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Carbon Nanotubes: An Example of Multiscale Development—A Mechanistic View from the Subnanometer to the Meter Scale

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Dedicated to the Bayer company on the occasion of its 150th anniversary

We summarize the catalytic synthesis of multiwall carbon nanotubes (MWCNTs). The current understanding of the reaction mechanism is presented, in particular the catalyst design for the CCVD process is analyzed. To complement that, kinetics and reaction engineering aspects are discussed along with the impact of the reaction and reactor operation on the product properties. All these issues are analyzed from the perspective of the industrial synthesis and implications for the application of carbon nanotubes. Carbon-nanotube technology is a perfect example of multi-scale development and covers challenges from the nanometer to the meter scale. Problems, methods, and solutions characteristic for different scales will be highlighted. The Co/Mn catalyst is used as reference as one of the first commercially used technologies for the scalable production of multiwall carbon nanotubes.

1. Introduction

The term carbon nanotube (CNTs) is used for graphitic, one-dimensional tubular structures with a diameter between 0.4 and 350 nm.[1] For materials with larger diameter and no hollow structure the term carbon nanofiber (CNFs) is generally preferred. However, this terminology is not universally accepted and, especially in older publications, CNTs, CNFs and terms such as fibrils were used. CNTs can also be differentiated in single-wall nanotubes (SWNTs) and multiwall nanotubes (MWNTs) depending on the numbers of graphitic layers. SWNTs have generally a smaller diameter between 0.4 and 2 nm. MWNTs tend to be larger and usually their diameter ranges between 5 and 50 nm.

Carbon nanotubes have been known for many years also under the term carbon filaments, carbon whiskers, or filamentous carbon. The deposition of carbon whiskers has been recognized as the primary cause of deactivation during conversion of hydrocarbons over metallic catalysts, such as, nickel during steam reforming.[2,3] However, for the last two decades the dedicated synthesis and application of carbon nanotubes has been the subject of extensive scientific research.

This scientific euphoria, culminated with the Nobel Prize in 1996, started when in 1991 Iijima reported formation of nanotubes during arc-discharge synthesis of fullerenes.[4] Since then CNTs, and more recently its two-dimensional cousin graphene, represents one of the most dynamic fields in nanotechnology. Literature searches indicate that by 2012 almost 10000 papers related to the development and application of CNTs has been published.[5] There is a vast patent basis, several monographs and Reviews.[6–19]

As it usually happens for a new material, the initial research was focused on characterization and screening of potential applications. The result was that carbon nanotubes were found to be suitable for almost every field of technology from electronic[20] and electrochemistry[21] to health care.[22] The spectrum of potential applications is very broad.[18] For example, in electronics, carbon nanotubes have been proposed for use in new generations of diodes and transistors, data storage media, field-emission displays, lighting and microwave amplifiers. A new generation of composite materials has been studied in which CNTs have been used to improve electrical conductivity and mechanical properties of polymers or ceramic materials. CNTs have also been proposed as new functional materials, for example, as catalysts, membranes, actuators, electrodes and additives in

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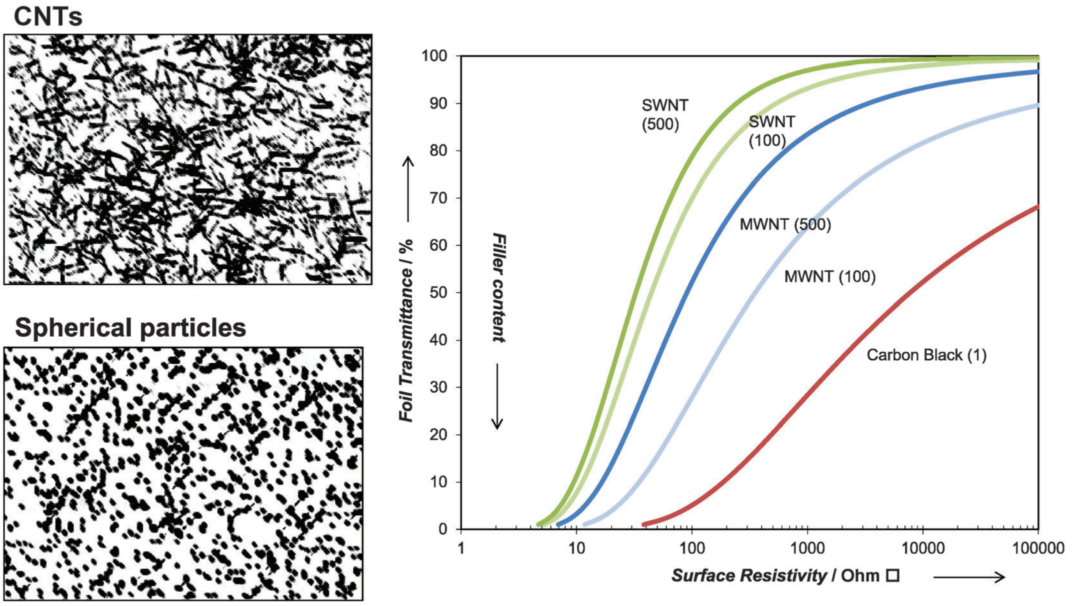

Figure 1. Illustration of percolation threshold for CNTs and spherical particles. Owing to the different aspect ratio, the required filler content to reach percolation varies. On the right side a percolation model for thin film composites is presented; the number in parenthesis represents the aspect ratio. (The unit of surface resistivity is Ohm per Square. It is graphically represented by the sign Ohm followed by an empty square.)

lithium-ion batteries. Also various applications as chemical, optical, thermal, and bio-sensors have been studied. A big, but unfulfilled hope has been evoked by reports about extraordinary capacity of CNTs for hydrogen storage. Finally, also life sciences could profit by applying carbon nanotubes as delivery systems, blockers for ion channels, or as skeletons for neuronal implants.

The broad spectrum for new applications results from exceptional properties of carbon nanotubes,[23] for example, their E-modulus/stiffness is up to five-times higher than steel (up to 1000 GPa), tensile strength can be 60 times higher than steel (up to 250 Gpa). These amazing mechanical properties have fuelled talk about projects such as the space elevator.[24] Beside mechanical properties, CNTs are excellent conductors: electric current density can be 1000 times higher than copper (1010 $\mathrm{A\,cm^{-2}}$), heat conductivity nearly twice as high as diamond (6000 $\mathrm{W\,m^{-1}\,K^{-1}}$), CNTs are very resistant to heat in an oxidizing atmosphere (up to 650 °C) and have specific surface area around 200–400 $\mathrm{m^2\,g^{-1}}$. No wonder that numerous applications were proposed to utilize these unique properties.[14]

One of the most important applications is the use of carbon nanotubes as additives for improving the electrical and mechanical properties of polymers and in Li-ion battery electrodes. The advantage of carbon nanotubes as an additive for improving electric conductivity, which is a serious issue for many polymer applications, is illustrated in Figure 1. The high aspect ratio (from 100–1000), that is, the length to diameter ratio, allows a conductive network to be obtained at a very low concentration of additive. High amount of additives, are not only uneconomical but deteriorate other properties of the material for example, elasticity or transparency. There are several obstacles to the wide utilization of this novel material. The most important are the price/performance ratio and the

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sustainable supply of large amounts of high quality CNTs. These two factors are of special importance for use in commodities applications such as polymer composites. In the last decade these needs pushed development technologies for carbon nanotube synthesis to pilot or commercial scale. Detailed discussion of the market and applications will not be discussed herein, except for few significant examples, because these topic have already been discussed in detail in some very recent Reviews.[6,8,9]

The aim of this Minireview is to summarize the current knowledge on the catalytic synthesis of MWCNTs. We decided to focus on the multiwall carbon nanotubes because, from the market perspective, at the moment they play a dominant role. For those who are interested in SWNTs the Review by Lamouroux et al.[15] is recommended. We review various technologies for CNTs synthesis but focus on the catalytic chemical vapor deposition (CCVD) process. The state of understanding of the reaction mechanism will be presented, especially the catalyst design for the CCVD process will be analyzed. All these issues will be presented from the perspective of industrial synthesis and implications for the application of carbon nanotubes.

Multiscale development has become a modern concept in the scientific literature. However, there are not many examples for the application of this concept. Zhang et al.[5] pointed out that CNTs are a good example of a development that has had to address challenges simultaneously on different scales. The catalytic synthesis of carbon nanotubes and the control of their chemical, structural, and morphological properties takes place on the nanoscale. Thus the catalyst active sites are defined at the nanoscale. The design of the catalyst extends the scale to the next level. Control of morphological properties of CNTs agglomerates takes place on the scale of micro- and millimeters. Mass transport processes influencing the effective reaction rate in the single-phase and multiphase reactors used for CNTs synthesis occurs on the scale millimeters and centimeters. The largest scale of meters is associated with the design of reactors used for CNTs production. Herein the issues associated with the technology developments at different scales are discussed.

