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Interdependency of Gas Phase Intermediates and Chemical Vapor Deposition Growth of Single Wall Carbon Nanotubes

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The main gas phase intermediates, leading the efficient chemical vapor deposition (CVD) growth of single wall carbon nanotubes (SWCNTs), have been explored through systematic experimental and theoretical studies. The growth efficiencies of the basic radical/neutral species (sp^2 C_2: C_2H_3/C_2H_4, sp^3 C_2: C_2H_5/C_2H_6, and sp^3 C_1: CH_3/CH_4) have been compared by supplying C_2H_4, C_2H_6, and CH_4, as carbon sources to grow SWCNTs. The gaseous composition of the exhaust was analyzed by an in situ direct sampling mass spectrometric technique using vacuum ultraviolet (VUV)-single photon ionization (SPI)-time-of-flight mass spectrometry (TOFMS). For verification via theoretical prediction, a CHEMKIN calculation was performed. A kinetic analysis of the experimental and theoretical results was compared with thermal decomposition phenomena of the used hydrocarbons, and hence, it was concluded that the key gas phase intermediates produced from the complex gas phase reactions as a final and efficient species capable of initiating the CVD growth of SWCNTs are sp^2 C_2 species, C_2H_3/C_2H_4. Additional significance is the production of highly pure SWCNTs from C_2H_6 since to date production of either only multiwall carbon nanotubes (MWCNTs) or a mixture of MWCNTs and SWCNTs have been reported. This result will be beneficial for selecting suitable hydrocarbons for the efficient growth of SWCNTs.

Introduction

Although efficient and selective chemical vapor deposition (CVD) growth of single wall carbon nanotubes (SWCNTs) has attracted much attention, it is still in the trial and error stage. One of the reasons might be the unclear role of the chemical reactions involved in the CVD process which has not received sufficient attention. Although reports focusing on chemical reactions[1−6] are limited, CVD growth of SWCNTs from hydrocarbons has been suggested to be initiated via hydrocarbon decomposition into reactive species, free radicals, and intermediates. This is strongly supported by the presence of many hydrocarbons as byproducts in the exhaust gas.[1,7−10] These studies clearly indicate the involvement of gas phase chemical reactions in the CVD growth of SWCNTs.

However, the importance of gas phase chemical reactions in the growth of SWCNTs has not been fully explored yet. Very recently the molecular structure of the hydrocarbons used as a carbon source has been found to greatly affect the efficiency of growth by producing specific intermediates with varying concentrations from their gas phase decompositions.[11] Other studies have similar opinions about the impact of the gas phase composition of the reaction mixture on growth efficiency.[12,13] These studies indicate that growth efficiency strongly depends on the reactivity and concentration of gas phase intermediates produced as a result of complex gas phase reactions. On this basis, it can be expected that the most efficient intermediates, that have the potential of chemisorption or physisorption on the catalyst surface to initiate CNT growth, should be produced in the gas phase. The overall kinetics of the growth process depends on the interaction/competition of gas phase and surface

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reactions. Thus, a detailed analysis of gas phase reactions is unavoidable.

Of course, gas phase carbon precursor enabling SWCNT growth has been speculated by some recent studies on the basis of the presence/absence of particular species in the mass spectra in their mass spectrometric analyses of gas phase composition of the exhaust/reaction mixture. For example; Franklin el al.[14] and Tian et al.[15] proposed C_6H_6 while Kim et al.[16] proposed radical species: C_5H_9, C_6H_{13}, and C_6H_9. However, other studies[17,18] reported that C_1 or C_2 radical/neutral species should be the key species because of their greater activity caused by fewer hydrogens and smaller size,[2] facilitating higher mobility on the catalyst surface compared to larger species. Since in the substrate CVD technique, also, many groups have realized the significant enhancement in the growth of SWCNTs upon direct supply of C_2 species as a primary carbon source[16,19] or by the addition of an enhancing agent,[12,13,20,21] the smaller radical/intermediate species seems to be the more probable key species.

Moreover, the above-mentioned studies are concerned with CVD growth on a substrate, while the reaction dynamics/environment in floating catalytic CVD, used in this study,[21] is different from that of substrate growth. Particularly, floating catalytic CVD involves a quasi-homogeneous reaction environment and, hence, provides very short reaction time to final key intermediates and each catalyst particle. Thus, probability of conversion of a radical/intermediate species into a larger species before surface interaction is negligible. Due to the reaction complexities in this process, it is not so easy to clarify the gas phase reactions directly. Therefore, analysis of the thermal decomposition phenomena of hydrocarbons used, in comparison to the experimental observation of SWCNT growth, should be taken into account for extracting some useful information about the key gas phase intermediates initiating the real growth process.

Stimulated by this necessity and the results of our previous study,[11] the present study is aimed at the investigation of key gas phase intermediates through the experimental and theoretical studies. Briefly, in our previous study,[11] sp^2 C_2 species C_2H_3/C_2H_4 were proposed as the efficient carbon precursor based on the experimental observations in which especially aromatic hydrocarbons efficiently producing SWCNTs were found directly/indirectly producing C_2H_3/C_2H_4 from their gas phase decompositions. A total of nine aromatic hydrocarbons differ in functional groups such as: toluene, *p*-xylene, ethylbenzene, *n*-propylbenzene, styrene, allylbenzene, 1.4-divinylbenzene, phenylacetylene, and 3-phenyl-1-propyne, which were used as the carbon sources for growing SWCNTs. Interestingly, hydrocarbons (*n*-propylbenzene, styrene, allylbenzene, and 1.4-divinylbenzene) capable of producing directly/indirectly the smallest sp^2 C_2 species were found to efficiently produce SWCNTs while other hydrocarbons capable of producing sp^3 or sp species could not produce SWCNTs. On the basis of these results, the peculiarity of sp^2 C_2 species as an efficient precursor was deductively proposed.

