Hidden features of the catalyst nanoparticles favorable for single-walled carbon nanotube growth

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Combining in situ studies of the catalyst activity during single-walled carbon nanotube (SWCNT) growth by mass spectrometry with differential scanning calorimetry and Raman spectroscopy results, the authors expose the favorable features of small catalyst for SWCNT growth and their relationship with synthesis parameters. The sequential introduction of $^{12}$C and $^{13}$C labeled hydrocarbon reveals the influence of catalyst composition on its lifetime and the growth termination path. Ab initio and molecular dynamics simulations corroborate “V”-shape liquidus line of metal-carbon nanoparticle binary phase diagram, which explains observed carbon-induced solid-liquid-solid phase transitions during nanotube growth. © 2007 American Institute of Physics. [DOI: 10.1063/1.2730730]

Elucidating the catalyst features suitable for single-walled carbon nanotube (SWCNT) growth is extremely complex due to the wide variety of catalyst compositions, crystallographic and electronic structures, size, phase during growth, preparation methods, and adhesion to substrates. In addition, the synthesis parameters are related to the catalyst properties. We have undertaken a systematic in situ parametric study of the catalyst activity time evolution during nanotube growth by using chemical vapor deposition synthesis augmented by an attached mass spectrometer (MS). Combining these results with differential scanning calorimetry (DSC) and Raman spectroscopy, we elucidate the common features of the catalysts responsible for nanotube growth and their relationship with synthesis parameters.

Fe or Fe/Mo catalysts supported on alumina were prepared by impregnation method. Since direct estimation of catalyst particle size by transmission electron microscopy is extremely difficult, we use magnetic characteristics (blocking temperature and Langevin function) and estimate catalyst particle size distribution to be 1–3.5 nm. SWCNTs are grown passing a mixture of CH$_4$ diluted in Ar over the prereduced catalyst. A MS is used to measure the catalytic activity during the growth by monitoring H$_2$ production. In addition, gas chromatography is used to study the growth kinetics by monitoring the outlet gas.

Previously, our DSC studies on samples synthesized using Fe catalyst revealed solid→liquid and solid→liquid→solid phase transitions of the catalyst during SWCNT growth, depending on synthesis duration. [Fig. 1(a)], a widely debated issue in the literature. Based on the calculated Fe–C liquidus lines discussed below, we explain these phase transitions due to the carbon-induced liquifaction of the particles at low carbon concentration and subsequent solidification upon further uptake of carbon. However, for relatively larger particles (>3 nm) the diffusion through the surface cannot be excluded. It is important to mention that in our studies we use methane gas. Unlike methane, the dehydrogenation reactions of other common hydrocarbons

FIG. 1. (Color) (a) Evolution of melting point of Fe and Fe:Mo supported catalysts during nanotube growth, measured by DSC. (b) Hydrogen concentration (normalized) evolution during SWCNT growth, with Fe:Al$_2$O$_3$ obtained with a mass spectrometer. The insets correspond to experiments with sequential introduction of $^{12}$CH$_4$ and $^{13}$CH$_4$ gas, for (b1) 3 and 17, (b2) 7 and 13, and (b3) 10 and 10 min, respectively.

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used for nanotube growth are highly exothermic\(^9\) and therefore can dramatically affect on catalyst local temperature, while synthesis temperature can be relatively low.\(^8,19\)

In situ monitoring of pure Fe catalyst activity shows an initial rapid increase in \(H_2\) concentration until \(t \sim 7 \pm 2\) min [Fig. 1(b)] followed by a slow decrease to an almost constant value, which is consistent with the concentration of noncatalytic decomposition of \(CH_4\) (see Ref. 14). Comparison of Figs. 1(a) and 1(b) suggests that significant activity occurs when the catalyst melting point becomes lower than the given synthesis temperature, and thereby is liquified, and that the liquid → solid phase transition initiates the deactivation of the catalyst. Similarly, the ratio of the SWCNT G-band and D-band Raman spectra intensities measuring graphitic order in the carbon deposit, increases rapidly for \(t < 7 \pm 2\) min and decreases after \(t > 7\) min. In addition, about 70 wt\% of the overall carbon yield (measured by temperature programmed oxidation) is obtained for \(t < 7 \pm 2\) min.