2. CNTs Synthesis

2.1. Synthesis Methods

There are several methods that can be applied for synthesis of carbon nanotubes.[11,23] Originally CNTs were synthesized by means of arc discharge and laser ablation. In the arc discharge technology two graphite rods are used as electrodes under an inert gas atmosphere and reduced pressure. By applying a voltage between the electrodes, a plasma arc is generated. The positively charged vaporized carbon atoms are moving through the arc from the anode to the cathode. During this process the anode is consumed whereas on the cathode, carbon containing mainly soot but also carbon nanotubes is deposited. This technology is very challenging for scale-up. The rule of the economy of scale hardly applies. Also the automatization of electrodes exchange is very complex. From the operational point of view, high energy costs and low selectivity for graphitic carbon (generally below 80%) are disadvantageous.

These remarks are also valid for the laser ablation method. In this method a target made of graphite is placed in a quartz tube operated under an inert gas flow at reduced pressure and high temperatures (ca. 1500 K). Carbon atoms are vaporized from the target by pulses of a high-energy laser beam. Carbon nanotubes are formed in the gas phase and transported from the reaction chamber with the flow of an inert gas to a cooled collector. Laser ablation produces shorter carbon nanotubes compared to the arc discharge method but exhibits higher selectivity to single-wall nanotubes. Furthermore fullerenes are formed in a significant amount.

Arc discharge or laser ablation would not allow the production of carbon nanotubes in large amounts at competitive costs. It should be noticed that until now, for many applications, carbon nanotubes are a replacing another material, for example, CNTs used for improvement of electric conductivity have to compete with carbon black which is already widely used. The most promising option for a cost-competitive process is a catalytic process. There are two major alternatives, that is, floating catalyst technology and catalytic chemical vapor deposition.

In the floating catalyst technology a metal–organic solution, for example, ferrocene in benzene, is sprayed into a hot tubular reactor. Hydrocarbons evaporate and catalytically pyrolyze over the metal. This process usually yields large nanotubes with a diameter in the range of 100 nm or more which are covered by amorphous carbon. In-spite of the low space-time-yield this technology is industrially applied and the products are used commercially.[12]

The largest potential to achieve the development targets, that is, to produce a "high quality product" (see Section 6.2 for definition and measurement of quality parameters) at competitive costs, is associated with the CCVD technology. This technology is based on the catalytic decomposition of a carbon-containing gas over a transition-metal catalyst. The process can be performed in the classical fixed bed, rotary drum furnace, or in a fluidized-bed reactor. These last two reactor types are well known in the chemical industry for continuous solid processing with great economy of scale. Other technologies such as plasma-enhanced CVD or flame pyrolysis,[14] which are primary used for synthesis of aligned carbon nanotubes, are of minor importance compared to the CCVD process. With the CCVD both SWNTs and MWNTs can be industrially synthesized.[25–30]

In addition to the scalable reactor technology used, the economic advantage of the CCVD process is strongly related to the applied catalysts. Heterogeneous catalysts, either bulk or supported are used. As mentioned above catalyst development is a multi-target process. Catalyst functions can be divided into chemical and morphological. Chemically high catalytic activity and selectivity are desired. A high specific activity of the catalyst is necessary to obtain high space-time-yield and thus reduce investment costs for the reactor. Whereas the high selectivity means that mainly graphitic carbon should be formed and the formation of amorphous carbon should be suppressed. To measure the activity and selectivity towards CNTs, the main parameter is carbon yield. It is defined as the amount of carbon nanotubes produced related to the amount of the catalyst used in the synthesis. Since the catalyst is consumed in the reaction, a high carbon yield means high utilization of the catalyst, that is, low specific costs of the catalyst. High carbon yield is also very important for the product quality since the rest of the catalyst and other carbon impurities generally remain in the product. These "residues" from the process might be critical in certain applications, for example, they can cause depolymerization in polymer composites.

The catalyst also affects the final morphology of the product. Generally speaking it controls the diameter, shape, and number of defects in the carbon nanotubes and the morphology of the CNTs agglomerate.[31] The diameter and the length of CNTs determine the aspect ratio, which is a critical parameter for many CNTs applications. A high aspect ratio is important for good electrical and thermal conductivity of CNT-containing composites. The catalyst design influences their microscopic and macroscopic morphology. Examples of different morphologies of carbon nanotubes are presented in Figure 2, CNTs made on a Ni catalyst show internal fragmentation like bamboo, whereas CNTs made on an Fe catalyst, show a more regular tubular structure. Carbon nanotubes synthesized by CCVD process usually form stable agglomerates that, for most applications, have to be disaggregated. The stability of the CNTs agglomerates is thus an important quality feature, for example, to disperse entangled carbon nanotubes high shear forces have to be applied, which results in broken and shortened CNTs.

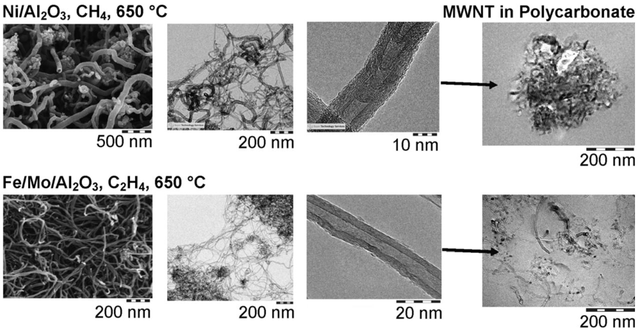

Figure 2. Effect of the different microscopic and macroscopic morphologies of carbon nanotubes and their effect on CNTs processing in polycarbonates by screw extrusion. Entangled and defective CNTs (top row) results in agglomerates of broken nanotubes, while straight and less entangled CNTs (bottom row) results in long and free nanotubes.

2.2. Microscopic Aspects of CNT Growth (Mechanistic View)

The first general model of the synthesis of carbon nanotubes on the molecular level was proposed by De Jong and Geus.[13] More recent validations are supported by in situ observations.[32] Hydrocarbon gas, representing the carbon source, dissociatively adsorbs on the surface of transition-metal particles. Hydrogen desorbs while carbon dissolves and reacts with metal yielding carbide (probably sub-stoichiometric). This carbide is metastable and precipitates out as graphitic carbon: the growing CNTs is a thermodynamic sink for the system.[33] The metal particle is then squeezed out because of pressure buildup arising from the formation of the graphite layers. As soon as the metal is pushed out the fresh surface is exposed to the hydrocarbons in the gas phase and growth continues. A schematic mechanism is illustrated in Figure 3.

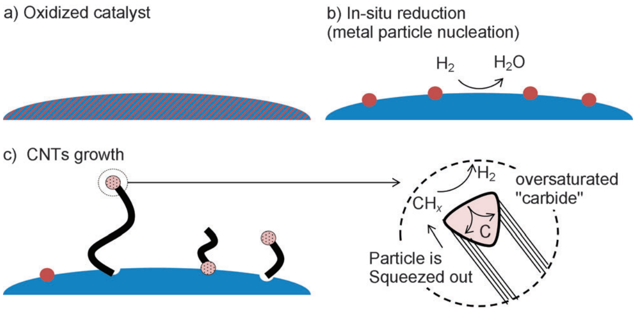

Figure 3. Schematic mechanism of the growth of CNTs. a) Homogeneous mixed oxide: the active metals (Co, Ni, Fe) are finely dispersed as oxides onto/into the support (Al$_2$O$_3$, MgO). b) Under a reducing atmosphere, the active metal is reduced and nucleates onto the support's surface, forming small active domains from which the CNTs can grow. c) The carbon source is decomposed and the carbon dissolved in the metal (forming supersaturated carbide phase). The excess carbon precipitates out in the form of CNTs, growth can be at the tip or root depending upon the interaction with the support.

For the active metal particles, three basic models are commonly used. The vapor–solid (VS) model assumes that the active particle is in the solid state. An alternative vapor–liquid–solid (VLS) model assumes that the particle has liquid-like character.[34,35] This model is supported by the fact that the metals are already at about half of their melting temperature, and because of the nanometer size of the particle, higher atomic mobility is expected.[36–38] Even if this mechanism has been accepted, there is still no general understanding for transport and precipitation of carbon in the metal particles. According to Baker et al.,[39] the driving force for the formation of the graphite at the underside of the particle is a temperature gradient. Because the decomposition of the hydrocarbons is exothermic, the accessible upper surface can have a higher temperature than the lower side which, in turn, can dissolve less carbon. This explanation has been questioned, at least for the endothermic methane decomposition. Alstrup[40] proposed a model based on the concentration gradient as the driving force for the transport of metal carbide. De Jong and Geus[13] propose that the particle is in a liquid-like state. Formation of the graphite layer at the bottom of the particle causes a pressure built up which, in turn, pushes metal to the top. According to Madroñero,[41] coronenes also come into consideration as seeds, so that the metal particles only act as an initiator for the formation of the superbenzenes. This theory explains why carbon nanotubes were found without metal particles in the tips. Recently, a three step mechanism: vapor–solid–solid (VSS) has also been proposed.[19] According to this mechanism, the carbon-donating gas dissociates on the metal surface to give carbon atoms that diffuse on the metal surface to the place where carbon precipitates forming a nanotube. In this model there is no carbon transport in the bulk of metal particles.

