[Carbon 130 \(2018\) 607](https://doi.org/10.1016/j.carbon.2018.01.072)-[613](https://doi.org/10.1016/j.carbon.2018.01.072)

Contents lists available at ScienceDirect

Carbon

journal homepage: <www.elsevier.com/locate/carbon>

An effect of gas-phase reactions on the vertically aligned CNT growth by temperature gradient chemical vapor deposition

Carbon

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article info

Article history: Received 29 April 2017 Received in revised form 31 December 2017 Accepted 18 January 2018 Available online 19 January 2018

Keywords: Vertically aligned carbon nanotubes Activation energy Gas-phase reaction In-situ mass spectrometry

Thermally rearranged secondary species

ABSTRACT

Gas-phase reactions among carbon precursors could have a significant effect on the catalytic synthesis of vertically aligned (VA-) carbon nanotubes (CNTs). State-of-the-art adjustment of the gas-phase reaction conditions is done ad hoc with low reproducibility, ascribed partly to an incomplete understanding of the mechanism how the gas-phase reaction influences the growth kinetics of VA-CNTs. Here, we investigate this mechanism and propose that in the presence of prominent gas-phase reaction, the growth kinetics characterization shifts from a single rate-limiting reaction to a multi-route reaction with each pathway having its own rate-limiting step. The rate of the gas-phase reaction could be tailored by the partial pressure and thermal history of a carbon feedstock (e.g., acetylene). According to in-situ mass spectrometry and numerical simulation, a rich set of thermally rearranged secondary species (e.g., C_4H_4 and C_6H_6) are found above the catalyst surface. It appears that these secondary species, along with a chief precursor (C2H2), can give variation to a yield of CNTs through various reaction pathways with altering the overall growth rate of VA-CNTs. Our findings would further the current understanding of the VA-CNT growth from thermally rearranged precursors, instrumental to applications such as diameter-controlled growth and CMOS-compatible low-temperature growth.

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1. Introduction

Chemical vapor deposition (CVD) growth of vertically aligned carbon nanotubes (VA-CNTs) has garnered great interest because of its scalability [[1](#page-6-0)], low-cost, and high production yield. Despite the effort in the CVD of VA-CNTs in the past decades, the fundamental mechanism of the CNT growth is still not well understood, leading to low reproducibility and controllability [[2](#page-6-0)]. Previous studies have thus far suggested a sequential process of four steps: (i) mass transport and reaction in the gas phase $[3-5]$ $[3-5]$ $[3-5]$ $[3-5]$ $[3-5]$, (ii) surface reactions on the catalyst, (iii) carbon diffusion on the catalyst particle surface [\[6](#page-6-0)] or through bulk [\[7\]](#page-6-0), and (iv) carbon incorporation into CNTs. While the other steps have been extensively investigated, active discussions on the aspect of the gas-phase reactions and its impact on the growth result are rare.

Due to the transport time from a gas inlet to a catalyst substrate, a CVD process unavoidably involves thermal rearrangement of feedstock gases. During this step, common feedstock gases such as

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 C_2H_2 (acetylene) and C_2H_4 (ethylene) can generate a combination of secondary species [\[8](#page-6-0)], which influences VA-CNT growth rate and quality $[9-12]$ $[9-12]$ $[9-12]$. The more reactive the gases and the chamber conditions, the more thermally rearranged the precursor gases. The extent of the gas-phase reactions depends primarily on gas pretreatment temperature, gas dwell time [[13\]](#page-6-0), and gas composition [\[14](#page-6-0)]. We have previously proposed temperature gradient CVD (TG-CVD), which can effectively modulate the gas-phase reactions for a $C₂H₂$ -based CVD. In particular, by introducing a linearly decreasing temperature gradient from the gas inlet to the catalyst substrate, TG-CVD can condition the optimal gas-phase reaction environment for an efficient and high-quality CNT growth [\[11](#page-6-0)].

