Review

The use of organometallic transition metal complexes in the synthesis of shaped carbon nanomaterials ☆

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ABSTRACT

A review of the use of organometallic complexes in the synthesis of shaped carbon nanomaterials (SCNMs), in particular carbon nanotubes (CNTs) has been undertaken. This review reveals that a limited number of organometallic complexes have been used as catalysts (typically ferrocene, $Fe(CO)_5$) to make carbon materials that have distinctive shapes. Depending on the reaction conditions employed, ferrocene can be used to synthesize single walled (SWCNTs), double walled (DWCNTs) and multiwalled nanotubes (MWCNTs) as well as fibres and other SCNMs. The type of reactor used as well as the reaction conditions (temperature, pressure, gas flow rates, etc.) and the presence of hydrogen and heteroatoms (N, O, S, P, etc.) also play a role in determining the final carbon types (and their sizes) that have been synthesized. The influence of the various chemical and physical factors on the carbons produced are discussed. The current mechanism used to explain the formation of CNTs is described.

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Content

1. Introduction

Whilst numerous organometallic complexes were known prior to 1950, the synthesis of ferrocene (FcH) is regarded as the pivotal event that led to the field of organometallic chemistry as practiced today [1]. The realisation that transition metal–carbon bonds were indeed facile to make and had reasonable stability was coupled to the implementation of appropriate characterization techniques that were being developed and used at the time [2]. These included IR and NMR spectroscopy as well as X-ray crystallography [3]. The clear link between homogeneous catalysis and organometallic chemistry has ensured the continued interest in this area of chemistry [4].

A recent development in the field of organometallic chemistry has been the use of organometallic complexes in the high yield catalytic synthesis of carbon nanotubes (CNTs) [5]. The development of appropriate characterization techniques, for example transmission and scanning electron microscopes (TEM, SEM), has assisted in the development of this field. Again, the area is driven by the potential uses of CNTs; in this instance, their use in interconnects, nanosensors, nanobalances, field emission displays and in the manufacture of strong and lightweight composites, etc. Indeed, today CNTs are made industrially in the tons pa level [6].

CNTs can be made by a variety of procedures and these include numerous variations of the arc-discharge [7], the laser ablation [8], and the CVD (chemical vapour deposition) processes [9]. While organometallic complexes can be used to make the catalysts required for the former two synthesis methods, the catalysts are generally made from metals or metal salts. Both these methods do produce relatively pure CNTs but are currently not easy to scale up to industrial levels of production.

The CVD processes, by contrast, do allow for easy scale up. There are two main approaches to the CVD synthesis of CNTs: one method entails passage of a gas phase carbon source over a supported catalyst whilst in the other both the catalyst and carbon source are in the gas phase. This latter process is called the 'floating catalyst' method. The catalyst used in the first CVD method can be derived from any metal source including an organometallic complex. But it is the floating catalyst method that typically requires volatile organometallic complexes to make CNTs. Remarkably, much of the work in this area of synthesis entails the use of very simple organometallic complexes (ferrocene and $Fe(CO)_5$) and the emphasis has not been on studying ligand effects on CNT synthesis. Indeed most studies to date involve catalysts purchased from manufacturers with studies focused on variation of CNT synthesis parameters or on reactor design.

It is to be noted that another type of CNT synthesis method has also been developed in recent years that does not use a gas flow system. Rather the reaction to make CNTs takes place in a closed container (e.g. autoclave or sealed quartz tube), at elevated pressures. Typically, in this method, organometallic complexes (at times containing an external carbon source) are used as starting materials to synthesize CNTs [10].

CNTs are but one type of carbon nanomaterial that is synthesized by the procedures described above, and the control of the morphology and type of CNT produced is a non-trivial task. Using typical reaction conditions, it is highly unusual to obtain >95% pure material in any current synthetic process. Thus, in a typical synthesis it is not uncommon to synthesise a mixture of single walled (SW), double walled (DW) and multiwalled (MW) CNTs with a range of diameters, lengths and helicities, together with amorphous carbonaceous materials and carbon fibres. Under appropriate conditions, it is also possible to synthesise carbon horns [11], spheres (filled [12], hollow [10i,13]), onions [14] and cages [15] or metal filled tubes or core shell spheres [16]. Some of these various shaped materials are shown in Fig. 1. Much work is still needed to unravel the chemistry that is taking place and that leads to control of the synthesis of these various carbon nanostructures.

All of these shaped carbon nanomaterials (SCNMs) are of interest in their own right but the high yield synthesis of 'pure' materials is still to be achieved. The outcome of making mixtures is that subsequent purification processes are needed to remove impurities but these methods can also modify/destroy the required materials.

In this review, we have attempted to evaluate some of the factors that control the synthesis of the shaped carbon nanomaterials. In particular, we have attempted to evaluate the literature and to indicate the current status of the field from the perspective of organometallic chemistry.

We have reviewed the current literature on this topic and incorporated many of the studies into tables that permit a quick evaluation of key information. As there are many hundreds of publications that use organometallic complexes to synthesise SCNMs we have not attempted to list, in this review, all the studies that have been reported. Indeed, in many publications the organometallic complex used to make the SCNMs is purchased and the interest in the actual catalyst is marginal; this is particularly true of studies in which the electrical, mechanical or optical properties of the CNTs are the key part of the study. We hope we have identified all the key reports and apologise to those authors whose work has been inadvertently been left out of the review.

Thus, this review will describe the SCNM synthesis and include conclusions on the

 (i) Types of organometallic complexes that have been used.
 (ii) Effects of the carbon source.
(iii) Effects of secondary elements (S, N, O, P).
(iv) Effect of physical parameters (temperature, pressure, etc.).
 (v) Reactor design issues.
(vi) Mechanistic issues.