Common for all models is that they assume that the metal particle is located at the tip of the nanotube. The tip-growth is the most common mechanism of CCVD. Besides the tip growth, so called bottom growth is also possible. In this case the metal particle is immovable on the inorganic support and a filament grows from the metal particle. This, so called, root-growth is much slower since only the metal surface between the growing tube and the support is available, thus the gas adsorption is much lower. The metal–support interface seems to be critical in determining the type of growth. The strength of the metal–support interaction determines how easy a metal particle can be separated from the carrier and if root- or tip-growth occurs.

Extensive characterization studies have been performed to try and confirm the above presented models. However, the best qualitative understanding of the CNTs growth is given by a fascinating video showing this process in real-time.[32,42] CNTs synthesis has been observed by means of time-resolved, high-resolution in situ transmission electron microscopy. The formation of carbon nanotubes from methane decomposition over supported nickel nanocrystals was filmed. The carbon nanotubes were formed through a reaction-induced reshaping of the nickel nanocrystals. Specifically, the nucleation and growth of graphene layers were found to be assisted by a dynamic formation and restructuring of mono-atomic step edges at the nickel surface.[43]

2.3. Macroscopic Aspects of CNTs growth

From the macroscopic point of view the mechanism of CNT growth is very similar to that of gas-phase polymerization (Figure 4). The porous catalyst particles disintegrate during the CNT formation process and their fragments become distributed in the CNT agglomerates ("expanding universe mechanism"). This mechanism is confirmed by the time dependence of particle density and diameter (Figure 5). When introducing catalyst particles into the reaction atmosphere, metal crystallites exposed to hydrocarbon gas are first reduced. Reaction is initiated on the reduced particles. Carbon nanotubes that grow on these crystallites disrupt the catalyst particle. This effect causes a large, almost an order of magnitude, drop of particle density. The disintegration of the particle causes the whole volume to become accessible to gas. New active centers are triggered. In this stage CNTs grow in the whole volume causing a slight but continuous increase in density. Furthermore, the diameter of the CNT agglomerates increases. The growth process takes place on the time scale of few minutes. This macroscopic growth of particles has also been filmed[44] and the critical stages, such as break-up of the catalyst particle and the growth of the CNT agglomerates, can be observed in real time (Figure 6).

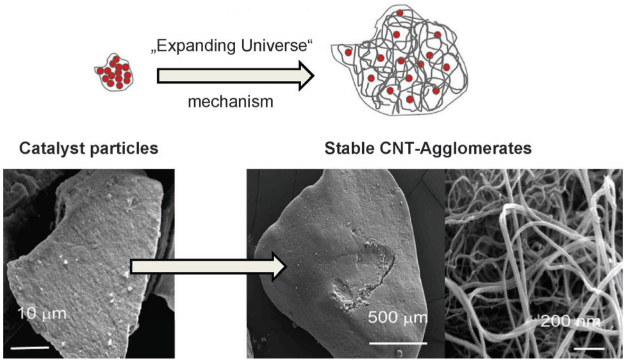

Figure 4. Macroscopic growth of carbon nanotubes. Top: representation of the "Expanding Universe" mechanism; Bottom: catalyst particle before and after CNT growth.

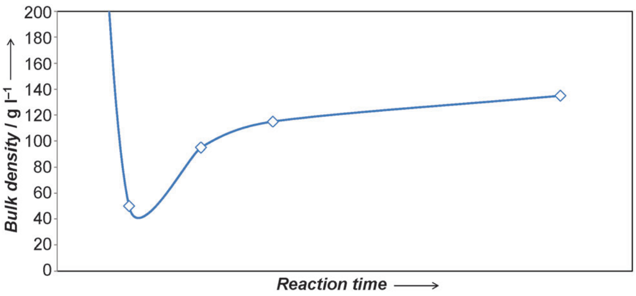

Figure 5. Change of particle density in a typical CCVD process.

The final product of the synthesis is a large, stable agglomerate of CNTs with a diameter in the millimeter range (see Figures 4 and 6). For many applications it is important that the final product is free flowing, for example, for feeding CNTs into extruders. Furthermore, it is important to have stable agglomerates to avoid product dusting, which is inconvenient for industrial handling and might even be critical for health and safety reasons.

Since CNT agglomerates show high compressibility, their density is difficult to determine in a correct manner, for example, in intrusion measurements, mercury often compresses the agglomerate before filling the free space. Therefore, bulk density is mostly used as a correlation for the agglomerate density. Generally, carbon nanotubes exhibit very low density (less than 300 $\mathrm{kg\,m^{-3}}$). For compounding CNTs with polymers low densities are often welcomed to allow good dispersion within the composite. This very low density, however, is a serious logistical and technical challenge for the large-scale production and processing.

On the other hand, in application of CNT agglomerates in heterogeneous catalysis, high densities are often desired to give a certain mechanical stability to the particles. Agglomerates with a density up to 1000 $\mathrm{kg\,m^{-3}}$ have been achieved. Carbon nanotubes are interesting for catalytic applications because of their reverse porosity structure as illustrated in Figure 7. In a typical catalyst particle, gas is transported by diffusion into the pores. This slow supply of reactants to active sites, and also concomitant removal of products, can sometimes limit catalytic activity. For fast reactions, the effective

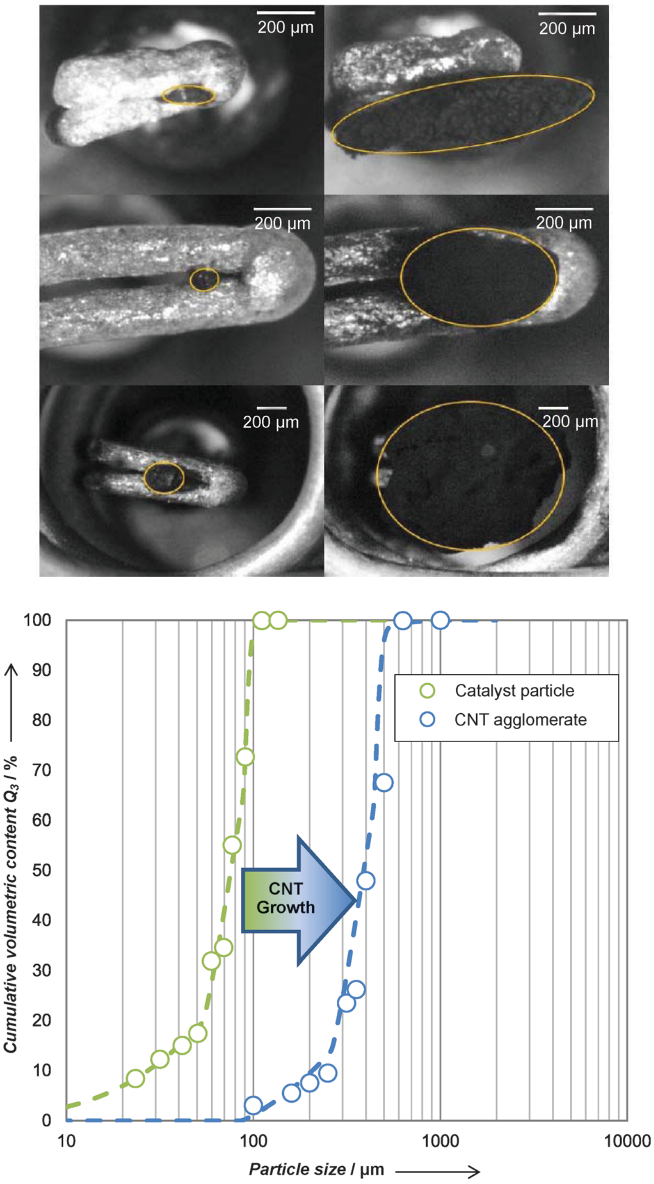

Figure 6. Change of particle diameter during CNT synthesis (pictures and data curtesy of Voelskov and Turek).[44]

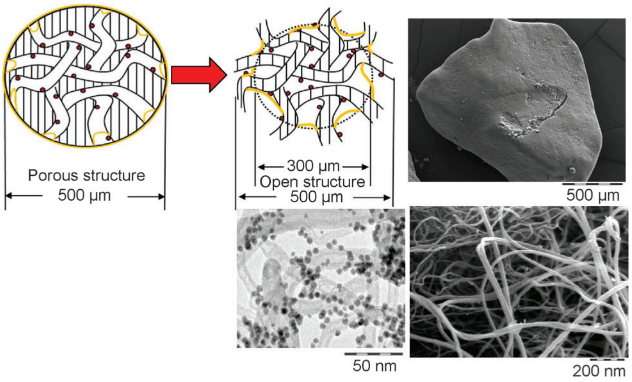

Figure 7. CNT agglomerates with deposited nanoparticles as catalysts with novel morphology. The typical porous structure of a conventional catalyst and the novel open structure of a CNT catalysts are shown. Right: TEM and SEM of the resulting catalyst at different magnification.

reaction rate can be determined by the rate of transport in the small pores, which limits the availability of the reactants. In the CNT agglomerates the catalyst is mostly placed on the large external surface of the nanotubes (over 100 $m^2 g^{-1}$). Owing to the high void volume of the agglomerates, the transport in and out of the particle is easier. Tessonier et al.[45] have tried to characterize this morphology. They measured BET isotherms and found that pore size distribution is bimodal. The first maximum was in the range 2 to 5 nm, that is, in the range that corresponds to the inner channels of the nanotubes. The second maximum was in the range 6 to 150 nm which is associated with the pseudo-diameter of channels between the entangled nanotubes. For applications in catalysis this second value determines the diffusion rate of the reactants from the bulk gas to the active site. However, selective catalysis in the inner channels might also be interesting.[46–48]

An alternative concept to the “expanding universe mechanism” has been explored by performing CNT synthesis in a nano-agglomerating fluidized bed.[49] A study performed over a Fe/Al_2O_3 catalyst confirmed that in spite of the growing carbon yield the particle diameter was kept constant whereas the bulk density showed a different behavior, it decreased. This unusual dependence can be explained by the continuous fragmentation of the agglomerates in the fluidized bed where the agglomerates are exposed to strong mechanical forces.[50] This mode of operation is only possible in a fluidized bed where particles have a high momentum.