Several studies have shown the significant impacts of gas-phase reaction products on the rearrangement of carbon precursors and subsequently the CNT growth. Meshot et al. have decoupled CVD temperature into catalyst substrate temperature and gas pretreatment temperature to observe that the substrate temperature determines CNT diameter, whereas that the thermal treatment generates a wide range of hydrocarbon species that either promote or inhibit the CNT growth [\[9\]](#page-6-0). Yasuda et al. have introduced thermal Corresponding author. history (dwell time) of feedstock gases as one of the CVD

parameters with which to report a strong correlation between the gas dwell time and various aspects of the growth results (e.g., conversion rate of carbon source to CNTs) [\[13\]](#page-6-0). Nessim et al. have observed a transition of the CNT crystallinity, from rather amorphous to single crystalline, under different thermal pre-treatment conditions of precursor gases [\[15](#page-6-0)]. Moreover, Matsumoto et al. have observed that the pyrolysis of C_2H_2 could strongly influence the growth efficiency of single-walled CNTs [[16\]](#page-6-0). These works provide a hint that some of these gas pyrolysis products are likely important reactants for the CNT production, while others could be detrimental to the growth efficiency and quality control. The subsequent work by Plata et al. has identified the alkyne types of the gas-phase reaction products (i.e., C_2H_2 , C_2HCH_3 (methyl acetylene), and C_4H_4 (vinyl acetylene)) as important precursors while excluding the previously suspected species such as C_6H_6 and CH₄ [[14\]](#page-6-0). Ma et al. have later found out that at CVD temperatures for the CNT growth, C_2H_2 polymerizes into unsaturated carbon chains, mainly comprising C_4H_4 [[12\]](#page-6-0). Although a number of theoretical and experimental observations have shown the potential influence of gas-phase reactions on the CNT growth, the underlying mechanism of VA-CNTs in the presence of prominent gas-phase reactions remains still to be elucidated.

Here, we investigate systematically the influence of gas-phase reactions on the VA-CNT growth by varying the ratio of the secondary carbonaceous precursors to initial C_2H_2 using TG-CVD. Temperature gradients were applied between the gas inlet and the catalyst substrate in the cold-wall CVD reactor. We observed extra growth rate enhancement for high C_2H_2 partial pressure, high gas pre-treatment temperatures, and long dwell time. In the presence of a thermal zone for active precursor rearrangement, the apparent activation energy of VA-CNTs deviates from its value for no such rearrangement as the C_2H_2 partial pressure varies. The deviation of the activation energy indicates an alteration of the growth mechanism. Based on these findings, we propose a mechanism of the gas-phase-assisted growth with a model by taking multiple parallel reaction pathways into account.

2. Experimental

2.1. Temperature gradient CVD

CNT growth experiments were performed in a vertical, cold-wall CVD reactor (Black Magic Pro™, Aixtron AG) with dual heaters. In this reactor, a gas mixture injected downward from a top shower head impinges on a sample stage 41 mm below. While passing the reactor chamber, the gas mixture undergoes a pre-defined temperature gradient, a characteristic of TG-CVD. Dual heaters, one (top heater) placed next to the shower head and the other (bottom heater) right beneath the sample stage, are employed to determine and control thermal boundary conditions for the temperature gradient inside of the chamber. Two boundary temperatures at the gas shower head and at the sample stage are measured by a thermocouple and an infrared pyrometer, respectively. The infrared radiation pyrometer has accuracy of ± 6 °C and can measure the sample stage temperature using a two-wavelength ratio method. A detailed description of the TG-CVD system could be found in Ref. [\[11\]](#page-6-0).

We separate our growth conditions into two categories: top heating (TH) mode and bottom heating (BH) mode. In a TH mode, the top heater is used as the main heat source creating a negative temperature gradient toward the catalyst substrate, whereas in a BH mode, the bottom heater is used as a main heat source generating a positive temperature gradient toward the catalyst substrate. Therefore, in the BH mode, the precursor gas flows through thermal zones cooler than the catalyst before reacting with it. In the TH mode, the gas passes through thermal zones hotter than the catalyst that is indirectly heated by the top heater via thermal radiation.

In order to analyze the gas mixture composition from the thermal treatment of the gas precursor, we collected mass spectra in situ by a quadrupole mass-spectrometer residual-gas analyzer (Vision 2000-C/Microvision 2, MKS), demonstrating relative changes in the abundance of selected compounds. The mass spectrometer probe is inserted $5-8$ mm above the catalyst substrate to detect the gas composition right above the catalysts (Fig. S5), measuring, for the first time, the gas-phase reaction products in the vicinity of the catalyst in a single CVD chamber setup.

