2 exposure, the initial C 1s line at 284.7 eV increases in intensity, and a strong peak arises at 285.3 eV (Figure 5). However, in contrast to metallic Fe, SEM, Raman, and XPS detect no nanotubes or C 1s component around ∼284.45 eV.

Figures 3–5 allow the following C 1s peak assignments. The peaks at 284.45 eV for Fe and 284.3 eV for Ni reflect CNT growth. This is in agreement with our previous XPS results for low-pressure CVD4 and the peak positions reported for sp2-bonded carbon.43,44 We assign the initial C 1s signatures to more disordered C–C bonding.45 The later appearance of a C 1s CNT signature for Fe may be due to an initial screening by disordered carbon. A clear C 1s peak at 284.45 eV is measured only when long SWNTs become abundant. We interpret the C 1s line at 285.4 eV for Fe, 285.3 eV for Fe oxide, and 285.55 eV for Ni as being due to disordered C with partially increased sp3 hybridization and possibly being hydrogenated. Such defect lines
are often observed for CNTs, graphite powder, and nanocarbon samples. We note that our previous C 1s data for in situ deposited Fe exposed to ∼2 × 10⁻⁷ mbar C₂H₂ background pressure initially showed a peak at 282.6 eV, which we attributed to chemisorbed carbon, and then a carbide peak at 283.2 eV. Here, our catalyst preparation involved transfer in air, and we observe adsorbed C for as-loaded samples, which converts into disordered C during heating. Our fitted spectra for the carbon and the metal core-level lines contain no contributions from metal carbides (Figures 3b, 4b, and 5). For Fe, however, a carbide peak at 708.1 eV (Fe 2p₃/₂) with low intensity could be added to the fit, assuming a lower asymmetry for the metallic Fe peak. Carbide formation is endothermic for Ni and Fe and strongly dependent on processing conditions. The catalytic activity of Fe₃C for the decomposition of C₂H₂ has been found negligible, and no carbide formation has been reported for graphene formation on Ni(111). At our conditions, the XPS information depth is ∼2 nm; i.e., 95% of all detected electrons originate from 3λ, where λ is the electron mean free path. Hence we also probe the “bulk” of the catalyst nanocrystals. However, once covered by a growing CNT, the XPS signal of a catalyst particle depletes, and hence we cannot exclude the presence of carbodic domains for active Fe particles.

We emphasize the integral nature of XPS probing; i.e., the XPS signatures also include catalyst particles which did not catalyze CNTs. However, the relatively high CNT yield (Figures 3a and 4a) makes us confident that active particles contribute significantly to the convolved XPS spectra. ETEM indicates CNT nucleation for some Fe₃C particles; however, it is not clear if the carbide phase decomposes during the formation of the graphitic CNT layers. We have no evidence for carbide formation for any other probed metal.

Pd (silicide) and Au nanocrystals do not catalyze the formation of high-aspect ratio carbon structures upon C₂H₂ exposure at ∼500 °C (Figures 6 and 7). For Pd (silicide), we measure an initial broad C 1s peak at ∼284.4 eV, which increases in intensity but does not shift in peak energy (Figure 6). We measure a slight further Si reduction due to C₂H₂, but the broad nature of the Pd 3d₅/₂ signal does not change and is only slightly depleted as expected.

For Au, the C 1s region shows an increase of a broad feature at 284.4 eV during C₂H₂ exposure (Figure 7). The Au 4f₇/₂ line thereby slightly depletes, and the 84.5 eV satellite disappears. In the literature, a 284.2 eV C 1s peak was reported for graphitic carbon on Au. We therefore attribute the binding energy of 284.4 eV for Au and Pd (silicide) to disordered C. This is in agreement with electron microscopy showing small amounts of amorphous C on the surface of Au crystals, in contrast to well-graphitized C and SWNTs for Ni (Figure 8a, b).

For C₂H₂ exposure at higher temperatures (∼730 °C), however, we observe graphitic deposits on Au (Figure 8c), which appear to be more loosely bound than on Ni (Figure 8a). SWNTs nucleate on both Au- and Pd-based catalysts in our hot-wall quartz tube furnace at ∼900 °C in diluted CH₄, Figure 8d. This is consistent with previous reports of nanosized noble metals acting as catalysts for CNT growth. We also observe short carbon nanofibers on larger Au particles for plasma-enhanced CVD in NH₃-diluted C₂H₂ at ∼650 °C. This shows that effective precursor dissociation and C network formation are the key characteristics for a catalyst material in CNT CVD. We note that Au is not known to form carbides and that the C

Figure 4. (a) Postgrowth SEM and Raman radial breathing modes (633 nm excitation; see Supporting Information for full spectrum) and (b) in situ XPS C 1s and Fe 2p₃/₂ core level lines of 0.25 nm Fe film on SiO₂ heated to ∼500 °C, pretreated in ∼10⁻³ mbar O₂ and ∼0.8 mbar NH₃, and then exposed to ∼2–5 × 10⁻⁷ mbar C₂H₂ in two intervals, for ∼5 and ∼15 min, respectively. The time of C₂H₂ exposure is indicated. The C 1s intensities are normalized to the highest C 1s intensity after 990 s deposition time.
which also nucleate CNTs. Hence for solid Au, the observed solubility can be neglected for larger (\(>10\) nm) Au particles; however, we currently find no direct experimental evidence as to suggest that such a solubility change is a necessity for CNT formation.

The C solubility might be significantly different for sub-5-nm Au particles; however, we currently find no direct experimental evidence as to suggest that such a solubility change is a necessity for CNT nucleation.