However, to validate that experimental suggestion with reliability, a direct comparison of the growth efficiencies of sp^3 C_2 (C_2H_5/C_2H_6), sp^3 C_1 (CH_3/CH_4), sp^2 C_2 (C_2H_3/C_2H_4) and sp C_2 (C_2H/C_2H_2) seemed to be unavoidable to clarify this complex issue. Thus, as a following step, in this study, the growth efficiencies of sp^3 C_2, sp^3 C_1, and sp^2 C_2 were compared since the smallest sp C_2 species is known to be less efficient.[11,22] For this purpose, C_2H_4, C_2H_6, and CH_4 were used as the main carbon sources to grow SWCNTs. C_2H_6 was selected because of its unique capability to produce sp^3 C_1 radicals, CH_3 by C−C fission, sp^3 C_2 radicals, C_2H_5 by C−H fission, or sp^2 C_2 radical/neutral species, C_2H_3/C_2H_4 by direct H_2 elimination/H-abstraction while CH_4 and C_2H_4 were selected for direct comparison of growth efficiencies with that of C_2H_6. Exhaust analysis by vacuum ultraviolet (VUV)-single photon ionization (SPI)-time-of-flight mass spectrometry (TOFMS) and a CHEMKIN calculation were also performed.

Experimental Section

Details of the experimental setup have been described elsewhere.[21] Briefly, the direct injection pyrolytic synthesis (DIPS)−CVD system consists of a ceramic reaction tube of length 120.0 cm with inner diameter 52.0 mm. The tube is vertically adjusted at the top by the flange having a feedstock spray nozzle and sample collector setup at the bottom consisting of a steel mesh filter to collect the produced samples. The central part of the tube is covered with a sprit tube three zone electric furnace of length 61.0 cm. A typical experimental procedure involves the preparation of feedstock by dissolving 3.8 wt % of ferrocene into suitable organic solvents and further addition of 1.9 wt % thiophene.

For the present investigation, toluene with similar compositions was used as a feedstock, which was injected into the reactor from the top through the spray nozzle with the help of a microfeeder at a typical flow rate of 5.0 μL/min under a H_2 carrier gas flow rate of 6.93 L/min. The main reason for the use of toluene as a feedstock with the above typical flow rate is its inability to produce any carbon deposits in the absence of a secondary carbon source. In other words, it mainly works here as a catalyst carrier, since it cannot produce SWCNTs at this flow rate under the present experimental conditions.[11] Three separate series of experiments were performed by supplying C_2H_4, C_2H_6, and CH_4 at flow rates of 5.0, 7.5, 10.0, 11.0, 12.5, 15.0, and 18.0 sccm, respectively. The reaction temperature was

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maintained constant at 1200 °C, and the residence time was ~2.3 s. When the feedstock and carrier gas passed through the hot zone, due to thermal decomposition reactions followed by gas phase and surface reactions at catalyst nanoparticles, SWCNTs were grown and collected at the filter. The weight of as grown samples was measured, and they were further characterized by resonance Raman (JASCO, NRS-2100) with an excitation laser line of 514.5 nm wavelength, scanning electron microscopy (SEM; Hitachi, S-5000), thermogravimetric analysis (TGA; Rigaku, Thermo plus Evo), optical absorption spectroscopy (Hitachi, U-4100), and transmission electron microscopy (TEM; JEOL, JEM 1010F). For the analysis of exhaust gas composition, vacuum ultraviolet (VUV)-single photon ionization (SPI)-time-of-flight mass spectrometry (TOFMS) was used. The exhaust was sampled directly from the end point of the ceramic reaction tube and above the filter at which grown SWCNTs were collected. Observed mass peaks were calibrated using the well-known formula of the TOFMS system by comparing the flight times of observed species against the flight time of toluene used as the standard sample.

Results and Discussion

As mentioned above, in order to confirm the key gas phase intermediates responsible for the growth of SWCNTs, it is important to compare the growth efficiency among the most basic radical/neutral C_1 and C_2 species as they are significantly produced from the decomposition of most hydrocarbons used as a carbon source for growing SWCNTs. For this purpose, first C_2H_4 and C_2H_6, having sp^2 and sp^3 carbons, respectively, were separately supplied as the main carbon sources with similar flow rates under identical other experimental conditions so that their decomposition pathways as well as their impact on SWCNT growth characteristics could be compared. Surprisingly, both produced a similar quality and quantity of SWCNTs. It is worth noting that this is the first time that only SWCNTs have been produced from C_2H_6 since previous studies[23−25] have reported the production of either only multiwall carbon nanotubes (MWCNTs) or a mixture of MWCNTs and SWCNTs. The percentage of carbon contents produced with increasing flow rates of C_2H_4 or C_2H_6 is shown in Figure 1. The percentage of carbon contents was calculated as a product of total weight of as grown samples and carbonaceous content estimated by TGA divided by the total amount of carbon supplied from the source hydrocarbons including the toluene present in the feedstock and supplied C_2H_4 or C_2H_6.