2.2. Catalyst preparation and CNT growth

All CNTs are grown on the same catalyst, consisting of 2 nm Fe atop of 20 nm Al_2O_3 deposited on a Si substrate by e-beam evaporation (Univex 500, Leybold). Here, we chose $585-700$ °C as the parametric window for the catalyst substrate temperature, while fixing the temperature difference between top heater and catalyst substrate to be -160 °C for TH mode and 200 °C for BH mode for all experiments. Before the growth, the chamber was thermally cleaned under pure H_2 at 800 °C for 10 min. Then, the catalyst substrate were loaded onto to the sample stage, followed by chamber evacuation to sub-0.2 mbar. At a ramp rate of 300 \degree C/min, the catalyst substrates were first raised to $700\degree C$ by the bottom heater and maintained at that temperature for catalyst reduction for 300 s, with the total chamber pressure maintained at 10 mbar. A feed gas mixture included 400 sccm of $H₂$ and 600 sccm of Ar. We applied identical heating and feed gas conditions in this pretreatment process for all of our experiments to ensure the constant initial activity of catalyst. After catalyst pre-treatment, a quick thermal rearrangement was introduced under pure Ar. By changing the top and bottom heater temperatures, desired temperature gradient was developed in this period. During the CNT growth, C_2H_2 (5, 15 or 25 sccm) was injected into the chamber along with constant amounts of H_2 (200 sccm) and Ar (300 sccm). The total pressure during the growth was kept at 480 mbar $(\pm 0.2 \text{ mbar})$. The initial growth rate was obtained by averaging the VA-CNT heights of the initial 100-s-long growths. Since the VA-CNT growth rate may decrease with time $[3-5]$ $[3-5]$ $[3-5]$, we checked the variation of the growth speed by employing an ex-situ method of the stop-andstart (pulsed) measurement technique [\[1](#page-6-0)]. According to the stopand-start growth that supply C_2H_2 discretely to a constant flow of Ar with a time interval of 15 s between each growth segment of 100 s, the initial growth rate turned out to be the maximum growth rate (Fig. S4). As the growth kinetics of VA-CNTs can be altered by the catalyst evolution over time, the effect of the gas-phase reaction can be better revealed in the initial growth rate characteristics.

2.3. Reacting flow simulation

In order to resolve the gas composition impinging on the catalyst substrate during TGCVD, we simulated a reacting flow of 199 reactions and 56 gas species based on a Chemkin reaction library [[17](#page-6-0)] using a stagnation flow model. The CVD chamber was modelled as a one-dimensional system, based on a kinetic model of laminar premixed C_2H_2 and C_2H_4 flames [[18\]](#page-6-0) with excluding the oxygen-containing reactions. In this simulation, we neglected an influence of moisture or any $O₂$ source from the environment on unwanted contamination of the reaction chamber. The boundary conditions were as follows: at the shower head, the mole fractions of the reactants were imposed $(C_2H_2$: 0.0099, H_2 : 0.3960, Ar: 0.5941); the bulk axial velocity at the inlet was given based on the shower head flow area and the volume flow rate of the incoming mixture calculated from the given top heater temperature and

chamber total pressure (480 mbar); the substrate that holds the catalyst piece was assumed to be non-reactive and impermeable.

3. Results and discussions

3.1. Apparent activation energy

It is known that C_2H_2 -containing feedstock gases generate a wide varieties of secondary species via thermal rearrangement [\[11\]](#page-6-0). Various types and compositions of the carbonaceous species would eventually approach the catalyst and participate in the subsequent surface catalytic reactions, precipitating carbon products such as CNTs. For a given catalyst temperature (T_{cat}) , gas precursors in the TH mode experience much higher temperatures than in the BH mode during their travel to the catalyst, and therefore vigorous thermal rearrangement would occur to the precursors in the TH mode. Distinct thermal histories of C_2H_2 can result in different active reactant species atop the catalyst and hence influence the growth kinetics of VA-CNTs.

