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Preparation of thin carbon nanotubes by catalytic pyrolysis on a support

E G Rakov

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Abstract. The preparation of single-walled, double-walled and thin multi-walled nanotubes by hydrocarbon pyrolysis or carbon monoxide catalytic decomposition is considered. The versions of methods, reagents and catalysts are described systematically. The kinetics and mechanisms of processes are characterised. Trends in the development of methods for nanotube synthesis are shown: the increasing role of pyrolytic methods as compared with the graphite sublimation. The advantages of thin multi-walled nanotubes over single-walled ones are noted. Some unsolved problems are formulated. The bibliography includes 485 references.

I. Introduction

Carbon nanotubes (CNTs) and nanofibres (CNFs) belong to materials that attract the keenest attention of scientists and technologists all over the world (*e.g.*, see Refs 1 – 10).

In recent summarising publications,[11 – 16] the methods of preparation of these materials are divided into two main groups, where the first group includes the graphite sublimation followed by desublimation and the second group comprises hydrocarbon pyrolysis and decomposition of carbon oxides (monoxide and suboxides). The other methods such as electrolysis, chemical reduction of certain organic derivatives with alkali and alkaline-earth metals, chlorination of metal carbides or thermal exfoliation play far less important roles.

Two current trends in the development of synthetic methods and the application of carbon nanotubes and nanofibres are observed. One of them reflects the increasing interest in pyrolytic methods of CNT or CNF preparation, while the second concerns revision of the role and significance of single-walled CNTs (SWCNTs).

Indeed, pyrolytic methods do not require such high temperatures as sublimation, are amenable to scaleup and easier to control, provide means for the effective organisation of continuous processes and are more diversified and versatile. As regards the number of versions, these methods far surpass the electro-arc and laser-oven sublimation of graphite. A potential advantage of certain pyrolytic methods is that in addition to CNTs they allow one to produce hydrogen free of CO, which is very important for the development of hydrogen energetics [17] and chemical syntheses.[18]

Initially, the potential of pyrolytic methods was believed to be restricted to the synthesis of multi-walled CNTs (MWCNTs); however, it is already clear that this is wrong and these methods can be applied for the SWCNT production. Dai *et al.*[19] (1996),† were the first to demonstrate the possibility of the SWCNT synthesis by the catalytic pyrolysis of hydrocarbons, while the conditions for the synthesis of high-quality SWCNTs were found as early as in 1998.[23, 24]

The second trend reflects the fact that the opinion that SWCNTs have higher properties than MWCNTs has been shaken. Indeed, double-walled CNTs (DWCNTs) were the first to be appreciated as promising industrial materials.[25, 26] Particularly, DWCNTs were shown to surpass SWCNTs in mechanical properties.[27] In addition, DWCNTs exhibit the higher thermal stability, thermal and electric conductivity as compared with SWCNTs.[28] SWCNTs start coalescing at $\sim$1200 °C, whereas DWCNTs coalesce above 2000 °C. DWCNT-based nanopaper exhibits higher characteristics than a paper made of SWCNTs.[29]

The inevitable topological defects typical of all CNTs have a weaker effect on the DWCNT properties as compared with SWCNTs. Covalent addition of chemical groups to the surface drastically changes the electronic properties of SWCNTs and in certain cases makes their functionalisation (and, hence, their solubilisation and the possibility of using aqueous colloid solutions of SWCNT for purification, production of composites, *etc.*) extremely unwanted. In the DWCNT case, the groups are added to the external wall and have virtually no effect on the electronic properties of the internal wall.

Next, a concept of 'thin MWCNTs' (from here on; denoted as t-MWCNTs) has been formulated. These tubes gradually came to occupy a special place among other filamentous carbon nanomaterials. Tubes with diameters not exceeding 10 nm are classified as t-MWCNTs,[30 – 34] although certain authors place the upper limit of diameters at 5 nm. Tubes that contain from 2 to 8 – 10 walls fall into this category.

Incidentally, the first industrial production of CNTs organised by 'Hyperion Catalysis' (USA) in the mid-1980s was based on the hydrocarbon pyrolysis and allowed the production of t-MWCNTs with diameters of 8 – 10 nm. Later, other countries have also organised the pilot production of CNTs and CNFs by pyrolysis. In 2004, a pilot-line production of carbon nanotubes

E G Rakov D I Mendeleev University of Chemical Technology of Russia, Miusskaya pl. 9, 125047 Moscow, Russian Federation.
Fax (7-495) 490 75 23, tel. (7-495) 490 75 24, e-mail: rakov@rctu.ru; nanotube@mail.ru

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† The first syntheses of MWCNTs from hydrocarbons were carried out several years earlier,[20, 21] while their synthesis from CO was carried out more than 100 years ago, in the end of the XIXth century.[22]

was organised in Tambov based on the works from the D I Mendeleev University of Chemical Technology of Russia.

Certain versions of pyrolytic methods of the CNT synthesis resemble those of chemical vapour deposition (CVD) which are widely used in the production of coatings of pyrolytic graphite, diamond and diamond-like carbon and are characterised by certain versatility. Indeed, they have their drawbacks, particularly, those associated with the necessity of strict control over the synthetic conditions aimed at the production of pure and uniform CNTs.

Several reviews were devoted to the pyrolytic methods (*e.g.*, see the recently published reviews [35–42]); a survey that summarises studies on the plasma-enhanced pyrolysis has appeared.[16] However, the majority of these reviews did not dwell into the synthesis of thin CNTs (one exception is a paper [37] entirely devoted to SWCNTs) and did not include the most of recent data. The present review summarises studies devoted to the synthesis of thin CNTs, which were carried out in the past 4–5 years. The attention is focused on bimetallic catalysts. For the first time, an attempt is undertaken to generalise the data on the kinetics of CNT formation. Certain potentials of pyrolytic techniques are demonstrated by the example of MWCNT synthesis.

II. Versions of catalytic pyrolysis

Pyrolysis is the transformation of organic substances on heating, which can proceed *via* many routes to ultimately yield elemental carbon. The process is carried out under different conditions, namely, the temperature of the process may vary from nearly ambient to above 1000 °C, while the pressure may be both below and above the atmospheric pressure. Solid (polyethylene, *etc.*) and liquid (supercritical toluene) substances and also aqueous and non-aqueous solutions undergo the pyrolysis to evolve carbon. Pyrolysis of gases and vapours is very close to the CVD processes (although it may differ from such processes [43]), while the pyrolysis of aqueous solutions resembles the hydrothermal synthesis.

The CNT synthesis under hydrothermal conditions involves the introduction of organic precursors (polyethylene, ethylene glycol, *etc.*) and metal catalysts [44, 45] into the system. The process is carried out at 700–800 °C and a pressure of 60–100 MPa. It was employed for the production of only MWCNTs with the number of walls from 5 to 100 and more. The inner diameter of such MWCNT was 20–1300 nm.

MWCNTs were also synthesised by the pyrolysis of a ferrocene solution in toluene under supercritical conditions at 600 °C and a pressure of ~12.4 MPa (MWCNTs or CNFs were obtained).[46, 47] Resistive heating of the Si substrate covered with a thin Fe film up to 500–1000 °C in certain organic solvents (methanol, ethanol) also yielded CNTs.[48] Pyrolysis of organic substances in a gel matrix can be carried out at surprisingly low temperatures (300 °C).[49] The catalytic pyrolysis of liquid hydrocarbons under the conditions of supersonically induced cavitation stands somewhat apart from the above methods. This synthesis was first carried out to produce CNTs in 1999 as the pyrolysis of *o*-dichlorobenzene in the presence of $ZnCl_2$. Its new version was described recently.[50, 51]

The methods of catalytic pyrolysis of gases are divided into the following two groups according to the way of catalyst loading:

— pyrolysis with a supported catalyst;

— pyrolysis with a 'volatile' catalyst.

Based on this, two groups of processes performed under different condition are distinguished. In both cases, to minimise the non-catalytic decomposition of gaseous monoatomic and heteroatomic hydrocarbons, their pyrolysis is recommended to be carried out at a reduced total pressure in the system and a low partial pressure of the main reagent.

SWCNTs can also be prepared by the pyrolysis without a catalyst.[52, 53]

III. Pyrolysis with supported catalysts

1. Versions and specific features of processes

Pyrolysis on a supported catalyst has several versions and offers the widest opportunities. The pyrolysis with powder catalysts and the pyrolysis on smooth (flat) or relief (patterned) substrates can be assigned to its major versions.

The general possibilities may include the production of long CNTs, CNTs of a given diameter, CNTs of definite shapes, doped CNTs, CNTs with the diameter- and length-varying compositions and CNT-containing composites.

On smooth or patterned substrates, it is possible to prepare CNTs oriented in a definite way or various structures formed by CNTs, where oriented CNTs or their structures can occupy relatively wide areas.

The simplest and most frequently applied method is the pyrolysis with powder catalysts. The overwhelming majority of CNT syntheses were carried out in set-ups that represented a heated horizontal reactor in the central zone of which a combustion boat with a weighed portion of the catalyst was placed. The starting hydrocarbons were fed into the reactor. Upon the end of the process, the boat contents were taken out and the CNTs formed were washed from the catalyst remainders with acids and other reagents.

The large-scale pyrolysis with powder catalysts was performed in reactors of the following three types: reactors with stirred (mobile), suspended, and filter beds.[54] Horizontal vibroreactors used in the synthesis of carbon nanofibres pertain to the first-type reactors.[55, 56] Rotating tube reactors [38, 57] and screw-conveyer type reactors were also used. Suspended-bed reactors include vertical reactors [58] and reactors with fluidised beds.[11] The latter are most popular. They are intended to be used in the preparation of SWCNTs in the CoMoCAT (formed from the words Co–Mo-catalyst) processes [43, 59, 60] and also in the pyrolysis of C_2H_2,[61] $C_2H_4-H_2$ mixtures [62] and CH_4.[63]

Long (several mm or cm) CNTs and their bundles were prepared.[64–74] Such tubes can be used later in the CNT 'cloning' (the growth of SWCNTs with identical geometry and structure),[75] for example, in a cycle shown in Fig. 1. For this purpose, an array of open-end SWCNTs was synthesised, then, the catalyst particles were deposited on their ends and the pyrolysis was repeated. The scheme of 'cloning' may be more complicated. Thus the catalyst particles were attached to shortened and functionalised SWCNTs in solution, which was followed by the deposition of tubes onto the substrate. The process resembles the epitaxial growth of single crystals.[75]

Carbon nanotubes of equal lengths are used most often for growing arrays of identically oriented tubes ('forest') on smooth substrates. The use of calibrated catalyst particles allows one to synthesise CNTs of definite diameters. In this way, SWCNTs with diameters of 1.45 ± 0.50 nm (Refs 76 and 77) and 1.3 ± 0.4 nm

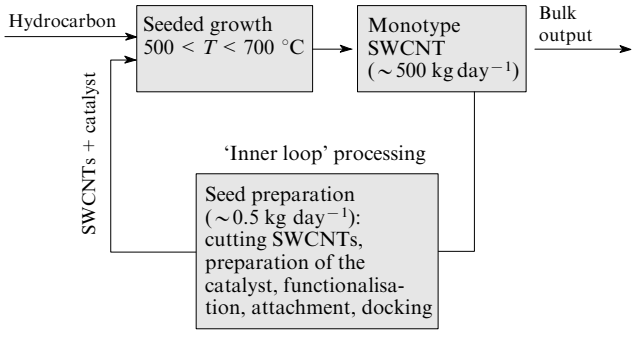


Figure 1. Block diagram of commercial production of SWCNTs of a definite diameter and desired morphology (chirality); [http://www.hydrogen.energy.gov/pdfs/review05/stp_37_smalley.pdf].

(Ref. 78) and also t-MWCNTs with diameters of 4–6 nm were prepared.[79] The use of the MSM-41 molecular sieves made it possible to control the SWCNT diameter within 0.5–0.8 nm with an accuracy of 0.05 nm.[80–82] By varying the concentrations of added thiophene in the CH_4 pyrolysis it is possible to control the SWCNT diameter within 0.88–1.18 nm.[83] The chemical treatment of zeolites allowed varying the diameter of the void in their crystal structure thus changing the size of catalyst particles incorporated into this void and the diameter of resulting t-MWCNTs.[84] When MWCNTs are synthesised on flat substrates with deposited catalysts, it is possible to regulate the diameter of tubes and their density on the substrate by varying the intensity of the catalytic film pretreatment in the NH_3 plasma.[85] Morphology and diameters of CNTs can be changed as a result of changes in the catalyst composition, for instance, by the addition of Co to the Ni/Al_2O_3 catalyst.[86]

Pyrolyses on flat and patterned substrates have their pecularities, making possible the preparation of oriented CNTs and CNT structures. The oriented CNT packing is possible in the cases of pyrolysis in electric field (the majority of papers describe the MWCNT preparation)[2,87–96] and magnetic-field orientation of catalyst particles,[97] as well as in a directed gas stream[66,69–71,98–100] and at a definite position of the substrate with respect to the gravity vector.[101]

The growth of oriented CNT was observed[2] in electric fields with the strength of ~ 1 V μm^{-1}. Somewhat weaker fields (0.4 V μm^{-1}) were used in the formation of SWCNT bridges as long as 25 μm between the electrodes.[91] The induced dipole moment was $\sim 10^6$ D for ~ 1 μm-long CNTs in a field of 1 V μm^{-1}.