Figure 1 seems to be clearly reflecting some remarkable points: (1) A similar nature of both profiles but with two different optimum points regarding their flow rates; 10 sccm in the case of C_2H_4 and 11 sccm in the case of C_2H_6. (2) A decreasing yield in both cases on decreasing or increasing the flow rates compared to optimized flow rates ~10 to 11 sccm. (3) A relatively lower yield below the optimum and higher yield above the optimum for C_2H_6 compared to C_2H_4.

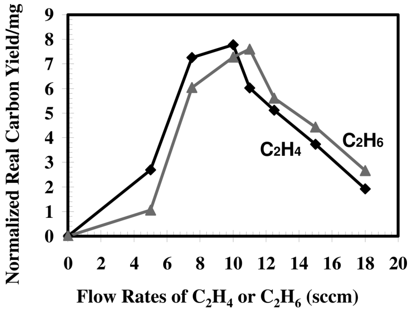

Figure 1. Carbon contents calculated as a product of total weight of as grown samples and carbonaceous content estimated by TGA and the resulting mass further divided by the total amount of carbon supplied from the source hydrocarbons. The resulting mass is normalized for 100 mg of used carbon.

It should be noted that the difference of carbon contents between C_2H_4 and C_2H_6 in their same volumes is negligible, even if we take account of actual effects of the real gas, such as van der Waals interaction. Contrary to this fact, the whole discrepancy between their profiles in Figure 1, especially below and above the optimum (above-mentioned point 3), indicates the meaningful impact of gas phase intermediates produced from C_2H_4 and C_2H_6. It also suggests that the observed ~9% difference in the optimum flow rates between C_2H_4 and C_2H_6 (above-mentioned point 1) should be more related to the key gas phase species produced from them than the difference in the carbon contents in their given volumes. Thus, these observed profiles in Figure 1 are very interesting for discussing the chemical kinetics of the gas phase reactions of CVD growth of SWCNTs.

For more clarification, the qualities of as grown samples were also characterized. Typical SEM images of as grown products produced at optimum flow rates are shown in Figure 2, and they reflect very clear and similar netlike structures of CNTs. Then, the TEM images of as grown products were also observed as shown in Figure 3. It clearly shows that the majority of CNTs are SWCNTs.

Moreover, Figures 2 and 3 do not show any visible differences verifying the production of similar qualities of SWCNTs from both ethylene and ethane. Similarly, thermogravimetric analyses (TGA) were also performed for all as grown products from C_2H_4 and C_2H_6. Typical TGA profiles of products especially produced at optimum flow rates of C_2H_4 (10 sccm) and C_2H_6 (11 sccm) have been presented in Figure 4.

It clearly shows a similar nature of profiles with a minor difference in percentage weight loss, confirming the similar qualities of products in terms of existing metallic impurities. The observed percentage metallic impurities in the as grown samples from C_2H_4 was ca. 3.5% while in the samples produced from C_2H_6 it was ca. 5.3%.Similarly, smooth lines in lower temperature regions verify that the changes induced by the feed gaseous hydrocarbons are not reflected in the mass accumulation of

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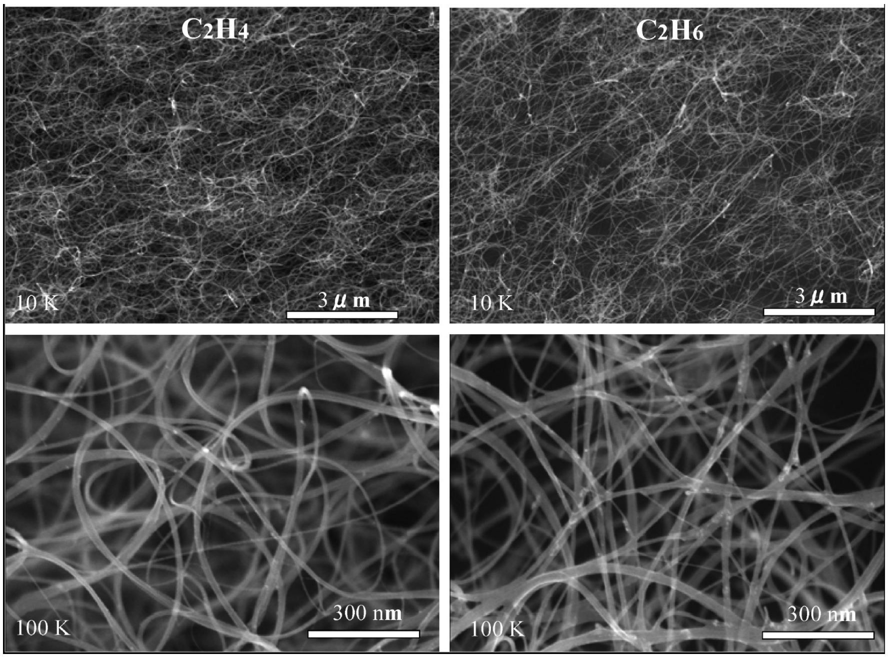

Figure 2. SEM images of as grown products produced at optimum flow rates of C_2H_4 (10 sccm) and C_2H_6 (11 sccm) showing clear netlike structures of CNTs.

