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Review

Fluidized bed catalytic chemical vapor deposition synthesis of carbon nanotubes—A review

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ABSTRACT

Carbon nanotubes (CNTs) are pure carbon in nanostructures with unique physico-chemical properties. They have brought significant breakthroughs in different fields such as materials, electronic devices, energy storage, separation, sensors, etc. If the CNTs are ever to fulfill their promise as an engineering material, commercial production will be required. Catalytic chemical vapor deposition (CCVD) technique coupled with a suitable reactor is considered as a scalable and relatively low-cost process enabling to produce high yield CNTs. Recent advances on CCVD of CNTs have shown that fluidized-bed reactors have a great potential for commercial production of this valuable material. However, the dominating process parameters which impact upon the CNT nucleation and growth need to be understood to control product morphology, optimize process productivity and scale up the process. This paper discusses a general overview of the key parameters in the CVD formation of CNT. The focus will be then shifted to the fluidized bed reactors as an alternative for commercial production of CNTs.

1. Introduction

Carbon nanotubes consist of rolled graphene, a hexagonal sp^2 carbon layer, which forms cylinders with diameters of nanometer sizes and length of up to several millimeters. Unusual properties of CNTs derive from the curved sp^2 graphene layers by imposing additional quantum confinement and topological constraints in the circumferential direction of the cylinders [1]. Carbon nanotubes form in three main categories, single walls, double walls and multiwalls. The structure of single wall CNTs (SWCNTs) can be conceptualized by wrapping one-atom-thick layer of graphite into a seamless cylinder and multiwall CNTs (MWCNTs) are a collection of concentric SWCNTs (Fig. 1). Basically, SWCNTs properties are directly influenced by the way the graphene sheets are wrapped around. A SWCNT can be classified as either metallic or semi-conducting based on its chiral vector [2,3]. However, SWCNTs exhibit more distinctive electrical and optical properties when compared to MWCNTs. On the other hand, MWCNTs show more chemical resistance than SWCNTs [4]. This characteristic is of significant importance when functionalization is required which means the surface structure of pristine CNTs is modified by chemical methods to meet the requirements of desired specific application.

Carbon nanotubes are produced by quite diverse methods such as arc discharge, laser ablation and CCVD. However, CCVD has been widely applied, as it offers a promising route for bulk production of CNTs, which can lead to commercialization [3,5–7]. The attraction and development of CCVD for growing CNTs by the scientific community can be attributed to the following facts: lower reaction temperature so lower cost, high purity, possible aligned carbon nanotubes production, relatively high yield of products, and the good potential for large-scale production [6–10]. Considerable efforts have been made to study the key parameters on CNTs productivity and morphology in CCVD process. It is prudent to note that CNTs are currently produced with a relatively high quality, as it is depicted in Fig. 2 [11], but in limited quantities. In this review, the findings of more than 100 published papers for the development of engineering solutions for CNT manufacturing are presented and discussed.

2. Carbon nanotube synthesis by catalytic chemical vapor deposition (CCVD)

Carbon nanotubes growth by the CCVD method is accomplished in a reaction furnace with flowing gaseous carbon feedstock in the presence of catalyst. There are mainly two processing system configurations for CCVD of CNTs, i.e., horizontal and vertical. The illustration of a typical horizontal system, which is used in the floating and fixed-bed catalyst technique, is depicted in Fig. 3. Floating catalyst technique utilizes a mixture of catalyst and reactants

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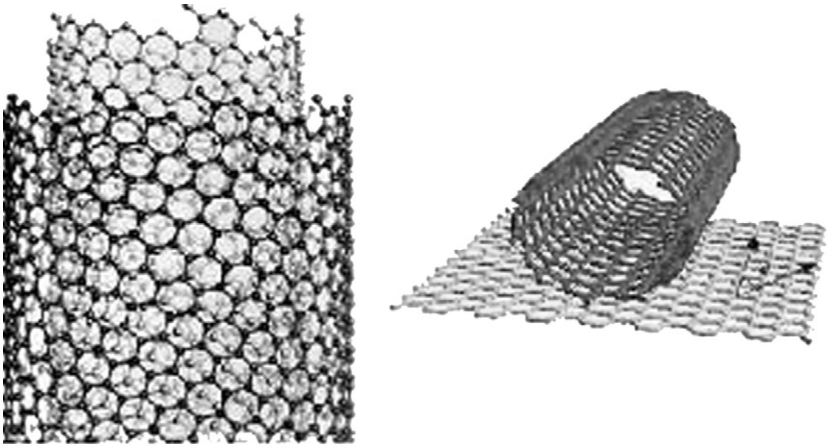

Fig. 1. (a) Synthesis of SWCNT from a graphitic sheet, (b) computer-generated image of multi-wall carbon nanotubes [1] (reproduced with authorization from publisher).

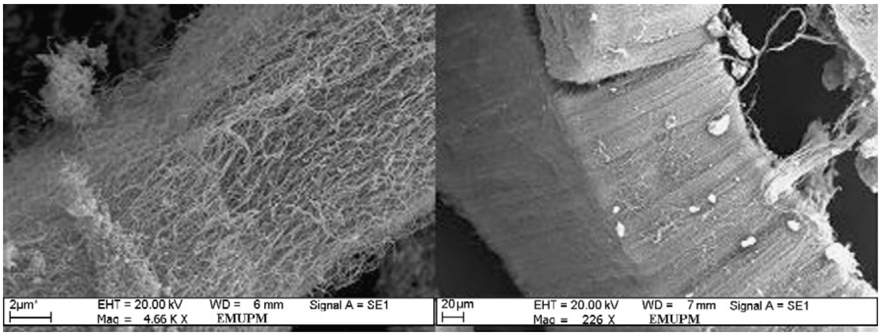

Fig. 2. SEM image of produced carbon nanotubes bundle by floating CCVD technique [11] (reproduced with authorization from publisher).

which are introduced in the gas phase to the reactor maintained at an elevated temperature where the CCVD reaction takes place. The gas phase catalyst undergoes transformation in the reactor and forms nano-sized solid phase active catalyst particles in situ. One of the drawbacks of this method is the difficulty in preventing particle coalescence. Only when these solid nano-catalysts adhere to the reactor surfaces will they have sufficient residence time to grow CNTs. Any unreacted gas phase catalyst and solid nano-catalysts which have not been able to adhere to the reactor walls at sufficiently high temperatures are swept away with the unused reactants and carrier gases or reaction product gas (hydrogen) thus thereby dramatically reducing the process efficiency.

