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The mass production of carbon nanotubes using a nano-agglomerate fluidized bed reactor: A multiscale space-time analysis

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Abstract

The scaled-up mass production of carbon nanotubes (CNTs) was reviewed by a multiscale analysis from the delicate catalyst control needed at the atomic level, CNT agglomerate formation at the mesoscopic scale, to the continuous mass production process on the macroscopic scale. A four level analysis that considered CNT assembly, agglomerate structure, reactor hydrodynamics and coupled processing was used. Atomic scale catalyst design concepts were used to modulate the CNT structure. On the reactor scale, the design consideration was on getting suitable CNT and catalyst agglomerates with good fluidization behavior and transport properties. A pilot plant with high yield (15 kg/h) and purity (>99.9%) was demonstrated, which made a great stride for extensive applications of CNTs. Other nano-agglomerate structures can also be considered using the multiscale time and space analysis, which will benefit mass production and applications of nanomaterials in future. © 2007 Elsevier B.V. All rights reserved.

Keywords: Carbon nanotube; Mass production; Fluidized bed; Multiscale; Nanotechnology

1. Introduction

The carbon nanotube (CNT) was discovered by Iijima [1]. It is an attractive material because of many unique properties originating from the small size, cylindrical structure, and high aspect ratio of length to diameter. Single-walled carbon nanotubes (SWCNTs) consist of a single graphite sheet wrapped around to form a cylindrical tube. Multiwalled carbon nanotubes (MWCNTs) comprise an array of such nanotubes that are concentrically nested like the rings of a tree trunk. CNTs have extremely high tensile strength (≈ 150 GPa), high modulus (≈ 1 TPa), large aspect ratio, low density, good chemical and environmental stability, and high thermal and electrical conductivity. It is a new type of high performance carbon nanomaterials that is in demand for different potential applications, including the making of conductive, electromagnetic and microwave absorbing and high-strength composites, fibers, sensors, field emission displays, inks, energy storage and energy conversion devices, radiation sources and nanometer-sized

semiconductor devices, probes, and interconnects [2–9]. Recently, strong and stretchable CNT fibers were spun from 0.65-mm-long CNT forests, which have the strength and Young's modulus of 1.91 GPa and 330 GPa, respectively [7]. SWCNT/PVA composite fibers are tougher than any natural or synthetic organic fiber described so far [8]. For these applications to be feasible, a controllable synthesis of CNTs at a low cost in a scalable way is needed. There are urgent needs for large amounts of CNTs.

Various CNT synthesis methods have been developed, which can be classified by the way the carbon is assembled into the tubular structure according to the energy input. According to the way of energy input, three main CNT synthesis methods – arc discharge, laser ablation, chemical vapor deposition (CVD) methods – have been developed [2]. The common feature of arc discharge and laser ablation methods is that high energy is input with physical means such as an arc discharge and laser to induce the reorganization of carbon atoms into CNTs. The temperature used is even higher than 3000 °C, which is beneficial for good crystallization of the CNTs, thus, the products are always produced with good graphite alignment. However, the basic requirements of these systems, including vacuum conditions and continuous graphite target replacement, pose difficulties to the large-scale

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production of CNTs. In CVD methods, the carbon source is deposited with the assistance of a catalyst at temperatures lower than 1200 °C. Tubular CNTs are deposited at the catalyst site. The CVD process can operate at a mild condition such as normal pressure and low temperature with a proper carbon source, catalyst and atmosphere. The CNT structure, such as its wall number, diameter, length, and alignment, can be well controlled during the CVD process. Thus, the CVD method has the advantages of mild operation, low cost, and controllable process, and is the most promising method for the mass production of CNTs. Various scalable processes had been reported with CVD methods, including "Carbon Multiwall Nanotubes" of Hyperion Company [10], "CoMoCAT[™] Process at SWeNT" of the University of Oklahoma [11,12], "HiPCO Process" of Rice university [13-15], and "Nano Agglomerate Fluidized" process of Tsinghua University [16,17].