3. Catalyst: Nanometer to Micrometer Scale

3.1. Catalyst Development

Various catalysts have been applied for the carbon nanotube synthesis by the CCVD process. Many materials have been tested and the results collated in several Reviews, for example, by Tanaka et al.,[11] Biro et al.,[12] Lamoroux et al.,[15] or Zhang et al.[5] The scientific literature is more or less equally abundant on in production of SWNTs, which are academically more interesting, and MWNTs. The industrially backed contributions focus mainly on MWNTs, which are commercially more interesting. However the growth mechanism and the basic principles behind catalyst development are common and independent from the focus. Usually catalysts based on Fe, Ni, Co, or on combinations of these three metals are used alone or combined with promoters. These metals are dispersed on the supports or distributed in the bulk catalysts. Oxides of Al, Mg, or Si are applied as the support or inert filler. Carbon can also be used as a support. According to the patent literature $Fe/Mo/Al_2O_3$,[31,51–56] $Co/Fe/Al_2O_3$[57,58] and $Co/Mn/Al_2O_3/MgO$[27–29] are used in the commercial operation by established manufacturers.

From the mechanistic point of view all metals that form metastable carbides are suitable, at least if the model of reaction proposed by De Jong and Geus[13] is valid. Analysis of the formation enthalpy of the metal carbides and carbon–metal alloys indicates that the following metals have potential to be catalytically active: Mn, Fe, Co, Ni, Mo, Tc, Ru, Rh, Pd, Re, Os, Ir, Pt.[59] From this list the noble metals are for cost reasons not suitable. Practically used are only Fe, Co, and rarely Ni, using Mn and Mo as promoting additives. Ni et al.[60] studied onset temperature for the CNT growth which might be used as measure for the catalytic activity. They found that carbon nanotubes started to grow at the lowest temperature over nickel catalysts, then cobalt, and finally iron. For these metals a number of commercial catalysts are available. To check their suitability for CNTs synthesis, screening has been performed in a micro-catalytic fixed-bed reactor. Their performance has been compared with that of catalysts in the patent literature. Results of this study are presented in Figure 8. The carbon yield obtained in these investigations varies between 1 kg of carbon and more than 200 kg of carbon per kg of the catalyst. Impregnated Ni catalysts underperform compared to Fe or Co, but also co-precipitated Ni catalysts exhibited low yield. This is only an apparent contradiction to the activity order mentioned above, since Ni is known to deactivate easily, for example, as a result of the formation of encapsulating carbon. Over the Ni catalysts, thick and defective carbon nanotubes were also formed (Figure 2). The yield could be significantly improved by the catalyst design, also for the Ni based catalysts yields of 84 $kg_C/kg_{cat.}$ have been achieved.[61] With the iron-based catalysts higher yields were obtained (Figure 8) and better CNTs were formed (Figure 2). This statement partially differs from the results of Luo et al.[62] who compared the performance of iron- and nickel-based catalysts in experiments performed in a fluidized bed. They found that Fe exhibited a slow carbon deposition rate and low yield compared to Ni. But with Fe, nanotubes of higher quality and with smooth walls were obtained. The highest yields have been achieved with the cobalt-based catalysts.

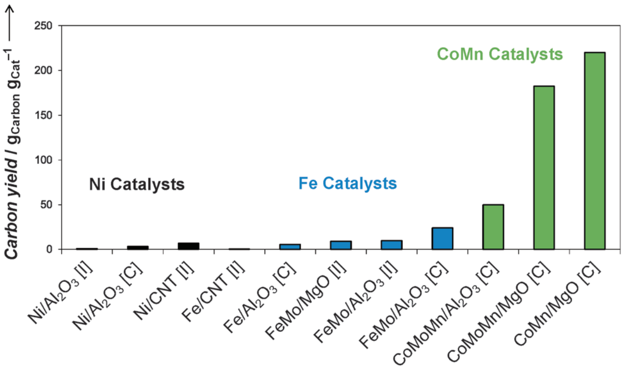

Figure 8. Carbon yield (productivity) for various catalytic systems based on Ni (black), Fe (blue), and Co (green) made by impregnation [I] and coprecipitation [C]

Most of the catalysts used for CNT synthesis are doped with molybdenum. Lamouroux et al.[15] and Alvarez et al.[63] assign Mo several functions. For Fe based catalysts Mo anchors iron and prevents it from sintering. Furthermore, Mo acts as a carbon reservoir and promotes catalytic formation of aromatics. The promoting effect of Mo has been confirmed by Ni et al.[60] who studied the effect of Mo on the threshold temperature of CNT growth. This temperature was different for Ni, Co, and Fe. However, when these catalysts were doped with Mo, all of them exhibited the same temperature threshold for CNT growth. A similar function is assigned to Mn.[64,65] Manganese is used for anchoring Co and to increase surface area (structure promoter). Since, MnO is hardly reducible, at least compared to Co, it keeps its oxidized structure after catalyst reduction. This stable matrix prevents Co from sintering. This concept has been applied for the development of the commercial CNT catalysts[27,29] and has been confirmed by Tessonier et al.[64] who found, in a small fixed-bed reactor, that spinel-type cobalt–manganese-based mixed oxide catalysts produced carbon nanotubes with 2–9 times higher yield than Mn-free catalysts. In addition, the CNTs were exceptionally homogeneous in diameter with the standard deviation being only 4 nm around the average diameter of 14 nm. They proposed that the ideal catalyst should be a mixed oxide containing a high loading of the desired active phase homogeneously distributed in the matrix, but which can also be easily extracted from the matrix to form the desired nanoparticles. The particular properties of Co and Mn allow phase segregation to be avoided during calcination, enabling the collapse of the spinel structure to release Co nanoparticles during reduction. To the same conclusions came Becker et al.[65] who studied a quaternary Co-Mn-Al-Mg oxide catalyst. The mixed oxides obtained were found to have mainly spinel-type structures after calcination. During reduction in H_2 the spinel structure collapsed and formed a Co-Mn-Al-Mg oxide matrix, from which the metallic Co nanoparticles segregated at temperatures above 700 K. An increase of the Mn content in the mixed oxides changed the redox properties of Co and led to an increased reduction temperature. It was found that the activity for CNT growth strongly depends on the Mn content of the catalysts, giving a maximum CNT yield at a Co:Mn ratio of 1:1. A higher Mn content results in a narrower CNT diameter size distribution. The high activity and selectivity of the catalyst may be attributed to strong interactions between the metallic Co nanoparticles and the Mn-Al-Mg oxide matrix. Investigations on the surface-near region confirm the presence reduced Mn^{II} oxide in the working catalyst. The close contact between MnO and the metallic Co nanoparticles is assumed to decrease the tendency to generate amorphous carbon thus slowing down the deactivation by encapsulation of the metallic Co nanoparticles. Over this catalyst an extraordinary high carbon yield up to 250 $g_C\,g_{cat}^{-1}$ has been achieved.

Carbon nanotubes and carbon nanofibers can also be synthesized using active carbon (AC) as the support.[66–68] Hierarchically structured carbon has been obtained by deposition of Fe in the pores and on the external surface of active carbon particles. In the first step iron particles have been used as oxidation catalysts to modify the pore structure of the active carbon. In the next step immobilized carbon nanofibers grew. In this procedure carbon yields up to 105 $g\,g^{-1}$ were obtained. The final product is well suited for applications in which having residual inorganic carrier in the product might be detrimental, for example, by promoting depolymerization. In analogy, CNTs can be grown on larger carbon fibers, resulting in a hierarchically structured secondary growth[69,70] that enhances the adhesion with the polymer matrix.

3.2. Industrial Catalysts

Let's analyze more in detail the requirements of an industrially applied catalyst and process. Bulk catalyst with an active metal content above 50 wt% are generally preferred because they have an increased carbon yield compared to a supported system with just a few wt% active metal. The bulk catalyst is prepared by co-precipitation of the metal precursors, followed by filtration, drying and calcination. Therefore, the catalyst after manufacturing consists of bulk mixed-metal oxides. To activate it, the catalytically functioning metal (i.e. Co) has to be reduced. This reduction can be performed before CNTs synthesis, for example, in a hydrogen atmosphere, or in situ in the reactor using the hydrogen that is generated during the CNT growth by decomposition of the hydrocarbon precursor. There is evidence that separate reduction can improve catalytic performance and the catalyst can yield CNT agglomerates with lower density.[71] Furthermore, the morphology of the catalyst has to be controlled. Mechanical stability of the catalyst is critical for the initial disintegration and formation of the domains of CNTs growth. If the catalyst is too "soft" the particle can be fully disintegrated by the growing CNTs and, at least in case of a fluidized-bed reactor, entrained (leached) from the bed. If the catalyst is too "hard" the particle cannot expand and the carbon yield is thus limited. The amount of binders (i.e. MgO and Al_2O_3) must be tuned to give the optimum performance.

