

Multiple Alkynes React with Ethylene To Enhance Carbon Nanotube Synthesis, Suggesting a Polymerization-like Formation Mechanism

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In spite of broad industrial development and significant research efforts over 20 years,¹ surprisingly little is known about the formation mechanism of carbon nanotubes (CNTs).^{2–4} Synthetic efficiencies still do not exceed 3%,⁵ and recent studies have shown that undesirable byproducts are formed during CNT production *via* catalytic chemical vapor deposition (CVD) of ethylene,⁶ a common route for high-volume manufacture. Lack of knowledge regarding chemical formation mechanisms of CNTs (1) limits true nanometer-scale control of CNT structure (*e.g.*, chirality and defect density), (2) precludes advances in carbon conversion and energy efficiency, and (3) threatens the ultimate success of the CNT-based product market due to real and/or perceived environmental or public health threats.

We aim to surmount these limitations through an improved mechanistic understanding of CNT formation. In general, CNT growth by CVD involves the introduction of a gaseous carbon precursor (*e.g.*, C₂H₄ or CH₃CH₂OH) to a heated (*e.g.*, 450–1300 °C) reaction zone that contains a free-floating or substrate-supported “catalyst”. The catalyst is typically a transition metal or oxide nanoparticle that is thought to mediate the reaction, although true catalytic activity has not been demonstrated. While the current understanding is limited with respect to chemical details,^{2–4} the prevailing notion is that the carbon-containing precursor adsorbs onto and then dissociates at the catalyst. Initially, a closed carbon network is thought to form the CNT “cap”, and then carbon adds to the growing lattice by con-

ABSTRACT Thermal treatments of feedstock gases (*e.g.*, C₂H₄/H₂) used during carbon nanotube (CNT) synthesis result in the formation of a complex mixture of volatile organic compounds and polycyclic aromatic hydrocarbons. Some of these are likely important CNT precursors, while others are superfluous and possibly degrade product quality, form amorphous carbon, and/or contribute to growth termination. To simulate the effect of thermal treatment without this chemical complexity, we delivered trace amounts of individual hydrocarbons, along with ethylene and hydrogen, to a cold-wall atmospheric pressure reactor containing a locally heated metal catalyst (Fe on Al₂O₃). Using these compound-specific experiments, we demonstrate that many alkynes (*e.g.*, acetylene, methyl acetylene, and vinyl acetylene) accelerate multiwalled CNT formation with this catalyst system. Furthermore, ethylene is required for enhanced CNT growth, suggesting that the alkyne and ethylene may react in concert at the metal catalyst. This presents a distinct CNT formation mechanism where the chemical precursors may be intact during C–C bond formation, such as in polymerization reactions, challenging the widely accepted hypothesis that precursors completely dissociate into C (or C₂) units before “precipitating” from the metal. Armed with these mechanistic insights, we were able to form high-purity CNTs rapidly with a 15-fold improvement in yield, a 50% reduction in energetic costs, and order of magnitude reduction in unwanted byproduct formation (*e.g.*, toxic and smog-forming chemicals and greenhouse gases).

KEYWORDS: carbon nanotube growth · catalytic chemical vapor deposition · alkyne · acetylene · methyl acetylene · vinyl acetylene · efficiency · environment

tinual dissociation at, diffusion into or over, and precipitation from the catalyst.^{2,7}

As a result of the focus on precipitation from the catalyst, few studies have evaluated the role of gas-phase reactions in CVD reactors. However, these gas-phase reactions play a critical role in CNT growth. We demonstrated that independently heating the carbonaceous feedstock prior to impingement on a metal catalyst accelerates CNT formation by up to a factor of 20.^{8,9} The thermal pretreatment step generates a suite of volatile organic compounds (VOCs),^{6,10–12} some of which may be responsible for enhanced CNT formation,⁶ while others may diminish CNT quality.¹⁰ Identifying the critical CNT precursors would

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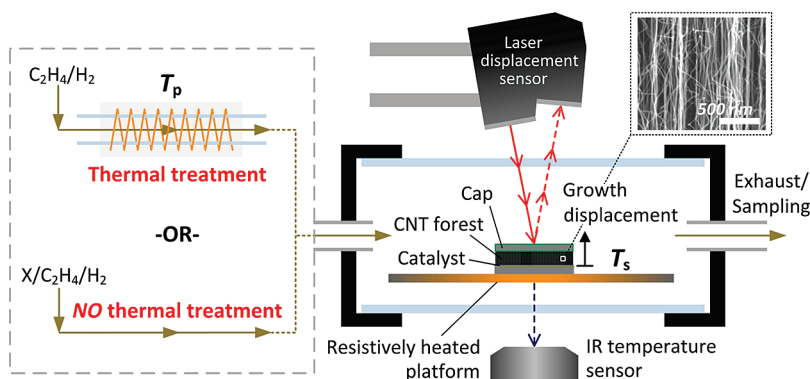