2. A multiscale space-time analysis on the mass production of CNTs

For the mass production of CNTs, the process covered large time and length scale. On the microscopic scale, as shown in Fig. 1, it is a process in which the carbon source self-assemble into a one-dimensional tubular CNT structure with the help of a catalyst, while on the macroscopic scale, it is the continuous mass production of a chemical product on the tons scale and is closely related to the modern processing industry in the processes, including the processing for the high purity of the MWCNTs and SWCNTs, and the processes of heat and mass transfer [18]. Thus, the continuous mass production of nanomaterials, including CNTs, is a great challenge for chemical engineers. This is due to that the product has such a high molecular weight (10^6-10^{13}) , must have definite structures and morphology, and has complex physical and chemical properties. CNTs have a large surface area, can be present in many structures and morphology, and the interaction between the nanomaterials or CNTs is more complicated than that in small organic or inorganic molecules. For example, in terms of the morphology, the product cannot be treated as a uniform substance. Its momentum, heat, and mass transfer properties are obviously different from those of common fluids or powders, and pristine CNTs are very difficult to handle from a processing point of view. In the work described here, this was solved by the use of a delicate control of the pristine CNTs into an agglomerated structure. The agglomerated structure significantly affected the properties and applications of the CNTs. The CNT structure is grown in a bottom-up self-assembly way from the atom scale, which is considered as a discrete event. However, the mass production is a continuous operation with macroscopic flow, reaction, and heat and mass transfer. For robust mass production, the bottleneck is not only the CNT growth at the atom scale and the macroscopic continuous operation, but also the mesoscopic nanostructure and architecture modulation, which has a strongly coupled relationship with both atomic and macroscopic scales. It may seem that like traditional chemical engineering processes and powder technology, the CNTs can be treated as a continuous fluid, but this is not good enough for treating the CNT structure. There is a gap between the microscopic and macroscopic scale which needed further studies. This is shown in the proposed time and length scale analysis of the mass production of CNTs shown in Fig. 1. The mass production process is decoupled into four scale levels:

 CNT self-assembly at the atomic scale, including the growth condition and growth mechanism of the CNTs, catalyst design, and controllable synthesis of the structure of individual CNTs. Many characteristics of CNTs, including wall number, diameter, length, defects, chirality, crystallinity or graphitization, are determined at the atomic scale.



Fig. 1. Multiscale space-time analysis of the mass production of CNTs.

- 2. As CNTs grow longer, due to the large aspect ratio, various CNT agglomerated structures are formed. This is the mesoscopic level that considers the behavior of agglomerated nanostructure, including agglomerate morphologies, agglomeration mechanism, and ways to control the agglomerates. Due to interactions between the CNTs, there are various CNT agglomerated structures, including CNT agglomerated particles, CNT arrays, suspended single CNTs, etc. For the mass production of CNTs, the control of the morphology is important. In this contribution, CNT agglomerated particles are used as an example to show a process for mass production of CNTs.
- 3. The flow behavior scale considers the transport properties of CNT agglomerates. Due to the unique properties of CNTs and CNT agglomerates, the traditional facilities have to be modified for CNT production, the modification of the hydrodynamic behavior of the nanomaterials in the reactor was a basic problem and the key for the scale up of this process. In order to realize the industrialization of CNT production, the hydrodynamic behavior of the CNT agglomerate powder has to be analyzed in detail.
- 4. Integrated CNT process engineering, including the process operation, the relationship between the macroscopic operation and microscopic CNT structure, environmental and ecological considerations, and the delivery and application of CNTs. These are macroscopic objects and various traditional chemical engineering concepts are involved at this level.

This analysis is a way to decouple the complex mass production of CNTs into the close connections among the various levels. For example, the macroscopic process operation is affected by the CNT structure, which can be modulated using the various interactions in the CVD growth process. This multiscale analysis may provide a common methodology for the scale up of nanomaterials and nanostructure.