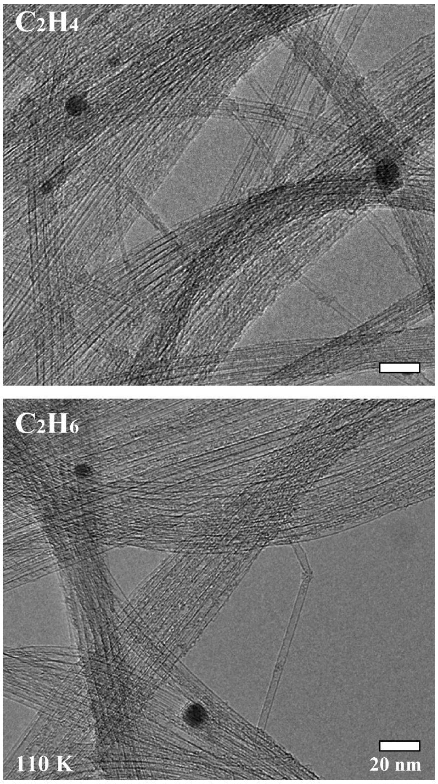

Figure 3. TEM images of as grown products produced at optimum flow rates of C_2H_4 (10 sccm) and C_2H_6 (11 sccm) showing the majority of CNTs as SWCNTs.

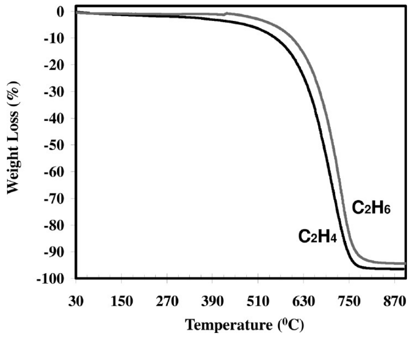

Figure 4. TGA profiles of as grown products produced at optimum flow rates of C_2H_4 (10 sccm) and C_2H_6 (11 sccm) showing a similar level of metallic impurities.

amorphous carbon. Thus, it also supports similarities in the qualities of products produced from C_2H_4 and C_2H_6.

These resemblances in produced SWCNTs in terms of carbon contents and qualities examined by electron microscopy and thermogravimetric analysis (Figures 1−4) are of great importance for determining the most responsible gas phase intermediates for CVD growth of SWCNTs, and thus, three possibilities about the key gas phase intermediates can be deduced: (A) Without any further gas phase reactions, both C_2H_4 and C_2H_6 by themselves play the role of final intermediates with a minor difference in their efficiencies for growth of SWCNTs. (B) The final and effective intermediates produced from C_2H_4 and C_2H_6 should be the same species but differ in concentrations depending on rate of their decompositions. (C) Either C_2H_6 is converted to C_2H_4 or vise-versa by dehydrogenation/hydrogenation, resulting in the same final species but slightly differing in concentration.

On the basis of very low efficiency of sp^3 carbons compared to sp^2 carbons for producing SWCNTs,[11] the observed minor differences in yield profiles (Figure 1) and a higher degree of similarities in qualities examinations (Figures 2−4), scenario (A), seems rather unlikely due to the basic difference in the molecular structures of C_2H_4 and C_2H_6. On the other hand, Figure 1 seems strongly favoring scenarios (B) and (C). For example, the lower yield of SWCNTs from C_2H_6 compared to C_2H_4 below the optimum flow rates could be due to a lower concentration of the resulting

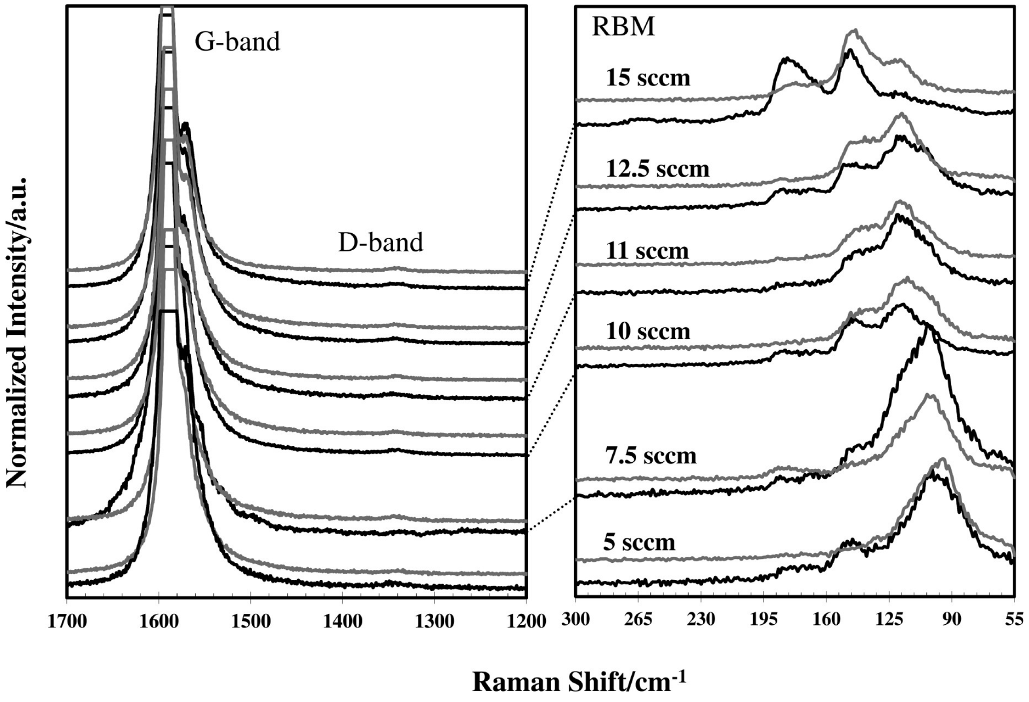

Figure 5. Resonance Raman spectra of as grown SWCNT samples on addition of C_2H_4 (black lines) compared to the addition of C_2H_6 (gray lines).