In order to verify this hypothesis, we collected the initial growth rates of VA-CNTs in the two heating modes at various C_2H_2 partial pressures (P_{C2H2}). Acquisition of such kinetics data allows the comparison among different heating modes in detail by drawing Arrhenius plots accurately and determining the activation energy of each heating mode. We varied P_{C2H2} in the range of 1-5 mbar. In the TH mode, we observed a change of the apparent activation energy, E_A , of the VA-CNT growth with respect to P_{C2H2} : $E_A = 1.18$ eV at $P_{C2H2} = 1$ mbar and increases to 1.37 and 1.51 eV at $P_{C2H2} = 3$ mbar and 5 mbar, respectively (Fig. 1a). In contrast, no such dependency of apparent E_A on P_{C2H2} was observed in the BH mode (Fig. 1b, black lines); our CNT growth data in the BH mode shows E_A with a constant value of 1.42 ± 0.01 eV as P_{C2H2} triples. Wirth et al. have also reported a constant E_A independent of P_{C2H2}, in the BH mode and under the isothermal conditions, indicating an invariant rate-limiting mechanism [\[7\]](#page-6-0). Under the assumption of bulk-diffusion-limited growth, a constant E_A around 1-1.7 eV is expected. However, the bulk-diffusion-limiting mechanism is insufficient to explain the P_{C2H2} dependency of the apparent E_A . Such a dependency of E_A indicates an out-of-proportion increase of the growth rate with P_{C2H2} in the TH mode, in which gas thermal rearrangement is enhanced.

We postulate that the gas-phase reaction of C_2H_2 may introduce a cumulative impact on the growth kinetics of VA-CNTs by altering the composition and concentration of actual gaseous reactants. In the BH mode, the gas-phase reaction is suppressed by low temperatures of the pre-treatment gas thermal zone; consequently, the cumulative effect of the gas-phase reactions is eliminated, manifested by a constant E_A .

3.2. Gas-phase reaction

To support our postulation that the products of the gas-phase reaction of C_2H_2 influences the CNT growth kinetics, we first measure the gas-phase composition directly above the catalyst substrate by in-situ mass spectrometry ([Fig. 2\)](#page-3-0). This measurement reveals that a wide range of gas species are actually arriving at the catalyst. Among them, we selected 6 mass-to-charge $(m|z)$ ratio values (i.e., 16, 26, 28, 40, 52, 78) to monitor CH₄, C₂H₂, C₂H₄, Ar, C_4H_4 , and C_6H_6 , respectively. C_4H_4 and C_6H_6 are supposed to be the most dominant products of thermal C_2H_2 polymerization [[17,19](#page-6-0)]. Ar as a carrier gas maintains the constant flow rate and partial pressure and is employed to normalize the other species and calculate the relative abundance.

First, we compare the gas compositions and concentrations in the BH and TH modes for a fixed P_{C2H2}. At T_{cat} of 600 °C and P_{C2H2} of 3 mbar, the relative abundance of the secondary species $-$ especially C₄H₄ and C₆H₆ (m/z 52 and 78) – is much higher in the TH mode [\(Fig. 2,](#page-3-0) red) than in the BH mode (Fig. 2, blue). When T_{cat} is increased to 750° C, we observe a similar tendency of more secondary species in the TH mode than in the BH mode with all of their partial pressures increased by at least half an order of magnitude ([Fig. 2b](#page-3-0)). Next, we varied P_{C2H2} in the TH mode. When P_{C2H2} is decreased from 3 mbar to 1 mbar at a fixed T_{cat} of 600 °C, the relative abundance of C_4H_4 decreases by about an order of magnitude, and that of C_6H_6 drops below 10⁻⁶ [\(Fig. 2](#page-3-0)a, red vs dark red). The P_{C2H2} reduction at T_{cat} of 750 \degree C also decreases the abundance of the secondary species including C_4H_4 and C_6H_6 . On the other hand, an increase of P_{C2H2} in the TH mode results in out-of-proportion elevation in the abundance of the secondary species. Finally, we compare the gas-phase reactions at various T_{cat} while fixing P_{C2H2} and heating mode ([Fig. 2a](#page-3-0) vs 2b). For all P_{C2H2} and heating modes (BH and TH), higher partial pressures of the secondary species are observed in 750 \degree C than in 600 \degree C, likely related to an overall increase in the average pyrolysis temperature. In general, heating mode, P_{C2H2} and T_{cat} can all influence the carbon precursor to vary the active carbonaceous reactant species atop the catalyst.

Fig. 1. Activation energy of the CNT growth for various heating modes and C₂H₂ partial pressures. (a) Different P_{C2H2} associate with different apparent activation energies (E_A) in the top heating (TH) mode (blue for 1 mbar, red for 3 mbar and green for 5 mbar of C₂H₂). The denoted temperature for Arrhenius plots are the catalyst temperature, $T_{\text{cat.}}$ (b) E_A is observed to be independent of P_{C2H2} in the bottom heating (BH) mode, based on both data from our study and others [[7\]](#page-6-0), whereas it clearly depends on P_{C2H2} in the TH mode. (A colour version of this figure can be viewed online.)