The most perfect packing of CNTs on a substrate in electric field requires the optimisation of the electrode shape and the elimination of van der Waals interactions between the tubes. Periodic changes in the electrode position and in the direction of the constant electric field during the CNT growth allow one to change the CNT morphology, *viz*., form bended and zigzag tubes.[102–104] For CNTs to continue their growth upon a change in the electrode position, the carbon capping that passivates the catalyst particles should be etched away.

A method of SWCNT orientation (aligning), which involved the deposition of Al_2O_3 islets, has been developed.[93,105] In this process, the tubes grow perpendicular to the boundary due to the appearance of a space charge. The deposition of a local thin SiO_2 coating on the catalyst film allowed CNTs aligned along the silicon substrate to be grown.[106]

Orientation under the effect of the gas flow made it possible to form networks of crossed SWCNTs (in a two-step process)[66,69] as well as more complex structures based on 1-cm long tubes.[70] The best results were achieved at rapid heating of the substrate. Here, a 'kite' mechanism was assumed to operate, *i.e*., the temperatures of the substrate and the gas increased at different rates, which gave rise to upward convection flows. It is these flows that lift up the ends of growing SWCNTs from the substrate.[71]

CNT deposition on silicon, quartz or sapphire single-crystal substrates can also be accompanied by the CNT orientation, which resembled the epitaxial orientation. The growth of oriented SWCNTs coordinated with the surface orientation of silicon single crystals was first observed by Su *et al*.[107] (later, analogous studies were performed with sapphire[108–112]). It was shown that when ferritin clusters were used as the catalyst and sapphire served as the substrate, the formed SWCNT deposits were ordered on the A and R faces of sapphire and disordered on its M and C faces. Such behaviour was attributed to the different packing of Al atoms on different faces. Sapphire is widely employed as the substrate material in microelectronics; hence, the further development of studies in this direction can lead to the appearance of a new integral circuit technology.

The oriented deposition of CNTs also occurs along atomic steps of vicinal faces of α-Al_2O_3.[108,113] The directed growth of SWCNTs was also observed on the Y-cut of a quartz single crystal.[114]

As compared with the CNT deposition on flat or powder substrates, the method of growing of arrays of oriented CNTs in Al_2O_3 matrices with cylindrical pores arranged perpendicularly to the external surface was used less often. The vast majority of studies that employed this method were aimed at the MWCNT preparation.[115–118] Mesoporous silicates were used for the same purposes.[119,120] On the other hand, the use of $AlPO_4$ single crystals,[121–126] molecular sieves MSM-41 (Refs 80–82 and 127–129) and ordered films of mesoporous SiO_2 (Ref. 130) made it possible to prepare SWCNTs. Zeolites (see Section III.5) and porous silicon served as the matrices in the SWCNT growth. In Al_2O_3 matrices with crossed pores, branched CNTs were synthesised.[131]

The method of preparation of a CNT 'forest' described by Dai[2] is more popular. Catalyst particles of the given size and density were deposited onto inert substrates thus providing the tube growth in only one direction. This allowed SWCNTs to be grown on different substrates in the pyrolysis of ethanol,[131–135] methane,[136] ethylene[67] and mixtures of different gases.

The use of photolithography, methods of substrate profiling or other methods in the deposition of patterns of catalyst particles on substrates made it possible to grow 'columns', 'towers', 'rods', 'tubes' and other CNT structures aligned perpendicularly to the surface. The growth of individual SWCNTs on the patterns formed by photolithographic or microprinting techniques is very promising.[12,23,130,136]

The preparation of structures of the 'power-line' type, namely, submicron Si or SiO_2 columns with CNT-connected vertices was a remarkable achievement.[2,12,136–141] To synthesise such structures, catalyst particles were preliminarily deposited on column vertices. The formation of 'wires' was explained by swaying of the growing CNTs.

Patterned growth of CNTs on 100 (Refs 142–144) and 150 mm Si wafers [http://www.elecdesign.com/Articles/Index.Cfm?AD=1&ArticleID=2462] was documented.

The pyrolytic method of CNT preparation can be employed in the formation of two- and three-dimensional structures.[145–147] A procedure of preparation of 'pellets' from CNTs aligned in parallel and transplantation them onto any substrate chosen has been developed (Fig. 2).[148]

The catalytic pyrolysis allows, in principle, a process similar to the chemical deposition with infiltration to be carried out. Particularly, attempts were undertaken to prepare carbon–carbon composites built of carbon fibres and CNTs.[149]

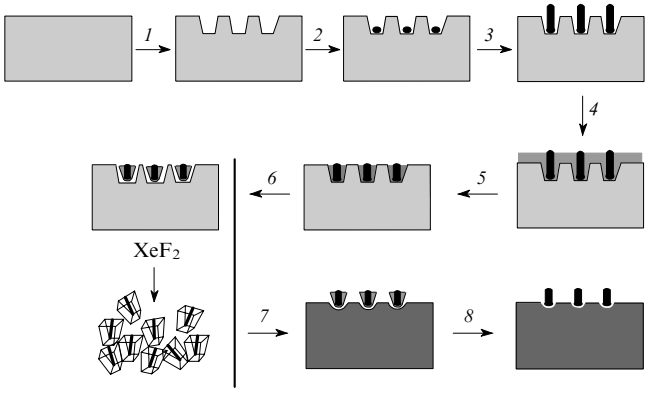


Figure 2. Sequence of operations in the preparation and packing of 'pellets' with CNTs (nanopelleting processes).
(*1*) Etching trenches, (*2*) filling trenches with the catalyst, (*3*) CNT growth, (*4*) spin casting[42] an epoxy polymer, (*5*) planarising and polishing the outer layer to create isolated pellets with uniform-length CNTs, (*6*) withdrawal of pellets, (*7*) transplantation of pellets onto a new substrate, (*8*) etching in the O_2 plasma to remove the polymer.

In the pyrolytic synthesis, the yield of particular CNT types (SWCNTs or DWCNTs) can reach 90%–95% (*e.g.*, see Ref. 150). However, the realisation of the above-described 'cloning' of tubes would be the most remarkable achievement.[75]

Tube doping (with nitrogen, boron, *etc.*) was employed, as a rule, only in the production of MWCNTs or carbon nanofibres,[151,152] although examples are known where SWCNTs [52,153,154] and even DWCNTs [155] were doped with nitrogen.

The synthesis of CNTs with a composition varying along their lengths or diameters was achieved by changing the growth conditions, particularly, the starting gas composition. Thus CNTs covered with one or several concentric coatings with different compositions were grown.

Pyrolytic methods for the preparation of composites of a ceramic matrix filled with CNTs were actively developed in France.[156–166] The CNT synthesis was carried out on solid oxide solutions or spinels. In the course of their reduction, solid solutions and compounds based on Al_2O_3 or MgO with formulas of $Mg_{1-x}M_xO$ (M = Co, Ni) or $Mg_{1-x}M_xAl_2O_4$ (M = Fe, Co, Ni; $x \ll 1$) evolved Fe, Co or Ni nanoparticles which served as the catalysts of the CNT growth. Mixtures of SWCNTs with t-MWCNTs,[167,168] SWCNTs with DWCNTs,[169,170] DWCNTs,[159,160,171] and also DWCNTs with triple-walled CNTs [172] were prepared from the CH_4-H_2 gas mixture with appropriately chosen concentrations of Fe, Co or Ni (x values). Oxides CaO, Cr_2O_3, La_2O_3, *etc.* can also serve as the matrices.

The catalytic pyrolysis of the CH_4-H_2 mixture also allowed the formation of a composite film containing MgO and SWCNTs.[173] A composite containing long CNTs, Fe and ZrC was prepared by the pyrolysis of hydrocarbons on a Zr–Fe film.[174] A composite of SWCNTs and nanocrystalline Al was obtained.[175]

Actually, any process of hydrocarbon pyrolysis or CO decomposition on powder catalysts can be modified to produce composites.

2. Methods of enhancement of pyrolytic processes

Several methods of enhancement of catalytic pyrolysis were described, namely, thermal, plasma, hot-filament, and laser enhancement.

There are two versions of thermal enhancement, *viz.*, heating of the substrate (either directly or through the reactor walls) and heating of gaseous hydrocarbons by their partial combustion. In the second version, which is used very rarely, the substrate covered with catalyst is placed into a certain zone of flame. Heating of the substrate was used more often. As a rule, the heating is performed through the reactor walls; however, resistive heating of the substrate was described (the use of Joule heat) in which the reactor walls remain cold [176,177] and also heating of the substrate using high-frequency current.[178,179] To decrease the temperature of the process [180] and the velocity of the gas flow,[181] reduced pressure was used. Thus the pyrolysis of pure C_2H_4 at a pressure of 100 Pa made it possible to build SWCNT and t-MWCNT bridges between the electrodes of nitrided Ta.[182]

The pyrolysis activated by different types of gas discharges, namely, arc, microwave, corona, glow, high-frequency (with frequency from several kHz to several and even tens MHz) was also carried out at reduced pressure.[41] Two types of these processes are distinguished, *viz.*, in which the substrate is placed either immediately into the flame discharge zone or outside of it and it is the gases that are subjected to activation, while the substrate has a relatively low temperature. An example of the use of a plasma source at a distance from the substrate was described.[183] The elimination of the direct action of microwave plasma on the substrate favours the increase in the CNT growth rate.[184]

The plasma enhancement allows one to carry out syntheses at low temperatures of the substrate. Thus MWCNTs were prepared from CH_4 with addition of small amounts of O_2 under the action of high-frequency plasma at the substrate temperature of 350 °C [185] and also from a CH_4-H_2 mixture under the action of inductively coupled plasma at the substrate temperature of 200 °C.[186] This can be associated with the fact that charged species formed in plasma can change the mechanism of chemical reactions.

Presumably, the advantages of plasma enhancement over thermal enhancement are that the former allows the effective decomposition of starting hydrocarbons and a strict control over the concentration of reactive species; the drawbacks include the somewhat higher disordering of the product structure.[187]

Plasma enhancement was used most often in the MWCNT synthesis.[16,41,188–190] At the same time, the formation of SWCNTs and t-MWCNTs was reported. The microwave discharge plasma was used most extensively. Thus on a Fe catalyst, SWCNTs and DWCNTs with the packing density of $\sim 10^{12}-10^{13}$ cm^{-2} were formed from a $C_2H_2-NH_3$ mixture,[191] t-MWCNTs with diameters of 3–20 nm were prepared from a CH_4-CO_2 mixture,[192] SWCNTs or t-MWCNTs were obtained from a CH_4-H_2 mixture [http://www.nsti.org/Nanotech2005/Showabstract.html?absno=273] and MWCNTs were formed from a $CH_4-NH_3-H_2$ mixture.[193] The MWCNT diameter was regulated by varying the size of catalyst particles on the substrate. This could be achieved, for example, by changing the thickness of the deposited metal-catalyst film.[189,194–197] A method of preparation of a SWCNT 'forest' under the action of point-arc microwave [198] or 'diffusion' [199–201] plasmas was described.

An interesting feature of SWCNTs formed in the CH_4 pyrolysis activated by high-frequency discharge is the domination of tubes with semiconductor characteristics.[183,202]

For the first time, in the plasma generated at the electron cyclotron resonance, SWCNTs or DWCNTs were grown directly on silicon substrates, which were not preoxidised.[203]

The hot-filament activated pyrolysis, *i.e.*, activated by an incandescent tungsten wire heated with Joule heat up to ~2000 °C, is a purely laboratory method. This process is easily organised (Fig. 3). Such activation can be accompanied by the formation of plasma, provided a certain potential difference is applied between the cathode and the tungsten wire, which allows SWCNTs to be grown. The tubes were deposited onto low-melting substrates.[79,204–206]

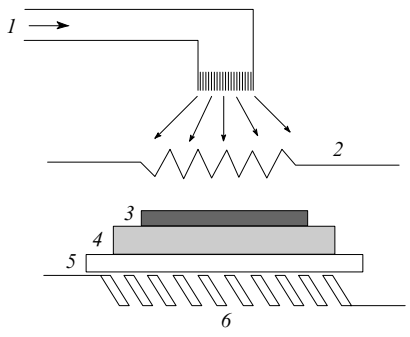


Figure 3. Illustration of CNT preparation in hot-filament activated pyrolysis.
(*1*) Gas mixture inlet, (*2*) hot tungsten spiral wire, (*3*) catalyst, (*4*) cathode, (*5*) substrate, (*6*) substrate heater.