effective intermediates produced from C_2H_6. Similarly, above the optimum flow rate, the lower yield of SWCNTs from C_2H_4 can be ascribed to the passivation of the catalyst nanoparticles by excess supply of carbon caused by higher concentration of effective intermediates while higher yield in the case of C_2H_6 would be due to a relatively lower degree of passivation because of a lower concentration of effective intermediates produced from it. This possibility reasonably supports the shifting of the optimum point in the case of C_2H_6 (~11 sccm) with respect to C_2H_4 (~10 sccm) with almost similar yields. As a conclusion, Figure 1 successfully indicates the production of the same key intermediates from C_2H_6 in a relatively lower concentration compared to C_2H_4 from their exactly same supplied volumes, and this expectation is strongly backed up by the similar qualities of products observed in electron microscopic and thermogravimetric analyses (Figures. 2−4).

To check the validity of the above expectation, resonance Raman spectra of as grown samples were recorded that are shown in Figure 5. It shows very clearly the similar type of G, D, and RBM peaks in samples obtained on addition of C_2H_4 and C_2H_6 separately. Negligible intensities of the D band suggest similar qualities of samples with fewer structural defects. Moreover, the notable variation in RBM peak position from 99.9 to 147.5 cm^{-1} (bottom to top) on addition of 5−15 SCCM of C_2H_4 is slightly higher than that of RBM peak positions 94.0 to 143.5 cm^{-1} on addition of C_2H_6. Similarly to the previous report,[21] the appearance of RBM peaks at higher Raman shift values from bottom to top can be ascribed to increased concentration of so-called key species from both C_2H_4 and C_2H_6. Thus, slightly lower values of RBM peak positions in the case of C_2H_6 indicate the production of relatively wider SWCNTs, most probably due to a lower concentration of similar effective species produced from C_2H_6 compared to C_2H_4.

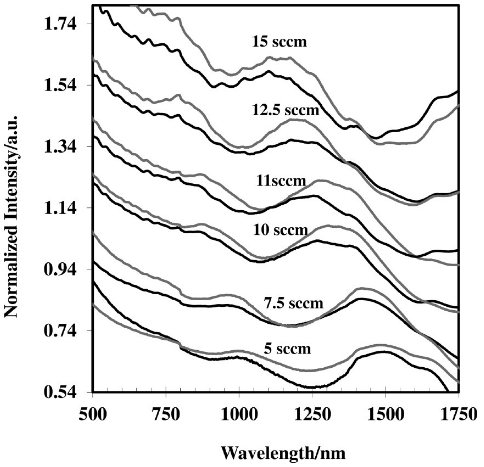

Figure 6. Optical absorption spectra of as grown SWCNT samples on addition of C_2H_4 (black lines) compared to that of C_2H_6 addition (gray lines).

Optical absorption spectra of those as grown products dispersed in D_2O with the help of sodium cholate were also recorded and are shown in Figure 6. Similarly to the Raman result, Figure 6 shows the tendencies of shifting of S_{22} and M_{11} peaks toward lower wavelengths, suggesting the sequential reduction in the diameter of produced SWCNTs. This can also be caused by increasing the concentration of the key intermediates due to increasing the flow rates of C_2H_4 and C_2H_6.[11]

It is hard to specify the reason for narrowing diameter with increasing concentration of C_2H_4/C_2H_6 in terms of chemical reactions. On the basis of the observed size of catalyst particles in the TEM images of as grown samples, it is expected that with increasing concentrations of efficient intermediates like C_2H_4/C_2H_6 the growth initiates comparatively earlier with smaller catalyst size and, thus, results in narrower diameter. Some detailed discussion on this matter

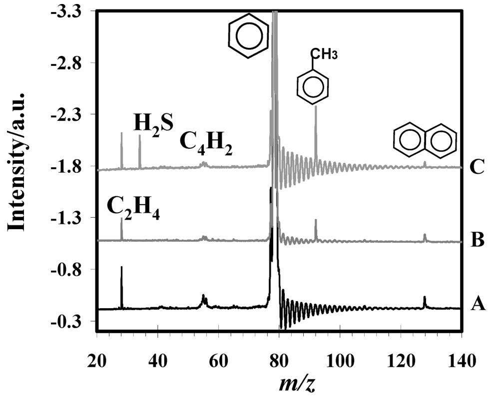

Figure 7. Mass spectra of gas phase products exhausted from DIPS-CVD and detected by in situ VUV-SPI-TOFMS. (A), (B), and (C) represent gas phase products of decomposition of only toluene, toluene + ferrocene, and toluene + ferrocene + thiophene, respectively.

can also be found elsewhere.[21] These characterization results fairly support the validity of above scenarios (B) and (C), that is, addition of both C_2H_4 and C_2H_6 produces similar active species through their gas phase reactions.

