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



Carbon

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#### 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, along with a chief precursor ( $C_2H_2$ ), 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], 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]. Previous studies have thus far suggested a sequential process of four steps: (i) mass transport and reaction in the gas phase [3–5], (ii) surface reactions on the catalyst, (iii) carbon diffusion on the catalyst particle surface [6] or through bulk [7], 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

\* Corresponding author. E-mail address: parkh@ethz.ch (H.G. Park).  $C_2H_2$  (acetylene) and  $C_2H_4$  (ethylene) can generate a combination of secondary species [8], which influences VA-CNT growth rate and quality [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], and gas composition [14]. We have previously proposed temperature gradient CVD (TG-CVD), which can effectively modulate the gas-phase reactions for a  $C_2H_2$ -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].

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]. Yasuda et al. have introduced thermal 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]. 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]. Moreover, Matsumoto et al. have observed that the pyrolysis of C<sub>2</sub>H<sub>2</sub> could strongly influence the growth efficiency of single-walled CNTs [16]. 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<sub>2</sub>H<sub>2</sub>, C<sub>2</sub>HCH<sub>3</sub> (methyl acetylene), and C<sub>4</sub>H<sub>4</sub> (vinyl acetylene)) as important precursors while excluding the previously suspected species such as C<sub>6</sub>H<sub>6</sub> and CH<sub>4</sub> [14]. Ma et al. have later found out that at CVD temperatures for the CNT growth, C<sub>2</sub>H<sub>2</sub> polymerizes into unsaturated carbon chains, mainly comprising  $C_4H_4$  [12]. 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<sup>™</sup>, 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  $\pm 6 \,^{\circ}$ 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].