Fig. 2. In-situ mass spectra collected by a mass spectrometer (MS) gas analyzer, demonstrating relative abundance of selected mass-to-charge (m/z) ratios. The m/z values of interest are related to CH₄ (16), C₂H₂ (26), C₂H₄ (28), Ar (40), C₄H₄ (52) and C₆H₆ (78). Two representative T_{cat} of 600 °C (a) and 750 °C (b) are compared. BH mode at P_{C2H2} = 3 mbar, TH mode at P_{C2H2} = 3 mbar, and TH mode at P_{C2H2} = 1 mbar are marked in cyan, red, and dark red, respectively. (A colour version of this figure can be viewed online.)

To analyze the gas-phase reaction in TG-CVD in a more comprehensive way, we compared the in-situ mass spectrometry result with a reacting flow simulation based on our chamber configuration and CVD conditions (see Methods 2.3). According to the simulation, the major gas-phase reaction products appear to be polymerized building blocks (C_3 and C_4 species), decomposition fragments (C_1 and C_2 species), C_2H_4 , unreacted C_2H_2 , and H_2 . The partial pressures of the feedstock (C_2H_2), reductant (H_2) and the carrier gas (Ar) are relatively constant due to their significantly high initial concentrations. Other carbonaceous species, such as C_2 species (ethane, C_2H_6 ; ethylene, C_2H_4 ; vinyl radical, C_2H_3 ; and the other C_2 intermediates), C_3 species (propene, C_3H_6 ; propadiene, C₃H₄; propyne, C₃H₄), C₄ species (vinyl acetylene, C₄H₄; butene, C_4H_8 ; butadiene, C_4H_6 ; butadiene radical, C_4H_2 ; and the other C_4 species) and benzene, change their partial pressures (mole fractions) drastically over a few orders of magnitude (Fig. 3a). Noticeably, P_{C4H4} changes over three orders of magnitude from 10^{-6} to 10^{-3} bar depending on temperature and initial P_{C2H2} (Fig. 3b). In principle, in order to clarify the respective impact of each gas species, it can be useful to observe the growth under the direct feeding of each species, e.g., via molecular beaming. In practice, however, most gas-phase reaction products are transient species with low stability and extremely short lifetime. For example, C₄H₄ has a lifetime (in vacuum) of around 3.5 μ s [\[20,21\]](#page-6-0). In the absence of a stable C4H4 supply method, the conduction of such an experiment is limited. As Ma et al. have reported, C_4H_4 has been recognized a key species to enhance the growth efficiency and quality of VA-CNTs [[12\]](#page-6-0). The structure of C_4H_4 with two sp²-hybridized carbon bond can be easily assembled to a CNT building block. Moreover, C_4H_4 contains a triple bond that can be easily opened for surface catalytic reactions. Although benzene shares the similar structural advantage, the high thermal stability of benzene prevents it from actively partaking in the CNT synthesis.

3.3. Generalized reaction kinetic formulation of the VA-CNT growth

The thermally rearranged secondary species have distinctive properties (e.g., structures, activities in catalytic reactions, etc.) and could participate in the surface catalytic reaction of the CNT growth through their own reaction pathways ([Fig. 4a](#page-4-0)). In the absence of gas-phase reactions, C_2H_2 arrives at the catalyst to dehydrogenate and dissociate into carbon monomers and yield CNT through bulk or surface diffusion [\(Fig. 4](#page-4-0)a, left) [\[22\]](#page-6-0). In the presence of a prominent gas-phase reaction, C_2H_2 undergoes thermal rearrangement to generate secondary species, largely comprising C_4H_4 [\[12](#page-6-0)]. Each of these species participates in individual catalytic surface reactions

Fig. 3. - Chemkin-based reacting flow simulation results. (a) Simulated partial pressure of major pyrolysis products approaching catalyst substrate (e.g., C₂H₄, C₄H₄, C₄H₄, C₁H₄, C₁H₄, and C_6H_6) as a function of the substrate temperature. (b) Contour plot of the predicted C_4H_4 partial pressure over the catalyst substrate as a function of the gas inlet P_{CHL} and the substrate temperature. (A colour version of this figure can be viewed online.)