3. CNT assembly at the atomic level

There is a long history to the production of carbon materials by CVD methods. Hyperion Company had applied for a patent for CVD synthesis of 3–75 nm "carbon fiber" comprising multilayer graphite sheets wrapped into coaxial cylindrical tubes in 1984 [10], which was 7 years earlier than the widely recognized discovery of CNTs [1]. The wall layer number, diameter, defects and alignment are the key objects in controllable CNT synthesis. Most of the problems require a focus on the atom arrangement mechanism, and the key lies in the atomic level. In this paper, the CNT growth mechanisms are introduced first, and then the concepts behind the MWCNTs and S/DWCNTs catalyst design rules are discussed to show how to finely modulate the CNT structure.

3.1. Growth mechanism for CNTs

In the CVD process, CNTs grow from the carbon atoms from a carbon source by the catalysis action of metal particles. The growth mechanism has been well discussed in the literature, but the complete mechanism of growth is still not fully understood. The most accepted model for CNT growth is similar to the vapor–liquid–solid (VLS) mechanism proposed by Baker and co-workers to describe the growth of carbon fibers [19,20,21]. In this model, the catalytic decomposition of a carbon feedstock into carbon atoms and hydrogen is initiated on an active transition metal surface. This is followed by the diffusion of carbon into the metal particles until the solution (metal–carbon) becomes saturated; when supersaturation occurs, there results the precipitation of graphite carbon from the metal surface, which under the right conditions forms a cylinder (CNT).

The catalyst particle may be located at the tip of a CNT (tip growth) or at the base (base growth), which depends on many factors. The strength of the interaction between the catalyst and substrate is a key factor. During a CNT array growth by the floating catalyst CVD process, the process was base growth [22,23]. For CNT growth on powder catalysts, both tip growth and base growth have been seen [24]. Helveg et al. [25] have shown *in situ* images of the growth of CNTs in a TEM, where the catalyst was pulled up from the substrate and tip growth was realized. Further studies are needed to further understand the complicated phenomena. The self-assembly of CNTs during the VLS process is needed to control the CNT diameter, chirality, length, and other characteristics. Here, based on VLS model, some catalyst design concepts at the atomic scale are proposed to achieve CNT structure modulation.

The catalyst is the key factor for CNT growth in CVD methods. The transitional metals, Fe, Co, Ni, V, Mo, La, Pt, Y are active for CNT synthesis [26]. These active elements can be loaded on a catalyst carrier by coprecipitation and other loading methods widely used in petroleum and chemical processes. However, the CNTs grow on the catalyst, that is, it is deposited on the catalyst surface, which means a one-time use of the "catalyst". The volume of the catalyst–CNT system increase during CNT growth, which is an obvious and important difference from when petroleum and chemical process catalysts are used [27]. Meanwhile, it can be deduced the VLS model above [19–21,25] that the CNT structure will have a close relationship to the active catalyst size and distribution, and the catalyst needs careful design.

Meanwhile, another important parameter in CNT growth was the carbon source. Until now, not only the pure carbon sources, including methane [28,29], ethylene [30], propylene [24], xylene [31], cyclohexane [22,23], camphor [32,33], ethanol [34–37], but also the mixtures such as liquefied petroleum gas [38], coal [39], natural gas [40], grass [41], can be used for CNT growth with proper catalysts. The carbon source with high conversion, low cost, stable supply is a good candidate for CNT mass production.