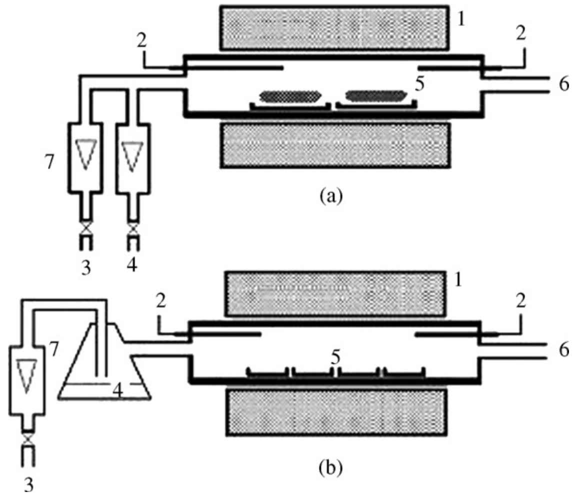

Fig. 3. (a) Fixed-bed technique: (1) furnace, (2) thermocouple, (3) carrier gas, (4) carbon source, (5) catalyst, (6) outlet. (b) Floating technique: (1) furnace, (2) thermocouple, (3) carrier gas, (4) catalyst dissolved in volatile carbon source, (5) empty boat for CNT deposition, (6) outlet.

In the fixed-bed process, the solid phase catalyst is placed in boats inside the reactor and the gas phase reactant is introduced when operational temperature is attained. The efficiency of CNTs growth in this process is limited severely by inhomogeneous gas–solid contact and temperature gradients. In a horizontal fixed-bed reactor, the diffusion of the carbon source gas to the catalyst particles becomes rate limiting because as more and more nanotubes are grown it will cover the surface thus reducing the effectiveness of the catalyst particles on the surface. The fluidized bed CVD (FBCVD) systems consist of a vertical furnace and reactor in which supported-catalyst particles are suspended by an upward flow of gas.

FBCVD process draws upon the advantages of both the floating and fixed-bed catalyst systems. It has excellent heat and mass transfer like the floating catalyst method and the catalyst nanoparticles are already anchored to support surface and are large and massive enough to be not swept away together with the reactant/carrier/product gas stream. Such a system provides a larger contact area among the reactants and catalyst powder, which leads to a more effective chemical reactions and heat transfer. Consequently, as the CNT formation rate is directly associated with the availability of the active catalyst sites, FBCVD compared to the other types of CCVD is more efficient for synthesis of large quantities of CNTs [8].

On the microscopic scale, the CCVD CNTs growth mechanism model consists of three relatively independent steps, which lead to the formation of tubular carbon solid in a sp^2 structure. These three phenomena include dissociation of hydrocarbon molecules by catalyst, saturation of carbon atoms in catalyst nanoparticle and precipitation of carbon from catalyst in form of CNT, respectively [1]. Produced CNTs features, including dimensions, wall number, chirality and graphitization are determined by the growth mechanism and process conditions. Therefore, parametric factors which affect the CCVD should be well considered in order to synthesize the desired clean CNTs. According to the literatures, the key parameters which are discussed in following sections include catalyst, temperature, carbon feedstock and time.

2.1. *Catalyst*

Catalysts play a crucial role in the CCVD synthesis of CNTs and therefore improving the desired characteristics of catalyst will enhance the obtained CNTs quality as well as the process yield. Materials with capability of decomposing hydrocarbon and CNTs formation are employed as catalyst in CCVD processes. However, it has been found that only the hydrocarbon molecules' decomposing ability of catalyst could not be accounted for CNT formation [9,12–14]. These results emphasize that careful selection of the catalyst is a dominating factor in CCVD synthesis of CNTs. Transition metals in the form of nanoparticles are considered as the most effective catalysts. The peculiar ability of transition metals to promote CNT growth is strongly related to these factors: (a) catalytic activity for decomposition of volatile carbon compounds, (b) ability of metastable carbides formation, and (c) diffusion of carbon through and over the metallic particles [7,15–19]. The CCVD process for CNTs growth utilizes heterogeneous catalysts, which are the catalytically active metal particles, typically with a diameter of 1–10 nm, anchored on a high surface inert area.

CCVD CNTs synthesis is essentially a two-step process consisting of an initial catalyst preparation step followed by the real reaction for which presence of catalyst is vital. It is worth reiterating that careful selection of the catalyst and support improves the process yield significantly. Interactions, either chemical or physical, between support and metal nanoparticles are significant for the catalytic properties of the nanoparticles. Size limitation and determination of metal particles by support porosity is physical interaction whereas chemical interaction affect the electronic structure of the nanoparticles thus their catalytic properties. Both physical and chemical interactions are contingent upon, not only, both support and catalyst materials but also on their crystallographic orientations, surface roughness and porosity of the support. As a rule of thumb, weak interactions yield tip-growth mode whereas strong interactions lead to base-growth, which are illustrated in Fig. 4 [15]. Stronger metal–support interactions will improve dispersion, narrow size distribution, and reduce sintering and agglomeration of active metal species. On the other hand, stronger metal–support interactions will hinder the reduction of the oxide precursors on the active catalytic metal species.

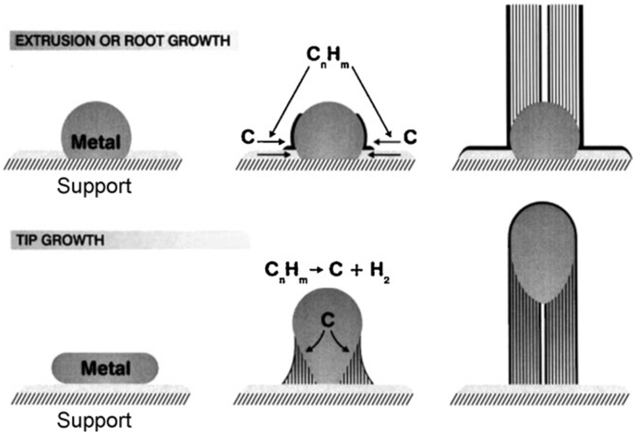

Fig. 4. Schematic diagram of CNT growth mechanisms: (a) root growth and (b) tip growth [15] (reproduced with authorization from publisher).