Figure 1. Atmospheric pressure, cold-wall CVD reactor with decoupled thermal control over feedstock and catalyst. Throughout this study, feedstock gases were delivered in one of two modes: (1) with thermal treatment ($T_p = 680\text{--}1040\text{ }^\circ\text{C}$, C_2H_4 and H_2 only) or (2) without thermal treatment (C_2H_4 and H_2 and a test gas, “X”). The catalyst substrate temperature (T_s) was $725\text{ }^\circ\text{C}$, unless otherwise noted. The height of the growing CNT forest was monitored with a laser displacement sensor.

enable selected delivery of those compounds, rather than relying on thermal generation to provide the necessary reactants within a complex mixture of chemicals. Indeed, others^{12,13} showed that direct delivery of unheated acetylene to a heated metal catalyst yields CNTs. Despite these investigations, it is unclear whether acetylene’s potency extends to other thermally generated materials and, if so, how the chemical functionality of distinct precursors affects CNT formation. Furthermore, direct delivery of critical precursor molecule(s) and avoidance of thermal treatment of the feedstock gas would (1) remove an energetically expensive component of the process,¹⁴ (2) potentially improve the precursor-to-CNT mass conversion efficiency, and (3) reduce the formation of unintended byproducts.

RESULTS AND DISCUSSION

Identification of Thermally Generated CNT Precursor Molecules.

Using an atmospheric pressure, cold-walled CVD reactor (Figure 1),^{9,10,15,16} we independently controlled the temperatures of the feedstock and catalyst. The $\text{C}_2\text{H}_4/\text{H}_2$ growth mixture was heated to various “pre-heat” temperatures, T_p ($860\text{--}1040\text{ }^\circ\text{C}$), and then cooled to room temperature prior to impingement on a substrate-affixed, locally heated metal catalyst (1 nm Fe/10 nm $\text{Al}_2\text{O}_3/675\text{ }\mu\text{m}$ Si with 300 nm thermal oxide).¹⁰ Simultaneously, we monitored the composition of gases evolved from the preheater by *ex situ* gas analysis,⁶ as well as the *in situ* CNT growth rate by monitoring the height evolution of a vertically aligned multi-walled CNT (MWCNT) “forest” using a laser displacement sensor.¹⁶ As preheat temperature increased, there were strong linear correlations between the growth rate and the partial pressures of methane, benzene, and vinyl acetylene (but-1-en-3-yne), each with a correlation coefficient (R^2) of 0.99 ($n = 4$, Figure 2). As the abundance of methyl acetylene (propyne) increased, the growth accelerated to a point of apparent saturation. Thus, at high methyl acetylene concentrations, something other than precursor availability limited the

rate of CNT formation. The hyperbolic behavior is characteristic of catalysis reactions, suggesting that the metal is acting as a true catalyst for CNT formation, rather than simply providing a template for highly ordered carbon precipitation.

Irrespective of the mechanism, some of these compounds have been suggested as important CNT precursors, while others have not. Methane is a common CVD feedstock gas, and recent simulations indicate it gives effective CNT growth *via* decomposition on Fe catalyst surfaces.^{17,18} Benzene has also been proposed as an important intermediate in CNT formation. However, the alkynes, methyl acetylene and vinyl acetylene, have not been explicitly recognized¹⁹ as active molecules in the CNT growth pathway. Acetylene (*i.e.*, ethyne) itself has been noted previously for its relatively efficient conversion to CNTs in molecular beam and vacuum experiments, where gas-phase reactions

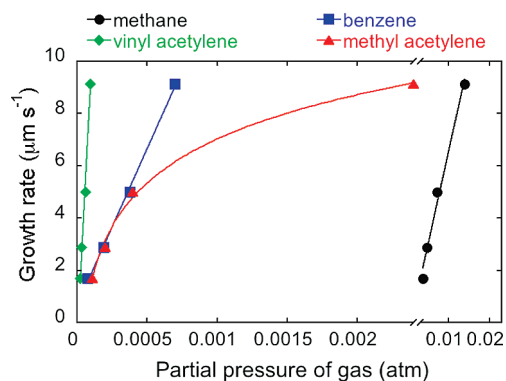


Figure 2. Thermally generated compounds correlate with CNT growth rate. Resultant concentrations from four different preheat temperatures (860, 920, 970, $1040\text{ }^\circ\text{C}$) are shown, and growth rate increased with temperature. The symbols are measured gas abundances just after the preheater tube, and the lines are the best-fit curves. The abundances of methane, benzene, and vinyl acetylene were linearly related to the growth rate (all $R^2 = 0.99$, $n = 4$). The relationship between methyl acetylene and the CNT growth rate was fit by a hyperbola ($R^2 = 0.99$, $n = 4$). In all experiments, the gas flow during growth was $\text{C}_2\text{H}_4/\text{H}_2/\text{He} = 70/330/0$ sccm (standard cubic centimeters per minute), and the catalyst substrate temperature was $840\text{ }^\circ\text{C}$.

are minimized.^{12,13} Unfortunately, in those studies, acetone (*i.e.*, 2-propanone) was present as a trace (<1%) component of the acetylene, and oxygen-containing compounds are known to enhance CNT growth.²⁰ Thus, it is unclear if the enhanced growth was an effect of the acetylene itself, the oxygen-containing acetone, or both.