To confirm the most probable scenario from scenarios (B) and (C), the understanding of decomposition phenomena of C_2H_6 and C_2H_4 seems unavoidable. Before that, it is necessary to know the impact of ferrocene (catalyst) and thiophene on thermal decomposition phenomena of used hydrocarbons. For this purpose, the gaseous composition of exhaust produced from toluene with and without addition of ferrocene and thiophene was analyzed by an in situ direct sampling mass spectrometric technique (VUV-SPI-TOFMS), and the observed mass spectra are shown in Figure 7. It clearly shows that benzene appears as a major product in all cases. Moreover, the number of products produced from toluene, with and without addition of ferrocene and thiophene, is constant except for an additional noncarbon product, H_2S, in the case of thiophene addition.

The observed slight difference in concentrations of the products is certainly due to suppression in percentage decomposition of toluene on addition of ferrocene and ferrocene + thiophene. The most important information that can be deduced from this result is that catalyst and/or promoter does not alter the gas phase composition, indicating that their main contribution in the growth of SWCNTs starts when the final key intermediates approach them. This supports that the production of main gas phase intermediates depends on the molecular structure of used hydrocarbons and their thermal decomposition pathways. Thus, thermal decomposition phenomena of used hydrocarbons must be analyzed.

As it is well-known, the observed major product (Figure 7), benzene, is produced via reaction R1[23,24] while the efficiency of reaction R1 strongly depends on the supply of hydrogen atoms which is hard to obtain from the direct decomposition of H_2 used as carrier gas. In the highly concentrated H_2 atmosphere used in this study, the main source for producing hydrogen atoms might be the radical−molecule reactions (R2) for which radicals are produced initially from the well-known self-decomposition routes of hydrocarbons, for example reactions R3 and R4 of toluene.[26,27]

$$C_6H_5CH_3 + H \rightleftharpoons C_6H_6 + CH_3 \qquad (R1)$$

$$H_2 + R(=C_6H_5CH_2, CH_3, C_6H_5) \rightleftharpoons RH + H \qquad (R2)$$

$$C_6H_5CH_3 + M \rightleftharpoons C_6H_5CH_2 + H + M \qquad (R3)$$

$$C_6H_5CH_3 + M \rightleftharpoons C_6H_5 + CH_3 + M \qquad (R4)$$

Similarly, thermal decomposition of C_2H_6 in an inert atmosphere is well-known to be initiated through the C−C fission reaction R5,[28−35] producing methyl radicals while some studies reported the direct hydrogen elimination reaction R6[36−38] producing ethylene. Most studies have considered that methyl radicals produced via R5 initiate the radical−molecule reaction (R7) producing methane as the main product and consequently producing the unstable species, the ethyl radical, which is readily decomposed via reaction R8 to produce ethylene as the second product.

$$C_2H_6 + M \rightleftharpoons CH_3 + CH_3 + M \qquad (R5)$$

$$C_2H_6 \rightleftharpoons C_2H_4 + H_2 \qquad (R6)$$

$$C_2H_6 + CH_3 \rightleftharpoons C_2H_5 + CH_4 \qquad (R7)$$

$$C_2H_5 \rightleftharpoons C_2H_4 + H \qquad (R8)$$

On the other hand, decomposition of ethane in the presence of H_2S[39] and decomposition of hydrocarbons like naphthalene and cyclohexane in a H_2 atmosphere[40] with and without CS_2 also suggested ethylene as the second product. Especially, a study by Kemball et al.,[41] decomposition of ethane and ethylene in a H_2 atmosphere in the presence of nickel catalyst, is relevant to the present study; however, their reaction temperature was too low

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(215 °C), and the catalyst used is different from this study. Although, they completely ignored the gas phase as well as radical reactions, they have also reported methane as the main product and ethylene as the second product. They also found that the rate of production of methane and carbon from ethylene was higher than that of ethane, that favors the decomposition of ethane via ethylene (R8) rather than reaction R5. On the other hand, Nishiyama et al.,[28] suggested that in general a metallic catalyst initiates the radical chain reaction. In the present study, the temperature was quite high and a highly concentrated hydrogen atmosphere was used for the growth of SWCNTs. Thus, a radical chain reaction (R9, similar to R2) accelerated by methyl and ethyl radicals to produce sufficient hydrogen atoms can be easily expected. The hydrogen atoms so produced will propagate reaction R10, which finally results in the production of sufficient ethylene via reaction R8. Of course, such produced atomic hydrogens also promptly convert methyl radicals into methane via reaction R11 under ambient pressure used in this study.

$$R(=CH_3,C_2H5) + H_2 \rightleftharpoons RH + H \qquad (R9)$$

$$C_2H_6 + H \rightleftharpoons C_2H_5 + H_2 \qquad (R10)$$

$$CH_3 + H \rightleftharpoons CH_4 \qquad (R11)$$

Additionally, the chain termination reaction (R12) also produces ethylene

$$2C_2H_5 \rightleftharpoons C_2H_6 + C_2H_4 \qquad (R12)$$

At this point, it is quite clear that, because of involvement of a few steps in C_2H_6 decomposition reactions, the concentration of so produced C_2H_4 would be less than directly supplied C_2H_4 when supplied volumes of them are the same as in this study, and thus, scenario C seems to be the most probable.