This review will not describe the properties associated with these materials as many excellent books are available that contain this information [17]. The review will also not describe the emerging chemistry associated with the purification and functionalization of these SCNMs [18]. Most of the studies on shaped carbon materials reported to date relate to the synthesis of CNTs as these are the complexes that have been most sought after. Two reviews by Rao and co-workers describe some early studies on the use of organometallic complexes on CNT synthesis, in particular from their own studies, and provide some discussion of early work in
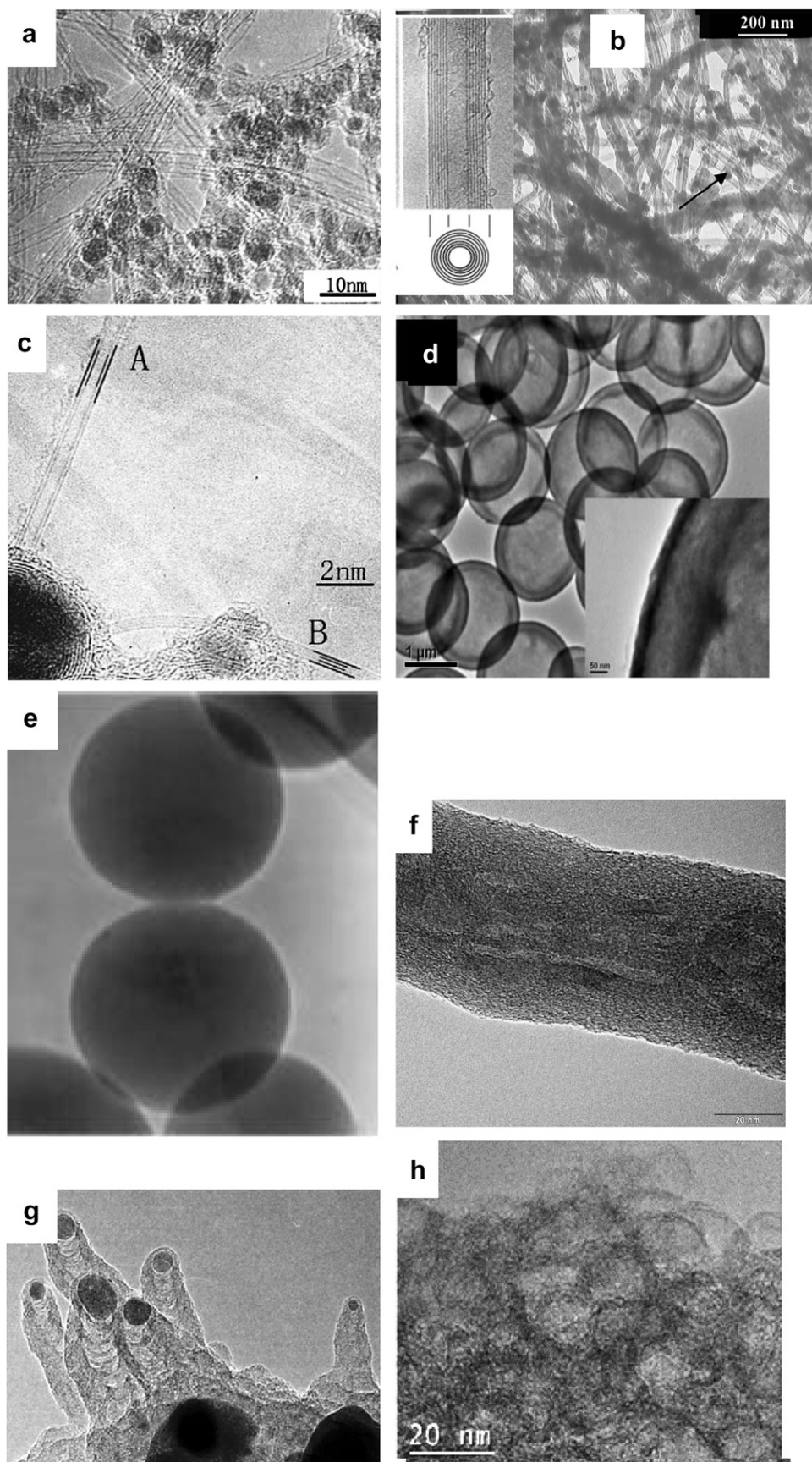
Fig. 1. Types of SCNMs: (a) SWCNTs [125]; (b) MWCNTs [30]; (c) DWCNTs [125]; (d) hollow carbon spheres [126]; (e) carbon spheres [127]; (f) nanofibre [128]; (g) nanohorns [11]; and (h) nanocages [129].
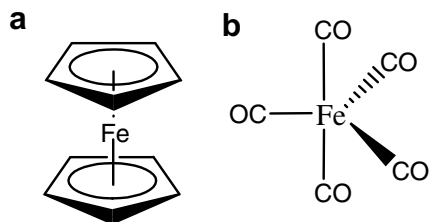
Fig. 2. Catalyst used for CNTs synthesis; (a) ferrocene and (b) Fe(CO)$_5$.

the area [5a,19]. A more recent review has focussed on the use of floating catalysts in the synthesis of CNTs [20].

2. Literature review

2.1. The organometallic catalysts

A patent by Komatsu and Endo in 1985 appears to be the first report of the use of an organometallic complex to prepare a shaped carbon material [21]. A report by Tibbets in 1993 described the use of ferrocene (Fig. 2a) in carbon fibre growth [22]. In the years that followed, numerous reports appeared in which ferrocene was used to catalyze carbon shaped structures from a range of hydrocarbons [20]. Since then hundreds of articles have appeared in which ferrocene has been used to make SCNMs. This arises from the easy accessibility, price, stability in air and volatility of ferrocene.

Another much used organometallic complex is Fe(CO)$_5$ (Fig. 2b) and again the advantages associated with ferrocene apply to Fe(CO)$_5$. Indeed, Fe(CO)$_5$ is used in the industrial HiPCO process to produce CNTs [23]. A listing of the conditions used, the products formed and other important information that relates to the use of ferrocene (Table 1), Fe(CO)$_5$ (Table 2) and other organometallic complexes (Tables 3–5) also indicates the wide range of carbon sources and physical parameters that have been used during the past 15 years. Noticeable from the tables are the limited range of organometallic complexes that have been studied. Other than ferrocene and Fe(CO)$_5$ few other organometallic complexes have been used to make SCNMs, and in particular CNTs.

It is quite remarkable that the use of a single catalyst, ferrocene, has led to the synthesis of such a wide range of carbon shapes (some examples are given in Fig. 1a–f). This reveals the rich chemistry in this field that is still being established. Other typical organometallic complexes that have shown good activity and selectivity towards SCNM synthesis, in particular CNTs include cobaltocene, nickelocene, their mixtures (Table 3) as well as metal (Fe, Co, Ni) phthalocyanines (Table 4). These latter complexes introduce nitrogen into the carbon structures and this issue is dealt with separately below.

Another approach has been to use substituted ferrocenes and this has permitted the exploration of ligand effects associated with the catalysts (Table 5). Here, both carbon and non-carbon elements can be introduced into the reaction using this procedure. The use of simple carbon ligand substituents impacts on ferrocene in terms of both physical (volatility) and chemical (electronic) factors and consequently SCNM synthesis. For example, a comparison of FcH with (C$_5$H$_4$Me)(C$_5$H$_5$)Fe as catalyst under identical reaction conditions, revealed the formation of MWCNTs with larger diameters when the Me group is present [24]. Further, Keller and co-workers have decomposed alkyne substituted ferrocenes to give CNTs with Fe embedded in the CNT [25].

Remarkably, few other studies have been reported in which other organometallic complexes have been studied. Some of these include (CO)$_5$W = C(OCH$_3$)(C$_6$H$_4$OCH$_3$) [26], [CpFe(arene)]$^+$[PF]$_6^-$ [10b], [CpFe(CO)$_2$]$_2$ [27], ruthenocene [28], Ru$_3$(CO)$_{12}$ [29],

[Co$_2$(CO)$_6$RCCR] and other related cobalt organometallic complexes [10d,10e,10f,10g], CpFe(CO)$_2$I [30] and Mo(CO)$_6$ [31]. Clearly, this is still an area ready for exploitation.

Pol and co-workers have reported that apart from thermal dissociation of hydrocarbons at autogenic pressure at elevated temperature (RAPET), organometallic precursors (Co, Ni, Mo, V, Zr or W) have also been reacted and typically yielded products in the nanometric range, either as core shell structures or well-dispersed particles [32].