Three types of laser activation are known. In the first method, a directed laser beam locally heats one or another substrate area (SWCNTs were obtained this way).[207,208] In the second method, by employing an appropriate frequency of laser radiation, one can selectively activate gases subjected to the pyrolysis or decomposition. Finally, laser beams can be used for heating of diathermic gases by adding to them substances capable of selective absorption of laser radiation.[209]

A specific feature of pyrolytic processes is that the CNT growth is accompanied by incorporation of only active metal particles [210] into CNT hollows, whereas the inert substrate (*e.g.*, oxide, see Section III.5) remains outside the tubes. This is the result of the effect of catalysts on the formation of tubes.

3. Starting compounds

The set of starting compounds used in the production of SWCNTs and t-MWCNTs is much more limited as compared with the production of MWCNTs or CNFs. Among hydrocarbons, methane is the most suitable for this purpose (Refs 23, 24, 27, 28, 83, 87, 92, 101, 105, 107, 114, 136, 141, 173, 185, 211–254). This hydrocarbon is thermally more stable as compared with others; this is why its catalytic pyrolysis produces smaller amounts of amorphous carbon impurities. Dilution with hydrogen, which is the main gaseous product of pyrolysis, inhibits the non-catalytic pyrolysis of methane even at relatively high temperatures.[74, 106, 142, 143, 156–172, 186, 189, 199–201, 233, 246, 255–262] In the plasma-enhanced CVD, the dilution with hydrogen is of vital importance; here, mixtures containing as little as 2 vol.%–6 vol.% CH_4 (*e.g.*, see Ref. 197) are often used. Dilution with inert gases also has a positive effect. The introduction of small amounts of C_2H_4 into the CH_4-H_2 mixture is a common practice.[88, 94, 109]

In addition to methane, unsaturated hydrocarbons, particularly, ethylene (Refs 67, 75, 176, 180, 182, 219, 240, 262–270), acetylene (Refs 61, 79, 84, 89, 182, 209, 215, 271–299) and propylene,[300] were pyrolysed to form SWCNTs, DWCNTs and t-MWCNTs. Mixtures of unsaturated hydrocarbons with methane [31, 64, 301–304] and benzene [227, 305] were also used.

As regards the CNT yield and purity, cyclic hydrocarbons, particularly, cyclohexane, naphthalene and anthracene, do not surpass methane.[305] This is also true for benzene.

Mixtures $C_2H_2-NH_3$ proved to be efficient in the synthesis of CNFs,[41, 306] MWCNTs,[41, 188, 283, 307, 308] t-MWCNTs [195, 196] and SWCNTs [191] in plasma. The role of NH_3 in the MWCNT preparation consists of the maintenance of the active surface state of catalytic particles due to the removal of amorphous carbon,[309] which accounts for the appearance of HCN is the gas [308, 310] or the increase in the concentration of hydrogen atoms.[193] The synthesised CNTs contained up to 10 at.% of nitrogen.[188]

The difference between the pyrolysis of C_2H_2 and the pyrolysis of other hydrocarbons is that the former process is highly exothermic. The catalytic synthesis of a CNT 'forest' was carried out using C_2H_2 molecular beams.[294] In the initial stages, before the thickness of the layer of products reached 50 μm, SWCNTs with diameters of ~1 nm were preferentially formed, which was followed by the growth of SWCNTs with larger diameters and DWCNTs.

In the last 3–4 years, keen attention was paid to the use of ethanol as the starting compound in the CNT synthesis. It was assumed that OH radicals remove amorphous carbon admixtures to yield much purer SWCNTs as compared with cases where other reagents were used. This line of research was actively explored by Japanese scientists of the Maruyama group.[132, 134, 135, 177, 311–320] Analogous syntheses were carried out by other scientific groups.[66, 72, 75, 78, 178, 179, 321–327] Low partial vapour pressures (0.7–1.4 kPa or 5–10 Torr) and a temperature of 800 °C were commonly used. Ethanol pyrolysis on a $Fe-Co/SiO_2$ catalyst selectively produced DWCNTs.[326]

The introduction of OH radicals into the gas phase can also be accomplished by the addition of O_2 (Refs 185 and 187) or H_2O vapours.[67] Presumably, the higher yields and formation rates of MWCNTs in the CH_4 pyrolysis on the oxide catalysts that were not subjected to preliminary reduction as compared with reduced catalysts were also attributed to the effect of H_2O vapours evolved in the oxide reduction during the pyrolysis.[244]

Single-walled CNTs were prepared from vapours of methanol [323] and mixtures $CH_3OH + H_2$ and $CH_3OH + Ar$.[71] The rate of MWCNT formation from methanol was substantially lower as compared with ethanol.[328] A synthesis of SWCNTs was carried out from methanol and propan-2-ol in a set-up with a hot filament.[329] Low SWCNT yields were obtained from camphor [330] and its analogues, namely, camphorquinone, norcamphor, norbornane, fenchone. These experiments did not reveal any beneficial effect of oxygen on the yield and quality of tubes.[331]

A matrix synthesis of SWCNTs was carried out using tripropylamine.[121, 125, 332] A mixture of SWCNTs and MWCNTs was isolated after the acetonitrile pyrolysis.[333] The synthesis of CNTs (with a fraction of t-MWCNTs) from associated gas was described.[236, 334]

In recent years, the CNT synthesis by the thermal decomposition of carbon monoxide was actively developed (Refs 19, 43, 59, 60, 68, 80–82, 127–129, 263, 335–349). The equilibrium of CO decomposition is such that the solid product yield decreases with an increase in the temperature. This makes the choice of conditions that suppress the formation of amorphous carbon much easier. An increase in the pressure substantially increased the yield of SWCNTs and made them more uniform in the diameter.[128] The addition of H_2 was observed to have a positive effect on the rate of CNT formation [69, 71, 335, 342] and, in the case of Co/MgO catalysts, the tube diameter was observed to decrease with the decrease in the Co concentration.[342] This method allowed one to prepare both ordinary [339–341] and long SWCNTs.[344]

A large-scale production of SWCNTs *via* the catalytic decomposition of CO was proposed based on the aforementioned CoMoCAT process (Fig. 4). The reaction is carried out at 700–950 °C and a pressure of ~0.5 MPa (5 atm). Stable operation of the set-up requires a low degree of CO decomposition in the reaction zone; this is why the set-up provides the CO recycling after the recovery of CO_2 formed. It was shown that the lower the temperature of the process the smaller the average diameter of SWCNTs formed, *i.e.*, the diameter approached 0.8 nm at 750 °C, 1.0 nm at 850 °C and 1.2 nm at 950 °C. The catalyst selectivity with respect to SWCNTs (the SWCNT fraction in the total CNT mass) was 80%–90%. The fraction of semiconductor CNTs in the total amount of tubes was 57%.

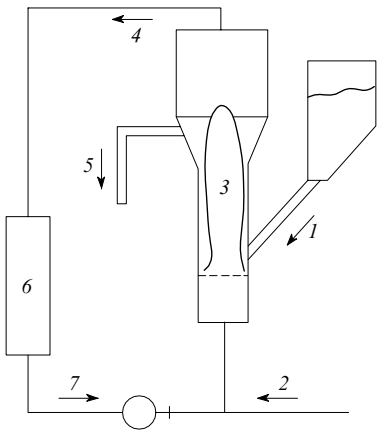


Figure 4. A principal scheme of the CoMoCAT process.
(*1*) Catalyst load slot, (*2*) fresh CO feed line, (*3*) fluidised catalyst bed, (*4*) outlet of reaction gases, (*5*) product output, (*6*) CO_2 trap, (*7*) inlet of recycled CO; [http://www.ou.edu/engineering/nanotube/comocat.html].

4. Catalysts

Among individual metals, Fe, Co and Ni exhibit the highest catalytic activity in the pyrolytic synthesis of CNTs. It is a wide opinion that the characteristics of metal–carbon systems are of the prime importance for the catalytic activity of metals in the pyrolysis.

In a review,[41] the catalysts used in the preparation of various filamentous carbon nanoparticles on substrates were tabulated and the original literature references (more than 60) were cited; however, only three of references are devoted to the synthesis of SWCNTs. This is why the present survey shows a new list of catalysts as applied to the synthesis of SWCNTs, DWCNTs and t-MWCNTs.

The preparation of SWCNTs, DWCNTs and t-MWCNTs involves most often the use of bimetallic catalysts, *i.e.*, active metals.[350] They exhibit enhanced activity, selectivity and thermal stability and are less susceptible to poisoning. Such catalysts allow the diameter and purity of CNTs obtained to be controlled within certain limits.

The major metal catalysts, namely, Fe, Co or Ni, are often supplemented with molybdenum compounds (Tables 1 and 2). Molybdenum as such, its oxides and certain other compounds also exhibit catalytic properties in the pyrolysis of hydrocarbons and the decomposition of CO; however, in the CNT synthesis, their effect is either weak or they impair the morphology of the solid products of the pyrolysis. In place of CNTs, non-tubular CNFs or wide-diameter CNTs are often formed. At the same time, the use of Mo as a promoting additive favours the decrease in the CNT diameter, the increase in the total yield of solid products and the decrease in the amount of admixed CNFs. Particularly, it is assumed that the addition of Mo to the Co/MgO system gives rise to small Co clusters that are formed due to the decomposition of $CoMoO_4$ and provide sites for the CNT growth.[288]

Table 1 shows examples of the use of binary powder catalysts Co – Mo on different substrates in the heat-activated pyrolytic synthesis of SWCNTs, DWCNTs, t-MWCNTs and CNFs. The data in Table 1 may be supplemented by the results on disproportionation of undiluted CO on the Co – Mo/SiO catalyst.[336] It was shown that this catalyst changes its chemical composition in the course of CNT formation. As reported in numerous publications, binary powder catalysts based on Co – Mo make it possible to synthesise SWCNTs from various carbon-containing precur-

Table 1. Composition and application conditions of binary powder catalysts Co – Mo/support (A) in the heat-activated CNT synthesis.

A	Co : Mo : A /mol (Co : Mo)	Process conditions			Products	Ref.
		starting compounds	T /°C	p /atm		
MgO	(0 – 5) : (5 – 0) : 95	CH_4 (20%) – H_2	1000	1.0	t-MWCNTs, CNFs	34
MgO	5 : 1 : 94	CH_4 (20%) – H_2	1000	1.0	t-MWCNTs, CNFs	32
MgO	2.5 : 2.5 : 95.0 [a]	C_2H_2 (10%) – H_2	800	1.0	SWCNTs	288
MgO	(1 : 4)	CO (100%)	700	1.0	SWCNTs	351
MgO	(1 : (2 – 30))	CH_4 (97%) – H_2	1000	1.0	t-MWCNTs	352
MgO	1.0 : 0.1 : 20.0	CH_4 (9%) – Ar	800 – 850	1.0	DWCNTs	239
SiO_2	0.5 : 1.5 : 98.0 [a]	CO (100%)	750	5.0	SWCNTs	60
SiO_2	2 : 4 : 94	CO (100%)	700	1.0	SWCNTs	59, 337
SiO_2 (see [b])	(1.0 : 3.5)	CO (100%)	850	1.0	SWCNTs	343
SiO_2	(2 : 1) – (1 : 4)	CO (20% or 50%) – He	700, 800	(1.0)	SWCNTs	337
SiO_2	~0.5 : 1.5 : 98.0 [a]	CO (100%)	700 – 950	1 – 10	SWCNTs	43, 345
SBA-16	(1.0 : (0.3 – 1.0))	C_2H_5OH – Ar (see [c])	850	1.0	SWCNTs	66
Zeol or Al_2O_3	(0 – 5) : (5 – 0) : 95 [a]	C_2H_2 (9%) – N_2	700	1.0	t-MWCNTs	353
Al_2O_3	1 : 4 : 50 [a]	CH_4 (50%) – Ar	550 – 850	1.0	MWCNTs	244

[a] Mass ratio. [b] Catalysts with Na additives were also tested. [c] The partial pressure of ethanol vapours was 0.0155 atm.

Table 2. Composition and application conditions of binary powder catalysts Fe – Mo/support (A) at thermal activation and atmospheric pressure.