To support the above-discussed decomposition phenomena with experimental evidence, the exhaust gas composition in both cases, particularly at optimum flow rates of C_2H_6 and C_2H_4, were analyzed by an in situ direct sampling VUV-SPI-TOFMS. The observed mass spectra are shown in Figure 8. It should be noted that the comparison of mass spectra is only to provide evidence for the probable conversion of the majority of ethane into ethylene before proceeding to the further gas phase reactions. This is not to speculate on the key intermediates involved in the growth of SWCNTs based on the presence/absence of certain species, as was done in other studies.[14-16] Interestingly, following the results in Figures 1–6 and 8 clearly reflects that the number of products detected in both cases is the same. Moreover, the concentrations of all detected species on addition of C_2H_6 are slightly lower than that of C_2H_4 addition, suggesting that ethane is mainly converted to ethylene before proceeding to growth of SWCNTs and producing other byproducts.

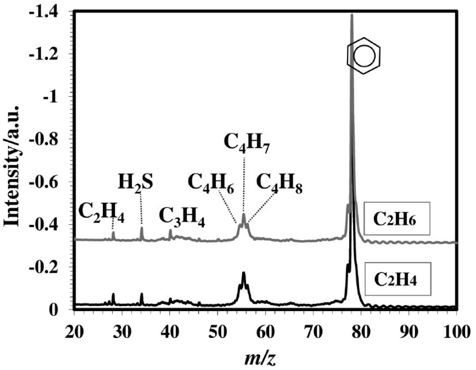

Figure 8. Mass spectra of gas phase species present in an exhaust gaseous mixture directly sampled during CVD growth of SWCNTs under optimum flow rates of C_2H_4 (10 sccm) and C_2H_6 (11 sccm).

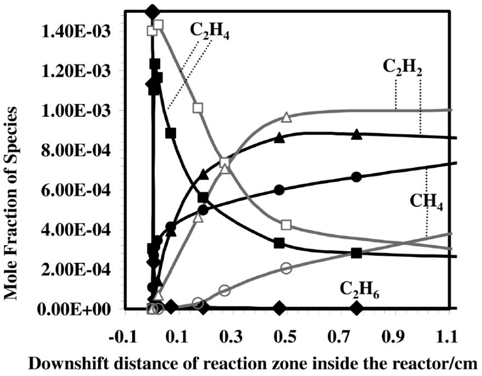

Figure 9. Variation of mole fraction of species, produced from the pyrolysis of C_2H_6 and C_2H_4, estimated by CHEMKIN-4 program, along the distance within the reaction zone where the zero (0) point is the entrance of the furnace around which growth is initiated. Since the temperature within the furnace was kept constant, the calculation has been performed at constant temperature of 1200 °C. Black lines represent products from C_2H_6, and gray lines represent products from C_2H_4.

For the purpose of obtaining some theoretical validation regarding the decomposition process, a CHEMKIN calculation was done under present experimental conditions with a reaction mechanism of pyrolysis of smaller aliphatic hydrocarbons that includes 68 species and 334 reactions;[42] and the result is shown in Figure 9. Interestingly, similarly to Figure 8, Figure 9 also clearly shows that the number of species produced from both ethane and ethylene is the same while the concentration of species produced from ethylene is relatively higher than that of ethane. One exception is methane, since methane is mainly produced from methyl radicals that are sufficiently generated by C–C fission of ethane (R5). The DIPS-CVD is a dynamic process, and typically, the total reaction time for this study was very short, ~2.3 s as previously mentioned in the Experimental Section. It should be noted that, in TEM images of as grown products, the increasing reaction time caused by decreasing flow rates at constant other experimental conditions led to increasing catalyst nanoparticle size and SWCNTs with relatively wider diameters. On this basis, it was suggested that nucleation starts in the early stage of

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(42) KUCRS 3c-model of reaction mechanism developed by Prof. Akira Miyoshi, Department of Chemical System Engineering, The University of Tokyo, Japan.

the reaction zone and the stage of nucleation determines the diameter of producing SWCNTs.[21] Because of this reason, a very short reaction time, that is short reactor length, has been compared in Figure 9, where zero point is the entrance of the furnace. On the other hand, at longer reaction time, production of methane was found to be enhanced and methane was found to be less efficient for effective growth of SWCNTs under present experimental conditions.

It is worth noting that the systematically presented experimental observations in Figures 1−6, corresponding to the physical characterizations of as grown SWCNTs, are consistent with the experimental observations in Figure 8 and the theoretical results in Figure 9, corresponding to chemical reactions taking place during the dynamic DIPS-CVD process. All of these results, which show minor differences in the profiles of C_2H_4 and C_2H_6, satisfactorily agree with the above-discussed decomposition phenomena in which C_2H_6 is converted into C_2H_4 and, thus, strongly supports scenario C.

Another interesting piece of information that can be deduced from the results and discussion is the role of the sp^3 C_1 species, CH_3/CH_4 in the CVD growth of SWCNTs. It appears that these species are not efficient sources for this process. The basis of this conclusion is the production of CH_3/CH_4 as the major gas phase product against its negligible contribution in growth. Because of preferential C−C fission in C_2H_6 via reaction R5, the amount of CH_3/CH_4 production from C_2H_6 compared to C_2H_4 will be certainly higher; thus, if CH_3/CH_4 could be an efficient producer of SWCNTs, the yield profiles in Figure 1 would be opposite to one another.