The results of CNTs growth with the same catalyst but on different types of supports suggest that substrates with larger surface areas, such as alumina and silica, will promote CNT nucleation and growth [20–34]. High surface area allows the carbon source atoms to diffuse readily to the metal catalyst particles. However, maximizing the surface area is not the only reason for using nanoparticles as heterogeneous catalysts. Basically the role of the supports can be summarized as: (a) to disperse the active phase, (b) to prevent sintering of catalyst, and (c) to improve mechanical strength.

The pore structure of the support, though important in heterogenous catalysis in general, does not play an important role in CNTs formation by CCVD. Fine pores are not active if they do not contain active metal catalyst species. If an active catalyst metal species is present within a fine pore, it will quickly form enough carbon to fill up the pore and block the entrance of additional reactant hydrocarbons.

There is a consensus in scientific literature that transition metals in the form of nanoparticles can produce CNTs and the outer diameter of formed nanotubes is directly correlated to the catalyst particle size. Another factor that influences the supported-catalyst activity is the level of nano-metals that are dispersed on the support. Large particles and aggregates as compared to fine and well-dispersed particles are inactive for nanotube formation. Optimization of the nano-metal particles and their dispersion in support leads to a maximum number of active points for hydrocarbon decomposition [35–44]. Accordingly, one of the scientific and technological challenges associated with heterogeneous catalyst system is to find the synthesis methods that fulfill the strong requirements in terms of their composition and structure.

There are numerous strategies for synthesizing supported metal catalyst; however the most common methods are sol–gel, impregnation, co-precipitation, and CVD. The effectiveness of the method mostly depends on the surface properties of the support through interaction with the active metal phases [9,20,21,23,42]. The sol–gel synthesis method has been reported to ensure a highly homogeneous distribution of transition metal in the matrix on which the aligned nanotubes grow [44–47]. However; every single applied condition affects the supported-catalyst activity, and it should be controlled meticulously to make the method reproducible. Dispersion of metal particles on the support also depends on the metal–support content ratio besides the preparation procedure. There is an optimal metal content ratio between catalyst and support, which leads to the CNTs synthesis with the desired properties at maximum yield. Increasing the metal percentage is fruitful only if it enhances the available active sites for CNT growth, instead of increasing the mean particle size of the metal [9,19,21,25,30]. At first, by increasing catalyst metal amount on support, carbon deposition rate and yield is ramped up since more active catalytic sites are available for carbon deposition. After the optimum point, the increased metal content makes the metal particles bigger resulting in lower specific area.

Iron (Fe), cobalt (Co), and nickel (Ni) have been enumerated as the most effective catalysts for CNTs growth. However, the challenge is that which metal is more active and provide better quality CNTs. Generally on the basis of the results in relevant studies, iron produces lower quality CNTs compared to Co and Ni [12–13,38,48–57]. An alloy of two transition metals with each other or with other non-transition metals can dramatically improves the catalyst performance in terms of CNT quality and lowering the reaction temperature [33,58–61]. Although catalyst selection and preparation is the most significant factor in CNTs synthesis, there are a number of mechanisms that can lead to catalyst deactivation, and hence loss of reactor performance. These mechanisms are

Table 1
Results from temperature study.

Carbon source	Carrier gas	Catalyst	Temp. (°C)	Technique	CNT diameter (nm)	Wall	Ref.
Ethanol	Ar	Co/alumina	550	Fixed bed	10–20	MW	[19]
Benzen	Ar/H_2	Ferrocene	600	Floating technique	10–30	MW	[68]
			550		2–20		
Methane	Ar	Fe–Mo/alumina	700, 750	Floating technique	2–45	SW	[63]
			600		0.8–1.2		
Acetylene	N_2	Fe–Co/alumina	700	Fixed bed	31–41	MW	[48]
Carbon monoxide	He	Co–Mo/SiO_2	700	Fixed bed	1	SW	[39]
Acetylene	Ar	Ferrocene	600–800	Fixed bed	10–20	MW	[17]
Ethanol	Ar	Fe–Co	700–800	Fixed bed	1	SW	[64]
Toluene	Ar/H_2	Ferrocene	800, 900	Floating technique	20–25	MW	[18]
Ethanol	He	Fe/alumina	800		0.78–1.05	SW	[30]
Methane	H_2	Fe–Mo/MgO	860	Fixed bed	N.M.	DW	[69]
Acetylene	N_2	Fe–Co/alumina	700	Fixed bed	31–41	MW	[48]
Methane	Ar/H_2	Fe–Mo/alumina	900	Fixed bed	0.9–2.7	SW	[23]
Methane	N_2	Fe/alumina–silica	900	Fixed bed	N.M.	MW	[41]
Acetylene	Ar	Ferrocene	900–1000	Floating technique	N.M.	SW	[67]
Ethanol	Ar	Ferrocene	1100	Floating technique	20–40	MW	[72]
Toluene	H_2	Ferrocene	1200	Floating technique	20–70	MW	[66]

N.M.: not mentioned.

poisoning, fouling and sintering of the catalyst due to elevated temperature or long reaction time. Phase change in catalyst support also sometimes occurs due to the high temperature and this can lead to a surface area reduction, and therefore reducing the reaction rate on account of impact on the access to active sites. Consequently other process parameters effects on CNTs synthesis should be taken into account, which are discussed in following sections.

2.2. *Temperature*

Each stage of CNT growth, discussed in Section 2.1, is a thermally activated process and therefore there must be a characteristic threshold temperature for each step [7]. The starting temperature of CCVD synthesis of CNTs has mostly reported higher than 500 °C but there is a conflicting result for maximum temperature. Early on, it was believed that a very high temperature (e.g., 1000–2000 °C) favors the formation of SWCNTs over MWCNTs [5], however, with the advent of new CVD methods, especially FBCVD, this opinion is changing as the SWCNT growth temperature keeps getting lower [62–67]. Some investigated conditions for the CVD growth of CNTs are displayed in Table 1.