Organometallic complexes have been used to synthesize SCNMs in a closed environment, typically in an autoclave or sealed quartz container. In these studies, performed at elevated temperatures, the organometallic complex can provide both catalyst and carbon source. Again, very few complexes have been studied with most based on Co and Fe metal catalysts [10]. The carbon source has been varied and the influence of reducing reagents has also been explored [33]. This approach has led to the synthesis typically of CNTs, fibres and spheres [10a,34].

Organometallic complexes have also been used to provide metal complexes for typical CVD processes, but this entails decomposing the complexes on a support prior to SCNM synthesis. Any source of metal (as a salt or coordination complex) can be used to achieve this result but organometallic complexes do have the advantage of not necessarily requiring the presence of a counter-ion.

2.2. Bimetallic catalysts

The control of catalyst nanoparticle size and distribution can be achieved by the use of bimetallic catalysts. In this approach, two or more metals can be either bonded to each other in a metal cluster complex or can be added as a mixture of two separate complexes. The latter approach is easier to use and indeed nearly all studies involving organometallic complexes, reported to date, have applied this approach. Generally the CVD method uses the former approach. For example, it has been observed that catalysts made by the addition of molybdenum to iron stabilized the active Fe nanoparticles [36]. The higher yield of CNTs achieved with bimetallic catalysts has been attributed to particle melting point reduction, increase in carbon solubility and the formation of well-dispersed metal clusters upon segregation during CNT formation [35].

The method involving a mixture of two metal complexes has been used in the floating catalyst process. Rao and co-workers reported a successful synthesis of SWCNTs by the pyrolysis of mixtures of acetylene with binary metallocenes in flowing Ar or Ar + H$_2$ at 1100 °C [37]. The diameter of the nanotubes was generally around 1 nm. They have also shown that the pyrolysis of a dilute acetylene–metallocene mixture gives rise to very fine metal particles essential for the formation of SWCNTs. Further, the use of hydrogen along with Ar, minimized the amorphous carbon coating on the nanotubes. Binary metallocene (nickelocene–cobaltocene) mixtures occasionally give bundles of nanotubes on pyrolysis with acetylene. Horváth et al. have studied the efficiency of bimetallic catalyst particles by investigating ferrocene–cobaltocene, ferrocene–nickelocene and cobaltocene–nickelocene mixtures against a ferrocene standard [38]. Their findings show that ferrocene–cobaltocene and ferrocene–nickelocene mixtures increased the carbon nanotube production compared to ferrocene on its own, and the highest yield was obtained using the ferrocene–nickelocene mixture. The samples contained mainly straight nanotubes and negligible amounts of amorphous carbon implying that these bimetallic catalysts also improved the quality and purity of the nanotube samples.

Mohlala et al. utilized bimetallic catalyst systems (Ferrocene/M(CO)$_5^t$BuNC, where M = W or Mo) to synthesis MWCNTs in 5% H$_2$ in Ar at temperature range 700–900 °C [39]. TEM analysis re-

Table 1
Ferrocene as a catalyst for the synthesis of CNTs and other SCNMs

SNCMs	Reactor design	Carbon source and FcH concentration	Temperature	Pressure and flow rate	Secondary elements	References
SWCNTs	High-pressure CVD reactor	Ferrocene	650–900 °C (pyrolysis)	Pressure 1–5 bars 2000 sccm Ar–FcH vapour mixture flow rate	None	[52]
	Horizontal CVD reactor	Ferrocene	1100–1150 °C (pyrolysis)	Ar flow rate 1500 ml/min H_2 flow rate 150 ml/min	H_2 Sulphur (Fe:S = 10:1)	[64]
	Horizontal CVD reactor two stage furnace system	Ferrocene and acetylene	T (F1) 350 °C (sublimation) T (F2) 1100 °C (pyrolysis)	Ar flow rate 1000 sccm C_2H_2 flow rate 50 sccm H_2 flow rate 25 sccm	H_2	[37]
	Horizontal CVD reactor two stage furnace system	Ferrocene (sublimation rate $3.74–4.68 \times 10^{-5}$ mol/h); Acetylene (3–10 sccm)	T (F1) 60–90 °C (sublimation) T (F2) 900–1000 °C (pyrolysis)	Ar flow rate 1200 sccm C_2H_2 partial pressure of 5.0 Torr (best) or less	None	[51]
	Horizontal CVD reactor two stage furnace system	Ferrocene; Acetylene (1 sccm)	T (F1) 55 °C (sublimation) T (F2) 1100 °C (pyrolysis)	Ar flow rate 300–2000 sccm C_2H_2 flow rate 1 sccm Total reactor system pressure held at 1 atm.	Sulphur Ratio FcH:S = 16:1	[67]
	Vertical CVD reactor	Ferrocene (0.018 g/ml) and Thiophene (0.4 wt %) in *n*-hexane	1150 °C (pyrolysis)	FcH/hexane/thiophene soln flow rate into reactor 0.5 ml/min H_2 flow rate 250 ml/min	H_2; Thiophene	[63] [106]
	Vertical CVD reactor	Ferrocene (0.025 g/ml) and Thiophene (0.6 wt %) in *n*-hexane	1200 °C (pyrolysis)	FcH/hexane/thiophene soln flow rate into reactor 0.6 ml/min H_2 flow rate 250 ml/min	H_2 200–250 mL/min; Thiophene	[46]
	Horizontal CVD reactor two stage furnace system	Ferrocene (vaporization rate $1.5–4.5 \times 10^{-7}$); Thiophene (0.5-5 wt%) in benzene	T (F1) 185 °C (sublimation) T (F2) 1100–1200 °C (pyrolysis)	H_2 70–90 ml/min (F2) H_2 150–225 ml/min (F1)	H_2	55 [63c]
	Vertical CVD reactor	Ferrocene; Benzene and thiophene soln	T (F1) 120 °C (sublimation) T (F2) 1150 °C (pyrolysis)	Ferrocene carrier gas flow rate 0.3-0.5 l/min Benzene carrier gas flow rate 0. 1–0.2 l/min	H_2(carrier gas) Sulphur (S/C = 1:200)	[63d]
	Horizontal CVD reactor	Ferrocene thiophene in benzene (3.0 wt%)	1150 °C (pyrolysis)	H_2 flow rate 1–10 ml/min	H_2; Thiophene	[63e]
	Horizontal CVD reactor with ultrasonic atomizer (850 kHz frequency)	Ferrocene and sulphur mixture (10:1 atomic ratio) in *m*-xylene to form 40 mg/ml.	1050 °C (pyrolysis)	Carrier gas ratio Ar:H_2 = 2:1 Total gas flow rate 300-1500 sccm	Sulfur H_2	[50]
	Horizontal CVD reactor with a sprayer system attached	Ferrocene in Ethanol 0.2–1.2 wt % FcHV (optimal 1.2 wt % FcH)	700–950 °C (optimal 950 °C) 30 min rxn time	FcH–ethanol flow rate 0.3 ml/min Ar flow rate 0.1-0.8 l/min	None	[107]
	Horizontal CVD reactor with ultrasonic atomizer (∼MHz, 20-30 W)	Ferrocene in Ethanol 0.1–3 wt% FcH(optimal 1.0–1.5 wt% FcH)	650–800 °C (pyrolysis)(optimal 700 °C) 30 min rxn time	FcH–ethanol flow rate ∼0.7 g/min Ar flow rate 0.5–2.5 L/min (optimal)	None	[54]
	Horizontal CVD reactor with a sprayer system attached	Ferrocene in Ethanol 1 g/100 ml to 1 g/800 ml	900–1100 °C (pyrolysis)	FcH–ethanol flow rate 50– 80 ml/hr Ar flow rate 80–120 l/h	None	[108]
	CVD vertical laminar flow reactor	Ferrocene CO	700–900 °C (pyrolysis)	Partial vapour pressure of FcH 0.8 Pa N_2/H_2 93/7 Vol%	FcH:SiO_2 = 1:4 CO_2 (Insitu)	[96]
	CVD vertical laminar flow reactor with a hot wire generator (HWG) for ferrocene aerosol	Ferrocene, CO, CO_2	575–600 °C (pyrolysis)	Partial vapour pressure of FcH 0.7 Pa CO flow rate 100 cm^3/min CO_2(600–8000 ppm)	CO_2 H_2O (150 ppm)	[61]
DWCNTs	Horizontal CVD reactor; two stage heating system	Ferrocene (vaporization rate = 6.45×10^{-6} mol/min) Tetraethoxysilane (TEOS) (vaporization rate = 1.28×10^{-4} mol/min)	T (F1) 120 °C (sublimation) T (F2) 1000–1100 °C (pyrolysis)	Ar flow rate 800 ml/min H_2flow rate 400 ml/min	H_2 $SiO_2$from TEOS decomposition	[105]
	Horizontal CVD reactor; two stage furnace system	Ferrocene Acetylene	T (F1) 60–90 °C (sublimation) T (F2) 900-1200 °C (pyrolysis) Reaction time 1.5 h	Ar flow rate 1200 sccm acetylene 8 sccm	Sulphur S:FcH = 1:8–1:64 range	[65]
	Horizontal CVD reactor; two stage furnace system	Ferrocene Acetylene	T (F1) 60–90 °C (sublimation) Furnace (2) 1100 °C (pyrolysis) Reaction time 1.5 h	Ar flow rate 300–2400 sccm C_2H_2 flow rate 2–20 sccm with a partial pressure of 0.25 Torr	Sulphur FcH:S = 512:1 to 6:1 range	[68a]