Accelerated CNT Growth by Direct Delivery of Key Precursors without Heating Feedstock Gases. To demonstrate that small alkynes ($C_{n \leq 4}$) were responsible for the accelerated CNT growth, we delivered each candidate precursor molecule to a heated metal catalyst without thermal treatment of the feedstock gas. To simulate the growth environment that would be generated by the preheater, but without the convolution of the more than 40 thermally generated compounds,⁶ we administered trace amounts of the test gas (*e.g.*, <1% by vol), along with a supply of ethylene (18.7% by vol) and hydrogen (51.3% by vol, balance He), to the heated metal catalyst. When equal partial pressures (9.8×10^{-3} atm) of each test gas were delivered, acetylene and methyl acetylene enhanced the growth rate of CNTs beyond rates achieved with thermal pretreatment (Figure 3a; growth rates of $4.1 \mu\text{m s}^{-1}$ for both acetylene and methyl acetylene, and $2.9 \mu\text{m s}^{-1}$ for “preheater on” growth). Note that online mass spectral analysis showed no acetone in our cryogenically purified acetylene, and thus, the rate enhancement was due solely to the presence of acetylene. Due to concentration limitations, vinyl acetylene was tested at a lower partial pressure (3.0×10^{-3} atm). Even with more than a factor of 3 dilution compared to acetylene and methyl acetylene, the CNT growth rate with vinyl acetylene was only 1.3 times slower (3.1 vs $4.1 \mu\text{m s}^{-1}$) and still faster than the “preheater on” case ($2.9 \mu\text{m s}^{-1}$). Thus, if these concentrations are within the linear range of vinyl acetylene’s effect on growth, then vinyl acetylene could be more active than both methyl acetylene and acetylene.

Vinyl acetylene accelerated the growth of CNTs to a greater extent than did ethyl acetylene (0.9 vs $0.6 \mu\text{m s}^{-1}$, respectively; Figure 3b). This suggests that the alkene group has a role in promoting CNT formation beyond the effects of the alkyne alone. Even so, the alkyne functional group is critically important, as its absence renders the molecule an inefficient promoter of CNT formation: 1,3-butadiene did not enhance CNT growth to the extent vinyl acetylene does (1.1 vs $3.1 \mu\text{m s}^{-1}$, respectively; Figure 3a). By logical extension, one might expect that diacetylene (1,3-butadiene; a thermally generated product with alternating triple bonds) would be an effective CNT precursor molecule. However, the compound is unstable and difficult to obtain commercially in the United States, so we were unable to test it directly. Nevertheless, we note that it was formed in all cases in which we observed accelerated growths (results shown below; see Figure 4a), and it may contribute to enhanced CNT formation.

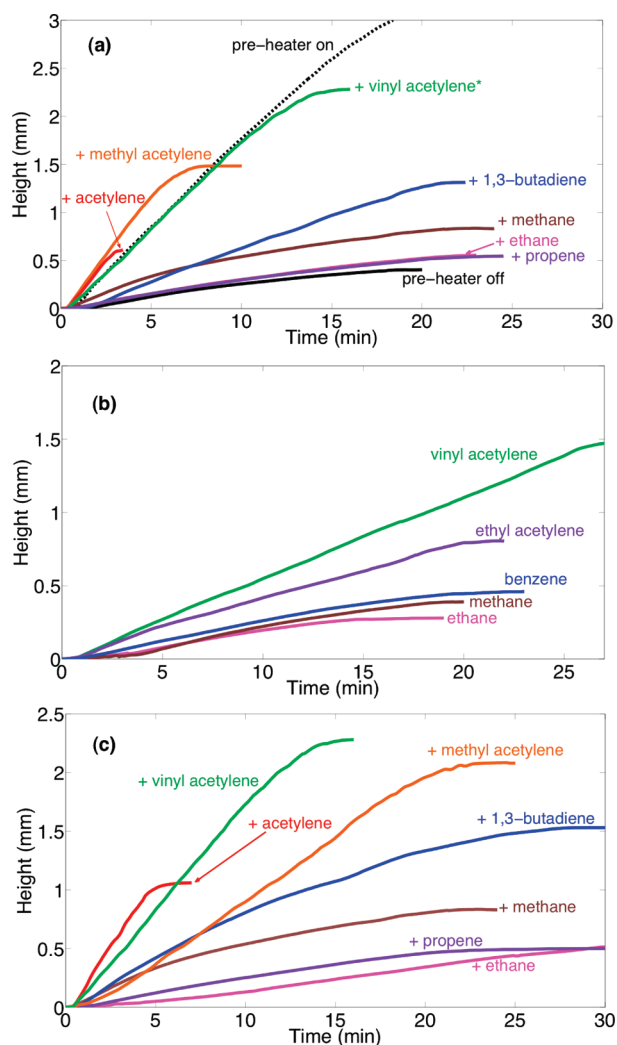


Figure 3. Effects of precursor chemical structure on CNT growth kinetics. In all experiments, standard growth gases ($C_2H_4/H_2 = 120/310$ sccm) were delivered without preheating in addition to either (1) no test gas (preheater off) or (2) a test gas (*e.g.*, methyl acetylene or methane). To provide a reference for typical growth conditions, a preheater on case (where only C_2H_4 and H_2 are delivered) is also shown. (a) Test gases were delivered at equal partial pressures (9.8×10^{-3} atm), except for vinyl acetylene, which was more dilute (3.0×10^{-3} atm). All alkynes significantly accelerated growth compared to when they were not delivered (preheater off case). Test gases were then delivered at (b) lower partial pressures (3.3×10^{-4} atm) or (c) equal masses ($5.5 \pm 0.4 \mu\text{g C sccm}^{-1}$).