CNTs morphology dependence on the temperature is one of the most popular topics under investigation. Muataz et al. [68] studied the role of reaction temperature in CNTs synthesis by floating catalyst method, in which benzene and ferrocene were utilized as carbon precursor and catalyst, respectively. They pointed out that MWCNTs synthesis occurs at temperatures greater than 500 °C and maximum wall numbers with less impurity is obtained at 850 °C (see Fig. 5). The higher the reaction temperature the more pronounced is the formation of non-tubular carbon like nanofibers. They also revealed that there is a positive correlation between the average diameter and the length of CNTs and temperature. As a result, they proposed that temperature is a dominating factor for CNT diameter control. The same conclusions have been also reported by other researchers [9,10,25,69–71]. The main effects of increasing the reaction temperature are to increase the metal particle size during the CVD growth of CNTs, and consequently the nanotube diameter. However there are some inconsistencies about the exact effect of the temperature on CNTs growth mechanism. Kim et al. [71] failed to observe any significant effects of temperature on average diameter of MWCNTs but observed that elevating the temperature had increased the length as well as the crystallinity of the nanotubes. Son et al. [65] concluded that the CNT diameters synthesized from methane in fluidized bed decreases as the reaction temperature increases. Nevertheless, the effect of temperature was evident on the growth rate, purity and the crystallinity of CNTs in all mentioned studies.

There is a great paradox of CNTs synthesis where even though the higher growth temperature is favored for less defective, well-crystallized nanotube, including such parameters of interest such as yield and purity, but a too high temperature is not suitable due to some disadvantages like deformation of catalyst, sintering of the supported catalysts, formation of alloy in bimetallic catalyst and the formation of pyrolytic amorphous carbon [7,10,47]. Although

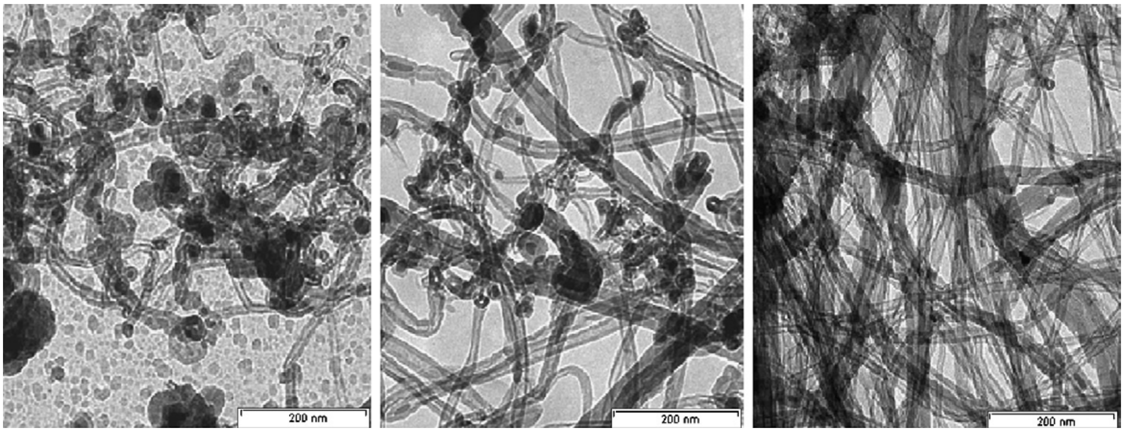

Fig. 5. TEM images of carbon nanotubes at (a) 550, (b) 650 and (c) 850 °C [68] (reproduced with authorization from publisher).

in a few rare cases, CNTs were produced at temperatures higher than 1000 °C [67,72], but most reported that the CVD products are in non-tubular form of carbon at these temperatures [12,47,48,68]. It can be attributed to the fact that not only pyrolysis of carbon sources is generally promoted around 1000 °C, but also pyrolysis of the CNTs will begin. Other effects of the reaction temperature are related to the diameter distribution and chirality issue especially in SWCNTs synthesis [29,73]. Indeed, it is likely that the size and shape of the catalytic nanoparticles should be more stable at lower temperatures, leading to better control of the size and chirality of the nanotubes.

2.3. Carbon feedstock

Besides catalyst and temperature, the carbon feed stocks also play an important role in the growth, characteristics and properties of CNTs, because of their own binding energy, type and role of reactive groups and thermodynamic properties. A comparison of produced CNT characterizations showed that there is a relationship between chemical structures of hydrocarbons and the CNTs formation [5,7,17,49,62,64,74–77]. Hernadi et al. [49] declared that unsaturated hydrocarbons have much higher yield and deposition rate than saturated gases. In addition, saturated carbon gases tend to produce highly graphitized filaments with fewer walls compared to unsaturated gases. Consequently, they suggested that saturated hydrocarbons are favored for SWCNTs growth and unsaturated hydrocarbons for MWCNTs. However, SWCNTs have been obtained from a highly diluted unsaturated hydrocarbon [10,19,23,38,40,47,75,76,78,79]. Li et al. [80] demonstrated that the chemical structure of hydrocarbons, i.e., straight-chained ring or benzene-like structures, is significantly more influential than the thermodynamic properties (e.g., enthalpy) of the carbon source on the type of CNT formation. Besides configuration, functional groups of hydrocarbons have a decisive influence on the quality of the produced material. The growth of clean SWCNTs was observed at relatively low temperatures using alcohols with various catalysts [19,25,30,64,81–85]. The authors concluded that alcohols are much better carbon sources for SWNTs than hydrocarbons and this is likely due to the ability attributed to OH– radicals to etch away amorphous carbon deposits. However Hernadi et al. [49] and Qian et al. [86] suggested that CNT morphology is independent of the carbon feedstock when a specific catalyst is used.

A kinetically stable carbon feedstock that undergoes the least pyrolytic decomposition at process temperature is desirable for CNT synthesis. The most commonly used carbon sources are ethylene [13,32,50,75,76], acetylene [16,33,47,58,70], methane [28,41,42,51,54,61,63], ethanol [19,30,64,80] and CO [21,46]. Recently, Yen et al. [84] reported that CNTs could be synthesis from solid-stated polymers—polycarbosilane and polyethylene using FBCVD. The experimental results indicated that the CNTs synthesized from PE were of better quality and had a higher degree of graphitization. Due to the low price and high availability of the natural sources, their use was proposed for the development of a high-scale, low-cost production of CNT. This is promising as pure carbon source are very expensive and have limited supply. Moreover, most organic gases are toxic, dangerous and difficult to store or transport. Accordingly, coal, liquefied petroleum gas and natural gas have been used successfully for CNTs synthesis [85–89]. However, there are some drawbacks due to the presence of impurities in natural sources as they affect the reaction and process, and also damage the equipment used for the production of CNTs. It is worth mentioning that more work is needed to improve the yield and quality of the CNTs from natural sources. The clarification of the possible synergic effects of gaseous species in the coal gas and natural gas is also required. To achieve commercial carbon nanotube synthesis carbon source with high conversion, low cost, stable supply, less defect on product is desirable.