A	Fe : Mo : A /mol (Fe : Mo)	Process conditions		Products	Ref.
		starting compounds	T /°C		
MgO	10.0 : 2.5 : 87.5	$CH_4 – C_2H_4 – H_2$	900	t-MWCNTs	31
MgO	(1.0 – 2.0) : (0.05 – 0.10) : 13.0	CH_4 (20%) – H_2 (N_2)	1000	SWCNTs	241
MgO	(0.5 – 2.0) : (0.05 – 0.2) : 11	C_2H_2 (1% – 13%) – Ar	850 – 950	SWCNTs	296
MgO	1.0 : 0.1 : 11.0 [a]	C_2H_2 (2%) – Ar	800 – 950	SWCNTs	287
MgO	1.0 : 0.1 : 12.0 [a]	C_6H_{14} – Ar	900	DWCNTs	354
Al_2O_3	9 : 1 : 90	C_2H_4 (0.06%) – Ar – H_2 (0.03%)	850	SWCNTs + DWCNTs	263
Al_2O_3	1.00 : 0.16 : 10.00	CH_4	900	t-MWCNTs [b]	355
Al_2O_3	1.00 : 0.16 : 10.00	CH_4 (50%) – H_2	950	SWCNTs [b]	355
Al_2O_3	1.00 : 0.17 : 10.00	CH_4 (60%) – H_2 (see [c])	700 – 900	SWCNTs	181
Al_2O_3	1.00 : 0.25 : 10.00	CH_4 (20%) – H_2	1000	SWCNTs	356
Al_2O_3	1.0 : 0.1 : 13.0	CH_4 (17%) – Ar	950	SWCNTs + DWCNTs	232
Al_2O_3	(5 : 1) [a]	CH_4 (10%) – Ar	680 – 900	SWCNTs	220
Al_2O_3	1.00 : 0.17 : 16.00	CH_4	900	SWCNTs	213
Al_2O_3	1.00 : 0.16 : 16.00	CH_4	850 – 1000	SWCNTs	215
Al_2O_3	(6 : 1)	CH_4 (2.2% – 35.2%) – Ar (see [d])	680 – 850	SWCNTs	223
Al_2O_3	9 : 1 : 90	CO (1.18 atm)	700 – 850	SWCNTs (+ DWCNTs)	263
$SiO_2 + Al_2O_3$	1.0 : 0.17 : (16.00 + 16.00)	CH_4	900	SWCNTs	213

[a] Mass ratio. [b] Depending on the catalyst synthesis conditions, MWCNTs and CNFs can be obtained. [c] The total pressure was 0.13 atm. [d] The total pressure was 0.79 atm.

Table 3. Composition and application conditions of binary powder catalysts M – M′/A (M, M′ = Fe, Co or Ni; A is support).

M – M′/A	M : M′ : A /mol (M : M′)	Process conditions			Enhancement method	Products	Ref.
		starting compounds	T /°C	p /atm			
Fe – Co/Zeol (or Al_2O_3)	(0 – 5) : (5 – 0) : 95 [a]	C_2H_2 (9%) – N_2	700	1.0	thermal	t-MWCNTs, MWCNTs	353
Fe – Co/$MgAl_2O_4$	6.5 : 3.5 : 90.0 [b]	CH_4 (18%) – H_2	700 – 1070	1.0	"	t-MWCNTs, CNFs	359
Fe – Co/$MgAl_2O_4$	(0 – 0.1) : (0.1 – 0) : 0.9	CH_4 (18%) – H_2	1070	1.0	"	SWCNTs, DWCNTs	170
Fe – Co/$MgAl_2O_4$	80 [c]	CH_4 – H_2	1070	1.0	"	SWCNTs, t-MWCNTs	167
Fe – Co/Al_2O_3 (see [d])	2.5 : 2.5 : 95.0 [a]	C_2H_4 (27%) – N_2	1080	1.0	"	SWCNTs	264
Fe – Co/Zeol	2.5 : 2.5 : 95.0 [a]	C_2H_5OH – Ar	700 – 800	6.6×10^{-3}	"	SWCNTs	311
Fe – Co/Zeol	2.5 : 2.5 : 95.0 [a]	C_2H_5OH	850	1.3×10^{-4}	plasma	SWCNTs	177
Fe – Co/Zeol	2.5 : 2.5 : 95.0 [a]	C_2H_5OH	800	0.013	thermal	SWCNTs	313
Fe – Co/Zeol	2.5 : 2.5 : 95.0 [a]	C_2H_5OH – Ar	800	6.6×10^{-3}	"	SWCNTs	316
Fe – Co/Zeol	2.5 : 2.5 : 95.0 [a]	C_2H_5OH – Ar – H_2	800	6.6×10^{-3}	"	SWCNTs	315
Fe – Co/Zeol	2.5 : 2.5 : 95.0 [a]	C_2H_5OH – Ar	900 – 1000	1.0	"	SWCNTs	178, 179
Fe – Co/Zeol	2.5 : 2.5 : 95.0 [a]	C_2H_5OH	900	0.05 – 0.08	hot filament	SWCNTs	360
Fe – Co/MgO	(10 – 0) : (0 – 10) [e]	C_2H_5OH, CH_3OH	450 – 950	$(6.6 – 13.1) \times 10^{-3}$	thermal	SWCNTs	323
Fe – Co/Zeol	(1 : 1)	C_2H_2 (0.4% – 1.6%) – Ar	900	1.0	"	DWCNTs	280
Fe – Ni/$MgAl_2O_4$	6.5 : 3.5 : 90.0 [b]	CH_4 (18%) – H_2	700 – 1070	1.0	"	t-MWCNTs, CNFs	359
Fe – Ni/$MgAl_2O_4$	80 [c]	CH_4 (18%) – H_2	1070	1.0	"	SWCNTs, t-MWCNTs	167
Co – Ni/$MgAl_2O_4$	80 [c]	CH_4 (18%) – H_2	1070	1.0	"	SWCNTs, t-MWCNTs	167
Co – Ni/SiO_2 (Al_2O_3)	(1 : 1)	CH_4	1000	1.25	"	SWCNTs	23

[a] Mass ratio. [b] Ratio Fe : Co : Mg or Fe : Ni : Mg. [c] Content of $MgAl_2O_4$ /mol. [d] Good results were also obtained for the Fe – Co – Ni/Al_2O_3 catalyst. [e] The MgO content was about 97 mass %; Si and SiO_2 supports were also used.

sors. Moreover, after certain changes in the conditions, even DWCNTs, t-MWCNTs and CNFs can be isolated. In the pyrolysis of $CH_4 – H_2$ mixtures, the highest yield was achieved for the molecular ratio Co : Mo = 1 : 3.[34, 357]

In addition to studies cited in Table 2, the use of the Fe – Mo/MgO catalyst in the synthesis of DWCNTs from $CH_4 – H_2$ deserves mention.[358]

As follows from Tables 1 and 2, the lowest temperature of the SWCNT synthesis is 680 °C [*e.g.*, from CH_4 with a catalyst based on Fe and Mo oxides deposited on Al_2O_3 at the mass ratio Fe : Mo = 5 : 1 (Ref. 220)];‡ however, such tubes are conventionally obtained at temperatures not lower than 800 °C.

The pyrolytic synthesis of CNTs employs Fe – Co, Fe – Ni and Co – Ni catalysts on different substrates (Table 3). In addition to catalysts shown in Table 3, Fe – Co/MgO (preparation of DWCNTs in the CH_4 pyrolysis),[245] Fe – Co/Zeol (SWCNTs, C_2H_2)[278] and Fe – Co/SiO_2 (DWCNTs, C_2H_5OH)[326] were described. The use of the Ni – Mo composition was also mentioned.[361]

Besides Mo, the additions of platinum metals, *e.g.*, Ru,[213] Pt[71, 317] and also compounds of tungsten,[280, 345] vanadium,[353] chromium[280] and manganese[280] was used in the preparation of bimetallic catalysts based on Fe, Co or Ni. It was shown that the Co – Mo catalyst is more efficient than Co – Pt[317] and the Co – Ni catalyst is more efficient than Co – V, Co – Cr and Co – Mn.[280]

A series of iron-based catalysts with different additives were tested,[359] namely, Fe – Cr/Al_2O_3, Fe – Ni/Al_2O_3, Fe – Ru/Al_2O_3, Fe – Cr/Cr_2O_3, Fe – Co – Ni/Cr_2O_3, Fe – Co – Ni/MgO and Fe – Co – Ni/$MgAl_2O_4$.

In addition to binary powder catalysts based on Fe, Co or Ni, more complex catalysts and supported binary catalysts were also

‡ Iron oxides are inactive under these conditions but can be activated by pre-reduction with a He – H_2 (10%) mixture.

Table 4. Composition and application conditions of multilayer catalysts sputtered on flat and patterned substrates in the heat-activated pyrolysis (the sequence of layers begins with the external layer).

M – M′ – M″ or M – M′	Layer thickness for M, M′ and M″ /nm	Process conditions				Products	Ref.
		substrate	starting compounds	T /°C	p /atm		
Mo – Fe – Al	0.2, 1.0, 10	Si	C_2H_2 (0.3%) – Ar (83.0%) – H_2 (16.7%)	600 – 1100	1.0	SWCNTs, DWCNTs	282
Mo – Fe – Al	0.2, 1.0, 10	Si	C_2H_2	1000	$(0.7 – 2.7) \times 10^{-3}$	SWCNTs	289
Mo – Fe – Al	0.2, 1.0, 10	Si	C_2H_2	700 – 1000	2.5×10^{-3}	SWCNTs	290
Mo – Fe – Al	0.2, 1.0, 10	Si	C_2H_2 – H_2 – Ar	535 – 900	1.0	t-MWCNTs	298
Mo – Fe – Al	2, 1, 20	see [a]	CH_4 – Ar	950	1.0	SWCNTs, t-MWCNTs, MWCNTs	237
Mo – Fe – Al	(0 – 0.2), (0 – 0.2), 10 [b]	Si	C_2H_2	730	1.0	t-MWCNTs	362
(Fe, Ni, Co) – Al	(1 – 10), (10 – 1) [d]	glass	CO (6%) – H_2	550	1.0	t-MWCNTs	363, 364
Ni – Al	1, (2 – 10)	SiO_2/Si	CH_4	800	0.13	SWCNTs	365
Co – Pt	2, 10	SiO_2/Si	C_2H_5OH (4.7%) – Ar	not specified	2.6×10^{-3}	SWCNTs	321

[a] 15 Substrates of different compositions were tested. [b] The best properties were observed for $Mo_{0.06}Fe_{0.94}$ with the total layer thickness of 0.5 – 2.0 nm. [c] Simultaneous sputtering was carried out. [d] The limits of layer thickness variation are shown.

Table 5. Composition of catalysts deposited on substrates from the gas phase or from solutions and suspensions and the conditions of their use in the heat-activated pyrolysis.

M – M′	Pyrolysis conditions				Ref.
	substrate	starting compounds	T /°C	p /atm	
Co – Mo	Si or SiO_2	C_2H_5OH	600 – 850	1.3×10^{-2}, 2.6×10^{-2}	312, 314, 320
Co – Mo [a]	SiO_2	C_2H_5OH	800	0.9×10^{-2}	132
Co – Mo	Si_2	C_2H_5OH	800	1.3×10^{-2}	134, 135
Co – Mo [b]	SiO_2	C_2H_5OH	800	not specified	317
Co – Mo	SiO_2	C_2H_5OH	800	1.3×10^{-2}	133
Co – Mo	SiO_2	C_2H_5OH	800	1.3×10^{-2}	318
Fe – Mo – Al_2O_3	SiO_2/Si	CH_4	900, 1000	1.0	24, 212, 214, 369 [d]
Fe – Mo – Al_2O_3	SiO_2/Si	$CH_4 - H_2$	900	1.0	142
Fe – Mo [c]	Si or SiO_2	CH_4	900	1.0	218
Fe – Mo	SiO_2/Si	CO (80%) $- H_2$	900	1.0	98, 99
Fe – Mo	Al_2O_3/Si	CH_4	900	1.0	370
Fe – Mo	Al_2O_3/Si	CH_4	900	1.0	107
Fe – Mo – Al_2O_3	SiO_2/Si	$CH_4 - H_2$	950	1.0	230
Fe – Mo	SiO_2/Si [e]	$CO - H_2$	950	1.0	339
Fe – Mo	Si_3N_4 (see [f])	CH_4 (50%) $- H_2$	950	1.1	257
Fe – Mo – MgO	SiO_2	$CH_4 - H_2$	950	1.0	173
Fe – Mo – Al_2O_3	Cr/Au/SiO_2/Si	$CH_4 - H_2$	900	1.0	65

[a] Thickness of the layer on the substrate was 1 – 2 nm. [b] Particles measuring 10 ± 1 nm were deposited. [c] A promoting catalyst deposited as a powder was also used. [d] In this work,[369] the deposition was carried out onto Si tips. [e] Substrates of Al_2O_3 and MgO were also tested. [f] The substrate was hydrophilised in the O_2 plasma.

used (Table 4). The synthesis of CNTs from CO on Co – Mo films deposited on quartz [344] and also by plasma-enhanced pyrolysis on the Al_2O_3 (thickness 0.7 nm) – Fe (0.5 nm) – Al_2O_3 (5.0 nm) film sputtered on silicon [198, 348] was described.

The studies by a group of Japanese scientists on the pyrolysis of hydrocarbons on sputtered Fe catalysts deserve mention.[366 – 368] In particular, they have shown that the CNT diameter can be regulated by varying the thickness of the sputtered catalyst film.

In certain cases, the catalysts were applied onto substrates by the methods simpler than sputtering, *viz*., by dipping in solutions or suspensions, chemical vapour deposition, *etc*. Table 5 shows the examples of CNT syntheses on such catalysts.