For completeness, benzene was delivered to the catalyst as a test gas (at 3.3×10^{-4} atm, within the range expected from thermal generation), but it did not enhance CNT formation ($0.4 \mu\text{m s}^{-1}$, Figure 3b). Similarly, relevant concentrations of methane did not promote CNT formation rates (0.7 or $0.4 \mu\text{m s}^{-1}$ at 9.8×10^{-3} and 3.3×10^{-4} atm, respectively). Thus, while methane and benzene were both correlated with growth rate, they did not enhance CNT growth at the catalyst. We conclude they were synthesized in concert or sequence with another critical component (*e.g.*, benzene formation *via* methyl acetylene-derived radicals).²¹

To ensure that the observed rate enhancements were not merely the result of differences in carbon mass (*e.g.*, methane’s low molar mass relative to

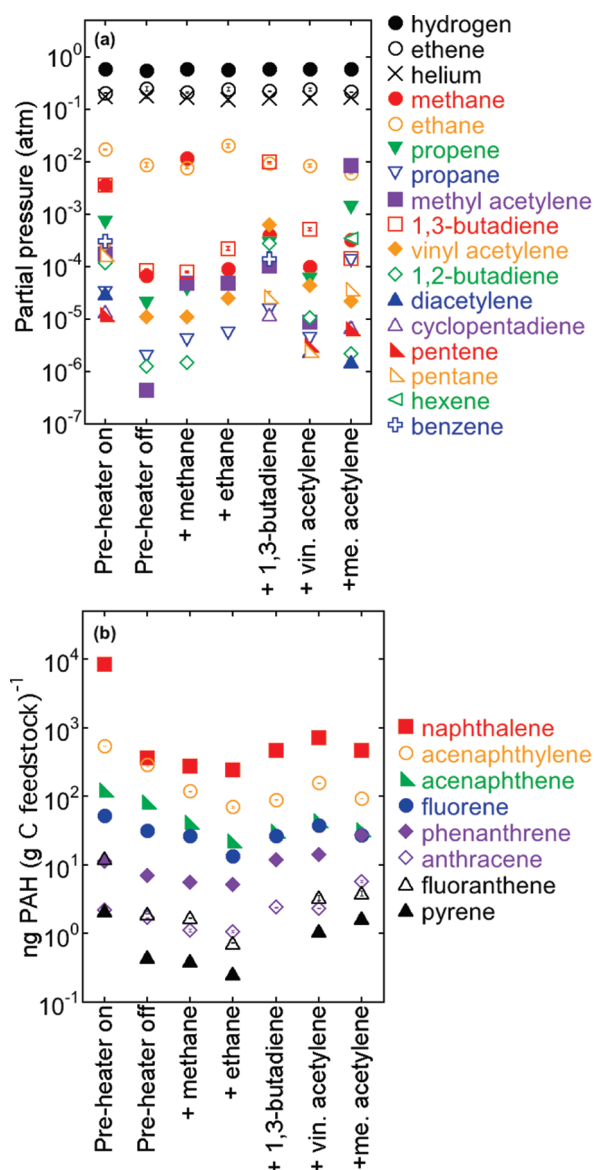


Figure 4. Eliminating thermal pretreatment of feedstock gases reduced (a) VOC and (b) PAH formation. Labels shown on the abscissa indicate the identity of the test gas and correspond to the growth curves shown in Figure 2a. “Me. acetylene” and “vin. acetylene” are methyl and vinyl acetylene, respectively. In the preheater on and preheater off case, no test gas was added to the typical feedstock gas ($C_2H_4/H_2/He = 120/310/174$ sccm). Error bars represent one standard deviation on multiple measurements, and invisible error bars are smaller than the symbol. (a) VOC concentrations are reported as partial pressure. (b) PAH abundance was integrated throughout the CNT growth, and so, concentrations are reported relative to total grams of C delivered.

alkynes), we delivered each test precursor at a constant mass ($5.5 \pm 0.4 \mu\text{g C sccm}^{-1}$). On a mass basis, vinyl acetylene enhanced the rate most, followed by acetylene, methyl acetylene, 1,3-butadiene, and methane (Figure 3c). Thus, the accelerating effects of alkynes on CNT growth are not simply due to their relative carbon contents; rather, they are intimately related to chemical structures.