Carbon feeding rate obviously affects the reaction and hence there is a critical flow rate for the process. Clearly at low flow rates, there is not enough reactants to react with the catalyst, and the carbon source concentration controls the rate of decomposition. A higher flow rate will increase the decomposition rate, however, after a critical point, increasing the flow does not significantly affect the decomposition rate or CNT growth, as it is controlled by the catalyst particles availability [21,25,37]. Single or multiwall carbon nanotubes growth, in fact, could be achieved by carbon feeding rate control and any excess of carbon will result in disordered structures [82].

2.4. Carrier gas

In CNT synthesis process, a specific amount of carbon precursor is continuously fed into the reactor in gaseous form. To reduce the formation of amorphous carbon and decrease the contact time between carbon feedstock and catalysts, the carbon feedstock is diluted by a carrier gas [7,90]. The chamber is also kept free of oxygen by using the carrier gas during the process to avoid carbon oxidation. It is worthy to stress that; the carrier gas should be a non-reactive gases. Argon, hydrogen and nitrogen are the most common carrier gases because they easily form inert atmosphere, however other kinds of gases like helium [38,39] or NH_3 [90] has also been used. It is generally considered that the carrier gases could affect the growth of CNTs and hence the structure and properties of the resulting assemblies [37,69,73,91–97].

Qingwen et al. [74] investigated the influences of carrier gas on the CVD process of cyclohexane. When argon was used as a carrier gas, MWNTs was produced whereas when hydrogen was used, some SWNTs were formed. In a relevant study, Mi et al. [91] compared the effects of NH_3 and nitrogen as carrier gases on the structure and morphology of CNTs. In the case of using ferrocene as catalyst and acetylene as a carbon source, the growth of bamboo-like structures was observed in NH_3 with larger diameters compared to CNTs obtained in nitrogen. The above findings are in fair agreement with Kukovitsky et al. [37] results. Authors noted that the nature of gaseous environment has a profound influence on the mobility and sintering process of the catalyst particle and therefore the strength of the metal–support interaction is altered.

Considering the CVD synthesis of CNTs, the sequence of events taking place is: reactant gases enter the reactor by forced flow, gases diffuse through the boundary layer, gases come into contact with the surfaces of substrate, deposition reaction takes place on the surfaces of substrate, and gaseous by-products of the reaction are diffused away from the surface through the boundary layer. Various transport phenomena, either diffusive or convective, and reaction processes underlying CVD involve many intermolecular collisions. These collisions transfer momentum and energy between the collision partners, or lead to net transport of mass from one part of the system to another. Transport properties of multi-component gases, including viscosity and thermal conductivity as well as heat and mass diffusion coefficients, are directly influenced by temperature, pressure, and mixture composition. To make it more clear, CNTs growth process occurs in a diffusive regime where hot gases surrounding the catalyst force a viscous media and slow down the CNTs growth [98]. Thus it can be inferred that, gaseous environment nature has an intense effects on all steps of the CVD synthesis of CNTs.

It is worth mentioning that, H_2 is mostly considered as a reactive gas rather than carrier. It is believed that hydrogen provides a reducing environment for the catalytic metals and hence prevents poisoning of the catalytic surface by carbon deposition which lessens undesirable carbon deposits formation [7,69,95,92,93].

However, Qian et al. [54] illustrated that there is no any obvious difference in the morphology of CNTs using the unreduced catalyst or reduced catalyst. They also reported that when the unreduced catalysts were used, the conversion of methane as a carbon feedstock was significantly increased. In accordance with their observations and based on representative results obtained by different groups, CNTs of good quality have been obtained by just argon [25,67,74,99–102] or nitrogen [84,103,104] as carrier gas.

Although the presence of H_2 is counted essential for SWCNTs production, the best results in Son et al. [102] in terms of lower diameter and higher crystallinity were achieved in cases of no H_2 were utilized. Furthermore, a relative comprehensive study conducted by Liu et al. [105] to examine the effects of H_2 concentration on CNTs morphology, clearly emphasize that increase in H_2 concentration leads to larger CNTs in terms of walls number and diameter. High concentration of hydrogen accelerates the sintering of the metal particles and consequently, enlarges their diameters. Conclusive evidence on the dependence of catalyst size on the formation of CNTs was reported earlier. These observations regarding the effects of hydrogen concentration on the carbon layer structure are in accord with Xiong et al. [69]. Accordingly the synthesis of single and/or double wall CNTs with high selectivity was attributed to the effective control of the low concentration of H_2. Besides that all, it is well known that the growth of nanofibers is enhanced in a hydrogen atmosphere [7].

The results presented here indicate that the gas flow compound strongly influence the CVD synthesis of the CNTs. It plays role in CVD reaction steps as well as catalyst stability and activity. Accordingly carrier gas has impact on the morphological and structural characteristics of the as-grown CNTs and their uniformity. As the profound influences of the gaseous environment on the CCVD synthesis of CNTs have been established, therefore a more meticulous and detailed investigation is strongly recommended.

2.5. *Time and space velocity*

The best operation period determination with respect to product quality and process yield is vital from the economic point of view for any process. In the CCVD process, there is an optimum time that beyond this, nucleation becomes more difficult and a progressive deactivation of the catalytic nanoparticles starts to occur. However, there is a great disparity in the proposed optimum time of CCVD with respect to process parameters and nature of catalyst as well as carbon source [10,19,58,65,75,94,100,106]. To nucleate CNT, accumulated carbon atoms must reach a critical concentration inside the catalyst particles, which is related to the deposition rate. Kouravelou and Sotirchos [31] in a systematic study proved that the rate of deposition depends on carbon precursor nature and the catalyst composition as well as temperature.

Meanwhile, it has been reported that CNTs possess different morphologies for different reacting times. Lamouroux [107] believed that short reaction time is adapted to SWCNT growth. Kim et al. [66] reported that CNTs diameter is determined by duration time of tubes in the hottest zone of reactor. In accordance with their statement, Roman and Somenath [108] showed that the mean diameter of MWCNTs increase with the CVD durations, possibly due to sintering and agglomeration of particles. Furthermore, CNTs length is controlled by the length of the deposition time [7,47,109]. Qian et al. [75] concluded that CNTs sampled at different periods have different thermal stability, i.e., the initially grown CNTs have a low thermal stability and serious defects as compared to the fully grown tubes. In view of that, better understanding of the reaction kinetics is needed for a controllable CNTs synthesis.