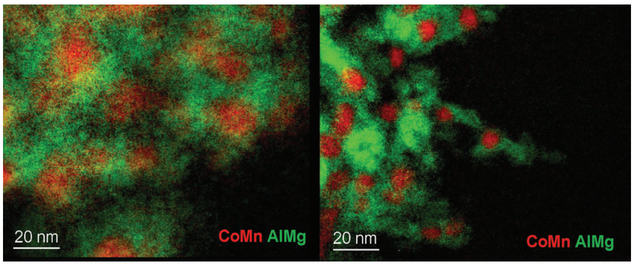

Figure 9. Metal particle dispersion of catalysts from batch and continuous catalyst preparation measured by TEM-EELS.

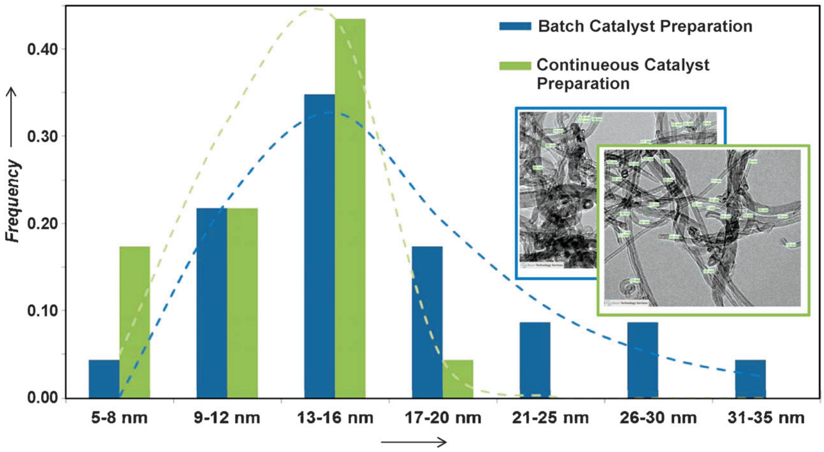

Figure 10. Diameter distribution for CNTs obtained over catalysts with different metal dispersions, produced by batch or continuous catalyst preparation (see also Figure 9). Inset: example of processed TEM used to determine the distribution. Sample size $N = 200–300$.

The technical catalyst used in CNT synthesis differs from the catalyst usually applied in the heterogeneous catalysis, at least of those applied in the fixed-bed reactors. The technical CNT catalyst should be a powder. However, it must be free flowing to be used in a fluidized bed or in rotary kiln. This property can be obtained for particles of group A according to the Geldart classification.[72] Therefore CNT-synthesis catalysts usually have diameters in the range of 50 to a few hundred micrometers.

The main target of the development of a technical catalyst is the control of the size of metal crystallites. According to the model presented in Section 2.2[13] the primary size of the metal clusters should control the diameter of the carbon nanotubes. To confirm this concept two $Co/Mn/Al_2O_3/MgO$ catalysts with different metal dispersions have been prepared. After reduction the catalysts were characterized by TEM-EELS (Figure 9). Clear metal spots can be recognized in the metal oxide matrix. Depending on the metal preparation, the metal crystallites differ in their diameter. These two catalyst batches have been applied for CNT synthesis in a micro-catalytic fixed bed reactor and the diameters of carbon nanotubes synthesized determined by means of TEM (Figure 10). The resulting distribution for both batches differs significantly and shows a clear correlation between the diameter of the carbon nanotubes and the crystallite size, that is, for the carbon nanotubes with a small diameter fine metal crystallites are necessary.

For the effective use of the catalyst it is important that it yields not only tubes with a small average diameter but also a product with a narrow tube size distribution. Especially the tailing at large diameters is not desired, since these thick tubes take an over-proportional amount of the carbon. Yu et al.[73] studied the effect of the size of metal particles for Fe_2SiO_4 catalysts using CO as the carbon donating gas. They found a strong maximum for growth rate as a function of the size of a metal particle which was located in the range between 10 and 20 nm. Therefore, this issue has to be addressed in the catalyst synthesis, for example, special technologies such as using micro-mixers have been proposed to obtain metal crystallites with a narrow size distribution.[74]

Carbon yield can be improved by increasing the metal amount in the particles (Figure 11). This dependence has a maximum at a metal content of around 80%. The increasing carbon yield with metal content is because the inert material is replaced by carbon-producing metal. However, the inert material is necessary to keep the catalytically active metal well distributed. Therefore, at very high metal content this

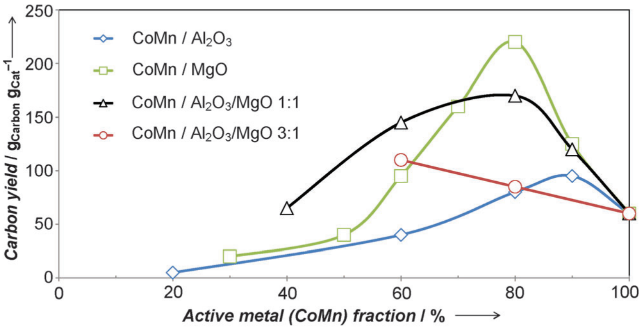

Figure 11. Effect of active metal content on the yield of CNT catalysts.

function can't be fulfilled. For the various applications of carbon nanotubes it is useful to minimize the content of the inert material. This impurity can be harmful in further processing, for example, in case of polymer processing at higher temperatures in extruders, it can promote depolymerization.

4. Optimization of Reaction Conditions: Nanometer to Meter Scale

4.1. Reaction Conditions

Optimal reaction conditions are determined by the partial pressure of the carbon source gas and the temperature which control the reaction rate, growth, and deactivation rate. The usual temperature range is between 650 and 950 °C depending on the metal system and carbon source. Reactors are operated at near atmospheric pressure. A notable exception is the HiPCO process for SWNTs synthesis that is operated at more than 100 bar CO.[75] Generally the reaction is performed in the kinetically controlled regime. However, because of the high temperatures, very fast reaction rates are expected and observed. Careful attention should be taken in preventing mass-transport limitations and keeping a homogenous gas distribution in the reactor.[76] However, the maximum conversion might be also influenced by the thermodynamic limitations. Jess et al.[77] reported that the maximum CO conversion in the CCVD process might be limited due to the Boudouard reaction.

Yu et al.[78] studied the effect of different carbon-donating gases. The effect of catalyst support and reactant on the yield and structure of carbon growth has been investigated over powder Fe and Fe/Al_2O_3 catalysts using CO/H_2, CO, CH_4, and C_2H_6/H_2 as gas precursors. No dramatic differences in the productivity have been obtained for all the investigated gases. However, the structure of the carbon nanotubes differed from tubular to fish-bone to bamboo. Hydrogen played an essential role in the processes by surface reconstruction, keeping the catalyst surface clean of carbon, and saturating dangling bonds. The strikingly different carbon nanostructures produced from CO and CO/H_2 can be explained by the impact of hydrogen which influenced surface orientations of the catalyst by lattice restructuring. This, in turn, influenced the structure of the deposited carbon.

4.2. Catalyst Poisons and Promoters

The main source of poisons for the CNTs growth is the catalyst manufacturing itself. Very important is the level of alkali metals after washing of the precipitated catalyst, these metals have a detrimental effect on carbon yield. In Figure 12 are shown the results of the dedicated experiment to determine the sensitivity of a Co based catalyst system to Na impurities from the catalyst preparation procedure. Similar dependence has been identified by Qian et al.[79,80] who tested the effect of Na_2CO_3, Na_3PO_4, and $CaCl_2$ on the performance of the Ni catalyst. All these components poisoned the catalyst, that is, carbon yield decreased. Furthermore, for sodium carbonate and sodium phosphate they found CNTs partially or totally destroyed. Many CNTs did not maintain a tube-like shape and many flat ribbon-like structures were formed. Qian et al. explained this effect as a result of the inhomogeneity of carbon precipitation. When the external surface of the metal particle is in contact with the poison, part of the metal particle loses its activity to decompose the carbon source. This local inhomogeneity propagates through the carbon concentration field in the metal particle. This, in turn, causes inhomogeneity in the carbon precipitation.

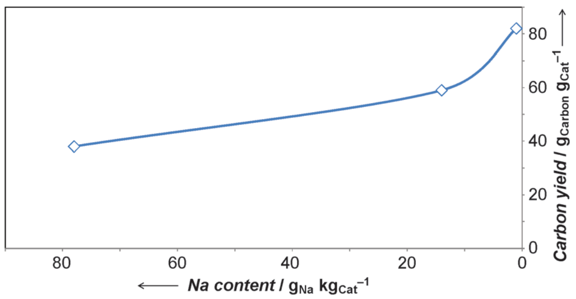

Figure 12. Effect on the carbon yield of remaining Na impurities in the precipitated catalyst.