Table 1 (continued)

SNCMs	Reactor design	Carbon source and FcH concentration	Temperature	Pressure and flow rate	Secondary elements	References
	Horizontal CVD reactor two stage furnace system	Ferrocene Acetylene	Ferrocene/sulphur T (F1) at 60–90 °C (sublimation) T (F2); 1100 °C (pyrolysis)	Ar flow rate 1200–1600 sccm C_2H_2 flow rate 8–12 sccm Total pressure of the system was held at 1 atm	Sulphur; FcH:S = 8:1– 192:1 molar ratio	[68b]
	Horizontal CVD reactor; with a three-section quatz tube with a two stage heating system	Ferrocene Acetylene	T (F1) 60–90 °C (Preheationg) T (F2) 950–1150 °C (pyrolysis) Reaction time 1.5 h	Ar flow rate 300–2400 sccm C_2H_2 flow rate 1–20 sccm with a partial pressure of 0.25 Torr system pressure at 1 atm	Sulphur FcH:S = 512:1 to 6:1 range	[66]
	Horizontal CVD reactor; two stage furnace system	Ferrocene Acetylene	T (F1) 60–90 °C (Preheating) T (F2) 900-1150 °C (pyrolysis) Reaction time 1.5 h	Ar flow rate 1600 sccm C_2H_2 flow 8 sccm	Sulphur S:FcH = 1:8– 1:64	[69]
	Horizontal CVD reactor two stage furnace system	Ferrocene Methane	Ferrocene/sulphur T (F1) 100 °C (Preheating) T (F2) 1150 °C (pyrolysis) Reaction time 30 min	Ar flow rate 1500–2500 sccm	Sulfur FcH:S = 10:1	[70]
	Horizontal CVD reactor two stage furnace system with a an injector attached	Ferrocene/sulfur mixture in xylene (conc of 0.03– 0.12 g/mL)	Reactor temp 900–1180 C (pyrolysis) Reaction time 10–20 min	Feeding rate 0.05–0.15 ml/min Ar flow rate 2500–3500 sccm H_2 flow rate 500 ml/min	Sulphur Fe:S = 10:1	[71]
MWCNTs	Horizontal CVD reactor with a an injector attached	Ferrocene in xylene 8.25% mole fraction of FcH (i.e. 1.00 % Fe/C ratio)	T (F1) 350 °C (sublimation) T (F2) 875 °C (pyrolysis)	Injection rate 4.0 ml/min FcH Total flow rate Ar/H_2 1500 sccm	H_2 10 % H_2 in Ar	[33b]
	Horizontal CVD reactor with two stage furnace system	Ferrocene to benzene ratio 4.2–8.6 % thiophene 0.55 wt %	T (F1) 115–125 °C (sublimation) T (F2) 1150 °C (pyrolysis)	Carrier gas (H_2) total flow rate 700 ml/ min	Sulfur H_2	[43b]
	Horizontal CVD reactor two stage heating system with a an injector attached	Ferrocene in xylene 6.5 mol % of FcH in xylene i.e. ~0.75 % Fe/C ratio	T (F1) ~175 °C (sublimation) T (F2) ~675 °C (pyrolysis)	1Carrier gas (Ar:H_2 = 10:1) Ar/H_2 1688/188 sccm Feed rate FcH–xylene 2.5 ml/h Partial pressure for xylene was 4 mbar	H_2	[45c]
	Horizontal CVD reactor with a nebulizer (1.54 MHz ultrasonic)	Ferrocene 2 g in 100 ml xylene	900 °C temp (pyrolysis) (30 min)	1000 sccm Ar flow rate	Ar	[45b]
	Two stage horizontal CVD reactor with a an injector attached	Ferrocene 0.02 g/ml of xylene	T (F1) 300 °C (sublimation) T (F2) 850 °C (pyrolysis)	Reagent injection flow rate 0.4 ml/min Ar/H_2 flow rate 2000/400 sccm	H_2 Ar	[45a]
	Two stage horizontal CVD reactor	Ferrocene 2-9.6 wt% in toluene	T (F1) 200 °C (sublimation) T (F2) 700–760 °C (pyrolysis)	H_2 10% in Ar total flow rate 750 ml/ min	H_2 Ar	[44b]
	Two stage horizontal CVD reactor	Ferrocene 1-9.6 wt% in toluene	T (F1) 200 °C (sublimation) T (F2) 590–840 °C (pyrolysis)	H_2 10% in Ar total flow rate	H_2 Ar	[44c]
Amorphous Carbon nanotubes (ACNTs)	Horizontal CVD reactor with a boat	Ferrocene	200 °C (30 min)	Pure Cl_2 gas	Cl_2	[88]
	Teflon-lined autoclave (50 ml)	Ferrocene (2.97 mmol, 0.552 g) Sodium (13 mmol, 0.3 g) Benzene 3/4 of autoclave	210 °C (pyrolysis) (24 h)	Autogenic pressure	Under air	[98b]
	Vertical quartz CVD reactor	Ferrocene Benzene thiophene	1100–1200 °C	H_2 Flow rate 100 cm³/min	H_2	[63b]
	Teflon-lined Autoclave (50 ml)	Ferrocene (1 mmol) Sulphur (2 mmol) Benzene 90% of autoclave	200 °C (pyrolysis) (70 h)	Autogenic pressure	Under air	[98a]
Hollow carbon nanosphere (HCSs)	Stainless steal autoclave (2 ml)	Ferrocene (0.186 g)	700 °C (pyrolysis) Reaction time 1 h	Reaction under N_2 atmosphere Total pressure 2.2 MPa	Reaction under N_2 atmosphere	[13b]
	Horizontal CVD reactor with two stage heating system	Ferrocene Camphor	T (F1) 50 °C (Preheating) T (F2) 1000 °C (pyrolysis)	12.5 g of solution transferred to reactor per hour with the aid of Ar gas	Ar	[101a]
Filled sphere	Horizontal CVD reactor with two stage heating system	Ferrocene Camphor	T (F1) 50 °C (Preheating) T (F2) 1000 °C (pyrolysis)	12.5 g of solution transferred to reactor per hour with the aid of Ar gas	Ar	[101a]
	Horizontal CVD reactor with two stage heating system	Ferrocene/ Anthracene (1:7)	T (F1) 160–200 °C (sublimation) T (F2) 580-700 °C (pyrolysis)	H_2 flow rate 300-400 ml/min	H_2	[47b]