A two-step mechanism was proposed [371] to explain the effect of bimetallic catalysts in the formation of SWCNTs. The role of the second metal, *e.g*., Mo, may consist of the promotion of the formation of an intermediate CNT precursor. This promoter can be spatially separated from the main metal on which CNTs are formed. For instance, a 'conditioning' catalyst or 'pre-catalyst' placed immediately in the gas stream fed into the pyrolysis reactor was observed to substantially increase the CNT yield. [28, 29, 249, 372] It was found that the 'pre-catalyst' favours the formation of small amounts of C_6H_6 from CH_4.

5. Catalyst supports and substrates

In powder catalyst composition, an inert support separates the active metal particles preventing their aggregation. In the preliminary stages of the preparation of compositions, due to the formation of solid solutions, the support favours more uniform distribution of catalyst precursors. This is why attention is focused on the choice of supports and the selection of the composition. A combinatory method for the selection of the composition of catalysts for the synthesis of MWCNTs,[373, 374] t-MWCNTs [374] and SWCNTs [375, 376] was described.

Based on a large number of examples, the relationship between the diameters of a CNT formed and a catalyst particle was studied and these diameters were shown to be similar.[79, 277, 322] For instance, it was assumed that the size of metal particles should be limited to 3 nm.[319] At the same time, it was shown that SWCNTs with diameters of 1.45 ± 0.50 nm grow on uniform Ni particles with diameters of 4.7 ± 1.4 nm,[76, 77] tubes with diameters of 1.3 ± 0.4 nm grow on Fe particles with diameters of 1.7 ± 0.6 nm [78, 377] and CNTs with diameters of 1 – 2 nm grow of Fe particles with diameters of ~5 – 14 nm.[260] The experimental results have not yet been brought in complete agreement with one another. It was shown [376] that the ratio of diameters of a catalyst particle and a SWCNT approached 1.6; however, in the MWCNT preparation (diameter 27 – 57 nm), a considerably smaller ratio of diameters, namely, 1.2 – 1.4, was observed.[378]

Testing of various powder catalyst supports has shown that MgO surpasses SiO_2, ZrO_2, Al_2O_3, CaO, *etc*. in the stability and the SWCNT yields reached.[227] For powder MgO with mesopores of a certain size (d = 12 – 16 nm), the specific surface area (S_{sp}) of the powder is related to the SWCNT purity, as evidenced by the changes in the intensities of *G*- and *D*-modes in the Raman spectra of tubes (Fig. 5). At the same time, no unambiguous relationship between S_{sp} of the support and CNT characteristics was revealed, *viz*., on a SiO_2 support with the pore diameter of 7.2 nm, no

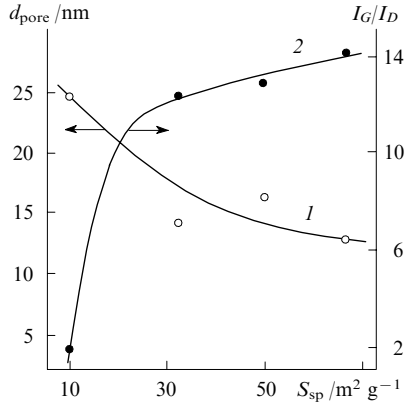


Figure 5. Effect of the specific surface area of MgO powder prepared by different methods on (*1*) the average size of powder pores and (*2*) the ratio of intensities of *G* and *D* modes in the Raman spectra of SWCNTs synthesised.
Points correspond to experimental data.

Table 6. Properties of catalyst supports and the pyrolysis products of the CH_4-Ar mixture at 850 °C (reproduced with permission of the Royal Chemical Society).

Material	S_{sp} /m^2 g^{-1}	d_{pore} /nm	RBM peak [a]	I_G/I_D
SiO_2	446	7.2	absent	–
CaO	4.8	38	"	–
ZrO_2	102	22	"	–
Al_2O_3	155	15	present	2.3

[a] RBM is the radial breathing mode that characterises the presence of SWCNTs.

SWCNTs or t-MWCNTs were formed at all even if S_{sp} of the support was as large as 446 m^2 g^{-1} (Table 6).

The increase in the active metal content in the catalyst entailed the increase in the deposit yield (Fig. 6) [156] but impaired the CNT quality, as follows from the S_{sp} of the carbon product (Fig. 7).[156]

For sputtered catalysts, the chemical composition of the substrate surfaces affects the CNT formation. Thus on hydrogenated silicon substrates, the formation of tube nuclei occurred easier than on oxidised substrates or those treated with tetramethylammonium hydroxide.[205] A buffer layer (Al_2O_3, TiO_2, *etc.*) between the substrate (Si) and the active metal (Fe) is not less significant, because it can determine the chemical composition of the catalyst.[379, 380] For example, under similar conditions, iron deposited on an Al_2O_3 layer exists as FeO and can catalyse the formation of SWCNTs, DWCNTs and t-MWCNTs, whereas in an iron layer deposited on TiN and TiO_2 layers, iron is present in the metal form and causes the growth of thick MWCNTs with more than 20 layers.[379, 380]

To prepare t-MWCNTs with diameters of less than 10 nm on metal electrodes, it was recommended to sputter a silicon interlayer between the metal electrode and the catalyst particles.[381]

By changing the composition and thickness of sputtered layers, one can regulate the CNT density on the substrate.[382] The results of a systematic study [237] point to the strong effect of the substrate on the morphology and quality of CNTs formed (Table 7).

The different effects of substrates on the CNT growth were attributed [237, 383] to the different roughness of their surfaces. The surface roughness affects the S_{sp} value, the density of defects and, as a consequence, the size of catalyst particles. Rough supports should be preferred. In the case of powder catalysts, the important

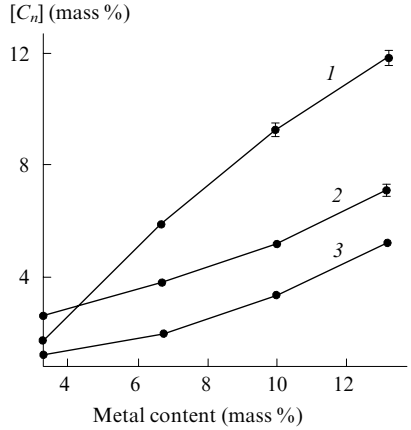


Figure 6. Effect of the content of transition metals in a powder catalyst on the carbon yield in the deposit.[156]
(*1*) Fe, (*2*) Co, (*3*) Ni.
(Reproduced with permission of Prof. Rao and the Materials Research Society.)

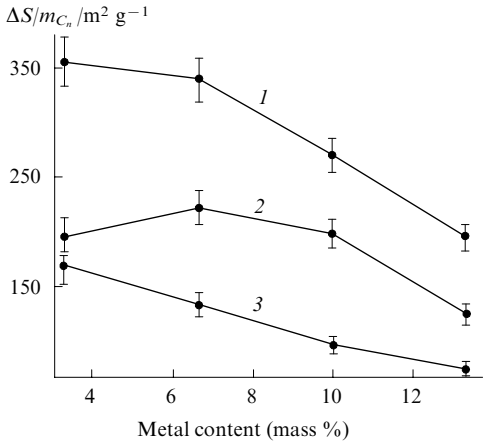


Figure 7. Effect of the content of transition metals in a powder catalyst on the quality of CNTs obtained (the ratio of the carbon deposit specific surface area to the deposit mass).[156]
(*1*) Co, (*2*) Ni, (*3*) Fe.
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Table 7. Characteristics of CNTs prepared on the Mo(thickness 2 nm)–Fe(1 nm)–Al(20 nm) catalyst (reproduced with permission of the Elsevier Publishers).[237]

Substrate	I_G/I_D	Diameters of SWCNTs /nm	Diameters of MWCNTs /nm
Deposited Al_2O_3	16.0	1.5–3.5	–
SiC	6.0	1.4–2.2	~ 9
Si(001)	4.1	1.3–3.75	5.4–20
Quartz	4.1	1.5–2.4	5.0–13.6
Sapphire	3.2	1.7–2.7	9.0–24
Si/SiO_2	1.7	1.2–4.3	7.5–18
MgO	1.4	2.3–4.3	11.0–27.7
Porous Si	1.4	⩽ 5.0	5.6–7.4
Aerogel (80%)	1.4	–	5.9–15.7
Aerogel (50%)	1.2	–	7.1–19.9
Aerogel (30%)	1.1	–	9.4–20.8
Fused SiO_2	1.1	–	5.5–12.5
Etched Si(001)	1.0	–	6.3–10.4
Plasma SiO_2	1.0	–	5.6–25.9
Si/Si	0.99	–	6.1–22.4

role was assigned [238] to the interaction of the metal with the support.

For the plasma-enhanced catalytic pyrolysis of hydrocarbons, the substrate can become the source of radicals, *i.e.*, take part in chemical reactions and also be sputtered with the transfer of the substrate material to the CNF surface.[41]

To obtain SWCNTs with small diameters (0.4–0.5 nm), $AlPO_4$-5 molecular sieves were used.[384] The pore size in the Co-substituted molecular sieves MSM-41 and, therefore, the SWCNT diameter could be regulated by varying the composition of liquid matrices in the sieve preparation.[81]

An unordinary substrate, namely, uniform SiO_2 microspheres with diameters from 300 to 700 nm was used in the synthesis of SWCNTs.[251] After the application of Fe particles on these spheres (the spheres were impregnated with a $FeCl_3$ solution), the CH_4 pyrolysis at 900 °C produced SWCNTs that formed 'nanoclaws' patterns on the spheres.

6. Methods of synthesis of catalysts

In the preparation of catalysts for the synthesis of SWCNTs, DWCNTs and t-MWCNTs, it is necessary to produce active-phase particles with sizes not exceeding 3–5 nm.[76–79,319,377,385] The methods of preparation of such catalysts are less abundant as compared with those used in the synthesis of ordinary MWCNTs and CNFs. The co-deposition of hydroxides, impregnation of fine-grain or mesoporous supports with metal salt solutions followed by the salt decomposition and the reduction of metals with hydrogen, and also the reduction of metallates, the method of 'wet combustion' and the sol–gel process were used in the catalyst preparation. Ion exchange processes were employed much more rarely.[272,386]

In particular, the co-deposition was used in the synthesis of catalysts deposited on MgO[228] and Al_2O_3.[334]

Metal salt solutions were utilised in the impregnation of zeolites[84,177,178,267,271,272,311,316,353,360] (including the thermally stable Ti-containing zeolite TS-1),[280] molecular sieve MSM-41,[80,127,128,387] MgO,[227,228,231,256,288,323,354] silica gel,[59,60,63,264,337,343] Al_2O_3 powder and foam (Refs 19, 23, 24, 30, 223, 232, 263, 264, 353), $Mg_2(OH)_2CO_3$ (Ref. 333) and powders of different compositions.[227] Catalysts were prepared by the hydrolysis of tetraethylorthosilicate in the presence of Al_2O_3 nanoparticles followed by impregnation.[213] An aerogel of Al_2O_3 impregnated with Fe and Mo salts proved its worth in the production of SWCNTs from carbon monoxide.[340] Impregnation is conventionally carried out under conditions of ultrasonic activation. Salt melts can also be used for the impregnation.[63] The impregnation is carried out together with thermal decomposition and reduction of metals.

The reduction of solid solutions $M_xMg_{1-x}Al_2O_4$ (M = Fe, Fe–Co, Fe–Ni),[158,159,169,358] $Fe_xMg_{1-x}O$ (Refs 159, 388, 389) and $Co_xMg_{1-x}O$,[159,168,216,390] $Fe_xAl_{2-x}O_3$ (Refs 159, 162, 255, 391 and 392) and also solid solutions of Co in MSM-41,[80,81,127,128,388,393–395] compounds $FeLaO_3$ (Ref. 396) and $NiLa_2O_4$ (Refs 397 and 398) was carried out. A linear correlation between the diameter of Fe particles formed in the reduction of $Fe_{0.3}Al_{1.7}O_3$ and the specific surface of the catalyst was revealed.[391] The reduction of solid solutions can also occur immediately in the course of pyrolysis.[399]

The method of 'wet combustion' consists of the preparation of a homogeneous aqueous solution of metal nitrates and an organic reducing agent, its rapid heating (an open vessel with the solution is placed into a heated furnace), evaporation of water and spontaneous ignition of the residue.[400] Thus the reaction of Fe and Mg nitrates with citric acid yielded a highly efficient catalyst for the synthesis of t-MWCNTs, namely, Fe–Mo/MgO (Mo salts were also added to the starting mixture).[31] The syntheses of a Co/MgO catalyst that involved the use of urea[216] and citric acid[342,401] were described. This method was also used in the synthesis of the following catalysts: Ni/MgO,[402–404] Co–Mo/MgO (with the use of citric acid),[352] Fe–Mo/Al_2O_3 [with the use of poly(ethylene glycol) (PEG)],[356] Fe–Mo/MgO[241] and Fe–Co/MgO (with the use of urea).[169,170]

The CNT quality and yields on catalysts prepared in such a way were largely determined by the treatment of the combustion product. In the presence of excess of a reducing agent, the catalyst contained carbon black admixtures, which were removed by annealing in air. In the Co/MgO synthesis, the annealing of the reaction products of Co and Mg nitrates with an organic reducing agent resulted in the formation of a solid solution $Co_xMg_{1-x}O$, which was difficult to reduce in the H_2 or CO medium (especially for low Co contents) and which proved inefficient in the synthesis of MWCNTs from CO.[342] A much more efficient catalyst was synthesised in the preliminary reduction of the uncalcined primary product in H_2. However, it is $Co_xMg_{1-x}O$ from which Co particles necessary for the SWCNT production were formed.[288]

Active bimetallic catalysts based on alumogel were prepared by the sol–gel method.[215,233,340,355]

The catalysts were applied on flat or patterned substrates by sputtering (*e.g.*, magnetron), aerosol deposition, the 'drop' method, spin-coating of liquid compositions followed by thermal treatment (drying, calcination, reduction), pneumatic spraying of solutions or suspensions,[258] microprinting. A method of dipping of the substrate into a solution followed by its withdrawal at a certain rate[133,318] (*e.g.*, at 4 cm min^{-1}) was also employed. This method is also suitable for the deposition of catalysts on fibres or wires.