However, this effect can also be used to control morphology. The cavities of carbon nanotubes can be used as nanoreactors or as containers for delivery systems. Qian et al.[79,80] poisoned Fe/Mo/Al_2O_3 with a small amount of Na_2CO_3 to produce carbon nanotubes with very large internal diameter. By this means they enlarged the inner diameter from 3–7 to 40–60 nm while the outer diameter of about 60–80 nm remained unchanged. Furthermore, nanotubes with large diameters exhibited stable carbon structures without increased distortion in the carbon layers. This effect has been explained by the lower carbon solubility in the metal particle.

Sulfur is another element which usually has an impact on the performance of metal catalysts. Qian et al.[81] studied the performance of Fe/Mo/Al_2O_3 catalyst in CNT synthesis from liquified propane gas (LPG) containing 13 ppm of sulfur. They did not find any significant effect on the carbon yield. This result is in-line with results of Tibbets et al.[82] who even found a promoting effect of H_2S on the synthesis of vapor-grown carbon fibers. This effect has been explained by the promoting effect of S on iron. The dissolved S reduces the Fe melting point, increases mobility, and encourages fiber growth.

5. Kinetic Modeling and Reaction Engineering: Millimeter to Meter scale

5.1. Kinetics

Yu et al.[73] proposed a simply mechanistic model to describe the growth of a carbon nanotube. The model assumes that there is an effective diffusion path length, such that the carbon concentration gradient from the front of the particle to the rear of the particle can be approximated as the difference between carbon concentrations at these two locations divided by the diffusion path length. In that case the rate of carbon diffusion and thus the CNTs growth rate can be represented by this simplified formula [Eq. (1)]:

$$r = \frac{D_{\mathrm{C}}}{d_{\mathrm{Fe}}} \alpha_{\mathrm{Fe}} \left(D_{\mathrm{C-Fe},f} - C_{\mathrm{C-Fe},r} \right) \tag{1}$$

where r is the CNT growth rate, D_{C} the effective carbon diffusivity, α_{Fe} the specific surface area of Fe, d_{Fe} the effective diffusion length, $C_{\text{C-Fe},f}$ the carbon concentration at the gas side, and $C_{\text{C-Fe},r}$ the carbon concentration at the rear side of the catalyst particle. Assuming that segregation of carbon is a fast process, $C_{\text{C-Fe},f}$ will be in equilibrium with surface carbon, which is determined by surface reactions. Provided that precipitation is also a fast step, the carbon dissolved at the rear side of the particle will be in equilibrium with the growing CNTs. $C_{\text{C-Fe},r}$ is therefore identical to the saturation concentration of carbon in the CNTs (C_{sat}). The smaller the CNTs diameter, the higher the C_{sat}.

Bellinghausen et al.[83] developed kinetics for the CNT synthesis. Conversion of the carbon-donating gas to carbon nanotubes can be well described with a first-order rate equation. The first-order dependence has also been reported for Co/MgO and Mo/Co/MgO catalysts.[77] It indicates that dissociation of the carbon-donating gas on the surface of the active metal is the rate-determining step. Only in the kinetic model developed for the Fe-Co/Al_2O_3 catalyst was the effective reaction order lower because inhibition by the C_2H_4 used as the carbon-donating gas was considered.[84,85] Philippe et al.[86] reported a reaction order of 0.75 and an activation energy of 120 kJ mol^{-1}. None of the kinetic models reported in the literature take into account the effect of hydrogen. However, Yu et al.[87] indicated that H_2 chemisorbs competitively on the catalyst surface and, in turn, lowers the so-called carbon affinity. This results in a lower carbon formation rate. Therefore at high partial pressures of H_2 an additional inhibiting term should be considered. Furthermore, hydrogen not only suppresses reaction rate but also influences CNT morphology. When hydrogen was added, the CNTs changed from cylindrical to hollow fishbone-tubular structure.[87] Observed activation energies of around 150 kJ mol^{-1} for Co/MgO and approximately 100 kJ mol^{-1} for Mo/Co/MgO were much higher than literature data for the decomposition of methane (ca. 66 kJ mol^{-1}), used as the carbon source in these experiments.[60]

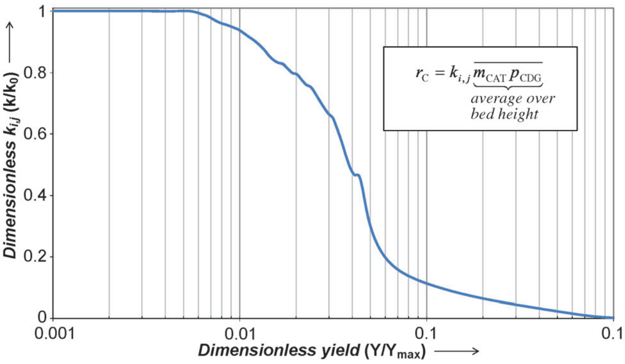

Figure 13. Kinetics of the CNT synthesis: rate equation, deactivation kinetics, and model validation.

In Figure 13 shows the predictions of the kinetic model of Bellinghausen et al.[83] The model was able to predict the particle size distribution of the carbon nanotube agglomerates based on the same distribution as for the catalyst (see Figure 6). The distribution curve for the product is almost parallel to the one of the catalyst. This relationship indicates that almost all the particles grow with a similar rate and that there is no significant disintegration of the particles. In other words particles keep their identity in spite of the attrition occurring in the fluidized bed.

The model of the particle growth has to account for the changes in the density of the "expanding universe mechanism" (Figure 4) and the deactivation of the catalyst. This is illustrated by the change of the rate constant with the time, which, in turn, can be correlated with carbon yield. In the first period, reduction of the catalyst takes place therefore CNT growth is negligible. In the second phase there is continuous fast deactivation of the catalyst which slows down with the time. There is no clear explanation for the deactivation process. Certainly, encapsulation of the metal has a significant impact. Yu et al.[87] postulated that formation of the encapsulating carbon plays an important role. They found that deactivation was accelerated with increased space velocity. At high space velocity, the supply of carbon atoms is at the highest rate. Furthermore, since they applied CO and H_2 mixture as feed gas high space velocity results in low concentrations of CO_2 in the reaction mixture, and CO_2 is a well-known carbon gasification agent. The combined effects result in higher site coverage of carbon on the metal surface, which in turn leads not only to a faster carbon deposition rate, but also to a higher rate of surface carbon polymerization. Therefore the encapsulating carbon forms at a higher rate, and the catalyst deactivates within a relatively short time. The effect of CO_2 was well demonstrated by Pinheiro and Gadelle.[88] They reported that addition of 1/3 CO_2 to pure CO reactant (equivalent to 25 mol%) increased the Fe-Co catalyst lifetime from 3 to over 13 h. Addition of CO_2 might be an effective reaction measure to moderate catalyst deactivation.

Ni et al.[60] postulates that deactivation occurs when the dissociation process is faster than the assembling of carbon into graphene sheets. In this case carbon species, such as amorphous carbon, will accumulate and cover the catalyst surface suppressing gas adsorption. Using this model it can be expected that the deactivation rate can be affected by modified reaction conditions. Indeed Becker et al. have shown that the mean active time can vary by orders of magnitude on varying temperature and carbon-donating gas.[89] Jess et al.[77] found that deactivation could be suppressed by increasing the partial pressure of hydrogen. They quantified this dependence and expressed it with the formal dependence on the partial pressure of hydrogen in power -0.4. Finally densification of the large CNT agglomerates causes the rate of the reaction to begin to be controlled by reactant diffusion, well known in catalysis as internal mass-transport limitation. In technical processes catalyst is not utilized to the maximum carbon yield achievable in order to obtain a product with the desired density. Generally, deactivation of the catalyst has a negative impact on the process. However, in the case of CNT synthesis it can bring some advantages. When performing the CCVD process in a continuously operated fluidized-bed, catalyst particles are very well mixed in the bed, that is, their residence time distribution is very broad. There is then the danger that those particles, with a longer residence time could grow to high-density particles that settle down and destabilize fluidization or cannot be disentangled in further processing steps. Fortunately, deactivation of the catalyst terminates densification of the CNT agglomerates, stabilizes the process, and yield products with more homogeneous properties.