3.2. MWCNT catalyst design

MWCNTs have diameters smaller than 100 nm, and it is hoped to be able to control this. The VLS mechanism implies that the diameter of the CNTs is similar to the size of the active catalyst particle. The important factors for a good CNT catalyst are the control of the loading of the active metal and to maintain a good metal dispersion on the catalyst support. However, at the



Fig. 2. Morphology of MWCNTs grown from a Fe/Mo/Al₂O₃ catalyst.

temperatures used for CNT growth, active metal particles tend to sinter to a large size due to the effect of Ostwald ripening. Generally, methods to highly disperse metal crystallites onto a support include tailoring the loading of the metal [42], protection using organic solvents during preparation [43,44], using promoters (e.g. Mo) [45-47], and using a stable and molecularlevel uniform structure for the support [48]. For example, Fe/ Al₂O₃ catalyst is an active catalyst for MWCNTs growth. The Fe catalyst nanoparticles are easily sintered, which caused large diameter CNT growth. If Mo is added, due to the segregation of Mo at the surface of the iron particle, there is a stable structure at high temperature, and a small size CNT is produced at a higher growth temperature (Fig. 2). This catalyst showed excellent carbon source cracking activity and gave high yields of small diameter CNTs. Thus, a synthesis catalyst was developed that gave a narrow size distribution of small diameter MWCNTs with the concept of phase segregation promoters. Various elements show a similar phase segregation effect, including Mo [49–51], W [52], C [53] etc.

Both the size and composition of the catalyst are key factors for the CNT structure. For a Fe/Al₂O₃ catalyst, if Ni is added, a Fe–Ni alloy is formed and catalyst stability is increased due to the high activity and stable phase [54]. However, the addition of Ni caused more defects in the CNTs products. The addition of Ni tends to produce fish bone type CNTs. Thus, this is a method to modulate the graphite arrangement in CNTs [54].

Meanwhile, it has been noted that some catalyst can be inhaled into the tube such that the Fe/Al_2O_3 catalyst forms coaxial carbon-metal nanowires [55]. This is due to the aggregation of metal particles, and the lift-up of the metal particles into CNTs and deformation of the metal. If a copper microgrid without a catalyst carrier was used as a catalyst, CNTs with totally hollow channels and/or totally filled copper nanowires can be fabricated [56]. This shows the MWCNT structures were modulated by the relationship between the catalyst active phase and carrier, the details of which need further studies.

Another aspect of catalyst design involves rules about modulating catalyst activity during CNT growth. For example, if we introduce some materials, including Na_2CO_3 , Na_3PO_4 , CaCl₂, etc. intentionally to tailor the activity of the Ni/Cu/Al₂O₃ catalyst, then collapsed CNTs, and even large inner diameter CNTs were obtained [57]. By this method, namely, the addition of specific amounts of Na_2CO_3 onto a Ni/Cu/Al₂O₃ catalyst, the inner diameter of the CNTs was enlarged from 3–7 to 40– 60 nm, while the outer diameter of about 60–80 nm remained unchanged [58]. Thus, the inner diameter and degree of collapse can be modulated by this method.

From the above concepts of controlling the catalyst particle size, composition, carrier and catalyst activity and by the introduction of poisons, various controllable CNT structures were obtained and fine control of the growth was realized. This was a basic development for the mass production of definite MWCNT structures.

3.3. S/DWCNT catalyst design

S/DWCNTs only have one or two walls, thus, have a smaller diameter compared with MWCNTs. The key to the control of the wall number was to maintain 2–5 nm catalyst nanoparticles at high growth temperatures. Due to the small diameter and high surface energy, S/DWCNTs more easily form bundles and rings, while the catalyst structure is not broken due to the flexible S/ DCNTs. A high void volume, low density catalyst is necessary for producing S/DWCNTs in high yields in a selective synthesis. It is noted that Fe/MgO is a stable, low cost catalyst and that it can be easily removed by a relatively mild acid treatment. But due to uniform precipitation or loading, the as-synthesized Fe/MgO catalyst has a relative low selectivity to S/DWCNT, which is bad for the mass production of S/DWCNTs in high purity. Here, the design concept for a high selectivity S/DWCNT catalyst was used.