Throughout the Roman and Somenath work [108], it has been shown that residence time of the flow, the time spent by the fluid in a reactor, also plays an important role in CCVD of CNTs. According to their results obtained in a fixed-bed reactor, at very low residence times only CNTs with practically no non-tubular form of carbon were formed. As the residence time increased, the concentrations of active radicals and intermediates in the gas phase increased, therefore they began to recombine, and formed larger molecules. Under these conditions, active radicals consumed the available C that would have otherwise formed CNTs and other forms of carbon.

The available specific surface area for CCVD reaction and hence its severity is mainly influenced by synthesis duration as well as space velocity. The space velocity is the volume flow rate relative to the catalyst mass. This parameter is important for any comparative measurements in catalytic process such as catalyst screening, determination of process parameters, optimization of catalyst production conditions, and deactivation studies [83,110,111]. Basically, space velocity eventually must be determined in a pilot plant [112]. It is worthwhile to note that as the space velocity in fluidized bed reactors is relatively high compared to fixed bed; hence selective synthesis of desired CNTs especially single or double wall is favored [105,113]. High space velocity avoids external diffusional effects in the catalyst particle and it can be obtained by using high gas flow rate or not vary dense bed of catalyst. A constraint may arise from high flow rates that it cools down the bed environment and thereby affect the deposition quality [8]. Moreover, high gas velocity makes some difficulties in process scale up as it influences the stable fluidization of catalyst and CNTs of low bulk density in the reactor [63,105]. Liu et al. [105] demonstrated a practical method to increase the space velocity for selective synthesis of DWCNTs. A very high space velocity achieved by feeding fresh catalyst in small amounts to the fluidized bed reactor. Nevertheless, this prominent parameter has been almost systematically occulted in the majority of studies regarding CCVD synthesis of CNTs in either fixed or fluidized bed.

3. CCVD synthesis of CNT using fluidization technique

Fluidized bed reactors are widely applied for several industrial purposes, such as different types of chemical reactors, fluid catalytic cracking, fluidized bed combustion, fluidized bed bio-filter or applying a coating on solid items [8]. Fluidized bed reactors afford excellent gas–solid contacting and particle mixing, facilitate the control of highly exothermal reactions, and provide good gas-to-particle and bed-to-wall. Recently, fluidized bed reactors with supported nano-metal catalysts were found to be equally effective for mass production of CNTs [8,96,105,114–138]. Typically a vertical reactor enclosed by an electrical furnace is used for FBCVD. An upward flow of carbon source and carrier gas mixture fluidizes the supported-catalyst particles in well-contact by the reactant (Fig. 6). In the mass production of CNTs, FBCVD techniques offer numerous advantages over fixed beds and floating catalyst thanks to the technology robustness, flexibility and high productivity [127,130,133,136]. Moreover, the FBCVD is easily scaled-up and can be operated continuously which is important for cost-effective large-scale production of CNTs.

Basically, fluidization provides higher space velocity which leads to efficient gas–solid contact, and hence high mass and heat transfer. In accordance with that high process yield, product homogeneity, purity and selectivity are attained [8,84,127–130,132,133]. Moreover, FBCVD is a flexible process in terms of operating conditions as parameters like gas mixture and temperature can be finely tuned according to the definition of the desired product [131,133]. Furthermore, available space for growing CNTs and their resistance times can be controlled accurately and the activity of the catalyst is utilized sufficiently [130,133] which favors the selective mass production of CNTs with uniform properties. Despite all mentioned advantageous, improper design and/or operation of fluidized bed

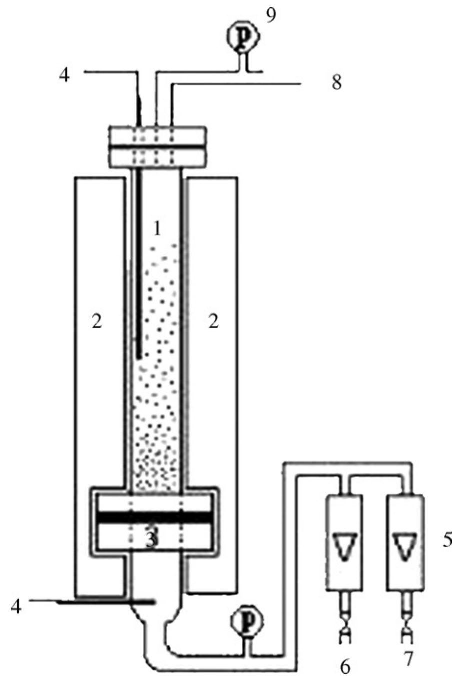

Fig. 6. General schematic of fluidized bed for CNT synthesis. (1) Reactor, (2) furnace, (3) distributor, (4) thermocouple, (5) rotameter, (6) carbon source, (7) carrier gas, (8) outlet, (9) pressure sensor analytical instruments like gas chromatography also can be used for outflow.

reactors can lead to conversions that fall well below the theoretical lower limit of perfectly mixed flow.

Another facility provided by fluidized bed reactor was demonstrated by Xu and Zhu [137] which emphasis the superiority of these kinds of reactors for mass production of CNTs. They developed a new technique of fluidized bed metal–organic chemical vapor deposition (MOCVD) as a one-step preparation of highly dispersed metal-supported catalysts followed by FBCVD to synthesis CNTs. This method has some advantageous over the conventional methods (such as impregnation, ion exchange, co-precipitation and co-crystallization) since it eliminates the drying and the subsequent calcinations/reduction operations, and hence minimizes the aggregation or growth of crystalline size of the supported metal particles caused by these operations. Prepared supported-catalyst particles activities were tested for CNTs synthesis through FBCVD using acetylene. Results proved that for all the metal-supported catalysts the deposited metals were highly dispersed on the surface of the support particles. In a relevant attempt regarding development of FBCVD toward the mass production of CNTs, See et al. [132] explored that the technical viability of using $CaCO_3$ as a soluble support material for the synthesis of CNTs via FBCVD. They achieved MWCNTs of similar quality to those synthesized via traditional CVD techniques. These models also showed the versatility of FBCVD which fulfill the priority of this method for large-scale production.