The 'drop' method is very simple;[74] however, it can be applied only in laboratory syntheses. Spinning is more efficient and was used, *e.g.*, in the large-scale production of cantilevers with CNTs[369] and in the growth of large CNT arrays.[142] Particles of Al_2O_3 (Ref. 142) and polysiloxane solutions are sometimes added to the composition to be deposited.[260] This method allows one to prepare size-uniform Fe_2O_3 particles that are used in the synthesis of SWCNTs with diameters around 1 nm.[405]

A unique version of the spinning method was used.[228] A homogenised ethanolic solution of Mg and Fe nitrates and PEG was spread over the substrate, which rotated at 3500 rpm. After evaporation of ethanol, the substrate was placed into a furnace heated to 600 °C.

In the evaporation method, a block co-polymer is often added to the starting solution.[173] Dilute (0.01 mass %) ethanolic solutions of metal nitrates are commonly used.[133,134] Thus a solution of $Fe(NO_3)_3 \cdot 9\,H_2O$ in propan-2-ol was utilised.[268] Immersion of the substrate for a certain time into an aqueous $FeCl_3$ solution with preliminarily added $NH_2OH \cdot HCl$ was described.[303]

Nanosize catalyst particles can be prepared by the thermal decomposition of salts. Such particles are stored in organic solvents and deposited by spin-coating.[286] Monodispersed particles Fe–Mo with diameters of 3–14 nm were formed in the thermal decomposition of carbonyls of these metals in a medium of long-chain carboxylic acids or amines.[370] Iron particles of different diameters were synthesised by the thermal decomposition of $Fe(CO)_5$ solutions in dioctyl ether in the presence of oleic, lauric or caprylic acids.[219] Nickel formate, which forms uniform nickel particles upon decomposition, is a good precursor of Ni catalysts.[222,406] A catalyst based on Fe particles was prepared by the plasma treatment of $Fe(C_7H_{15}COO)_3$ deposited on the substrate by spin-coating.[407] The methods based on the thermal decomposition of compounds containing metal clusters deserve special mention, *e.g.*, $[H_xPMo_{12}O_{40}] \subset [H_4Mo^{VI}_{72}Fe_{30}.$ $.(CH_3COO)_{15}O_{254}(H_2O)_{98}] \cdot 60\,H_2O$ (contains 84 Mo atoms and 30 Fe atoms), $Na_2[\{Mo^{VI}(Mo^{VI})_5\}_{12}\{Mo^{V}_6Fe^{III}_{24}\}(CH_3COO)_{20}.$ $.O_{258}(H_2O)_{84}] \cdot 150\,H_2O$ (78 Mo + 24 Fe), $[\{(Mo^{VI})Mo^{VI}_5.$ $.O_{21}(H_2O)_6\}_{12}\{Fe^{III}(H_2O)_2\}_{30}] \cdot 150\,H_2O$ (72 Mo + 30 Fe) and their analogues [http://www.hydrogen.energy.gov/pdfs/review05/stp_35_liu.pdf].

A procedure that involves the co-deposition of salts of two metals in the course of slow evaporation followed by thermal decomposition was used.[255]

The inverse micelle method[304,408–410] is usually combined with the deposition of a colloid solution by dipping, spinning or pneumatic spraying.

Very small (1–2 nm) individual catalyst particles of the same size may be supported with the use of ferritin, apoferritin[2,114,226,411–413] and ferritin-like proteins[414] or dendrimers.[302]

When annealed in an inert medium, thin metal films sputtered over flat substrates are transformed into islets or nanosize particles. The sputtering was performed using a magnetron,[194,195] by electron- or ion-beam evaporation[282] and the laser ablation of the target.[317] Usually, the thickness of the deposited film did not exceed several atomic monolayers, for example, corresponded to 5×10^{15} atoms per cm^2 (Ref. 92). According to a publication,[140] the sputtering and annealing of a Co-catalyst film with a thickness of 0.5–1.0 nm resulted in the formation of cobalt particles measuring 3–7 nm that favoured the growth of a dense 'forest' of SWCNTs. The results obtained in the plasma-enhanced pyrolysis of a mixture of NH_3 and C_2H_2 (Ref. 415) are quite demon-

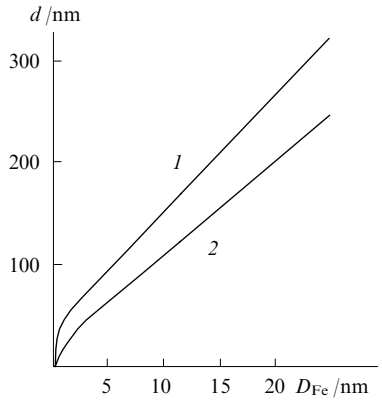


Figure 8. Dependence of (*1*) the average diameter of islets formed in film annealing and (*2*) the average diameter of filiform carbon particles grown on islets on the initial thickness of the sputtered Fe film (D_{Fe}) (according to Wang *et al.*[416]

strative (Fig. 8, Ref. 416). The pyrolysis products synthesised under similar conditions differed not only in the diameter but also in the morphology, namely, SWCNTs, DWCNTs, t-MWCNTs, MWCNTs and, finally, CNFs were obtained.

In the preparation of MWCNTs, it was found that on a catalyst islet, several (up to 7–8) tubes could be grown with diameters much smaller (2–3-fold) that the islet diameter.[417] Moreover, the smaller the diameter of the islet the smaller number of tubes can grow; this is why the elucidated feature does not always hold for t-MWCNTs.

A procedure that allows the determination of the optimum thickness of a layered film in few experiments has been developed.[362] Combinatory methods were proposed for the determination and optimisation of the deposition conditions.[319,418,419] Thermodynamic conditions for the transition of films (5-, 10- and 20-nm thick) into particles were considered.[189] According to thermodynamic calculations, in the case of Ni, the radius of a particle formed exceeded the thickness of the deposited film by a factor of 1.5.[420]

The deposition can be performed through masks to promote the growth of CNTs on definite areas on the substrate and their organisation into one or another type of structures (*e.g.*, see Refs 2, 136 and 291). Ordered arrays of SiO_2 microspheres can serve as a sort of masks in the preparation of individual SWCNTs or their bundles.[341] Polymeric spheres with diameters from 1 to 125 μm can also be used.[421,422]

Organometallic polymers deposited on the substrate as thin films can serve as the precursors of catalysts. Particularly, a polyferrocenylsilane block copolymer was used in the synthesis of SWCNTs.[423]

The synthesis of CNTs on catalysts deposited by the microprinting technique is of special interest (Fig. 9). In microprinting, polymethylsiloxane stamps are commonly used.[87,137,372] This method is relatively simple and versatile; it allows one to prepare a considerable number of copies on relatively wide (more than 1 cm^2) areas with the resolution varying from below 100 nm to above 1 μm. The catalyst deposition involves the use of 'ink', *i.e.*, alcohol (ethanol, isopropyl alcohol) solutions of metal nitrates, *e.g.*, $Fe(NO_3)_3 \cdot 9H_2O$ containing Al_2O_3 or SiO_2 particles and MoO_2Cl_2 or $MoO_2(acac)_2$ additives.[87,137,372] (The details can be found in numerous publications, *e.g.*, Refs 23, 99, 130, 138, 230, 257, 275, 273, 375, 424 and 425.) By changing the concentration of the applied solution and the pyrolysis temperature, it is possible to regulate the CNT diameter.[275] A gel catalyst was used in the synthesis of t-MWCNTs.[426]

The deposition of Fe nanoparticles of the same size (1.7 ± 0.6 nm) on the substrate surface with the accuracy of their positioning of ±5 nm was described.[377] An organometallic compound mixed with the resist served as the catalyst precursor. The diameter of SWCNTs formed was 1.3 ± 0.4 nm.

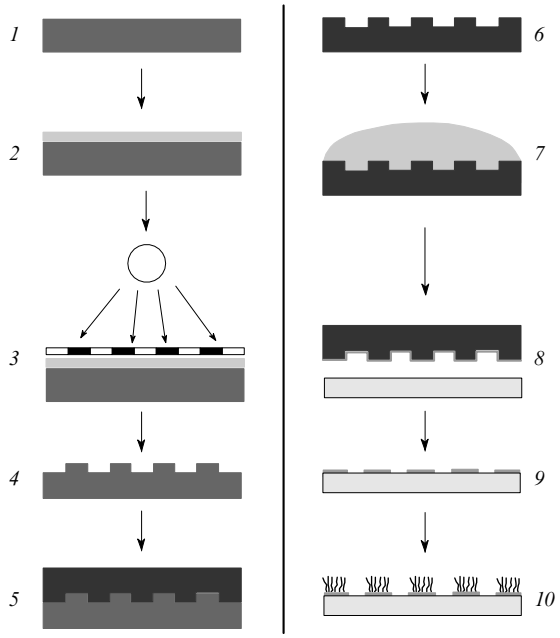


Figure 9. Sequence of steps in the production of stamps, microprinting and CNT growth.
(*1*) Substrate, (*2*) substrate with resist, (*3*) exposure with the use of a mask, (*4*) etched structure, (*5*) elastomer casting, (*6*) elastomer stamp, (*7*) inking of the stamp, (*8*) microprinting on the new substrate, (*9*) printed pattern, (*10*) growth of CNTs.

The positional packing of SWCNTs on a substrate can sometimes be carried out by an unexpected method. For instance, it was found that lithographically deposited islets of $Pb(Zr_{0.5}Ti_{0.5})O_3$ are capable of sorbing the Fe–Mo catalyst particles and initiating the local growth of tubes.[225] In this case, the stronger sorption of catalyst particles could be associated with the porous structure of islets. In the pyrolytic synthesis of CNTs on quartz or oxidised silicon surfaces, the localisation of tubes involves the creation of active sites by mechanically damaging the substrate (scratching).[427]

Studies devoted to the initial stages of CNT growth in the hot-filament activated pyrolysis demonstrated [428] the important role of the catalyst pre-treatment stage in the preparation of finer particles.

MWCNTs can be used as the substrate.[413]

7. Mechanism and kinetics

The catalytic growth of CNTs proceeds by the following three macroscopic mechanisms: base growth, tip growth and branched growth mechanisms.

In the base growth mechanism, a catalyst particle remains on the substrate. In the tip growth mechanism, the particle is detached from the substrate and removed from it as the CNT grows and the tube tip moves away from the substrate or the catalyst support. The branched growth can be a version of either base or tip growth mechanisms and is typical of MWCNT growth. In the first case, the catalyst particle is split to form a dendrite structure;[429] in the second case, octopus-like structures are formed. Sometimes, branched MWCNTs grow from a single catalyst particle.[430] The base and tip growth scenarios can occur simultaneously to form products with different morphology.[29,431] In many experiments, catalyst particles were observed to change their shape and size in the course of the process or to be in continuous or impulsive motion.

The base growth mechanism is typical of the preparation of SWCNTs, where the scheme of transformation of carbon or carbon-containing substances is described by a sequence vapour – liquid – solid.[432]

The rate of this process depends on several factors (seven factors have been proposed[296]), among which two most important factors can be outlined. First, the rate is determined by several reactions that occur both on the catalyst surface and in the gas phase. Precisely this factor was used for explaining the effect of the aforementioned 'pre-catalyst' (conditioning catalyst) on the formation rate and yield of SWCNTs.[249] An equally bright example of the effect of gas-phase reactions on the overall process of CNT formation is the experimental fact that the length of a thin-film catalyst sample can affect the rate of the process.[270] Thus, on a $Mo-Fe/Al_2O_3$ sample with the film dimensions of 1×1 cm, no CNTs were formed from CH_4, whereas the growth of a CNT 'forest' was observed on a sample of 1×15 cm. Moreover, the process strongly depends on the gas flow rate and the position of the substrate in the path of gases in the reaction zone.

Second, the rate is determined by the size of catalyst particles. In addition, it is important that the changes in the conditions of the process can cause changes in the CNT morphology.