Due to the difficulty of achieving a high dispersion of the Fe on the carrier surface with the precipitation or loading process, some large metal particle will be present. Then, MWCNTs will grow from the catalyst [59]. However, if the calcination of the Fe/MgO catalyst was conducted in air at high temperature, the selectivity to S/DWCNTs grown from the catalyst was much enhanced. This is due to that the calcination caused FeO_{x} clusters to be welldispersed in the MgO lattice, resulting in an MgFe₂O₄/MgO solid solution with more Fe element on surface of the particle. After the introduction of methane, many small iron-enriched particles with diameters less than 5 nm appear on the carrier surface [60]. Then, carbon from methane cracking is dissolved in these iron-enriched particles, which leads to the formation of CNTs at the same time as the formation of the particles. However, the S/DWCNTs yield is not higher than 15%. Then a hydrothermal treatment method was used to reform Fe/MgO catalysts with a cubic particle morphology into lamella-like Fe/Mg(OH)2 catalysts. A high dispersion of the iron species was found on the lamella-like Mg(OH)2 substrates that were several hundred nanometers in size. The materials prepared with the hydrothermally-treated catalyst were found to mainly comprise DWCNTs that had a high degree of cleanliness



Fig. 3. TEM images of DWCNT products [61].

without other carbon purities [61]. A high purity and a yield up to 49.1 wt.% with BET surface area higher than 800 m²/g was obtained by CH₄ cracking for 60 min over a catalyst with a 180–220 °C hydrothermal treatment (Fig. 3) [61]. This is significantly enhanced CNT yields by catalyst design at the atomic scale.

It was noted that the catalysts not only contain the active metal particle, but also contain the MgO carrier. If the surface of MgO was changed gradually, which can be done by the introduction of CO_2 during the reaction, the yields of S/ DWCNTs was also enhanced [62]. Also, minimizing the size of MgO by phase separation, which can decrease Fe particle sintering, were also effective in enhancing the production of DWCNTs [29]. In summary, the concept for enhancing S/ DWCNT production was discussed and the researches on the atomic scale have provided the opportunity for high yield mass production of S/DWCNTs at low cost.

4. CNT agglomerate structure and its controllable formation

The above catalyst design concept to make a definite catalyst site and structure was seen to effectively modulate the CNT structure. The CNTs can be grown into agglomerate particles, bundles and arrays. Various reactors, including fixed beds [63,64], floating catalyst process with a low solid density [65– 68], and fluidized beds [17,24,63,69-79] were used to produce CNTs on a large scale. The agglomerate CNT particles can be easily scaled up into the kilogram per hour scale by the fluidization technique with a powder catalyst. However, according to conventional fluidization knowledge a single CNT can't be fluidized because it is a linear nanometer material [80]. But by the control of the catalyst and a proper CNT agglomerate state, a macroscopic state can be formed that is easily fluidized during the growth. The CNT products are black granular particles with an average diameter of around 500 μ m and a bulk density of 40 kg/ m^3 , which is only 1/20 that of the original catalyst [24]. As shown

in Fig. 4, the CNT particles are a 3-dimensional network structure agglomerated from large amounts of CNTs, that is, they are not present in the form of individual CNTs. Due to the stronger interaction between the CNTs and the catalyst support, subagglomerates of about 1µm were formed. But due to van der Waals forces and entangling among CNTs, a further aggregation of these sub-agglomerates naturally occurs to form large CNTs agglomerates, some even as large as 400–500 µm. This structure can also be confirmed by the relationship between the pressure and density of the CNTs, shown in Fig. 5. When the CNT agglomerate is pressed, the density of the CNT increased. If there were no agglomerates or the agglomerate structure changed, a linear relationship between the density and log of the pressure existed. If agglomerates existed and they were cracked, the slope was changed. In Fig. 5, two turning points can be seen: in the low pressure area, agglomerates of hundreds micrometers were



Fig. 4. Agglomerate structure of MWCNTs.



Fig. 5. The relationship between the pressure and density of agglomerate MWCNTs, which reflect the multi-agglomerate structure.

pressed; when the pressure reached 10^5 Pa, the multi-agglomerate structure collapsed and the CNTs exist as sub-agglomerates; when the pressure reached 10^7 Pa, the CNTs were presented as hard agglomerates which were very difficult to destroy.