To validate the period of catalytic activity and its relationship with catalyst phase and nanotube growth, the \(^{12}\)CH\(_4\) feedstock was replaced by the \(^{13}\)C methane isotope at times when the catalyst is liquified and has high activity, as well as when the catalyst is less active. Specifically, \(^{12}\)CH\(_4\) is used for the first 3, 4, 7 (high activity), 10, and 13 min (low activity) while \(^{13}\)CH\(_4\) is used for 17, 16, 13, 10, and 7 min, respectively [insets in Figs. 1(b), b(1), b(2), b(3), and see Ref. 14]. Raman spectra of SWCNTs obtained from \(^{13}\)C methane are similar to those from the \(^{12}\)C isotope [Fig. 2(a)], with a frequency shift (12/13)\(^{1/2}\) times smaller, as the heavier carbon atoms yield smaller phonon energies.\(^20\) Raman spectra for our samples synthesized using \(^{12}\)CH\(_4\) for the first 3 and 4 min, followed by \(^{13}\)CH\(_4\) for the last 17 and 16 min, contain significant contributions from \(^{13}\)C nanotubes [Fig. 2(a)]. In contrast, samples grown from \(^{12}\)CH\(_4\) for the first 7 min and then \(^{13}\)CH\(_4\) for 13 min show little contribution from \(^{13}\)C nanotubes. Finally, Raman spectra for the sample obtained from \(^{12}\)CH\(_4\) for 10 min followed by \(^{13}\)CH\(_4\) for 10 min are identical to the spectra of \(^{12}\)C nanotubes. Comparing these results with DSC measurements [Fig. 1(a)] reveals that high catalytic activity corresponds to the liquified particles that are favorable for SWSNT growth. It is important to note that by increasing the growth time using \(^{13}\)C from \(t = 10\) to 20 min for the sample that was initially exposed to \(^{12}\)CH\(_4\) for 10 min, only changes the D band, responsible for disordered carbon [Fig. 2(a), dashed line]. Thus, the catalyst lifetime for SWNT growth is \(t \approx 7 \pm 2\) min even though the catalyst is active for CH\(_4\) decomposition until \(t > 20 \pm 2\) min. In addition, \(t = 7 \pm 2\) min coincides with the liquid → solid transition [Fig. 1(a)] of the carboide formation.\(^16\) The solidification of the catalyst particle reduces the diffusion of carbon into the particle\(^16\) and decreases the efficiency of hydrocarbon decomposition. Eventually, this leads to the formation of disordered carbon observed by Raman scattering measurements, common cause of catalyst poisoning [Fig. 2(c), gray arrow path].

Results from \textit{ab initio} and molecular dynamics (MD) simulations support the proposed mechanism of carbon-induced liquefaction and solidification of the iron nanoparticles. Density functional theory in the spin polarized projector augmented wave generalized gradient approximation formalism\(^21,22\) is used to calculate the adhesion between an Al-terminated Al\(_2\)O\(_3\) surface and an Fe cluster [Fig. 3(a)]. The results are used to fit a Morse potential between each Fe atom and substrate giving a binding energy of 150 meV/atom [Fig. 3(b)].\(^13\) MD simulations are then implemented by using Fe–Al\(_2\)O\(_3\), Fe–Fe, Fe–C, and C–C interactions as Morse, Born Mayer many body, Johnson- and Lennard-Jones-type interactions.\(^23\) The phase diagrams of free and supported metal clusters are calculated from changes in the internal energies and Lindemann indices as a function of temperature. Figure 3(c) shows, in agreement with previous studies,\(^24,25\) there is a linear decrease in the melting temperature \(T_M\) for pure Fe nanoparticles with decreasing particle diameter, and that the interaction with the substrate increases the particle’s melting point.\(^26\) The phase diagrams of the supported iron-carbide particles [Fig. 3(d)] reveal a similar “V”-shape \textit{liquidus} line to that of the bulk system that supports carbon-induced liquifaction. Also, reducing the cluster size shifts the eutectic point toward lower temperatures and carbon concentrations.