Table 1 (continued)

SNCMs	Reactor design	Carbon source and FcH concentration	Temperature	Pressure and flow rate	Secondary elements	References
Carbon nano-onions	Horizontal CVD reactor with two stage furnace system	Ferrocene (~0.7 g) Or mixture of FcH/ $Fe_3(CO)_{12}$	T (F1) 300 °C at of 40 °C min^{-1}(sublimation) T (F2) 900 °C (pyrolysis)	Ar flow rate 260 ml min^{-1}\ 0.5% and 1.0% of O_2 in Ar	$Fe_3(CO)_{12}$	[14]
Iron-included Carbon nanocapsules and nanotubes	Horizontal CVD reactor with two stage furnace system	Ferrocene	T (F1) 200 °C (sublimation) T (F2) 625 °C (pyrolysis)	Carrier gas (H_2) Flow rate 100–300 cm^3/min	H_2	[109]
	Horizontal CVD reactor with two stage furnace system	Ferrocene	T (F1) 200 °C (sublimation) T (F2) 900 °C (pyrolysis)	Carrier gas (Ar:H_2 = 3:1 Flow rate 50 sccm	H_2	[5b]
	Horizontal CVD reactor with two stage furnace system	Ferrocene	T (F1) 620 °C (sublimation) T (F2) 1000 °C (pyrolysis)	Carrier gas (Ar) Flow rate 1000 sccm	Ar	[110]
	Stainless steal autoclave (14 mm in inner diameter, 70 mm in length)	Ferrocene (FcH) Picric acid (PA) (PA:ferrocene = 8:1–2:1)	The detonation of explosive was initiated by heating (20 °C/min) and occurred at 290 °C; Reaction temperature 1000 °C	Autogenic pressure	None	[16c]

vealed the formation of large metal particles in the MWCNTs determined to be Mo/Fe alloys rich in Fe, indicating that an alloy had been formed under the reaction conditions. Under similar reaction conditions, ferrocene yielded MWCNTs and carbon balls (CBs) while the M(CO)$_5$^{t}BuNC complex yielded little carbonaceous material. It was observed that the diameters of the CNTs formed in the presence of ferrocene are smaller while the diameters of CBs are larger relative to the diameters of CNTs and CBs produced by the bimetallic catalyst systems.

2.3. The carbon source

The synthesis of SCNMs requires some source of carbon to create the carbon structures and this can be supplied by a catalyst and/or by an external source. When supplied by a catalyst such as ferrocene or Fe(CO)$_5$, C is derived from the Cp or CO ligands. It is generally believed that the ligands break down into C_1 (or similar small C radicals) in the gas phase and that these small species then 'condense' into the shaped materials. However, formation of larger gas phase radicals is also possible and these certainly play a role in the formation of SCNMs. This issue will be dealt with in Section 2.7.

In most studies the carbon used to make the SCNMs is derived from an external source and this can be any carbon containing material. Typically, hydrocarbons are used and include CH_4 [40], C_2H_4 [41], C_2H_2 [5c,42], C_6H_6 [5b,34,43], $C_6H_5CH_3$ [44], xylene [45], pentane [12c], hexane [21,46], anthracene [10a,47], etc. Factors such as C/H or C/M (M = metal) ratios, reactant volatility, reactant stability as well as radical and ion formation play key roles in determining the eventual products obtained.

The morphology of the SCNMs should be influenced by the carbon source, as indeed has been found when CNTs are synthesised. However, a range of hydrocarbons used in the synthesis of carbon spheres did not have a significant effect on their properties (e.g. size) [48]. However, in the presence of a heteroatom (e.g. oxygen from alcohols) the size and yield of the spheres were affected [49]. The common heteroatoms used in the synthesis of SCNMs are dis-

cussed in the following sections. Several studies have indicated that the diameters and distribution of the carbon spheres [48] as well as CNTs can be controlled by varying the reaction time, feed time and reactant flow rate [50]. Variation of these parameters not only affected the sizes but also controlled the product SCNM yields and distribution [24]. In addition, it has been reported that adjusting the partial pressure of the carbon source in the CVD synthesis of CNTs in the floating catalyst method, can control the mean diameters as well as the amount of material produced [51,52].

2.4. Other elements

The addition of heteroatoms to the reactant streams used to make SCNMs plays a key role in producing either doped materials or 'cleaner' materials. Thus, the heteroatom can be introduced by incorporation into the carbon source or into the catalyst ligand and this can lead to modified chemical and physical properties of the SCNMs formed from the reactants. Alternatively, the heteroatom can selectively react with debris or defects associated with the carbon products and lead to the generation of more perfect SCNMs.

2.4.1. Hydrogen
In general, the catalysed synthesis of CNTs requires the presence of a reducing agent to ensure the catalyst remains in a low oxidation state. This can be achieved by the use of ligands (CO) or the presence of H atoms. Most carbon sources used to make CNTs contain hydrogen, but in numerous studies hydrogen gas (H_2) is also added to the carbon source to act as a reducing agent. Many studies have been undertaken that indicate the role of hydrogen in CNT synthesis. Wasel et al. have carried out studies on the CVD synthesis of MWCNTs and investigated the role of hydrogen on CNT synthesis using ferrocene as the catalyst and xylene as the carbon source [33b]. The results revealed a competition between the formation of the different carbon products (soot, carbon fibres and CNTs) altered by the addition of hydrogen.