The multi-agglomerate structure that is formed is due to the CNT growth on the powder catalyst (Fig. 6). The catalysts were agglomerate nanoparticles. Their morphologies were changed by CNT growth and the catalyst particles were crashed. A model of this is in Fig. 7. In the initial period, growing CNTs with a base growth mode crush the catalyst particles, disrupt the structure, and form separated catalytic sites. Due to the release of the stress inside the catalysts in this period, disorder in the graphite layer and defects occur during the initial carbon deposition, as shown in the tips in Fig. 7b. With increased carbon deposition, the catalysts will have been crushed as much as they can be and the CNTs grow



Fig. 6. TEM images of CNT agglomerates from a Fe/Mo/Al₂O₃ catalyst. The catalyst has been crushed by CNT growth and a multi-stage CNT agglomerate was formed.



Fig. 7. Schematic mechanism of CNT agglomerate formation: (a) original catalyst particle; (b) the catalyst particle structure is crushed by CNT growth; (c) catalytic sites are adequately separated and sub-agglomerates form; (d) fully developed agglomerates [24].

around the catalyst sites. The growing CNTs will push away and separate the sites from each other, leading to increasing agglomerate size and decreasing density, until fragmentation by ablation dominates the growing process (Figs. 6 and 7c.d). It is noted that CNTs can be grown in a fluidized bed, where the solid catalyst with CNTs are present as a low density material. This reactor provides enough space for CNT agglomerate growth. However, some fast growing CNT can penetrate another CNT agglomerate, which cause the CNT agglomerate to ripen and grow fast. Then the material is difficult to fluidize, which is harmful to the fluidized bed. Thus, a well-designed catalyst is the dominant factor for this period. If the catalyst structure is too strong and it is difficult for the growing CNTs to destroy it, the formation of subagglomerates will be difficult, the inside of the catalyst can't be used for the reaction, and the carbon yield will be much lower. On the other hand, too loose a catalysts structure is easily broken into pieces and the sub-agglomerates will have difficulty in forming stable agglomerates, and remain in too small size and will be entrained out of the reactor.

Using this mechanism, we can conclude that the level of the CNT agglomerate development is closely related to the CNT microstructure due to the different stress states in the CNT agglomerates. It is to be particularly noted that the volume of the CNTs will increase and growth space is needed for this process. In a fixed bed, the agglomerated CNTs are stationary, which will cause the newly grown CNT to enter into the loose structure of another agglomerates, and the agglomerates to intertwine each other. Then, the reactor will get jammed, which causes significant heat and mass transfer problems. If the agglomerated CNT is kept moving in the reactor, then the weak connection between the agglomerate and newly grown CNT gets broken, which keeps the CNT material fluidized. Thus, the Nano Agglomerate Fluidized bed (NAFB) reactor has the advantages

of good mass and heat transfer, and provides a uniform temperature condition and a relatively large space for the growth of fluidized CNTs [24,27]. The CNT agglomerate structure and formation were controlled at a mesoscopic scale to make the mass production of CNTs possible.

5. CNT hydrodynamics in a NAFB

For the mass production of CNTs, it is not only the catalyst, reaction condition, growth space, and agglomerate modulation that are important, but other key factors are also the uniform distribution of the temperature and concentration, easy removal of CNTs from the reactor, and maintaining a constant catalyst concentration in the reactor. The key problem lies in the interaction of the CNT agglomerate and gas, which is the basis of the multiphase flow behavior. It is one of the most significant issues in fluidization science and technology [81–83].