On the surfaces of formed CNTs, secondary processes can occur. Thus the tubes can become thicker due to the deposition of amorphous carbon, polyaromatic compounds or graphitised particles on their walls; moreover, the increase in the temperature and the duration of the process results in the active growth of such deposits and substantially increases the CNT diameter.

This is why the catalytic pyrolysis differs substantially from the processes of chemical vapour deposition, although these processes are often confused in the literature. The optimum conditions for the CNT synthesis are developed in those cases where the temperature is sufficiently high for the rapid growth of tubes but too low for the formation amorphous carbon and other undesired forms.

The pyrolysis proceeds at different conditions on a powder catalyst, on a substrate with the catalyst deposit (the formation of 'forest') and on porous membranes of the Al_2O_3 type. Thus on a substrate, the secondary processes can be suppressed by building a 'shelter' over the catalyst particles.[270]

Table 8 shows the experimentally measured rates of the linear growth of CNTs under different conditions. As follows from these data, the rates vary in a very wide range, *viz*., from 0.2 to 660 μm min^{-1} [for the MWCNT growth, the rate was found to vary in the ranges of 60 – 600 μm min^{-1} (Ref. 436) and 0.4 – 50 μm min^{-1} (Ref. 298)]. This entailed no changes in the kinetics of formation of SWCNTs and MWCNTs. It is noteworthy that some studies[67,437] described the synthesis of high-quality SWCNTs that grew at a very high rate. The authors of those studies have explained this fact by the effect of small amounts of H_2O vapour that favour the prolongation of the catalyst service life. Still higher growth rates of SWCNTs with diameters of 4 – 6 nm (480 μm min^{-1}) were observed in the decomposition of CO at 880 °C.[68,349] Ultralong SWCNTs were grown at a rate of 660 μm min^{-1}.[72] Ultimately, at 700 °C the record-breaking rate of the MWCNT growth from C_2H_2, namely, 6000 μm min^{-1} was reached (although in the 1st second).[292]

It should be noted that very high rates of MWCNT growth (60 – 600 μm min^{-1}) were observed at rather low pressures.[436] The interpretation of these results requires their refinement.

So far, it is difficult to explain the wide deviations in the linear rates of tube growth found in different studies and relate the linear growth rates to the catalyst efficiency (a relative amount of CNTs formed before complete poisoning of the catalyst).

As seen in Fig. 10, the rate of CNT growth in the plasma-enhanced pyrolysis is associated with their diameter, the latter being determined by the thickness of the deposited metal-catalyst

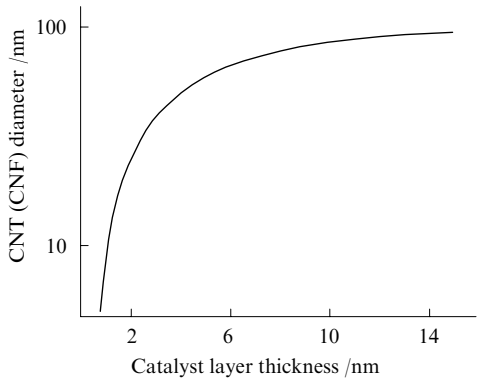


Figure 10. Effect of the average outer diameter of CNTs and CNFs on the thickness of sputtered Fe, Co or Ni films during the plasma pyrolysis.

Table 8. Linear growth rate of CNTs.

Reagent	Catalyst	T /°C	p /atm	Enhancement method	Morphology	Diameter /nm	Growth rate /μm min^{-1}	Ref.
CH_4	NiO_x	700	1.0	plasma	MWCNTs	50 – 80	0.2	433
CH_4+H_2	Fe – Ti	600	0.1	"	t-MWCNTs	~ 5	~10	197
CH_4	Fe	700	2.6×10^{-2}	"	MWCNTs	~ 20	5.4 – 16.8	184
C_2H_2	Fe	750 – 950	1.0	thermal	MWCNTs	30 – 130	0.5 – 2.0	434
C_2H_2	Fe	750	(1.0)	"	MWCNTs	10 – 15	20	291
C_2H_2	Fe – Mo	730	1.0	"	SWCNTs + MWCNTs	1 – 20	> 17	362
C_2H_2	Ni	480	$(2.6-13.0)\times10^{-5}$	"	MWCNTs	not specified	2.1 – 2.4	293
C_2H_2	Ni	480	$\leqslant 1.3\times10-5$	"	SWCNTs	3.5	0.4 – 0.5	293
$C_2H_2+Ar+H_2$	Fe – Mo	535 – 600	(1.0)	"	t-MWCNTs	not specified	12 – 30	298
$C_2H_2+Ar+H_2$	Fe – Mo	700	(1.0)	"	DWCNTs + SWCNTs	not specified	13.2	298
C_2H_2	Co – Ni	800 – 900	1.0	"	MWCNTs	~ 200	0.5	273
C_2H_4	Ni(Fe; Ni – Fe)	850 – 1000	3.2×10^{-4}	plasma	MWCNTs	10 – 50	0.25	176
C_2H_4 (see [a])	Fe	750	1.0	thermal	SWCNTs	1 – 3	250	67
C_2H_5OH	Co – Mo	800	1.3×10^{-2}	"	SWCNTs	1.0 – 2.0	0.3	134
C_2H_5OH	Fe	900	(1.0)	"	SWCNTs	1.3 – 2.2	660	72
$B_2H_6+CH_4+N_2+H_2$	–	600 – 650	0.02	plasma	nanofibres [b]	50 – 400	0.17	435

[a] 1 vol.% – 13 vol.% C_2H_4 in a mixture Ar (He) – 40 vol.% H_2 in the presence of additions of 0.0175 mass % H_2O vapours. [b] Nanofibres of boron carbonitride.

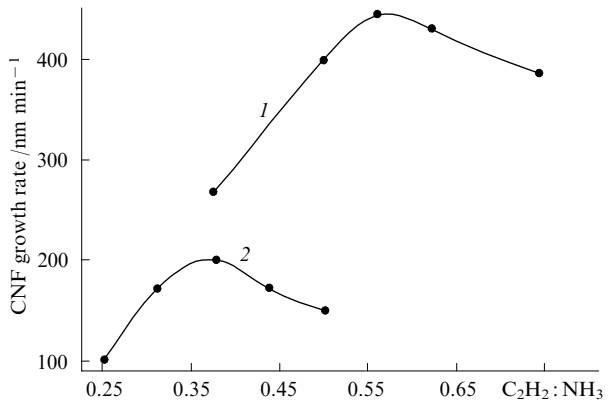


Figure 11. Effect of the gas mixture composition and the set-up geometry on the CNF formation rate during the plasma pyrolysis.
Nozzle diameter: (*1*) 1 mm and (*2*) 5 nm. [Reproduced with permission of the Elsevier Publishers according to V I Merkulov, A V Melechko, M A Guillorn, D H Lowndes, M L Simpson *Chem. Phys. Lett.* **361** 492 (2002).]

film.[195] In the $C_2H_2-NH_3$ mixture, the growth rate of nanofibres depended on the set-up design (the distance between the plasma source and the substrate) and on the reactant ratio (Fig. 11).[41]

The temperature of the SWCNT growth also depends on the diameter of catalyst particles. Thus, for Fe particles measuring 10–30 nm, tubes were formed at 900–950 °C, whereas for the 5-nm particles, the tubes started to form at 780 °C.[195]

Only few papers show the classical kinetic parameters of processes involved in the pyrolysis of organic substances to yield CNTs. Thus the activation energy (E_a) was assessed as 71–73 kJ mol^{-1} (Ref. 438) for the methane pyrolysis on a Ni/La_2O_3 catalyst to yield CNFs and as 95–98 kJ mol^{-1} (Ref. 244) for the same process on a Co–Mo/Al_2O_3 catalyst to form MWCNTs with diameters of 10–30 nm. At the same time, E_a of the formation of a pyrolytic carbon deposit on a Fe catalyst at 500–600 °C was much higher being equal to 150 kJ mol^{-1} (Refs 439 and 440). It was noted that the latter value is close to the E_a of the Fe_3C formation equal to 158 kJ mol^{-1}.

The formation of SWCNTs in the CH_4 pyrolysis on different catalysts at 900 °C has two periods, namely, a short period of a fast mass increase and a long period of a relatively slow mass gain.[301] The catalyst Fe–Mo/Al_2O_3–SiO_2, which was prepared by gelation of a SiO_2 sol in the presence of Al_2O_3 nanoparticles followed by impregnation of the calcined gel with Fe and Mo salts (the molar ratio of 1.00 : 0.17), proved to be the best for this reaction. Among all catalysts studied, this one has the largest specific surface area (S_{sp} = 196 m^2 g^{-1}) and the greatest pore volume (0.79 ml g^{-1}).

The results obtained by Choi *et al.*[302] were processed by Vinciguerra *et al.*[441] They described the reaction rate in terms of the extrusion-diffusion model and derived an empiric equation that adequately describes the experimental data but contains no standard kinetic parameters.

Our calculations based on experimental data obtained [255] have shown that the reaction order in CH_4 changed from 1.24 to 1.77 being in average 1.45. It seems that the deviation of the reaction order from unity is associated with the increase in the contribution of non-catalytic decomposition of CH_4 with the increase in its partial pressure. The formal reaction order of the pyrolysis to yield CNFs was also shown [438] to depend on the temperature and to increase from 1.05 at 600 °C to 1.3 at 700 °C. According to the results of another study,[439] the order of this reaction is equal to 1.

A threshold value of CH_4 partial pressure (0.4 atm at 850 °C) above which the rate of the catalytic pyrolysis to yield SWCNTs becomes independent of the partial pressure was observed.[233] Presumably, such behaviour is associated with the transition of the process into the region where the rate is limited by the surface or volume diffusion. It cannot be ruled out that the thermodynamic restrictions may also affect the reaction rate.

The kinetics of catalytic pyrolysis of CH_4 and C_2H_2 was also discussed by Nagy *et al.*[243]

Pulsed hydrocarbon feeding is one of the ways for the improvement of CNT purity and yield in the catalytic pyrolysis.[235, 368] However, this can also decrease the average rate of the process; hence, this method requires optimisation.

Somewhat different mechanisms are typical of the acetylene pyrolysis. The use of an interesting method of 'marks' allowed the kinetic parameters of the MWCNT growth to be determined in the pyrolysis of C_2H_2 on Fe islets.[297] It was shown that after a short interruption of the pyrolysis process due to the C_2H_2 feeding cutoff (by replacing it by Ar) followed by the resumption of the process on the grown tubes ('forest'), clear boundaries (marks) were left which could characterise the growth rate if one took into account the duration of individual growth stages. The position of 'marks' and the length of grown segments were determined using a scanning electron or optical microscope. As a result, it was found that the activation energy of the process was 159 ± 5 kJ mol^{-1} in the temperature range of 873–953 K (the partial pressure used in the calculation of the E_a value was not shown [297]) and the reaction order in C_2H_2 was unity for the C_2H_2 partial pressure of 2–10 kPa and a temperature of 953 K. The linear rate of CNT growth reached 20 μm min^{-1}. The E_a value of the MWCNT growth from C_2H_2 on a Fe catalyst at 800–1100 °C was 125 kJ mol^{-1}.[442]

The obtained E_a values made it possible to abandon the earlier assumptions that the process is limited by the carbon diffusion in a liquid or quasiliquid catalyst particle (a solution of carbon in a metal),[443] because E_a of this process should be substantially lower than the found values. It was assumed that a surface reaction at the gas–catalyst interface is the limiting stage of this process. At the same time, the experimentally observed involvement of the liquid phase in this process cannot be denied.[444, 445]

Yet another, optical method was used for measuring the growth rate of the MWCNT 'forest' in the C_2H_2 pyrolysis.[298, 446] A multilayer film Mo(0.2 nm)–Fe(1 nm)–Al(10 nm) on Si served as the catalyst, the gas mixture contained 0.25% C_2H_2, 16.62% H_2 and 83.13% Ar. It was shown that with the increase in the temperature from 535 to 900 °C, thinner CNTs were formed, *viz.*, 6–10-walled CNTs were mainly formed at 575 °C, DWCNTs predominated at 725 °C and the fraction of SWCNTs increased at higher temperatures. The highest growth rate ($\sim$12 μm min^{-1}) was observed at 700–730 °C; the effective E_a of this process in the low-temperature region was $\sim$2 eV ($\sim$190 kJ mol^{-1}). Under isothermal conditions, the pyrolysis occurred with deceleration. With the increase in the C_2H_2 concentration, this deceleration was more pronounced and the CNT growth stopped at a smaller ultimate length of tubes (the 'forest' height).

A simplified mechanism of C_2H_2 pyrolysis on a Fe catalyst involves the C_2H_2 dissociation on the Fe surface, the dissolution of carbon in the near-surface disordered 'fused' Fe layer and the diffusion of C atoms in this layer to the CNT formation site (with the diffusion coefficient that at 1000 K exceeds the diffusion coefficient in solid Fe by 3 orders of magnitude). CNTs grow until the near-surface carbon-containing layer is distributed throughout the surface of Fe particles. The equations that adequately describe the experimental results were derived.