Table 2
Fe(CO)$_5$ as a catalyst for the synthesis of CNTs and other SCNMs

SNCM	Reactor design	Carbon Source	Temperature	Pressure and flow rate	Secondary elements	Reference
SWCNTs	Horizontal CVD reactor two stage furnace system	Acetylene–Fe(CO)$_5$	T (furnace 1) 350 °C T (furnace 2) 1100 °C	C$_2$H$_2$ flow rate 50 sccm Fe(CO)$_5$ vol. 1 ml Ar flow rate 1000 sccm	None	[37] [19]
	Horizontal CVD reactor	CO mixed with small amounts of Fe(CO)$_5$	800–1200 °C	CO (1–10 atm) Fe(CO)$_5$ (1–25 mTorr)	None	[23] [111]
	Horizontal CVD reactor two stage furnace system	CO	T (furnace 1) 700 °C T (furnace 2) 900 °C	CO flow rate 800 sccm H$_2$ flow rate 200 sccm	None	[112]
MWCNTs (aligned)	Horizontal CVD reactor with atomizer	Acetylene–Fe(CO)$_5$	900 °C	C$_2$H$_2$ flow rate 100 sccm Ar flow rate 1000 sccm	None	[45b]
MWCNTs (helically coiled)	Horizontal CVD reactor two stage furnace system with vapourization chamber and an ice cooler	1 g Fe(CO)$_5$ dissolved in (1) 99 g Pyridine (2) 99 g Toluene	1050–1150 °C	H$_2$ carrier gas flow rate 350–400 ml/min	None	[113]
MWCNTs	Vertical CVD reactor	Methane	1050–1150 °C	CH$_4$ flow rate 125–250 sccm Fe(CO)$_5$ feeding rate 0.5–2.5 ml/h N$_2$ flow rate 1000–2000 sccm	None	[40c]
	Horizontal CVD reactor	Fe(CO)$_5$-pentane 3.3 wt% Fe(CO)$_5$	700–800 °C	N$_2$/Fe(CO)$_5$ flow rate 50–100 ml/min	None	[12c]
CNFs	Vertical CVD reactor	Methane	800 °C	Methane flow rate 5300 cm^3/min He with Fe(CO)$_5$165 cm^3/min H$_2$S flow rate 8 cm^3/min	Sulfur	[74]
CNBs	Horizontal CVD reactor	Fe(CO)$_5$-pentane 10 wt% Fe(CO)$_5$	900–1000 °C	N$_2$/Fe(CO)$_5$ flow rate 50 ml/min	None	[40c]

Increasing the hydrogen concentration resulted to an increase in the yield and quality of the MWCNTs produced. The role of hydrogen is to reduce the rate of carbon production by dehydrogenation so that the more ordered and thermodynamically stable MWCNTs can be produced rather than less ordered and less thermodynamically stable soot and carbon fibres. Recent studies have also indicated that the hydrogen can influence the radicals formed (e.g. radical condensates) from the carbon sources and this impacts on SCNM production [53].

2.4.2. Oxygen

Addition of ethanol to FcH has been shown to give SWCNTs at lower temperature than that found for hydrocarbon reagents [54]. This could be due to the lower decomposition temperature of ferrocene in ethanol [55] and/or the etching effect of OH radicals generated from the ethanol precursor [56]. Here, the presence of the OH radical formed from ethanol at high temperature is said to oxidize the amorphous C formed in the reaction and this has led to cleaner and more crystalline tubes covered with less debris [57]. In general, it appears that when the reactant C/O ratio is high, then cleaner tubes are formed. If the oxygen level becomes too high then the catalyst becomes oxidized and poor SCNM yields are obtained. Further, this effect does not hold when the oxygen is added via a sonication process. In this instance, low levels of oxygen kill all catalyst activity [58].

In recent work, it has been shown that the presence of CO$_2$ can be beneficial to MWCNT growth [59]. This could relate to participation of the water gas shift reaction influencing the composition of the reactants [60]. Nasibulin et al. showed that addition of a small amount of CO$_2$ and H$_2$O vapour to a ferrocene/CO reaction mixture resulted in an increase in the CNT length and a drop in the reaction temperature for CNT synthesis (from 890 °C to below 600 °C) [61]. Thus, the role of CO$_2$ and H$_2$O most likely can be explained by an etching effect during the formation of CNTs. The presence of both CO$_2$ and H$_2$O is believed to etch amorphous carbon that can poison catalyst particles needed for CO disproportionation as well as for CNT nucleation and growth. Hence, the function of these etching agents is to clean the catalyst particle surface and remove the carbon graphitic layer or amorphous carbon at the nucleation stage.

2.4.3. Sulfur

The impact of sulfur on SCNM synthesis has been known for decades [62]. The sulfur is typically added as part of a volatile complex (thiophene [63]) or even as sulfur [50,64–71] to a reactant stream required to make carbon materials. The addition of sulfur to FcH has led to the selective synthesis of SWCNTs, DWCNTs, MWCNTs, etc. and has even impacted on the quality and yield of CNTs produced [66]. Thus, addition of thiophene or pure sulfur to ferrocene has been found to be effective in promoting the growth of SWCNTs and in increasing the yield of SWCNTs under a range of different growth conditions [50,55,67]. Others have reported the growth of DWCNTs upon the addition of thiophene [72] or of pure sulfur [65,66,71,73] under similar conditions [55,66].

Tibbetts and co-workers described the role of sulfur in the production of carbon fibres in the vapour phase using Fe(CO)$_5$ as the catalyst [74]. The increase of filamentous carbon was influenced by the addition of small amounts of H$_2$S to the feed as this reagent enhanced the filament nucleation on the iron particles. Further

Table 3
Cobaltocene, nickelocene and ruthenocene as catalysts for the synthesis of CNTs and other SCNMs