Traditionally, when methane is used as a principle carbon source, it is heated to relatively high temperature

(e.g., 800–1200 °C or used in plasma CVD).^{2,3} Conversely, acetylene must be kept at a lower temperature for efficient production (e.g., 550–800 °C and with low partial pressures of acetylene).^{13,22} The use of methane for high-temperature growth and acetylene for low-temperature growth is not by scientific design, but rather, it is a consequence of empirical optimization. This thermal disparity may, in fact, reflect the generality of CNT formation mechanisms; if methane is not a critical precursor itself, it would require thermal conversion to become one. On the other hand, acetylene, as an alkyne, is an effective CNT precursor, and so it does not require thermal treatment. Thus, the broadly held understanding that different precursors require different temperatures may simply be an experimental artifact rather than a true distinction in growth mechanisms. If the actual chemical intermediates were used as direct feedstock, it is possible that a much narrower thermal range would be observed for distinct catalyst systems.

Reduced Byproduct Formation without Sacrificing CNT Growth.

In the typical CVD approach, where feedstock gases are heated, many volatile organic compounds are generated by the thermal treatment of ethylene and hydrogen (Figure 4a), including methane (a potent greenhouse gas), benzene, and 1,3-butadiene (hazardous air pollutants regulated by the Environmental Protection Agency). Omitting thermal pretreatment reduces the abundance of all VOCs (except ethane) by more than an order of magnitude (Figure 4a), and several compounds, including benzene, were not formed in detectable quantities (<0.1 ppmv). Thus, CNT production techniques that reduce the energy delivered to the feedstock gas offer substantial reductions in unnecessary emissions. Compared to preheating, methyl- and vinyl acetylene-assisted growth reduced methane formation by about a factor of 30, thereby limiting potential greenhouse gas emissions; 1,3-butadiene formation was reduced 60-fold; and benzene formation was effectively eliminated (below detection, <0.1 ppmv).

VOCs are the most abundant components of the CVD effluent, but several toxic polycyclic aromatic hydrocarbons (PAHs) are also formed and emitted.⁶ Eliminating thermal treatment of the feedstock gases reduced the total PAH load by an order of magnitude (Figure 4b). Naphthalene, fluoranthene, and pyrene were most sensitive to this change, reduced by 20-, 60-, and 40-fold, respectively. Interestingly, fluoranthene and pyrene were elevated in alkyne-assisted CNT syntheses relative to unassisted growths. Some have postulated that fluoranthene, whose structure resembles a CNT cap, is responsible for CNT nucleation.¹⁴ However, further studies are needed to establish the function of PAHs in CNT formation reactions.

Increased Carbon Conversion to High-Purity CNTs. Augmenting growth with trace amounts of alkynes offered substantial improvements in carbon conversion efficiency (grams of CNT per grams of C feedstock \times 100%, nor-

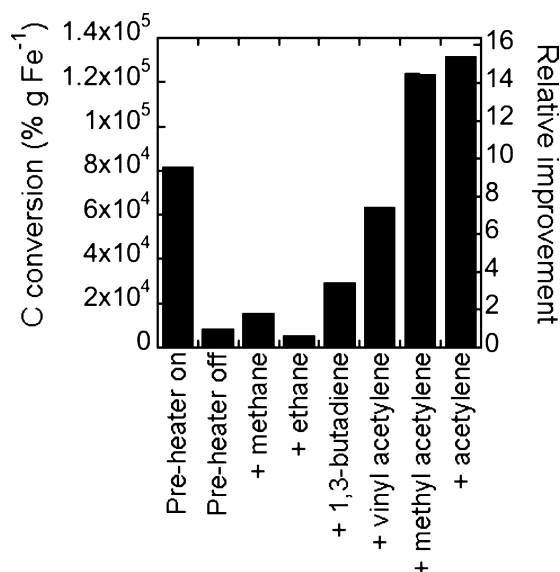


Figure 5. Alkyne-assisted CVD offers improved carbon conversion yields and catalyst efficiencies. Carbon conversion is normalized to the mass of catalyst used (grams of CNT per grams of C precursor) $\times 100\%$ /g catalyst. The catalyst was deposited by electron-beam evaporation at an estimated density of $7.9 \text{ ng Fe mm}^{-2}$.

malized to catalyst mass; Figure 5). Acetylene- or methyl acetylene-assisted growth improved C conversion by factors of 14 and 15 (1.2×10^5 and $1.3 \times 10^5 \text{ g catalyst}^{-1}$), respectively, exceeding the efficiencies that were achieved with thermal treatment approaches ($8.2 \times 10^4\%$ g catalyst⁻¹). In addition, dosing unheated feedstock with trace quantities of vinyl acetylene growth offered a 7.5-fold improvement in C conversion ($6.4 \times 10^4\%$ g catalyst⁻¹). In contrast, methane, ethane, and 1,3-butadiene did little to enhance CNT formation beyond what is achieved without preheating, further demonstrating that these compounds are not critical reactants for nanotube growth.

CNT yields have also been reported in terms of "catalyst efficiency" (grams of CNT per grams of catalyst), which does not account for carbon precursor mass. The highest observed efficiencies are for water- and ethanol-assisted CVD (10^{-1} to 10^4 grams of CNT per grams of catalyst).^{22,23} Here, without the use of oxidative etchants or thermal treatments, we observed catalyst efficiencies up to 1.1×10^3 . Thus, while we have made no efforts to optimize our synthesis for catalyst efficiency, we are within the range of the state-of-the-art. With further efforts directly aimed at improving catalyst efficiencies, we may see dramatic improvements beyond what has been possible in CNT synthesis to date.