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<sub>2</sub>O<sub>3</sub> 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<sub>2</sub> 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 °C/min, the catalyst substrates were first raised to 700 °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 H<sub>2</sub> 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<sub>2</sub>H<sub>2</sub> (5, 15 or 25 sccm) was injected into the chamber along with constant amounts of H<sub>2</sub> (200 sccm) and Ar (300 sccm). The total pressure during the growth was kept at 480 mbar ( $\pm 0.2$  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], we checked the variation of the growth speed by employing an ex-situ method of the stop-andstart (pulsed) measurement technique [1]. According to the stopand-start growth that supply C<sub>2</sub>H<sub>2</sub> 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] 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] with excluding the oxygen-containing reactions. In this simulation, we neglected an influence of moisture or any  $O_2$  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]. 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<sub>2</sub>H<sub>2</sub> partial pressures (P<sub>C2H2</sub>). 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<sub>C2H2</sub> 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  $P_{C2H2}$ :  $E_A = 1.18 \text{ eV}$  at  $P_{C2H2} = 1 \text{ mbar}$  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 EA on PC2H2 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  $1.42 \pm 0.01$  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]. 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<sub>C2H2</sub> 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). 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 CH<sub>4</sub>, C<sub>2</sub>H<sub>2</sub>, C<sub>2</sub>H<sub>4</sub>, Ar, C<sub>4</sub>H<sub>4</sub>, and C<sub>6</sub>H<sub>6</sub>, respectively. C<sub>4</sub>H<sub>4</sub> and C<sub>6</sub>H<sub>6</sub> are supposed to be the most dominant products of thermal C<sub>2</sub>H<sub>2</sub> polymerization [17,19]. 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<sub>C2H2</sub>. At T<sub>cat</sub> of 600 °C and P<sub>C2H2</sub> of 3 mbar, the relative abundance of the secondary species - especially  $C_4H_4$  and  $C_6H_6$  (*m*/*z* 52 and 78) – is much higher in the TH mode (Fig. 2, red) than in the BH mode (Fig. 2, blue). When T<sub>cat</sub> 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). Next, we varied  $P_{C2H2}$  in the TH mode. When  $P_{C2H2}$  is decreased from 3 mbar to 1 mbar at a fixed T<sub>cat</sub> 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. 2a, red vs dark red). The P<sub>C2H2</sub> reduction at T<sub>cat</sub> of 750 °C also decreases the abundance of the secondary species including C<sub>4</sub>H<sub>4</sub> and C<sub>6</sub>H<sub>6</sub>. 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 vs 2b). For all P<sub>C2H2</sub> and heating modes (BH and TH), higher partial pressures of the secondary species are observed in 750 °C than in 600 °C, likely related to an overall increase in the average pyrolysis temperature. In general, heating mode, P<sub>C2H2</sub> and T<sub>cat</sub> 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  $C_2H_2$  partial pressures. (a) Different  $P_{C2H_2}$  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  $C_2H_2$ ). The denoted temperature for Arrhenius plots are the catalyst temperature,  $T_{cat.}$  (b)  $E_A$  is observed to be independent of  $P_{C2H_2}$  in the bottom heating (BH) mode, based on both data from our study and others [7], whereas it clearly depends on  $P_{C2H_2}$  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 CH<sub>4</sub> (16), C<sub>2</sub>H<sub>2</sub> (26), C<sub>2</sub>H<sub>4</sub> (28), Ar (40), C<sub>4</sub>H<sub>4</sub> (52) and C<sub>6</sub>H<sub>6</sub> (78). Two representative  $T_{cat}$  of 600 °C (a) and 750 °C (b) are compared. BH mode at P<sub>C2H2 = 3</sub> mbar, TH mode at P<sub>C2H2 = 3</sub> mbar, and TH mode at P<sub>C2H2 = 1</sub> 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<sub>3</sub> and C<sub>4</sub> species), decomposition fragments (C<sub>1</sub> and C<sub>2</sub> species), C<sub>2</sub>H<sub>4</sub>, unreacted C<sub>2</sub>H<sub>2</sub>, and H<sub>2</sub>. 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<sub>2</sub> species (ethane, C<sub>2</sub>H<sub>6</sub>; ethylene, C<sub>2</sub>H<sub>4</sub>; vinyl radical, C<sub>2</sub>H<sub>3</sub>; and the other C<sub>2</sub> intermediates), C<sub>3</sub> species (propene, C<sub>3</sub>H<sub>6</sub>; propadiene, C<sub>3</sub>H<sub>4</sub>; propyne, C<sub>3</sub>H<sub>4</sub>), C<sub>4</sub> species (vinyl acetylene, C<sub>4</sub>H<sub>4</sub>; butene, C<sub>4</sub>H<sub>8</sub>; butadiene, C<sub>4</sub>H<sub>6</sub>; butadiene radical, C<sub>4</sub>H<sub>2</sub>; and the other C<sub>4</sub> 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<sub>C2H2</sub> (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, C<sub>4</sub>H<sub>4</sub> has a lifetime (in vacuum) of around  $3.5 \ \mu s$  [20,21]. In the absence of a stable C<sub>4</sub>H<sub>4</sub> supply method, the conduction of such an experiment is limited. As Ma et al. have reported, C<sub>4</sub>H<sub>4</sub> has been recognized a key species to enhance the growth efficiency and quality of VA-CNTs [12]. The structure of C<sub>4</sub>H<sub>4</sub> with two sp<sup>2</sup>-hybridized carbon bond can be easily assembled to a CNT building block. Moreover, C<sub>4</sub>H<sub>4</sub> 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). 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. 4a, left) [22]. 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]. 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.,  $C_2H_4$ ,  $C_4H_4$ ,  $CH_4$ ,  $C_3H_4$  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  $P_{C2H2}$  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,  $C_2H_2$  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).  $C_2H_2$  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]. 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].

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 particles [26]. 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]. 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]. 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]. 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  $C_4$  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:

$$\nu_1 = \sigma_{\rm S} A_1 e^{-E_{\rm A1}/k_{\rm B}T},\tag{1}$$

$$v_2 = \sigma_{\rm S} [C_{\rm C_4}] A_2 e^{-E_{\rm A2}/k_{\rm B}T}, \tag{2}$$

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). *v* is the reaction rate of the rate-limiting step in pathways 1 and 2;  $A_1$  and  $A_2$  are the preexponential factors;  $\sigma_s$  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 [6,32–35]. Concentration of the gaseous  $C_4$  species could be deduced from the result of the aforementioned 1D reacting flow simulation by

$$[C_{C_4}] = [C_{C_2}]A_{C_4}e^{-E_{AC_4}/k_BT},$$
(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,

$$v_{\rm o} = [C_{\rm S}]A_1 e^{-E_{\rm A1}/k_{\rm B}T} + [C_{\rm S}][C_{\rm C_4}]A_2 e^{-E_{\rm A2}/k_{\rm B}T} = A_{\rm o}e^{-E_{\rm Ao}/k_{\rm B}T}, \qquad (4)$$

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. 4c. 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). 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], 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]. 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  $(k_BT)^{-1}$ , the *RC* product to  $E_A^{-1}$ ; 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). At time t of the multiple-RC circuit (or given thermal environment of  $k_{\rm B}$ T), 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<sub>A</sub> 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<sub>C2H2</sub> value) of each pathway. Changes of the RC value in a circuit branch will thus lead to changes in the I<sub>total</sub> 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 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.

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#### 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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