As far as FBCVD synthesis of CNTs is concerned all parameters, which influence the reaction and fluidization quality, should be considered. The effective factors on CVD reaction efficiency have been addressed in previous sections. The conversion in a fluidized reactor depends on the basic features that together determine the fluidization quality. The term 'fluidization quality' is applied to describe the various fluid-dynamic conditions brought about by the fluidization process itself. Quantities, which determine the fluidization mode and characteristics, include intrinsic properties of particles, reactor geometry, superficial fluidizing velocity (U), and minimum fluidization velocity (U_{mf}).

The CNTs synthesis conditions and related results of different studies conducted in fluidized bed are summarized in Table 2. Unfortunately, the scattering of data and the diversity of the experimental equipments and procedures made a reliable comparison of results difficult. Moreover, there is a dearth of process parameters and large gaps exist between reported information, especially factors associated with fluidization criteria. See et al. [125] reported the first investigation of some process parameters and their interactions in FBCVD using fractional factorial design. However, FBCVD is in its infancy and further in-depth understanding of the impact of the operating parameters on product quality and quantity is strongly required for commercial production of CNT. In this contribution, the general study of fluidization principles is presented as well as published researches on FBCVD.

Fluidization quality is closely related to the intrinsic properties of particles, e.g., particle density, particles size as well as their size distribution and surface characteristics. Geldart [139] classified powders into four groups according to their fluidization behaviors at ambient conditions. Type A particles with sizes of about 20–100 μm, form a slightly cohesive structure. Type B are dense materials like glass and sand with diameters of around 150 μm. Type C particles are even smaller and lighter than type A, usually less than 20 μm in diameter. Type D particles are large, on the order of one or more millimeters. Nano-sized particles, corresponding to Geldart classification, fall in group C, but, their fluidization behavior differs from conventional C particles because of extremely small dimensions and bulk density [139,140]. The Geldart C particles are difficult to fluidize due to the large cohesive forces which lead to crack formations and channeling in the bed. Nanoparticles despite the anticipated large surface charge can be easily fluidized due to the formation of light agglomerates [140,141]. This type of fluidization has been termed as agglomerate particulate fluidization.

Fluidization quality is basically depicted by applied gas flow velocity to the minimum fluidization velocity ratio (U/U_{mf}). Minimum fluidization velocity is the superficial fluid velocity at which the upward drag force exerted by the fluid is equal to the apparent weight of the particles in the bed; the pressure drop of the gas across the bed becomes constant with increasing the gas velocity. Minimum fluidization velocity depends on particle size and particle density, Geldart group, and fluid properties as well. The value of U_{mf} is usually determined experimentally by measuring the pressure drop as a function of gas velocity. It also may be predicted by some empirical or semi-empirical correlations [142–145]. However, the result from these kinds of equation is not accurate due to different behaviors of particles in practice [129].

There is a prominent issue for FBCVD of CNTs related to its fluidization quality determination, because the bed characteristics change on account of reaction and elevated temperature. Catalyst particles initially provide fluidization, and their fluidization behavior can be easily predicted at ambient condition according to Geldart classification. However their fluidization characteristics at process temperature, which is above 500 °C, appear different from that which it occupies at ambient conditions. This is due to the effect of gas properties on the grouping and may have serious implications as far as the operation of the fluidized bed is concerned. Moreover, U_{mf} differs significantly from the size distribution in the fresh feed due to elutriation of fines, attrition, agglomeration of particles, bed solid characteristics change due to reaction, density and viscosity of fluids alteration due to reaction and temperature.

Venegonia et al. [96] in their parametric study for CNTs growth by FBCVD measured the U_{mf} of SiO_2 particles, belonging to B group of Geldart classification, both at 25 and 550 °C, and found that $U_{\mathrm{mf}} = 517\,\mathrm{cm\,min^{-1}}$ decreases to $57\,\mathrm{cm\,min^{-1}}$, respectively. In accord with this observation, Morancais et al. [116] pointed out during the synthesis of CNTs, U_{mf} is roughly divided by a factor 6 after 120 min of run, since the grain density sharply decreases;

Table 2
Parametric studies of published paper on CNT synthesis by fluidized bed.

Condition			Catalyst			Reactor		Fluidization parameters			Results		Ref
Carbon source	Temp. (°C)	*P* (atm)	Composition	dp (μ)	Amount (g)	ID (mm)	Height (m)	Total vol. flow (1000 × sccm)	U_{mf} (cm/s)	Fixed bed height (cm)	CNT dia. (nm)	Wall	
Propylene		1	Fe/alumina–silica			50	1		0.5–0.7	4.5	20–30	MW	[119]
Acetylene	700		Fe/silica		6	22	1.2	0.605			8–25	MW	[115]
Propylene			Fe–Mo/alumina			28	2		1.7				[104]
Acetylene	700	N	Fe/silica	N	10	22	1.2	0.7	N	N	8–16	NM	[58]
Ethanol	<600	–	Fe–Mo/MgO		0.1			0.2			0.8–1.8	SW	[99]
Ethylene	823	1	Fe/alumina									MW	[75]
Ethylene	650	1–1.3	Fe/alumina	110	50	53	1	2.29		1.8	10–20	MW	[116]
Ethylene	550–1050		Fe/silica			28						MW	[96]
Ethylene	650	0.004	Fe/alumina		100	53	1	1	0.14	3.5		MW	[120]
								1.455					
Methane	760	1	Ni/silica			22	1	1.01			0.86–1.35	SW	[101]
	860										50–200	MW	
Acetylene	600		Fe–Mo/alumina	114	30	50	1	3		10	15–20	MW	[118]
								2			50.4		
								3			15.4		
								4			16.9		
Ethylene	500		Fe/Cu/SiO_2		28.5	44	1				25–30	MW	[53]
Propylene			Fe/Cu		28.1						20–30		
Ethylene			Fe/Al		1.09						5–10		
Methane	800		Fe–Mo/MgO	45–150	5	50	1	3				MW	[65]
Methane					2.5						10.59		
Acetylene					5						12.12		
Acetylene					10						9.46		
Acetylene					20						10.05		
Polypropylene	450–850					110					15–40	MW	[51]
Carbon monoxide	800	6	Co–Mo/MCM41		1	25.4	635	0.43			2	SW	[129]
Ethylene/propylene	500–700	1	Fe/alumina		–	250	1	83–182	0.6		10	MW	[126]
Acetylene	600		Fe–Mo/alumina	150	30	53	1	3				MW	[123]
								1.998				MW	

and as a consequence, the fluidization ratio increases. Accordingly, they proved that at $U/U_{mf} = 0.87$ for a 5.3 cm diameter reactor, optimum conditions of run in terms of fluidization quality and MWCNTs formation is obtained. They also noted that carbon yield tends to increase when the U/U_{mf} ratio decreases for a similar amount of carbon introduced, because of the increase in residence time of the gaseous precursors into the bed. In contrast, Son et al. [118] reported that at gas flow rates corresponding to about $2U_{mf,}$ the heat and mass transfer are relatively low leading to lower carbon yield and bigger CNTs diameter than about $4U_{mf}$. In accordance with them See et al. [125], Corrias et al. [120] and Venegonia et al. [96] applied fluidization ratio higher than one. Recently Philippe et al. [127] in a comprehensive kinetic modeling study of CNTs by FBCVD indicated that U_{mf} decreases with run duration till 30 min and then regularly increases, in agreement with the Ergun relation for which U_{mf} depends on dp^3 $(\rho_p - \rho_g)$.