SNCM	Reactor design	Metallocene + carbon source	Temperature	Pressure and flow rate	Secondary elements	Reference
SWCNTs	Horizontal CVD reactor two stage furnace system	1. Cobaltocene–acetylene mixture 2. Nickelocene–acetylene mixture	T (F1) = 200 °C (sublimation) T (F2) = 1100 °C (pyrolysis)	Ar flow rate 1000 sccm C_2H_2 flow rate 50 sccm	None	[5a]
	Horizontal CVD reactor two stage furnace system	Cobaltocene–ferrocene/nickelocene–acetylene mixture	T (F1) = 200 °C (sublimation) T (F2) = 1100 °C (pyrolysis)	Ar flow rate 975 sccm H_2 flow rate 25 sccm C_2H_2 flow rate 50 sccm	None	[19] [37] [114]
	Horizontal CVD reactor with an atomizer	1. Cobaltocene–toluene mixture (20 g/l) 2. Cobaltocene–toluene mixture (20 g/l)	900 °C (pyrolysis)	Ar flow rate of 1000 sccm.	None	[45b]
MWCNTs	Horizontal CVD reactor two stage furnace system	1. Cobaltocene 2. Nickelocene	T (F1) = 200 °C (sublimation) T (F2) = 900 °C (pyrolysis)	Ar (75%)–H_2 (25%) flow rate 50 sccm	None	[5b]
	Horizontal CVD reactor two stage furnace system	1. Cobaltocene–benzene mixture 2. Cobaltocene–benzene mixture	T (F1) = 200 °C (sublimation) T (F2) = 900 °C (pyrolysis)	Ar (85%)–H_2 (15%) flow rate 1000 sccm	None	[5a] [19]
	Horizontal CVD reactor	1. Cobaltocene–benzene, toluene, xylene, cyclohexane, cyclohexanone, n-hexane, n-heptane, n-octane, n-pentane 2. Nickelocene–benzene, toluene, xylene, cyclohexane, cyclohexanone, n-hexane, n-heptane, n-octane, n-pentane	875 °C (pyrolysis)	6 g metallocene in 100 ml hydrocarbon catalyst 1 ml/min solution flow-rate Ar carrier gas flow 500 l/h	None	[38]
	Horizontal CVD reactor two stage furnace system	Cobaltocene–ferrocene mixture (1:2)	T (F1) = 120–140 °C (sublimation) T (F2) = 980 °C (pyrolysis)	Ar/H_2 mixture Total flow rate 150 sccm	None	[115]
	Horizontal CVD reactor	1. Cobaltocene in supercritical toluene with hexane or ethanol as supplemental carbon source 2. Nickelocene in supercritical toluene with hexane or ethanol as supplemental carbon source	600–645 °C (pyrolysis)	Pressure 8.3 MPa Solution injection flow rate 1 ml/min	None	[116]
	Horizontal CVD reactor two stage furnace system	Xylene–ruthenocene–ferrocene mixture	T (F1) = 200 °C (sublimation) T (F2) = 700 °C (pyrolysis)	Ar/H_2 (10%) carrier gas	None	117
	Horizontal CVD reactor two stage furnace system	Nickelocene–tetrahydrofuran mixture	T (F1) = 171–173 °C (sublimation) T (F2) = 600 °C (pyrolysis)	No carrier gas used	None	[118]
DWCNTs	Horizontal CVD reactor two stage furnace system	Cobaltocene–acetylene mixture	T (F1) = 60–90 °C (sublimation) T (F2) = 950–1150 °C (pyrolysis)	Ar flow rate 300–2400 sccm C_2H_2 flow rate 2–20 sccm	Sulphur	[68a]
Y-Junction MWCNTs	Horizontal CVD reactor two stage furnace system	1. Cobaltocene–thiophene mixture 2. Nickelocene–thiophene mixture	1000 °C	Ar flow rate 100–200 sccm H_2 flow rate 50–150 sccm	None	[75]
CNFs	Horizontal CVD reactor two stage furnace system	Cobaltocene–acetylene–thiophene mixture	T (F1) = 140–180 °C (sublimation) T (F2) = 1100–1150 °C (pyrolysis)	H_2 carrier gas flow rate 20 mg min^{-1}	None	[119]
CNBs	1. Stainless steel autoclave placed in a horizontal furnace 2. Horizontal CVD reactor two stage furnace system	Ruthenocene–ethylene mixture	T (F1) = 400 °C (sublimation) T (F2) = 900–1300 °C (pyrolysis)	Ar flow rate 200 sccm H_2 flow rate 150 sccm C_2H_4 flow rate 50 sccm	None	[28]

Table 4
Fe, Co and Ni phthalocyanines as catalysts for the synthesis of CNTs and other SCNMs

SNCM	Reactor design	Carbon source	Temperature	Pressure and flow rate	Secondary elements	Reference
SWCNTs	Two-zone CVD electrical furnace	Iron phthalocyanine	T (F1) = 480–520 °C (vapourization) T (F2) = 800–920 °C (pyrolysis)	Ar/H$_2$ flow (1:1v/v) 40 cc/min	None	[120]
MWCNTs	Horizontal CVD reactor two stage furnace system	1. Iron phthalocyanine 2. Nickel phthalocyanine 3. Cobalt phthalocyanine	T (F1) = 550 °C (vapourization) T (F2) = 700–1000 °C (pyrolysis)	Ar flow rate 30–150 sccm H$_2$ flow rate 5–10 sccm	None	[121]
Y-junction MWCNTs	Horizontal CVD reactor two stage furnace system	1. Iron phthalocyanine + thiophene mixture 2. Nickel phthalocyanine + thiophene mixture	T (F1) = 440–520 °C (vapourization) T (F2) = 1000 °C (pyrolysis)	Ar flow rate 100–200 sccm H$_2$ flow rate 50–150 sccm	None	[75] [81b] [19]

Table 5
Ferrocenyl derivatives as a catalyst for the synthesis of CNTs and other SCNMs

SNCM	Reactor design	Carbon source	Temperature	Pressure and flow rate	Secondary elements	Reference
MWCNTs	Horizontal CVD furnace	Ferrocenylethynyl benzenes	500–1400 °C	Ambient pressure under argon	None	[25a]
	Horizontal CVD furnace	1,4-Diferrocenylbutadiyne	500–1400 °C	Ambient pressure under argon	None	[25c]
	Horizontal CVD furnace	Butadiynyl–ferrocene-containing compounds	500 – 1400 °C	Ambient pressure under argon	None	[25b]
	Horizontal CVD furnace	1. Dimethylferrocene in toluene 2. Diethylferrocene in toluene	800–1000 °C	1. 5 wt% H$_2$/Ar flow rate 100 ml/min 2. Solution injection rate 0.2 and 0.8 ml/min	None	[24]
	Horizontal CVD furnace	CpFe(CO)$_2$Me in toluene	800–1000 °C	5 wt%H$_2$/Ar flow rate 100 ml/min Solution injection rate 0.2–0.8 ml/min	None	[30]
	Horizontal CVD furnace	Ferrocene and ferrocenyl disulfide mixture	800–1000 °C	5 wt%H$_2$/Ar flow rate 100 ml/min Solution injection rate 0.2–0.8 ml/min	None	[77]
	Two zone horizontal CVD furnace	1. Cyclopentadienyliron dicarbonyl dimer 2. Cyclooctatetraene iron tricarbonyl	T (F1) = 200 °C (sublimation) T (F2) = 685–750 °C (pyrolysis)	1. Solution injection rate 1.5–2.0 ml/h 2. 4 wt% H$_2$/Ar flow rate 1.5 slpm	None	[27]
	Two stage horizontal CVD furnace	Ferrocene–Fe$_3$(CO)$_{12}$mixture	T (F1) = 300 °C (sublimation) T (F2) = 900 °C (pyrolysis)	Ar carrier gas flow rate 260 ml/min	None	[14]
SWCNTs	Horizontal CVD furnace	Polyferrocenylsilane block copolymer	500 °C	Not applicable	None	[122] [123]
	Horizontal CVD furnace	Poly(ferrocenylsilane)-block-polysiloxane Diblock Copolymers	900 °C	1. H$_2$ flow rate 500 sccm 2. Methane flow rate 800 sccm 3. Ethylene flow rate 20 sccm	None	[124]
CNFs and CSs	Horizontal CVD furnace	1. Dimethylferrocene in toluene 2. Diethylferrocene in toluene	800–1000 °C	5 wt%H$_2$/Ar flow rate 100 ml/min Solution injection rate 0.2 and 0.8 ml/min	None	[24]
	Horizontal CVD furnace	Ferrocene and ferrocenyl disulfide mixture	800–1000 °C	5 wt%H$_2$/Ar flow rate 100 ml/min Solution injection rate 0.2–0.8 ml/min	None	[77]

addition of H$_2$S increased the filamentous growth but decreased the quality of the fibres as measured by length and straightness. Deepak et al. prepared Y-junction nanotubes in large quantities by carrying out the pyrolysis of a mixture of a metallocene with thiophene [75]. Pyrolysis of various organometallic complexes (e.g. Fe(CO)$_5$, ferrocene and cobaltocene) and sulfur containing compounds (thiophene) has yielded excellent Y-junction nanotubes. Buds can also be formed as seen in the low magnification TEM image of the products from the pyrolysis of a cobaltocene/thi-

ophene mixture (Fig. 3a). Many of the nanotubes shown in Fig. 3 show multiple Y-junctions. A TEM image of a single long Y-junction nanotube is shown in Fig. 3b.