The CNT materials were synthesized by propylene decomposition on a Fe/Mo/Al₂O₃ catalyst in a fluidized bed. A fluidized bed of plexiglass of 280 mm I.D. and 2 m high was constructed to investigate the hydrodynamics of the CNT agglomerates. The dependences of bed expansion and pressure drop on gas velocity in a CNT nano-agglomerate fluidize bed is shown in Fig. 8 [84]. A smooth and highly expanded fluidization was achieved, but a strong hysteresis existed in the CNT fluidization curve. On the defluidization branch, similar to Geldart-A particles, particulate fluidization, agglomerate bubbling fluidization, turbulent, and fast fluidizations can be successively observed and distinguished as shown in Table 1. However, $U_{\rm c}$ and $U_{\rm se}$ of the CNTs were relatively lower than that of Geldart-A particles, due to the weak interaction among the CNT agglomerates and their highly porous structure. This indicated that good fluidization behavior can be achieved only with strong turbulence of the fluidized bed, because of strong interaction between agglomerated CNT.

The particulate fluidization is not always uniform, and it depends on the gas velocity. In aggregative fluidization, the distribution of the time-averaged solids fractions also showed a



Fig. 8. Dependence of bed expansion and pressure drop on gas velocity in a CNT nano-agglomerate fluidized bed [84].

Table 1	
Fluidization parameters of the CNT agglomerates [84]	

	*							
	U _{mf} (m/s)	U _{mb} (m/s)	U _c (m/s)	Ut (m/s)	U _{se} (m/s)	d _p (μm)	$ ho_{ m p}$ (kg/m ³)	
Observed	0.017	0.038	~ 0.1	0.205	>0.2	416	61.1	

stronger radial non-uniformity than Geldart-A particles. An analysis of the transient density signals indicated that a nonuniformity in the radial solids distribution with a lot of aggregation among agglomerates near the wall with increasing volume fraction of the dense phase near the wall. However, on the microstructure scale, the gas–CNT flow is more homogeneous than Geldart-A particle fluidization. This is due to the small density difference between the bubble phase and emulsion phase, which is about one order of magnitude smaller than that of FCC fluidization. Then the turbulent heat and mass transfer was reduced. Gas phase and solid phase mixing experiments showed those transport phenomena.

6. Enhanced NAFB with a coupled process

Chemical engineering scale up seeks to develop a high efficiency process and is a complex system engineering, which needs to consider many factors. Here, the coupling to link the catalyst and reactor operation was an important aspect. Some work concerning a coupled process to enhance the NAFB has been performed [85-91]. CNT production in NAFB proceeds through a series of changes, including catalyst reduction, CNT growth, catalyst support crushing, CNT agglomerate formation, agglomerate densification, etc. In an effective process, changes in reactor concentration, solids density, catalyst deactivation, particle size growth, particle residual time, etc., have to be made that will influence the operation and quality of CNTs significantly. The combination of a multi-stage fluidized bed to make these changes is necessary so that an enhancement of the NAFB can be achieved in the reactor operation, coupled fluidized bed, and coupled CVD process.

First, it is noted that the catalyst is originally in the oxide state and reduction is necessary before CNT growth can occur. The carbon source, such as methane cracking into CNTs and hydrogen, will absorb 75 kJ/mol. However, catalyst reduction can produce 50 kJ/mol, and contributes to break the methane cracking equilibrium with its hydrogen consumption [92]. The combination of catalyst reduction and methane decomposition is a good way to get a higher conversion of methane, that is, to increase the yield of CNTs. The yield of CNTs in the combined process is about 3-4 times that in the separated methane decomposition process. The effect can be attributed to the lattice oxygen on the unreduced catalyst, the presence of which brings about a simultaneous catalyst reduction that provides energy for the endothermic methane decomposition and consumes part of hydrogen and carbon, making the equilibrium of methane decomposition shift to the direction of hydrogen and CNTs production, while the reduced catalyst has a much higher reaction rate [85].