Fig. 4. - Schematics, numerical prediction, and electrical circuit analogy for the VA-CNT growth kinetics. (a, b) With the help of enhanced gas-phase reactions, secondary products such as C_4 and C_6 species are produced to approach the catalyst substrate. Gaseous secondary products could participate in the CNT synthesis through reaction pathways, path 3 and path X, unseen in the CVD without the precursor thermal rearrangement. With no gas-phase reaction, C₂H₂ contributes to CNT growth though dissociation followed by bulk diffusion (path 1) or surface diffusion (path 2). (c) A resistor-capacitor circuit analogy for the CNT growth rate based on a multiple pathway mechanism. (d) The predicted values of the CNT growth rates (dash lines) in great agreement with the experimental data (black/white squares, circles and triangles for P_{C2H2 of} 1, 2, and 3 mbar, respectively). (A colour version of this figure can be viewed online.)

and diffusion pathways to incorporate into VA-CNT (Fig. 4a, right). $C₂H₂$ is known to bond very easily and strongly to a transition metal surface due to its strong interaction with the d-orbital, which leads to the exchange of electrons between the d-orbitals and the antibonding orbitals of adsorbed C_2H_2 [\[23,24](#page-6-0)]. In the range of P_{C2H2} applied in this study, the surface sites can be considered as a layer of adsorbed C species as a carbon reservoir in equilibrium comprised of molecules of C_2 species and their derivatives [\[25\]](#page-6-0).

Molecules of C_2 species adsorbed on Fe particle can either dissociate into two atomic carbons or a dimer, each possibility resulting in its individual reaction pathway (Fig. 4b). Through one pathway, C_2 molecules first dissociate into single C atoms and then diffuse through the bulk catalyst particle (Fig .4b, Path 1). Atomic carbons are prone to diffusion in the bulk catalyst rather than on the surface due to a large surface-to-volume ratio of catalyst par-ticles [\[26\]](#page-6-0). In addition, adsorbed C_2 dimers could bypass the dissociation step and incorporate directly into CNT through surface diffusion. Surface-diffusion-limited growth has E_A around 0.4 eV and are often observed in a plasma-enhanced CVD [\[6,27,28\]](#page-6-0). However, the observed apparent E_A in our study is much higher than E_A for surface diffusion and lies in the E_A regime for bulk diffusion, and thus we simply account for the bulk-diffusionlimited reaction pathway.

Alternatively, the adsorbed C_2 -species molecules can interact with the impinging gas species directly and undergo a polymerization-like reaction to construct CNTs [\[29\]](#page-6-0). In the transition metal catalysis, the cyclotrimerization of alkynes that combines three acetylene molecules into a hexagonal building block has been known for decades. We consider a simplified reaction mechanism based on carbon mass conservation. C_4H_4 , including their derivatives, are referred to as C_4 species groups, respectively. We assume that gas molecules can impinge and react directly with an adsorbed species on the catalyst site through capture, isomerization, and insertion, as in the Eley-Rideal reaction, often used to describe the selective C_2H_2 hydrogenation on the transition metal like Fe $[30,31]$ $[30,31]$ $[30,31]$. As a result, C_4 and other secondary species from the reactant gas mixture could possibly react with the adsorbed C_2 species via the Eley-Rideal mechanism and subsequently diffuse on the surface to participate in the CNT formation (Fig 4b, Path 2 in blue; also other pathways in green). Due to the nature of the Eley-Rideal mechanism, the reaction rate depends not only on the catalyst active site density but also on the impinging frequency of gaseous C4 species.

Through the above pathways, various forms of carbonaceous precursors contribute to the CNT growth. Each pathway contains a series of reactions with a distinct rate-limiting step, represented as follows:

$$
v_1 = \sigma_S A_1 e^{-E_{A1}/k_B T}, \tag{1}
$$

$$
\nu_2 = \sigma_S [C_{C_4}] A_2 e^{-E_{A2}/k_B T}, \qquad (2)
$$

where, two typical pathways are listed, namely, the diffusion limited pathway (Fig. 4a left and Fig. 4b Path 1) and a polymerization-like reaction pathway in the Eley-Rideal mechanism (Fig. 4a right and Fig. 4b Path 2). ν is the reaction rate of the rate-limiting step in pathways 1 and 2; A_1 and A_2 are the preexponential factors; σ_s is the areal density of the active catalyst sites; E_A is the activation energy of the rate-limiting step; C_{C2} and C_{C4} are the impinging concentration of gaseous C_2 and C_4 species, respectively. We assign $E_{A1} = 1.5$ eV and $E_{A2} = 1.25$ eV by referring to the literature [\[6,32](#page-6-0)-[35](#page-6-0)]. Concentration of the gaseous C_4 species could be deduced from the result of the aforementioned 1D

reacting flow simulation by

$$
[C_{C_4}] = [C_{C_2}] A_{C_4} e^{-E_{AC_4}/k_B T}, \qquad (3)
$$

which associates $[C_{C2}]$ with the rate of the reaction pathway 2. We extracted apparent activation energies (E_{AC4}) and their preexponential factors (A_{C4}) for various C_2H_2 partial pressures ([C_{C2}]). Combing eq. (1) and eq. (2) , the overall reaction rate as a sum of these pathways can be expressed as,

$$
\nu_0 = [C_S]A_1 e^{-E_{A1}/k_B T} + [C_S] [C_{C_4}]A_2 e^{-E_{A2}/k_B T} = A_0 e^{-E_{A0}/k_B T},
$$
(4)

where, v_0 is the overall reaction rate of VA-CNTs and can be described as a single Arrhenius function apparently; A_0 is the constant overall pre-exponential factor; E_{A0} is the overall apparent activation energy, which is a function of $[C_{C4}]$. Replacing $[C_{C4}]$ by eq. (3), we can obtain E_{A0} as a function of C_{C2} . The numerical prediction based on the multiple-reaction-pathway model for the CNT growth rate with respect to P_{C2H2} is shown in [Fig. 4](#page-4-0)c. The prediction shows that when enhanced gas-phase reactions of C_2H_2 are present, the overall E_A is positively correlated with P_{C2H2} . The model shows great consistency with our experimental data, as it considers the contributions from additional surface reaction pathways of the secondary species derived from the C_2H_2 feedstock. In other words, the contribution of C_4 species, for example, can render the overall E_A deviate from a constant value, in the presence of a prominent gas-phase reaction.

As the P_{C2H2} increases, one may expect that the catalysts are more prone to poisoning and might slow down the growth. If the severe catalyst poisoning took place, CNT growth kinetics may have appeared disproportionately influenced by the P_{C2H2} change. However, this scenario can be excluded for a few reasons. First, the P_{C2H2} do not change very much throughout our growths. Second, our observation of the unexpectedly high growth rate at high P_{C2H2} shows an opposite trend to the catalyst poisoning scenario. Third, as the stop-and-start method shows, our experiments are in the initial growth phase of CNTs with almost constant growth rate. Thus, we rule out the possibility of the P_{C2H2} -reliant catalyst poisoning in our growth conditions. To sum up, this parallelpathway model could possibly provide an explanation to our experimental observation of the apparent E_A variation with P_{C2H2} .

3.4. An electric circuit analogy incorporating the activation energy

In order to provide better insight to the multiple parallel pathway model, we visualize this parallel model by constructing an analogous electric circuit ([Fig. 4c](#page-4-0)). This electric circuit model comprises resistors (with resistance, R) and capacitors (with capacitance, C) driven by a voltage source. Compared with a simple, resistance-based linear circuit model [[36](#page-6-0)], the RC circuit model could reflect the complexity of the Arrhenius equation (e.g., eq. (4)) associated with variable activation energy by incorporating E_A to the exponential function of the circuit (Fig. S6). Hence, our proposed RC circuit offers a fine-grained model for the growth kinetics in contrast to the commonly used, simple resistor circuit [\[7\]](#page-6-0). Since E_A is the focal point of our investigation, this coordinate-transferred view through the circuit analogy helps to visualize physical representation of E_A .

In the RC circuit analogy, each resistor-capacitor pair (RC pair) is connected in parallel and share the same voltage across their endpoints. When voltage (E) is applied, the RC pairs draw a charging current to store electrical energy in the capacitor. The larger the capacitance, the more the transient current flows through that RC circuit.