For further experimental confirmation, methane (CH_4) was supplied as the carbon source under the same experimental conditions, but nothing was obtained as deposited material even at a very high flow rate, 100 sccm/min. This experimental observation and above-discussed reaction kinetics demonstrate that the inefficiency of CH_4 is most probably due to its extremely low rate of decomposition into C under present experimental conditions, especially in a highly concentrated hydrogen atmosphere[43] in which rate of reaction R11 might be overly dominating its rate of decomposition. As a final result, the majority of the CH_4 might exhaust as is, and a negligibly small decomposed fraction may be converted to C_2 species.[11,43]

At this point, a key question is whether C_2H_4 itself interacts with the catalyst or is converted to another smaller species which has the potential to react with the catalyst. Regarding this question, it will be interesting to know about the thermal decomposition of ethylene; unlike ethane, it is either polymerized or accelerates the bimolecular reactions rather than decomposing into smaller species in the gas phase.[36−38] Moreover, Kemball et al.[41] has reported that, in a hydrogen atmosphere, ethylene is decomposed on the catalyst surface into methane and carbon via reaction R13 rather than other products.

$$C_2H_4 + M(\text{catalyst}) \rightleftharpoons C + CH_4 \qquad (R13)$$

However, in addition to reaction R13, observation of C_4 species in the mass spectra of exhaust (Figure 8), especially C_4H_6 and C_4H_7, indicate that a certain fraction of C_2H_4 undergoes abstraction reaction to produce C_2H_3 radicals while C_4H_8 can be produced by the direct dimerization of C_2H_4. The surprising observation of the delocalized stable radical, C_4H_7, which is a product of C_2H_4 + C_2H_3-reaction,[44,45] as a dominant C_4 species strongly supports the existence of both sp^2 C_2 species C_2H_3 and C_2H_4 in the reaction zone where the growth of SWCNTs is initiated. Considering the difficulty in distinguishing the degree of contribution of C_2H_3/C_2H_4 in the growth, this entire discussion can be ended with the active role of sp^2 C_2 radical/neutral species as the key gas phase intermediates capable of initiating and accelerating the CVD growth of SWCNTs under an atmosphere of excess hydrogen on the basis of the following consequential order of the experimental observations and literature support.

Experimental observations are as follows: (a) The similarities in profiles of C_2H_4 and C_2H_6 reflected from Figures 1−6, 8 and 9 indicate the conversion of C_2H_6 into C_2H_4 in the beginning of the reaction, which is further supported by discussed decomposition phenomena. (b) The inefficiency of sp^3 C_1 species, CH_3/CH_4 in facilitating the growth of SWCNTs; either on direct supply or produced as major gas phase product, under present experimental conditions. (c) The observed narrowness in diameter of produced SWCNTs (Figures 5 and 6), because of minor decrease in reaction time caused by increasing flow rates of C_2H_4 (i.e even $\sim 3.6 \times 10^{-4}$ times of the total inlet flow rate of gaseous mixture), shows the peculiar impact of C_2H_4 in quality of produced SWCNTs. Similarly, its importance in quantity of produced SWCNTs is reflected from Figure 1. Thus, results presented in Figures 1,5, and 6 indicate the key role of C_2H_4 in the growth of SWCNTs. (d) The existence of C_4 species (C_4H_x) in the mass spectra of exhaust (Figure 8); supports the existence of both sp^2 C_2 species, C_2H_3 and C_2H_4 in the reaction zone where growth of SWCNTs is initiated.

Literature support is as follows: (1) Only hydrocarbons capable of producing sp^2 C_2 species C_2H_3/C_2H_4 can produce SWCNTs effectively and efficiently.[11] (2) In a hydrogen atmosphere, C_2H_4 decomposes on the catalyst surface into C.[41] (3) Nucleation of SWCNTs initiates as early as possible in the reaction zone,[21] where C_2H_3/C_2H_4 has been observed to be produced efficiently (see the above discussion).

Finally, the results of this study will be of benefit to carbon nanotube researchers who have been using different hydrocarbons in a trial and error process for the production of SWCNTs by CVD on mass scale. This study will help them to select proper hydrocarbon capable of producing

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C_2H_4 or C_2H_6 efficiently from their gas phase decomposition or they can use C_2H_4 or C_2H_6 directly under optimized conditions. Equally, it will be useful for developing a kinetic model of the reaction mechanism for CVD growth of SWCNTs.

Conclusions

The above-discussed systematic experimental and theoretical results can be summarized as follows: (1) CVD growth of SWCNTs strongly depends on the gas phase intermediates produced from the hydrocarbon used as a carbon source. (2) sp^2 C_2 species appear to be the main gas phase intermediates produced from thermal decomposition of most hydrocarbons used as carbon sources, capable of initiating and accelerating the CVD growth of SWCNTs. (3) sp^3 C_2 and C_1 radical/neutral species were found to be inefficient for initiating the growth of SWCNTs by themselves. (4) The quantity of sp^2 C_2 carbons produced either as a result of gas phase reaction or directly supplied was found to directly affect the yield and diameter of the produced SWCNTs. (5) High quality SWCNTs were grown from C_2H_6 for the fist time, and C_2H_6 is, therefore, a strong alternative to C_2H_4 for efficient growth of SWCNTs. (6) The main cause for variation in quality and quantity of produced SWCNTs from different hydrocarbons seems to be related to the variation in the rate of production of C_2H_3/C_2H_4 during their gas phase decompositions.