Lastly, and notably, CNT purity (% CNT) was maintained in spite of eliminating thermal treatment of the feedstock. Vinyl acetylene-, methyl acetylene-, and acetylene-assisted growths produced materials with CNT purities of 86 ± 2 , 84 ± 3 , and $91 \pm 7\%$, respectively, none of which are significantly different from the CNT product generated by feedstock heating ($87 \pm 1\%$; results determined by thermal gravimetric analy-

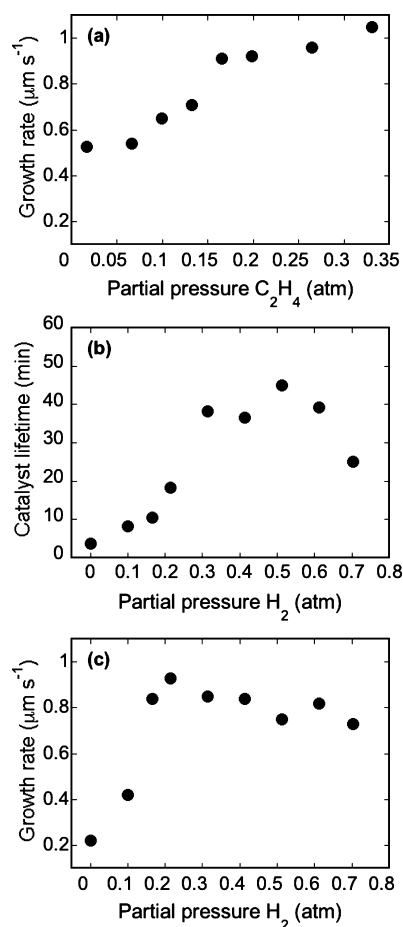
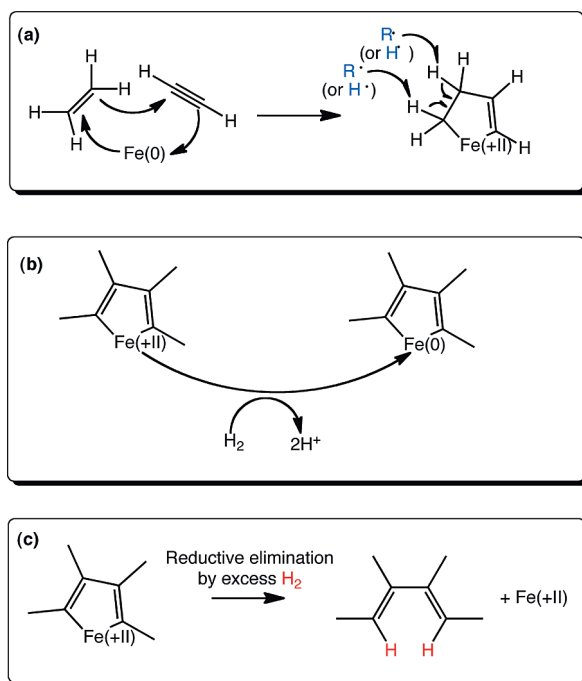


Figure 6. Effects of ethylene and hydrogen during acetylene-assisted CNT growth. Acetone-free acetylene was delivered at 1.0×10^{-3} atm in all experiments. As C₂H₄ was varied, H₂ was held constant at 0.51 atm. As H₂ was varied, C₂H₄ was constant at 0.20 atm. Helium was used to maintain a constant total flow rate of 604 sccm. The ethylene content (a) influenced the CNT growth rate but had little effect on the catalyst lifetime. The hydrogen content had a large impact on (b) catalyst lifetime at high and low p_{H₂} but only influenced (c) the growth rate at low partial pressure.

sis; Supporting Information Figure S1. Additional CNT characterizations, such as CNT diameter, Raman spectra, number of walls, and forest density are also available in the Supporting Information).

Ethylene as a Co-reactant and Hydrogen's Effect on Catalyst Lifetime. While a relatively small concentration of alkyne added to the unheated ethylene feedstock accelerated CNT growth, the mass of alkyne was not sufficient to account for the mass of CNT formed. Therefore, the principle feedstock, ethylene, must still serve as a co-reactant at the metal catalyst and add to the growing CNT. Indeed, alkynes have been shown to react with alkenes to form cyclic intermediates during homogeneous catalyses,^{24–27} and it is possible that alkynes are playing a similar role in CNT formation. In these reactions, the metal must be reduced in order to have catalytic activity, as the electrons are necessary to promote bond formation. In CNT synthesis, most catalysts are reduced (e.g., with H₂) prior to CNT growth.²⁸ If the



Scheme 1. Chemical effects of ethylene and hydrogen during acetylene-assisted CNT growth. Ethylene may co-react with acetylene to form a metallacycle intermediate (a). Hydrogen may play a dual role regulating the catalyst lifetime, where low partial pressures of H₂ limit catalyst turnover (b) and high partial pressures of H₂ terminate “chain” propagation (c).