It was not just the combination of catalyst reduction and methane cracking that can increase carbon source conversion, but also, the reactor form can enhance the NAFBR. The later can be achieved in a two-stage fluidized bed, which was beneficial

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for a high conversion of the reactant. A two-stage fluidized bed had been used to scale up the gaseous catalytic hydrogenation of nitrobenzene to aniline to a 0.7 million tons/vear operation [86]. For methane decomposition in a two-stage fluidized bed reactor, a low temperature is used in the lower stage and high temperature in the upper stage. This allowed the fluidized catalyst to decompose methane with high activity at a high temperature condition; then the carbon produced will diffuse to form CNTs in both the low and high temperature regions. Thus, the catalytic cycle of carbon production and carbon diffusion on the microscopic scale can be tailored by a macroscopic method, to have a catalyst with high activity and thermal stability. The multi-stage operation with different temperatures in different parts of a fluidized bed reactor is an effective way to meet both the requirements of hydrogen production and preparation of CNTs with relatively good crystallinity [87]. Thus, there is enough space for process enhancement on the single reactor scale.

The CNT structure can be modulated by a coupled CVD process. The dense fluidized bed and floating catalyst CVD can be combined to decompose propylene at 660 °C, using the CNTs as support and the metal particles from the *in situ* pyrolysis of ferrocene as the catalyst. The conversion of propylene in this process was close to 100% under an optimized condition. The growth of a new generation of CNTs was proved. It was demonstrated that short and thin CNT branches existed on the tips or sidewalls of the CNTs [88]. The *in situ* formed catalysts on the side wall of the CNT were the branch points and this was the benefit from the combination CVD process.

Here, various methods, such as reaction operation, coupled fluidized bed, and coupled CVD process that enhance the NAFBR process [85–91] were discussed. This is only an example of an enhanced process, but it is not yet the best and commercial process. Further work has to be done for the mass production of CNTs on this scale, including safety, environmental, ecological, and economical considerations.



Fig. 9. The facility for MWCNTs pilot plant production.

7. Mass production at the 15 kg/h scale

A multiscale controllable mass production were analyzed into the self-assembly into CNTs on the atomic scale, agglomerated structure and controllable formation on the mesoscopic scale, transport phenomena on the reactor scale, and an enhanced NAF process on the macroscopic scale. Generally, for a new chemical process, a pilot plant at the 100–300 tons/year is necessary, although this is difficult for its large amount of work and is uneconomical due to its small size. The pilot plant is the key engineering and technology for scale up. In an integration of the above researches, a pilot plant for producing high quality and purity MWCNTs was designed, and this plant is shown in Fig. 9. In this plant, MWCNTs were continuously synthesized at a yield of kilograms per hour. Ultrahigh purity (99.9%) MWCNTs were obtained, which were produced in the NAFBR and subsequently annealed under vacuum and a temperature of 2050 K [93–95].

8. Conclusions

In summary, the scale up of CNT mass production was solved by a multiscale analysis that considered the self-assembly into CNTs on the atomic scale, agglomerated structure and controlled formation of agglomerated CNTs on the mesoscopic scale, CNT flow hydrodynamics on the reactor scale, and enhancement of a NAF process on the macroscopic scale. An integration of the above researches resulted in a pilot plant that produced high quality and purity MWCNTs, where MWCNTs were continuously synthesized at a yield of kilograms per hour. This is a methodology for CNT mass production. Other nano-agglomerate structure — CNT bundles, CNT arrays and nano ZnO, WS₂, SnO₂, CdS, ZnS, GaAs, SiO₂, TiO₂ nanostructure can also be considered using the multiscale analysis. This will benefit mass production and applications of nanomaterials in future.

Nomenclature

- $d_{\rm p}$ Particle diameter, m
- *H* Height of fluidized bed, mm
- H_0 Initial height of fluidized bed, mm
- U_c Transition velocity, m/s
- $U_{\rm g}$ Superficial gas velocity, m/s
- $U_{\rm mb}$ Minimum bubbling velocity, m/s
- $U_{\rm mf}$ Minimum fluidization velocity, m/s
- Use Serious entrainment velocity, m/s
- $U_{\rm t}$ Terminate velocity, m/s

Greek

 $\rho_{\rm p}$ Particle density, kg/m³

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