Yet another method, laser diffraction was proposed [447] for measuring the kinetic parameters of the CNT 'forest' growth. The results obtained [447] point to the exponential increase in the CNT length in time. According to the field emission characteristics,[448] the growth rate of MWCNTs in the electric field measured at a low pressure (less than 10^{-2} mbar) was in the range of 60–600 μm min^{-1}. With the increase in the C_2H_2 partial pressure, the MWCNT growth rate increased.[448]

The addition of H_2 reduced the amount of amorphous carbon, favoured the decrease in the MWCNT diameter and increased the linear growth rate 1.85-fold.[276]

The growth rate of the CNT 'forest' from a mixture of C_2H_2 and NH_3 (the volume ratio 1 : 3, temperature 700 °C, total pressure ~0.2 kPa, or ~2 Torr) on a Ni catalyst increased in the initial plasma-enhanced stages, reached its maximum (6.5 – 8.5 μm min^{-1}) and began to decrease upon reaching the CNT length of ~2 μm.[449] Such kinetics of the process is associated with the mechanism of the CNT growth that involves the surface diffusion. Presumably, the process decelerates when the tube length exceeds the diffusion path.

The formation of the MWCNT 'forest' in the plasma-enhanced process can proceed at the substrate temperature of 120 °C.[283, 450] The E_a value at 120 – 527 °C turned out to be very low (22 kJ mol^{-1}) as compared with the value typical of the heat-activated process (116.4 kJ mol^{-1}).[451] This means that the process is limited by the surface diffusion of carbon over Ni particles. This mechanism can operate on Fe, Ni and Co catalysts in the pyrolysis of not only C_2H_2, but also CH_4.[452] It should be noted that a comparatively low E_a value (37 kJ mol^{-1}) was also found for the SWCNT formation at 1050 – 1200 °C under conditions of the laser-oven sublimation, which was associated with the following mechanism: vapour – liquid – solid.[453]

The MWCNT formation was observed *in situ* using transmission electron microscopy,[292, 293] which allowed the researchers to propose a realistic growth model. The tubes grow on individual faces of a Ni particle and with the highest rate on its (100) face. Catalyst particles rotate or are fused and recrystallised; hence, the growth direction can change.

The kinetics of ethylene pyrolysis was less thoroughly studied than that for methane; however, it is known that the rate of this reaction can be very high.[67, 437] The catalyst efficiency (the amount of CNTs formed per catalyst mass unit before its complete poisoning) in a process described by Japanese authors was 500 g g^{-1}, which exceeded the catalyst efficiency in the HiPco process (thermal decomposition of CO in the presence of volatile Fe carbonyl as a catalyst precursor) by two orders of magnitude. At the same time, the product contained less than 0.013% Fe.

The increase in the pyrolysis temperature narrows the region of C_2H_4 partial pressures at which SWCNTs are formed (Fig. 12).[180]

The relative rate of the ethanol reaction with metal clusters depends on the metal nature and the cluster size (Fig. 13).

Many studies[454 – 474] were devoted to the simulation of CNT formation; however, most of them dealt with high-temperature methods, namely, the graphite sublimation in an electric arc and in

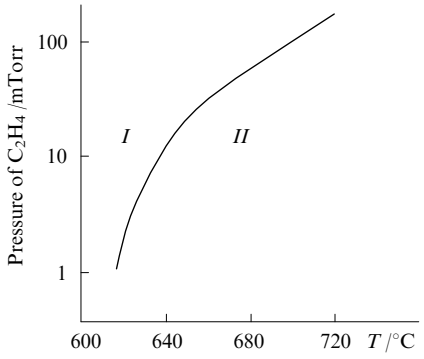


Figure 12. Effect of the pyrolysis conditions on the morphology of CNTs formed.[180]
(*I*) A region in which no SWCNTs could be obtained, (*II*) a region of SWCNT formation. (Reproduced with permission of the American Chemical Society.)

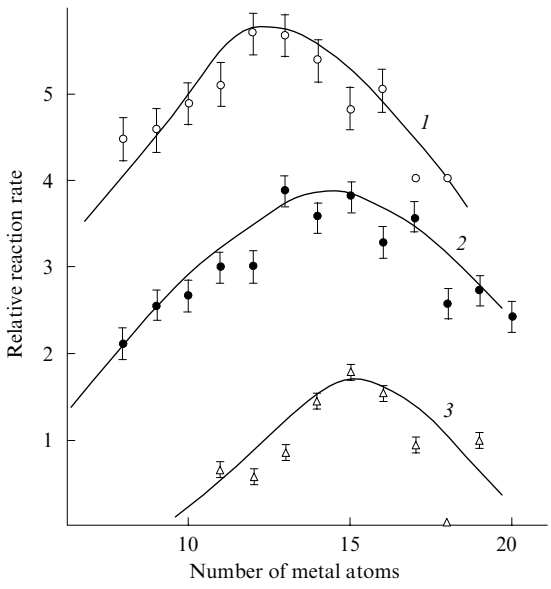


Figure 13. Relative reaction rate of ethanol vapours with clusters of (*1*) Fe, (*2*) Co and (*3*) Ni [http://www.photon.t.u-tokyo.ac.jp/~maruyama/papers/04/Inoue_JCP.pdf].

laser radiation. Particularly, a process in which mobile Ni atoms located on the tip of a growing CNT play the active role was considered.[454] Later,[456] a basically different mechanism of the effect of Ni atoms was substantiated and an attempt was undertaken to resolve the contradictions between these mechanisms.

A relationship between the Fe cluster size, the CNT diameter and the number of CNT walls was demonstrated.[455, 463] The processes of heat and mass transfer were considered as applied to the tip mechanism of CNT growth.[469]

The theoretical analysis of the catalytic pyrolysis of CH_4 mixed with H_2 arrived at the assumption that this method of SWCNT synthesis is a very difficult task.[474] As follows from the experimental data mentioned above, this conclusion should be corrected. Nonetheless, a model that takes into account not only the chemical stages of the process but its hydrodynamics and the heat transfer has been developed.[475] The authors of this model cited numerous publications and estimated the kinetic parameters for 47 gas-phase reactions, 19 reactions on powder Co catalysts and 15 surface reactions resulting in amorphous carbon, which may be useful for further calculations.

A thermodynamic model of the formation of MWCNTs with diameters of 5 – 35 nm in the C_2H_2 pyrolysis (this reaction releases a great amount of heat) assumes the presence of gradients of temperature and carbon concentration on a catalyst particle.[470] It was shown that the growth rate should be inversely proportional to the CNT diameter (d). This corresponds to experimental results,[434] although it was shown earlier[476] that for CNFs the rate is inversely proportional to $d^{0.5}$.

The formation of a liquid external layer on a catalyst particle and its effect on the SWCNT formation was discussed.[477] The SWCNT growth proceeds until the catalyst particle, which represents an eutectic metal – carbon mixture, remains liquid and stops when the catalyst becomes solid.

Presumably,[478] the key stage in the CNT synthesis is the formation of tube nuclei. It this case, the SWCNT growth is possible only on liquid catalyst particles.

The choice of the catalyst affects its specific efficiency. Thus under equal conditions, the alumogel-supported catalyst exhibited the selective efficiency with respect to SWCNTs at least 5-times higher (6 g g^{-1}) than a catalyst of the same composition prepared by impregnation of Al_2O_3.[215] The efficiency of ordinary

catalysts in the SWCNT formation was ~40 mass % (or 0.40 g g^{-1}).[213] The catalyst efficiency in the CoMoCAT process was ~0.25 g g^{-1}. The Fe–Mo/MgO catalyst exhibited the highest efficiency in the synthesis of t-MWCNTs (3000 mass %, or 30 g g^{-1}).[28]

It was noted [434] that the increase in the pyrolysis temperature accelerates the growth of MWCNTs in their length, and their average diameter increases. The hydrocarbon partial pressure affects both the pyrolysis rate and the morphology of CNTs prepared. The MWCNT diameter changes with variations in the total pressure in the system.[479] The length and the diameter of growing SWCNTs can be controlled by changing the duration of the process or by adding a promoter.[83] The effect of the temperature and the hydrocarbon partial pressure on the CNT morphology was also studied by the other researchers.[480] By the example of the C_2H_2–NH_3 mixture, it was shown that the decrease in the pressure favours the transition from bamboo-like nanofibres to cylindrical MWCNTs.[481]

The catalytic decomposition of carbon oxide decelerates in time,[340] and the product yield is proportional to $t^{0.5}$. The rate of MWCNT formation from the CO–H_2 mixture and the tube quality depended on the medium in which the catalyst based on the sputtered Fe–Co–Ni alloy was pre-treated.[364] Thus catalysts pre-treated in vacuum demonstrated poorer properties than the catalysts treated in Ar or N_2. After heating in these gases, the linear rate of MWCNT growth at 580 °C was about 0.4 μm min^{-1}, whereas after heating in vacuum the growth rate was ten times lower.

According to calculations,[346] in the CO decomposition, SWCNTs can grow by the adsorption of molecules on the open ends of tubes; catalysts favour the formation of nanotube nuclei.[346]

IV. Conclusion

While this review was in the stage of preparation for publication, several new publications have appeared that deserve mention. These are the materials of the 7th International Conference on Scientific Application of Nanotubes,[482] two Russian books [483, 484] and a monograph [485] in English.

The 7th International Conference on Scientific Application of Nanotubes in which only one participant from Russia took part confirmed in a certain sense the trend mentioned in the beginning of this review. Thus analysing the posters presented in the Session devoted to the CNT synthesis, Professor A Windle (Cambridge University) noted that the majority of the 76 reports presented were devoted to the catalytic pyrolysis. Moreover, the majority of reports dealt with supported catalysts and heat-activated processes. Among metal catalysts, attention was focused on Fe, followed by Co and Mo; the main substrates were SiO_2 and Al_2O_3, while the starting compounds included C_2H_5OH, CH_4, C_2H_4 and CO (shown in the order of decreasing citation frequency). The latter factor was apparently associated with the domination of scientists from Japan who focus their attention on the ethanol pyrolysis.

Windle has formulated the following 'five questions of science to answer:

1. Does surface of metal particle catalyse: (a) decomposition of hydrocarbon, (b) decomposition of futher metal precursor?

2. What is metallurgy of nano particles? (a) Melting point, surface melting, internal pressure, (b) carbon solubility (as function of radius), (c) phase diagram with carbon (modelling + experiment).

3. Does a region of metal particles have to remain free of a graphene coating? If it doesn't, is that a killer?

4. What determines rate of growth? (a) Diffusion rate in metal (surface), (b) supply of carbon to particle, (c) shape changes due to flow of small (not necessarily molten) particles, (d) interface modifiers such as sulphur, (e) do we have a reliable E_a yet?

5. What determines type and size of nanotube? (a) Metal particle diameter and/or composition, (b) temperature, (c) feedstock, (d) what is the difference in growth mechanism between (say) a double wall tube and an 8 ish layer multi-wall tube of similar diameter?'

Two Russian books are written from absolutely different standpoints and contain complementary information, *viz*., the monograph [483] is largely devoted to the quantum chemistry of carbon nanotubes, a subject absent in the textbook.[484] At the same time, the classification of nanotubes, their properties, synthesis and applications are described more comprehensively in the textbook [484] with substantial attention paid to pyrolytic methods.

The textbook [484] mentions the following most important challenges (some of them are beyond the frames of the present review):

— elucidation and mathematical description of the mechanism of formation of CNTs with different morphology and structure under different conditions;

— determination of the functional relationship between the kinetics of CNT formation and their morphology and structure;

— the search for the methods for regulation and control over the CNT morphology and structure during their syntheses;

— elaboration of methods for deep and selective as well as local functionalisation of CNTs;

— elucidation of mechanisms of the behaviour of CNTs with different morphology and structure in colloid solutions;

— determination of the influence of CNTs and modified CNTs on organisms.

According to the aforementioned book,[484] the most important unsolved technological problems include the following directions:

— development of a process for efficient industrial production of CNTs with the same morphology and structure;

— development of a process for CNT isolation (grading) with respect to morphology, structure and size, that allows scaleup;

— elaboration of methods for preparation of stable dispersions of individual CNTs in aqueous and organic media;

— the search for the methods of introduction of individual CNTs into polymeric, ceramic, and metal matrices and preparation of CNT composites;

— development of methods for the production of macromaterials from CNTs, especially, macrofibres and nanopaper with the oriented packing of individual tubes;

— development of methods of commercial production of functional devices with CNTs, namely, electron emitters, transistors, sensors, actuators, *etc*.

The third book,[485] which has an intriguing title, is destined, according to its summary and contents, for a learned reader and embraces both the main information on the subject, the latest achievements and potential application fields.

In the conclusion, I would like to express my gratitude to I V Anoshkin for making it possible for me to get acquaintance with the materials of the 7th International Conference on Scientific Application of Nanotubes, to Nguyen Tran Hung for his help in the preparation of this review and also to all colleagues who have sent me copies of their papers.

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