catalyst continually transfers electrons to carbonaceous reactants to form long CNTs, we expect H₂ is required as an electron donor to sustain catalyst activity. However, hydrogen’s influence will not be strictly limited to catalyst surface effects, as it is also important to gas-phase reactions during CNT synthesis.⁶

To explore the role of H₂ and C₂H₄ in CNT synthesis, we varied the concentration of each independently while fixing acetylene (which, incidentally, is the least expensive of the tested alkynes and a likely target for use on the industrial scale). Consequently, we identified the minimal H₂ and C₂H₄ quantities needed to obtain rapid CNT formation so as to minimize feedstock costs and waste.

As C₂H₄ abundance was reduced, there was a decrease in CNT growth rate (Figure 6a). This is consistent with ethylene acting as a key reactant with the alkyne in the CNT formation reaction (Scheme 1a). In contrast, the abundance of C₂H₄ delivered as feedstock gas did not have a clear relationship with the catalyst lifetime.

As we had anticipated, the partial pressure of H₂ (pH₂) had a significant impact on the catalyst lifetime (Figure 6b). At low pH₂ (<0.31 atm), there was a sharp decrease in the catalyst lifetime, consistent with hydrogen’s role as a sustained source of electrons necessary to re-reduce the catalyst after it has been oxidized during bond formation (Scheme 1b). While a minimum amount of hydrogen was necessary to sustain catalyst activity, excess pH₂ reduced the catalyst lifetime. In polyethylene polymerization, an abrupt increase in pH₂

can terminate chain propagation by adding H₂ to the metal catalyst, blocking monomer addition (Scheme 1c). As such, pH₂ is often used to control the ultimate length of the polymer.^{29–31} Alternatively, termination events could be induced *via* protonation by water to yield a reductive coupling product (e.g., adding H to the CNT and cleaving the metal–CNT bond), and recent observations of water-induced cleavage of CNT–catalyst contact support this mechanism for termination.²⁰

In addition to having a substantial influence on catalyst lifetime, lowering pH₂ (<0.17 atm) reduced the CNT growth rate (Figure 6c). In the gas phase, inadequate hydrogen can promote polyacetylene formation and subsequent soot production.³² While polyacetylenes have been suggested as candidates for CNT formation,³³ an excess abundance in the gas phase may promote soot formation rather than CNT growth.

While both ethylene and hydrogen are necessary for efficient CNT growth, we could reduce the delivery rate of each by 20 and 40%, respectively, without sacrificing CNT growth rate, catalyst lifetime, or yield. By delivering the necessary precursors directly, rather than relying on thermal treatment to generate trace quantities of the desired reactant(s), lower quantities of starting materials may be used. Such dramatic reduction in the requisite starting materials’ masses will not only reduce waste in high-volume CNT production but also translate to cost savings for manufacturers.

CONCLUSIONS

Within the complex mixture of thermally generated compounds (>40 distinct chemical species),⁶ we have demonstrated that the alkynes contribute to accelerated CNT formation while other previously suspected molecules (e.g., benzene and methane) do not. This has important implications for industrial-scale CNT production. For example, the reduced energetic and starting materials requirements could result in substantial cost savings. Further, if alkyne-assisted approaches are fully optimized for high volume synthesis, we could see dramatic improvements in CNT yield and mass-per-hour production rates. Lastly, the limited byproduct emissions could prevent unnecessary damage to the environment and public health as industrial CNT production continues to expand.

Many intriguing questions remain. The general reactivity of small molecules (C₂–C₄) containing triple bonds suggests a previously unrecognized chemical specificity during CNT synthesis. This could be a consequence of two scenarios: (1) alkynes have a higher adsorption affinity for the metal catalyst (here, Fe on Al₂O₃), and their enhanced presence at the catalyst facilitates dissociation into C units followed by bulk and/or surface diffusion across the catalyst,^{2,3} or (2) alkynes bond efficiently with the metal catalyst system, and their structures enable the formation of new C–C bonds between intact (nondissociated) precursors. The latter interpretation, while unprecedented in the CNT literature, has close analogues in the homogeneous

metal catalysis literature,^{24–27,29–31} where new C–C bonds are formed *via* cyclic intermediates. Rather than forming transient structures, these cyclic structures may persist and form the graphitic CNT lattice during nanotube synthesis. Such metal-mediated cyclizations can occur between an alkene and an alkyne.^{24,26} Indeed, mass balance calculations and experimental evidence suggest that both ethylene and an alkyne were re-

quired for CNT formation in our system. If such reactions are occurring, and the chemical precursors are largely intact during new C–C bond formation, then chemical moieties on the alkyne or alkene could influence the resultant CNT structure (*e.g.*, chiral wrapping or functional group incorporation). Thus, alkyne-assisted CVD might provide a novel route for exerting control on nanometer-scale synthetic processes.