5.2. Reaction Engineering

For the continuous synthesis of CNTs mostly either fluidized-bed or rotary reactors are applied. Fluidized-bed reactors have the advantage of isothermal operation arising from the very good mixing of solids. However, this effect causes the residence-time distribution for particles to be very broad, like, for example, in the continuously stirred tank reactor. This, in turn, results in a broad distribution of particle sizes. To obtain stable operation the entrainment of small catalyst particles and the sedimentation of large product particles has to be prevented. The operational challenge is to obtain a large average particle diameter which is synonymous to a high carbon yield and high product purity. With respect to the high conversion of the carbon-donating gas it has to be taken into account that a gas–solid fluidization is not homogeneous, that is, a significant amount of gas is flowing as particle-free bubbles. Therefore the effective reaction rate might be influenced by the mass exchange between the bubbles and the dense phase. The threat of this potential limitation for the overall reaction rate increases with the scale-up. Therefore a comprehensive reaction engineering model for fluidized bed technology was developed as the basis for scaling up.[83,90] The model includes kinetics, bed hydrodynamics, and also population balances for the description of the particle growth. Simulations have shown that in large reactors the effective reaction rate can be limited by the mass transport between bubbles and the dense phase. Fortunately, catalyst deactivation prevents particles from growing to very large diameters. This, in turn, prevents defluidization and helps to keep a stable operation. Model development has involved extensive hydrodynamic studies in a large-scale cold flow model. A similar approach has also been reported by Zhang et al.[5] for the development of continuous fluidized bed processes. To avoid the catalyst sedimentation in an operating reactor, the use of a few fluidized beds connected in series or a multistage fluidized bed has been proposed.[91] An overview of the reaction engineering aspects of CNTs synthesis in a fluidized bed is also given by Wu et al.[92]

In analogy to the fluidized-bed reactor, the modeling of carbon-nanotube production by the CCVD process in a continuous rotary reactor with mobile bed was performed by a rigorous chemical reaction engineering approach.[93] The geometric, hydrodynamic, physical, and physicochemical factors governing the process were analyzed to establish the reactor equations. The comparison between experimental and calculated production has shown a very good data fit. Furthermore, it has been found that the process is not limited by the mass-transport effects.

6. Product Properties: Subnanometer to Millimeter Scale

6.1. Microscopic and Macroscopic Structure

Carbon nanotubes formed in the catalytic process can have different morphologies. Multiwall carbon nanotubes from the CCVD process have generally an average diameter between 5 and 50 nanometers. Figure 2 shows carbon nanotubes exhibiting segmentation in which horizontal shelves close the inner channel. Carbon nanotubes of this sort are called bamboo type. Finally carbon nanotubes without an inner channel can grow by pillaring plates with geometry similar to the Chinese hats. This kind of CNTs is called the fishbone type. Jess et al.[77] reported that the morphology of CNTs could be controlled by varying the reaction conditions. They found by studying a Co/MgO catalyst that at high temperatures MWNTs were produced whereas at low temperatures fishbone-type material was formed.

Also agglomerates can exhibit different morphological structures (Figure 14). Generally one of the most important criteria, even if only qualitative and difficult to describe, is the extent of the entanglements. In the initial stage of growth many active domains in the catalyst particle are formed. From these independent domains CNTs grow in an uncoordinated manner in all directions (Figure 14a) and interpenetrate cross-linking the different domains. Such a high degree of entanglement causes structures that are called bird-nests and that are hard to disperse. Carbon nanotubes concentrated in isolated islands in a polymer composite do not improve the electric conductivity or the mechanical strength significantly. For an improvement a network of well-dispersed carbon nanotubes is necessary. To obtain a good dispersion of CNTs in various polymers, the applied shear forces have to be optimized.[90]

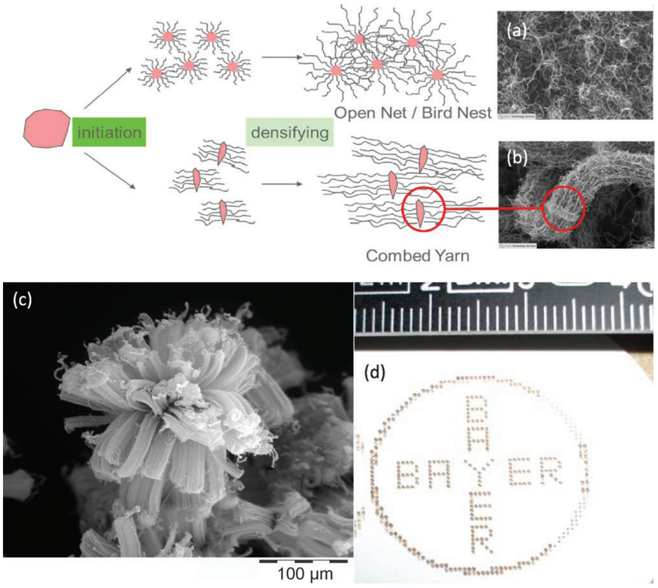

Figure 14. Different types of CNT agglomerates: a) bird-nest, b) combed yarn, c) aligned, d) structured growth.

The homogeneous dispersion of carbon nanotubes in a polymer matrix is easier to achieve when CNTs have similar growth orientation, as presented in Figure 14b. CNT agglomerates with this kind of structure are called combed yarn. To obtain not entangled or weakly entangled CNT agglomerates the synthesis can be stopped at low carbon yields. In this case, the additives in the catalyst, usually Al_2O_3 or MgO, act as spacers separating different domains. Alternatively this spacer function can be incorporated in the catalyst design.[94,95]

For various applications, especially in the electronic industry, for example, for flat-screen displays or in field emitting devices it is interesting to have straight, aligned carbon nanotubes (Figure 14c). This concept might be interesting for making conductive pathways or switches and can be realized by seeding the catalyst on flat substrates (Figure 14d). Vanhaecke et al.[96] discussed the interaction of Fe catalysts with different types of flat substrates, such as Ti, Al, stainless steel, or Cu_xO_y/Cu foils. However this approach suffers from low space-time yields. In an alternative idea, catalyst spots can be placed on nonporous surfaces such as glass spheres.[97]

6.2. Quality and other Characteristic Parameters

There are no generally accepted procedures for measurement and characterization of carbon nanotubes. Common techniques for catalysis and nanotechnology can be used. Tessonier et al.[45] performed a comprehensive analysis of a few types of commercially available CNTs. The results of this study show that mostly a combination of several methods is necessary and that many techniques can be only used for comparative studies.

One of the most important qualitative measures of carbon nanotubes obtained by the CCVD process is the aspect ratio which is defined as ratio between the length and the outer diameter. Since the diameter usually varies between a few nanometers, and the length of the carbon nanotubes can achieve micrometers, then aspect ratios up to 1000 can be achieved. For the multiwall carbon nanotubes the aspect ratio is generally lower than for SWNTs.

Another quality criterion is the purity of the product. Mainly amorphous carbon and catalyst residues are considered as impurities. Carbon nanotubes obtained by the CCVD contain only a small amount of amorphous carbon, often not even detectable. The level of inorganic impurities is inversely proportional to the carbon yield, that is, on the utilization of the catalyst. Generally, the purity from the CCVD processes, with a product yield up to 100 g CNTs per g catalyst, is above 98%. If needed, the catalyst residues can be removed by subsequent washing. However, not all the inorganic impurities can be removed completely. As shown in Figure 15 and the inset (EDX, energy dispersive spectroscopy), a large fraction of the catalytically active metal (in this case Co) remains trapped at the tip or root of CNTs and remains encapsulated. Only about 50% of the remaining Co can be washed out. The other 50% is encapsulated in the carbon nanotubes. This residual metal is not accessible and therefore not chemically active. This encapsulated metal offers the potential, for example, in life-science applications, to magnetically trace carbon nanotubes.

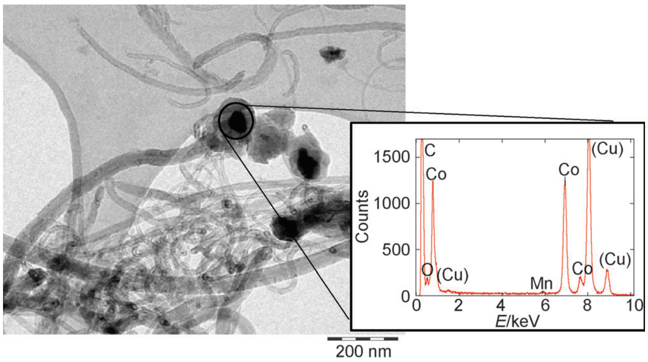

Figure 15. TEM image of CNTs washed in concentrated acid. The remaining metal particles are composed mainly of Co and encapsulated into the CNTs ends. Inset: EDX image.

The surface of the carbon nanotubes synthesized by the CCVD process is usually smooth. However, under transmission electron microscopy many defects can be recognized. The non-uniformity of the carbon precipitation from the metallic particle results in discontinuities in the graphitic walls. These defects can be generated by several factors, such as local and temporary limitations of the growth, arising from the carbon-source availability, reduced diffusion of the dissolved carbon in/onto the metal particle, or local supersaturation inside the particle itself. Hoffman et al made a highly enlightening study of defect formation related to CNT growth.[42] In a TEM movie, strongly pulsed growth of CNTs and subsequent generation of defects at every change of growth rate was observed. The defects can be limited to the external surface, however, they can also permeate through all the layers. Defects in the graphitic structure negatively influence the electrical conductivity by interfering with the transport of electrons. They also reduce mechanical strength.