### 4. Discussion

CNT formation from gaseous precursor sources is a heterogeneous, gas–solid catalytic process controlled entirely by its kinetics. The situation is complex, as a chemical potential of atomic carbon is required to feed CNT growth. Our data shows that the catalyst during CNT CVD is in the solid state and potential metal oxide phases require at least partial reduction; i.e., for the probed catalysts the active state is not the oxide. The carbon potential also feeds catalyst carbide formation, and carbides of Fe and Ni can be thermodynamically stable at CNT growth conditions. Carbon dissolution and the role of carbides have been previously studied in the context of deactivation mechanisms during Fischer–Tropsch catalysis and methane steam reforming. In particular for Fe, (metastable) carbides have been found and their participation as intermediates in the transformation of carbon into graphite has been suggested. During CNT CVD, we observe carbide formation only for Fe and with very small intensity. This suggests that a carbide phase is not a necessity for CNT formation. Furthermore, assuming that a carbide phase must be metastable in order to achieve a net growth of CNTs, we suggest that SWNT formation from supported catalysts is most favored under low pressures of the hydrocarbon source, and with a moderate hydrogen chemical potential providing a negative feedback. Low pressures always favor dehydrogenation, as is known from surface science studies predominantly finding dehydrogenation products under UHV conditions and requiring high-pressure experimentation for observing hydrogenation.

Ni and Fe differ in terms of their ability to activate hydrocarbons. Figures 3 and 4 clearly reveal that, on the scale of our experiments, Ni quickly and completely dehydrogenates the adsorbed C\(_2\)H\(_2\) whereas Fe is slower. XPS detects the almost complete dehydrogenation on Ni with very little hydrogenated material present, whereas for Fe this unwanted side product is much more prominent. This supports the idea that on Fe the hydrogenation activity is higher than the dehydrogenation activity.

It has been previously speculated that C network formation and defect healing and hence CNT formation are prevented on Au, because of a lower binding energy of C atoms and graphene-like fragments on Au than on Fe. Similarly, it has been argued that CNT–metal adhesion must be comparable to C cap formation energies to maintain an open-ended CNT on the metal catalyst. Our data does not support these arguments. Our previous experiments for Ni showed that graphitic planes anchor to step edges to the catalyst surface and that SWNT growth requires the liftoff of a carbon cap facilitated by a catalyst particle deformation. We think that for Au the rate of carbon incorporation is usually slower than the speed of step withdrawal; hence, the carbon cap does not become stabilized for tangential SWNT formation. Further we think that the weak adhesion of graphitic planes on Au effectively impedes cap nucleation and thus nanotube growth.

The cause of self-termination of nanotube growth is a key question for CVD. When carbon grows so fast that it overcomes the kinetic selection of crystal facets, catalyst deactivation can occur by site isolation through graphitic encapsulation of its active surface. Figure 8 clearly shows that an adhering graphitic overlayer forms on Ni, whereas for Au carbon forms a “balloon”. This is in agreement with a very weak carbon–gold interaction, except for a few special locations where Au is modified from its metallic state and hence can form a binding interaction with carbon. The present observations agree with literature data and also fit well with the inhibiting effect that Au alloying has on the carbon formation activity of Ni catalysts.

The strong wetting of silica to Au (Figure 2) and the particle shapes after growth (Figure 8) indicate that the metal may be defective and contain subsurface species. Active particles may contain defective surfaces with nonequilibrium terminations, strain, and subsurface modifiers such as hydrogen, nitrogen, or carbon, which do not form covalent compounds. Such species are known to greatly modify the catalytic reactivity and thus an additional level of complexity may discriminate pure and “optimized” metal particles under different CVD conditions.

The shift of the C 1s peak is a useful indicator for the binding states of metal particles and SWNTs. The C 1s peak shift to
lower binding energy after the initialization period marks the formation of SWNTs. As the metal spectra remain unchanged, this C 1s shift does not indicate a ground-state change in charge density at the carbon (i.e., no carbide formation), but rather a change in the core hole relaxation mechanism. Activated carbon is only weakly bonded to the metal and thus retains its reactivity. This causes an atomlike relaxation with a substantial contribution of a relaxation shift to the observed line position. As soon as SWNT growth begins, the electronic structure of the nanotube and the metal particle become coupled, and thus a relaxation channel opens for the C 1s line through the metal valence electrons. Consequently, the relaxation shift in the atomic carbon spectrum changes and so does the binding energy. The fact that we observe this also for the hydrocarbon byproduct indicates that this unwanted product is in electronic contact with the metal and that it is a conducting species rather than a C—H polymer. It is important to note that Ni is more selective than Fe in the type of carbon it catalyzes, which again is consistent with the kinetic balance of nanocarbon production and the hydrogenation of the activated carbon.

Figure 6. In situ XPS C 1s and Pd 3d₃/₂ core level lines of 0.25 nm Pd film on SiO₂ heated to ~500 °C, pretreated in ~10⁻² mbar O₂ and ~0.8 mbar NH₃, and then exposed to ~10⁻³ mbar C₂H₂ for ~3.5 min. The time of C₂H₂ exposure is indicated. The C 1s intensities are normalized to highest C 1s intensity of Figure 4b.

Figure 7. In situ XPS C 1s and Au 4f₇/₂ core level lines of 0.25 nm Au film on SiO₂ heated to ~500 °C, pretreated in ~0.1 mbar O₂ and ~0.6 mbar NH₃, and then exposed to ~3 × 10⁻³ mbar C₂H₂ for ~15 min. The time of C₂H₂ exposure is indicated. The C 1s intensities are normalized to highest C 1s intensity of Figure 4b.
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Supporting Information Available: Post-growth Raman spectra (633 nm excitation) for samples shown in Figures 3 and 4, and plot of subsidiary peak in in situ XPS C 1s core level lines of sample shown in Figure 3. This material is available free of charge via the Internet at http://pubs.acs.org.

References and Notes

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