The RC circuit analogy transforms the Arrhenius plot of the CNT

growth from the growth-rate-thermal-energy domain to the charging-current-time domain. In the RC circuit analogy, the total charging current (I_{total}) is analogous to the overall initial growth rate in the CNT growth kinetics. The total charging current is the sum of charging currents out of each branch (I) of the parallel RC circuit. The current in each branch is a function of R and C values as

$$
I = \frac{E}{R}e^{-t/RC},\tag{5}
$$

and thus the total current equals to

$$
I_{total} = E\left(\frac{1}{R_1}e^{-t/R_1C_1} + \frac{1}{R_2}e^{-t/R_2C_2} + \cdots\right)
$$
 (6)

In this analogy, the charging time, t , corresponds to an inverse thermal energy $({\rm k_B T})^{-1}$, the RC product to $E_{\rm A}^{-1}$; and the voltage over resistance, E/R, to the pre-exponential factor of the CNT growth kinetics model.

Indeed, the RC circuit model can successfully explain the E_A variation of our experimental observation [\(Fig. 4d](#page-4-0)). At time t of the multiple-RC circuit (or given thermal environment of k_BT), the branch of higher RC value (or smaller E_A) yields large charging current than the branch of lower RC value (or higher E_A) does; see Supplementary Information for details. Analogously, among parallel reaction pathways for the VA-CNT growth, the pathway with lower E_A would contribute more to the growth rate than the pathway with higher E_A does, noting that $RC \sim 1/E_A$. If we use eq. (6) to calculate an apparent RC value for the entire circuit, the apparent overall RC value depends on the R and C values in each branch. Similarly, the apparent E_A calculated for the CNT growth having multiple reaction pathways depends on the E_A and the proportionality constants (pre-exponential factor and/or P_{C2H2} value) of each pathway. Changes of the RC value in a circuit branch will thus lead to changes in the I_{total} and the apparent overall RC value. Likewise, variation in the A value (caused by a change in P_{C2H2}) of a certain reaction pathway will also affect the apparent E_A value of the CNT growth. In brief, the RC circuit analogy can provide an illustrative model to analyze the P_{C2H2} -dependent E_A and the accumulative effect of complex chemical reactions in the CNT growth. Furthermore, the RC circuit analogy offers a flexible platform to model CNT growth kinetics, as it can be extended to cover multiple parallel reaction pathways. This aspect becomes of particular utility when the gas-phase reactions are even more complex or when multiple species behave as precursor gases. It is to be noted that this electric circuit analogy is nothing more than a coordinate-transformed illustration of the equivalent Arrhenius expression for the multiple reaction pathways (e.g., eq. (4)).

4. Conclusions

The activation energy of the VA-CNT growth deviates from a constant value to higher ones at increased C_2H_2 concentrations when gas-phase reaction of the feedstock gas is enhanced. In-situ mass spectra and the reacting flow simulation results support our postulate that gas-phase reaction products such as C_4H_4 do exist and along with the chief precursor, C_2H_2 , have a significant influence on the VA-CNT growth. By correlating this deviation of activation energy with a cumulative effect of the secondary species, we propose a parallel reaction pathway model in conjunction with the Eley-Rideal mechanism. Our parallel reaction model supports the observation of the P_{C2H2} -dependent activation energy, which cannot be explained by simply assuming a single rate-limiting step. Our proposed electric circuit analogy illustrates the parallel reaction pathway model by projecting the overall CNT growth rate to the total charging current and the E_A to the inverse RC value in the resistor-capacitator circuit. Our work unveils a complex aspect of the catalytic CVD process and enables rational design of the thermal reaction process for an effective CNT growth at an industrial scale. Further refinement of this model could lead to a deeper understanding and a better control of the CNT CVD. Besides, the growth data and the simulation results can collaborate to engender new knowledge on the diameter-selective VA-CNT growth.

Acknowledgments

The major part of this work was carried out in Binnig and Rohrer Nanotechnology Center of ETH Zürich and IBM Zürich. The authors acknowledge the support from the Microfabrication Center (FIRST) and the Microscopy Center (SCOPE-M) of ETH Zürich. This work was funded by Swiss National Science Foundation (Contract Nos 200021-137964 and 200021-146856), Switzerland, and Agency for Defense Development (ADD-14-70-07-06), the Republic of Korea.

Appendix A. Supplementary data

Supplementary data related to this article can be found at <https://doi.org/10.1016/j.carbon.2018.01.072>.

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