In FBCVD synthesis of CNTs, the initial amount of catalyst corresponding to the static bed height, H_s, provides the operability characteristics of fluidized beds. Therefore, the challenge associated with the catalyst mass placed in the reactor is not only its effects on CNTs formation but also on fluidization condition. First, the heterogeneous catalyst should carefully be prepared with respects to its activity for CNTs formation. Then appropriate catalyst amount should be chosen to obtain required fluidization properties. However, the utilized initial amount of catalyst, as it is clear from Table 2, is rather different. Son et al. [118] comment that if static bed height (H_s) is smaller than the inside diameter of the reactor, (i.e., a shallow bed), fluidization quality is poor. Adding 114.3 μm alumina powders as inert particles, in their study, improved CNTs production and the mean CNTs diameter and agglomerate size of synthesized CNTs decreased as a result of attrition of the inert particles. In accordance with their comment, See and Harris [132] also applied 40 g pure $CaCO_3$ in addition to the 70 g catalyst (Fe–Co supported) on $CaCo_3$. In contrast, some researchers insist on a small initial bed heights are sufficient for effective synthesis of CNTs in FBCVD because of the significant decrease in bed density and rapid bed expansion [65,131,132]. Moreover, large amount of catalyst demands a very high flow rate of gas for organization of homogeneous condition in the reactor and for its transportation into the reactor. Recall that very high gas velocity leads to the complexity in the process scaling-up [63,105]. Accordingly, such peculiarities require appropriate reactor design and finely tuned operating conditions.

Considering the CNTs structure, it possesses both nano-metric (related to its radius) and microscopic (related to its typical length) dimensions. The apparent feature of CNTs as an end product of FBCVD is a black spongy powder with low bulk density. Further microscopic observation showed that produced particles are a 3D network structure from large amounts of CNTs rather liner structure of individual CNT (Fig. 7). Wang et al. [126] found CNTs in tangled and loose agglomerates with broad size distribution, which belongs to Geldart-A classification. Further observation made by Hao et al. [104] revealed that during the process larger agglomerates break into smaller one; therefore the average agglomerate diameter in the reactor remains nearly constant. Correspondingly they deduced that agglomerate morphology of nanotubes provides good fluidization during the growth process and cause high-quality CNTs production in large-scale at low cost. Morancais et al. [116] also observed MWCNTs in the form of 3D randomly oriented chunks of 110–225 μm size. Contrary to the former observation, they annotated that if agglomeration phenomenon occurs, carbon conversion and MWCNTs growth rate decreases and agglomeration happens in low fluidization quality condition, which less mixing of powders due to low gas flow exists.

As mentioned earlier, FBCVD does not allow the production of aligned CNTs that might be considered as an obstacle for this process [8]. However the comparisons of CNTs grown on a same catalyst in a fixed bed and fluidized bed showed that CNTs produced by FBCVD has a higher specific surface area [105] and better thermal stability [134]. Moreover, due to effective mass and heat transfer, longer CNTs with smaller diameter and fewer lattic defects is formed in an FBCVD compared to fixed bed [130,134]. It is worth mentioning that, the smaller the mean diameter and the higher the crystallinity of the CNTs, which are achieved in FBCVD, the better the field emission properties [102].

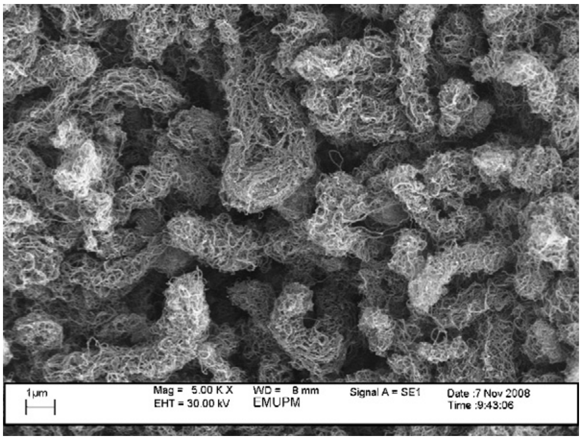

Fig. 7. Three-dimensional structures of CNTs produced in FBCVD.

Considering the presented results, it seems reasonable to declare that, the prominent features of FBCVD for CNTs production are blurred. The hydrodynamic and thermodynamic behaviors of CNT growth in fluidization have not been understood yet. This review presents achievement toward there are especially some distinctive topics to be solved before large-scale production of CNTs using FBCVD can be implemented.

(1) optimization of fluidization characteristics for CNTs production, namely supported-catalyst diameter, static bed height and total flow rate;
(2) investigation of heat, mass and momentum properties of CNTs;
(3) investigation of parametric factors interactions;
(4) investigation of end products particles morphology and their effects on the process, especially agglomeration; and
(5) designing a continuous process.

4. Conclusion

Mass production of CNTs is the major challenge and critical for their future applications. Significant advances during the last few years include the development of new CVD methods for commercial production. This has been significantly boosted through the use of fluidized bed reactors. A fundamental key to further control of FBCVD is the understanding of different mechanisms of CNTs formation, which can determine their structure and characteristics. However, the FBCVD is in its infancy and further research will improve the yield, purity and selectivity of CNTs growth. Many of the challenges and ambiguity associated with CVD and FBCVD synthesis of CNTs have been highlighted in this paper. It has been demonstrated that further investigations, both theoretical and experimental, are required to study the effective parameters on FBCVD process. This will contribute to the design and operation of commercial production facilities of CNTs. Currently it is still too much of an art requiring practical experience particularly during scaling-up where the cost factor is crucial.

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