Raman spectroscopy is frequently used to study the microstructure of carbon nanotubes.[16] In the Raman spectrum the ordered graphitic structure (sp^2 hybridization) yields a strong band in the range of 1570–1610 cm^{-1} called the graphitic band (G). The disordered structure or lattice defects (sp^3 hybridization) have a peak centered at approximately 1340 cm^{-1} called the diamond or disordered band (D). Generally, the intensity ratio (R) of the D line to G line is used to evaluate the defects in carbon nanotubes. This approach has been shown to give very good quantitative results when applied to SWNTs, as a result of their strong Raman resonance, which enhances every deviation from the ideal structure.[98] However, when applied to MWNTs, this method has shown some limitations. Owing to the lack of resonance, the intrinsic mismatch between the rolled graphitic layers, and the higher number of imperfections, it is difficult to quantify the extent of defects. Moreover the Raman fingerprint varies with laser energy, intensity, and other experimental conditions, making the method only valid for relative comparison. Heise et al.[99] have compared several MWNTs, graphite, and active carbon materials, using different experimental conditions (e.g. filters) and laser frequencies and intensities. They found that the D/G ratio varies by orders of magnitude with measurement conditions. Many times Raman evaluation needs to be coupled with thermogravimetric analysis to be conclusive (see below).[100] The typical range of R for multiwall carbon nanotubes is 0.3–2.7. For a high-quality product a lower ratio is required.

A quite good evidence for the quality of carbon nanotubes is their thermal stability. However, it strongly depends on the CNT diameter as well as on the amount of impurities, particularly the nature and amount of catalyst residue. High amounts of transition metals lower the thermal stability, catalyzing combustion reactions, while larger CNTs diameters increase the stability. For the purified carbon nanotubes thermal stability depends on the number of defects. In Figure 16 thermogravimetric analysis of several types of CNTs is presented. Only nanotubes containing amorphous carbon were not stable below 300 °C in air. Pure CNTs are very stable, there is no decomposition until at least 300 °C. Carbon nanotubes synthesized using the Co/Mn catalyst has been stable even up to 400 °C. These data are in agreement with the results of Tessonn et al.[45] who found in the temperature-programmed oxidation (TPO) the temperature of 50 % mass loss is approximately 500 °C. Long-term experiments performed with CNTs doped with 1 wt% Ru confirmed their stability in a highly oxidizing atmosphere at 300 °C for more than 600 h.[101] The TPO results can be used as measure for the quality of nanotubes since it appears that oxidation mainly takes place on the edges of the surface graphene sheets. Therefore the nature and the density of defects play a crucial role for the burning of CNTs in a TPO experiment.[45]

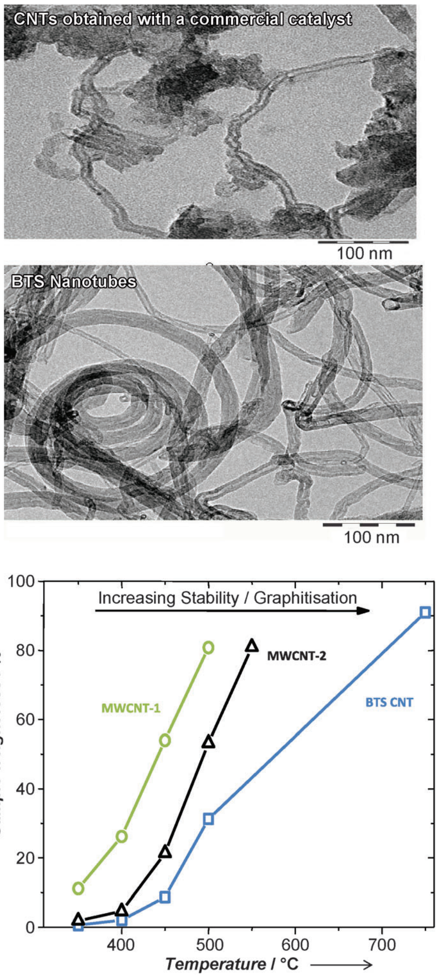

Figure 16. Top: CNT obtained with a commercially available Ni/Al_2O_3 catalyst. Middle: CNT obtained with an optimized CoMn catalyst. Bottom: Oxidative thermogravimetric analysis (TGA) of different carbon nanotubes.

6.3. Doped CNTs

Functionalized or doped carbon nanotubes represent a new class of materials with novel properties that is based morphologically on the CNTs structure. Their properties are very different and depend strongly on the type and amount of functionalization. We need to distinguish between chemically functionalized (for example oxidized CNTs) and doped CNTs.

In the chemically functionalized CNTs it is the surface that is mainly affected while the bulk of the material remains untouched and similar to a pristine CNT. The first step in the functionalization is often oxidation, where some defects on the surface of the CNTs are oxidized (with HNO_3, H_2O_2, O_3, etc…) to, for example, carboxylic acid groups. From this chemical moiety a subsequent functionalization can take place using the techniques known from organic synthesis. This method is often used to make the nanotubes compatible with a polymer matrix. The field of functionalization and application of these materials is so broad that many Review articles have been written on the topic. A very comprehensive one, from the different chemistries to the applications in polymer materials, was written recently by Spitalsky et al.[102]

Herein we would like to focus more on the second class of functionalization (properly called doping). In this case heteroatoms or functional groups are embedded in the CNTs structure and they modify not only their surface chemistry but also their inner walls. As in the semiconductor industry, the addition of elements with a different number of electrons than the element that compose the crystal, results in injection of electrons in the conduction band or depletion of electrons from the valence band of the material, resulting in n and p doping. In this case the crystal is represented by the carbon graphitic lattice and the heteroatoms that are employed are, generally, the neighboring elements B and N. The effect on semiconducting SWNTs, that have a well-defined electronic structure and controlled crystallinity, is in perfect agreement with the theory. It is possible to add electrons or holes in the electronic structure of semiconducting SWNTs. For MWNTs, owing to their intrinsic more disordered electronic structure, this effect is masked.

Incorporation of boron has been shown to be more challenging and is generally done by post treatment of the CNTs at high temperatures with boron oxide.[103] Nitrogen can be incorporated either by post treatment or even by in situ growth of the CNTs using nitrogen-containing organic precursors. This last production process has the advantage that can be scaled up industrially to several hundred tons per years. At Bayer Technology Services, in a process analogous to the one used for the production of MWNTs, N-doped CNTs (NCNTs) can be synthesized in several kg per day.[104]

Even if the N-doped MWNTs do not have a perfectly well-defined electronic structure, with Van-Hove singularities, like the corresponding N-doped SWNTs, they have special properties that derive from the coexistence inside the CNTs, and particularly on the surface, of different nitrogen species. These represent high energy, highly reactive sites. Coupled with the high surface area of the CNTs, this make them an ideal material as a catalyst support or a catalyst itself.

It has been observed that NCNTs alone are able to catalyze several reactions, such as hydrogenation of nitro groups to the corresponding amine.[105] As a support for metal nanoparticles, they not only stabilize the particles and improve their dispersion, but form catalysts that perform many times better than the metal-supported on normal CNTs.[106] They are also widely used in electrochemistry where they were used as oxygen depolarized cathode for chlorine-alkali production with results comparable to state of the art silver oxide.[107] The reports on their use in catalysis, especially in the growing field of fuel cells, increase day after day.[108]

7. Conclusions

In the last decade several companies developed CCVD technologies for the commercial production of nanotubes. Worldwide a number of suppliers offer their products, not only start-ups but also major chemical companies. Many of them have the ability to supply carbon nanotubes in two-digit ton amounts.[6] Not mentioned are the undisclosed capacities in Asia. On the other hand, general trends like electromobility, which creates demand for light and strong polymer composites, as well as the growing importance of renewable energies, with the need for energy storage, should give a new push for the development of applications based on carbon nanotubes.[9] Clearly, one of the main obstacles from the early development has been eliminated, that is, high-quality carbon nanotubes with reproducible properties are now available for the development of applications. Furthermore, they are available at competitive prices. The aim of this Review was to show that there is now a good understanding of the basics of the synthesis, especially the chemistry and catalysis. This is a good basis to overcome the remaining obstacles. A numbers of CNT applications have been developed in the last decade.[6,7] However, further effort is necessary to utilize the intrinsic advantages of CNTs in marketable products.

It is clear that for any new technology, its safe and environmentally sound handling is essential.[8] The technological development of CNTs has been accompanied by toxicological and eco-toxicological studies.[109,110] Life-cycle assessments were performed and concepts for safe production, for example, closed systems, automated filling, or exhaust-gases treatment were developed. The same is valid for CNT processing in applications, for example, procedures for proper use to ensure safe handling, use of engineering controls, and of personal protection measures (see MSDS) were elaborated. Impact of the use of products containing CNTs was analyzed for various applications. Finally, concepts for product disposal were proposed.

Altogether, the carbon nanotube synthesis by CCVD process is becoming a mature technology. This general development was strongly influenced and supported by the Bayer Company. It is a good example for the multiscale development which always takes place when not only the chemistry, but also product properties are important, and both are strongly dependent on reactor design and operation. These challenges have been addressed by a multidisciplinary team of scientists and engineers that made use of 150 years of tradition at Bayer in the development of new technologies and products.

In this Review we used results obtained in the projects aiming at the development and optimization of the fluidized-bed CNTs technology. The results presented have been obtained by a large team of scientists and engineers. It is not possible to list all of them but the special thanks go to A. Wolf, V. Michele, S. Buchholz, O. F. K. Schlüter from Bayer Technology Services GmbH and H. Hocke, R. Weber from Bayer MaterialScience AG. Special thanks should be given also to BMBF, Inno.CNT, and the supporting initiatives from the German Federal Government.

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