The mechanism by which the addition of Mo to the Fe catalyst significantly improves SWCNT yield\(^6,11\) is still not fully understood. Similar experimental studies to those described above, but using bimetallic Fe–Mo:Al\(_2\)O\(_3\) catalyst, show that the catalytic activity of the bimetallic particles is observed to be larger than the monometallic ones. The rate of \(H_2\) formed on the bimetallic catalyst is qualitatively and
An upper limit on the synthesis temperature and composition at grown have been reported. The number of Fe atoms in the particles is shown. The black and red dashed lines represent interpolations for the free and supported clusters, respectively. Phase diagrams, $T_M$ versus $C$, in atomic percent ($\%$), for supported particles of size $N_{Fe}=80, 100, 200,$ and $1000$. Carbon concentration is defined as $N_C/(N_{Fe}+N_C)$.

Quantitatively different to the linear combination of Fe:Al$_2$O$_3$ (1:15) and Mo:Al$_2$O$_3$ (0.21:15) products, which is attributed to the substantial intermetallic interaction between Mo and Fe. Interestingly, the catalyst is liquid for synthesis duration up to 90 min [Fig. 1(a)] and capable of growing nanotubes. In contrast to the pure Fe particles, Raman spectra of nanotubes obtained from Fe/Mo catalysts with sequential introduction of $^{13}$CH$_4$ for 13 or 20 min and $^{13}$CH$_4$ for 10 min show clear contribution of $^{13}$C atoms [Fig. 2(b)], and see Ref. [14]. However, no contribution from $^{13}$C atoms is found when $^{13}$CH$_4$ is introduced into the reactor after $t > 20$ min and the catalyst is not active. Although the bimetallic catalyst is liquid for longer than the pure Fe catalyst, it is inactive for SWCNT growth after $t > 20$ min. We attribute this to the simultaneous growth of SWCNTs and other sp$^2$ carbon structures, which gradually cover the surface of the catalyst deactivating it [14] [Fig. 2(e), blue arrow path]. Hence, adding Mo retards solidification of the pure Fe particle and consequently enhances the catalyst lifetime for nanotube growth by almost a factor of 2.

Production of SWCNTs also requires identification of appropriate synthesis conditions for a particular catalyst. We observed detectable activity of the Fe catalyst for CH$_4$ decomposition at $T \sim 700$ °C, while bimetallic Fe/Mo particles are already significantly active at $T \sim 650$ °C. Minimum synthesis temperature ($T_{\text{synthesis}}$) below which nanotubes are not grown have been reported. An upper limit on the synthesis temperature is set by the noncatalytic decomposition of the carbon feedstock ($T_{\text{decomp}}$) which rapidly poisons the catalyst. In addition, when $T_{\text{synthesis}} > T_M(Fe)$ an exothermal peak is detected by DSC with an enthalpy of 161 J/g, probably due to chemical reaction of Fe with Al$_2$O$_3$ resulting in deactivation of the catalyst. Therefore, the boundaries for appropriate synthesis temperature can be summarized as

$$T_M > T_{\text{synthesis}} > T_{\text{eutectic}} \quad \text{and} \quad T_{\text{decomp}} > T_{\text{synthesis}}. \quad (1)$$

In summary, we found that carbon-induced liquifaction is an important feature for growth of SWCNT. Proper modification of the catalyst composition prevents solidification due to carbide formation, and this prolongs its lifetime for the growth of SWCNTs. Preventing the formation of disordered carbon on the catalyst surface and applying the appropriate synthesis conditions with respect to catalyst features [Eq. (1)] are also required for growth of carbon SWCNTs. While this letter was under review, another family of elements (Ag, Au, Pt, Pd, and Cu) was reported as catalysts for growth of SWCNTs, where the growth was explained based on carbon solubility and liquifaction mechanisms.

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References

14. See EPAPS Document No. E-APPLAB-90-031716 for description of experimental methods, theoretical calculations, and additional figures. This document can be reached via a direct link in the online article’s HTML reference section or via the EPAPS homepage (http://www.aip.org/pubservs/epaps.html).