METHODS

Chemical Supplies. Helium, hydrogen, ethylene, methane, acetylene, and 1% acetylene (balance helium) were purchased from Metro Welding (MI) or AirGas (all ultrahigh purity grade). Before use, pure acetylene was filtered through a Porasil-C packed column immersed in a cryogenic solution (acetone/N₂(l) or acetonitrile/N₂(l), both –39 to –41 °C) to remove acetone. Mass spectral analysis indicated that acetone was removed to below the detection limit (<1 ppmv; manufacturer reported, Pfeiffer OmniStar). To our knowledge, this is the first CNT growth study where acetone has not been present as a co-reactant in acetylene-fed CVD experiments. The 1% acetylene mixture did not require purification. All other high-purity gases were purchased from Air Liquide America Specialty Gas. Benzene-saturated He was prepared by adding liquid benzene to a stainless steel tank, flushing, and then pressurizing with He.

CNT Synthesis. To measure *in situ* MWCNT forest height during the reaction progress, we utilized a custom-built CVD reactor^{9,10,15,16} with a laser displacement sensor mounted above the growth chamber (see Supporting Information). Gases were premixed and introduced to a resistively heated quartz preheater tube (4 × 300 mm (i.d. × length)), cooled to room temperature, and then delivered to a quartz reactor tube (4.8 × 22.9 cm). Inside the reactor tube, CNT forests were grown from electron-beam-deposited Fe (1 nm) with an Al₂O₃ (10 nm) under layer on a Si (675 μm) support. The catalyst substrate was locally heated on a Si platform (725 °C, except where noted), thereby minimizing gas-phase reactions in the growth chamber.¹⁰ The outer temperature of the cold-wall reactor did not exceed 70 °C.

The preheater was operated in two modes: (1) “on” at 1000 °C or (2) “off” at room temperature (21 °C). In both modes, reactant gases (C₂H₄/H₂) traveled through the preheater tube. With the preheater off, specific VOC test gases (*e.g.*, methyl acetylene or vinyl acetylene) were introduced to the reactant stream after the preheater tube and prior to impingement on the catalyst. The sum of these flows (He + test gas) was constant, but the distribution varied. Given the varying He delivery, we sought to remove effects associated with trace contaminants (*e.g.*, methane or water) by purifying the carrier gas using a N₂(l) cold trap with Porasil-C silica beads.

A typical program included the following: He flush at 1000 sccm for 8 min, He and H₂ at 174 and 310 sccm, respectively, for 4 min, and C₂H₄ (120 sccm), H₂ (310 sccm), the VOC test gas, and He were introduced for the duration of the CNT growth (where the summed flow rate of all gases was 604 sccm, except where noted).

VOC Analysis. VOCs were collected and analyzed as detailed in Plata *et al.*⁶ Briefly, stainless steel canisters were placed downstream of the reactor tube and flushed for the duration of CNT growth. Gas samples were collected just after growth termination and sealed with stainless steel ball valves. VOCs in the stainless steel canisters were quantified by gas chromatography with a flame ionization detector and thermal conductivity detector (GD-FID-TCD) calibrated with standard gas mixtures. Detection limits were approximately 0.1 ppmv. He and H₂ were quantified using an additional GC-TCD with a N₂ reference gas.

PAH Analysis. PAHs were collected and analyzed as detailed in Plata *et al.*⁶ Briefly, PAHs were concentrated on two consecutive, precleaned polyurethane foam (PUF) filters (3 in. length ×

1 in. diameter). These filters were in place for the entire duration of CNT growth, and the reported PAH abundances represent an integrated signal throughout the growth period. PUFs were extracted by triplicate accelerated solvent extractions (100 °C, 1000 psi, 5 min) with a 90:10 dichloromethane/methanol mixture. Extracts were concentrated and then analyzed by GC-mass spectrometry. Analyte recoveries were assessed using internal standards (acenaphthalene-*d*₁₀, *m*-terphenyl, and perylene-*d*₁₂) and ranged from 75 ± 1% for low molecular weight PAHs (128 to 154 amu) to greater than 90 ± 1% for higher molecular weight PAHs (>166 amu). Detection limits were around 1 ng g_C feed-stock⁻¹ (0.001 parts per trillion by volume for average PAH).

TGA and Raman Measurements. Results are shown in the Supporting Information. TGA measurements were performed using a TA Instruments Q50. Samples were oxidized in 20% oxygen and 80% helium from room temperature to 900 °C at a ramp rate of 5 °C min⁻¹ with a 30 min hold. The relative abundance of CNTs and amorphous carbon was calculated using a linear least-squared fit of the differentiated mass loss plot.

CNT structural quality was evaluated by Raman spectroscopy (Dimension P2, Lambda Solutions, λ = 533 nm), with a laser power of 20 mW and spot size of ~25 μm. Several spectra per sample were acquired, both horizontally along the midpoint and vertically along the height of the forest side wall. *G/D* values were determined by calculating the area under each peak, and averages were reported.

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Supporting Information Available: Material purity assessment (TGA and Raman analysis); Raman spectra; CNT diameter; forest density; diagram of experimental apparatus; tabulated VOC and PAH contents of reaction effluents. This material is available free of charge *via* the Internet at <http://pubs.acs.org>.

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