A comparison of the reactivity of ferrocene–benzene and ferrocene–thiophene mixtures, without hydrogen addition, has been made [76]. The diameter of the tubes decreased with increasing reactant flow rate in the high temperature range (above 850 °C). The use of thiophene instead of benzene yielded a significantly narrower diameter distribution for the straight nanotubes with a con-

siderable yield of L and Y carbon nanotube junctions being observed (Fig. 4). The inner core of these straight tubes was frequently continuously filled with the catalyst material and indicated that the presence of sulfur may facilitate the filling of tubes.

The use of ligand modified catalysts allows for introduction of doping atoms in a CNT synthesis, e.g. addition of S as part of a ferrocene ligand (e.g. $(C_5H_4SMe_2)(C_5H_5)Fe$) has been reported and indicated that the proximity of the S to the Fe plays a role in affecting the MWCNT product formed [77].

2.4.4. Nitrogen

Doping of CNTs by heteroatoms may lead to an increase in the electrical conductivity of CNTs by formation of electron excess n-type (e.g. N-doped CNTs) or electron deficient p-type (e.g. B-doped CNTs) semi conducting nanotubes [78].

The presence of nitrogen in SCNM formation has been well studied [79]. Addition of nitrogen as NH_3 and carbon via a 'carbon' source provides a simple route to adding nitrogen to the SCNM. The presence of nitrogen leads to a major change in the morphology of the carbon structures formed, since the N atom is incorporated into the structure. For example, the presence of nitrogen in MWCNTs is detected by the presence of 'bell shaped' structures (Fig. 5). N can be present as a pyridinic or pyrrolic N atom, detected by XPS (X-ray photoelectron spectroscopy) studies and the N content can be as high as 10% in a MWCNT. The presence of nitrogen also leads to a modified chemical behaviour of the SCNM. The addition of N atoms derived from the pyrolysis of pyridine with ferrocene as the catalyst with either pure NH_3 or a mixture of NH_3 and
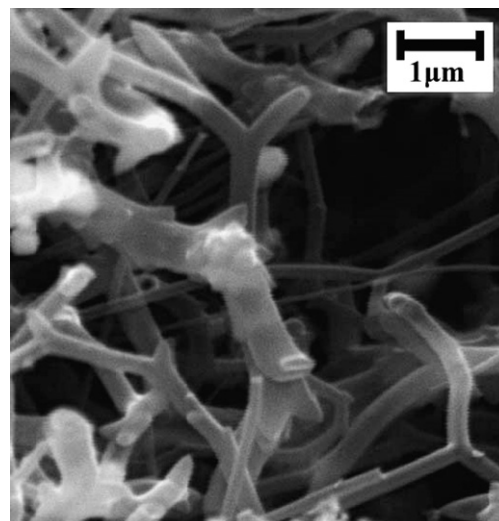

Fig. 4. SEM image showing a significant yield of carbon nanotube junctions, in the samples grown at 875 °C, 60 ml/h active solution flow rate and 0.06 g/ml solution of ferrocene in thiophene [76].

argon atmosphere using an injection CVD method has been reported [80].

Nitrogen addition has also been achieved by adding the N atom as part of a metal ligand. Indeed, early studies by Rao and co-workers achieved success using metal phthalocyanines (metal = Fe, Co, Ni) [19,75,81]. A recent comparative study on the use of 4-ferrocenylaniline and a ferrocene/aniline mixture revealed that using a constant Fe/N ratio, a higher N content was achieved using the substituted ferrocene compound as the catalyst [82].

2.4.5. Boron

Presently boron doped nanotubes have been produced using an arc-discharge method [83] or by a CVD method [84]. However, the use of volatile organometallic catalysts and boron containing reactants has not been exploited. The use of ferrocenyl containing boron ligands to produce boron substituted CNTs was not successful [85].

2.4.6. Phosphorus

Whereas nitrogen can be incorporated into SCNMs the role of phosphorus is to modify the catalyst. In a study using ferrocene and benzene, spheres were formed while the addition of PPh_3 led
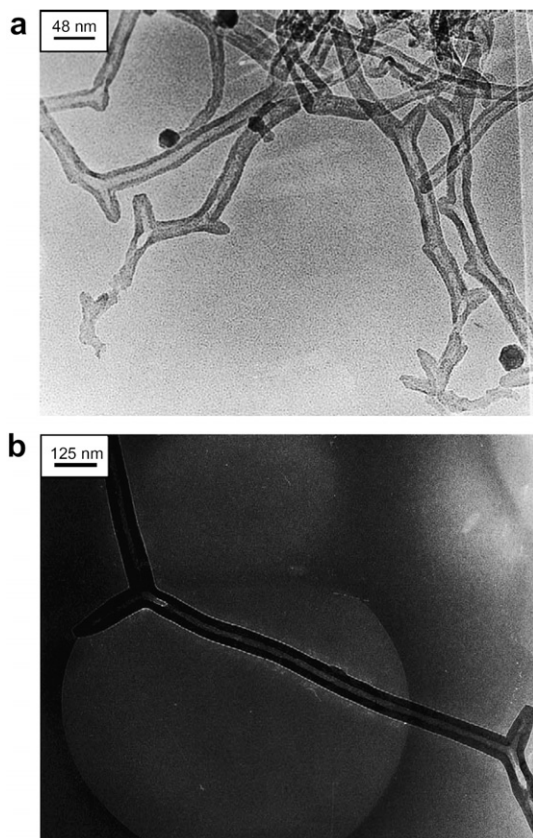

Fig. 3. TEM images of Y-junction nanotubes obtained by the pyrolysis of cobaltocene–thiophene mixtures: (a) image with several Y-junction nanotubes and (b) image showing a single multiple junction nanotube [75].
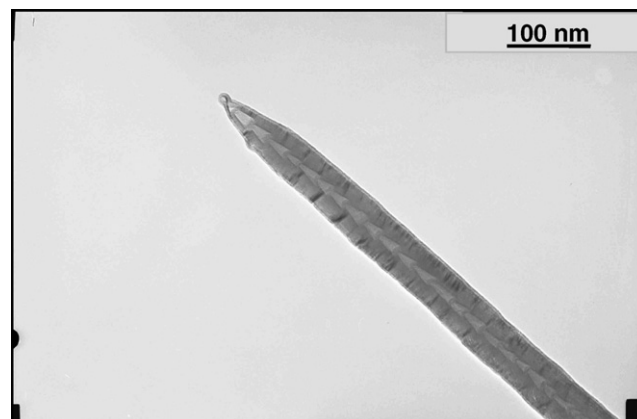

Fig. 5. TEM image of a MWCNT with 'bell shaped' structures synthesized using pyridine [130].
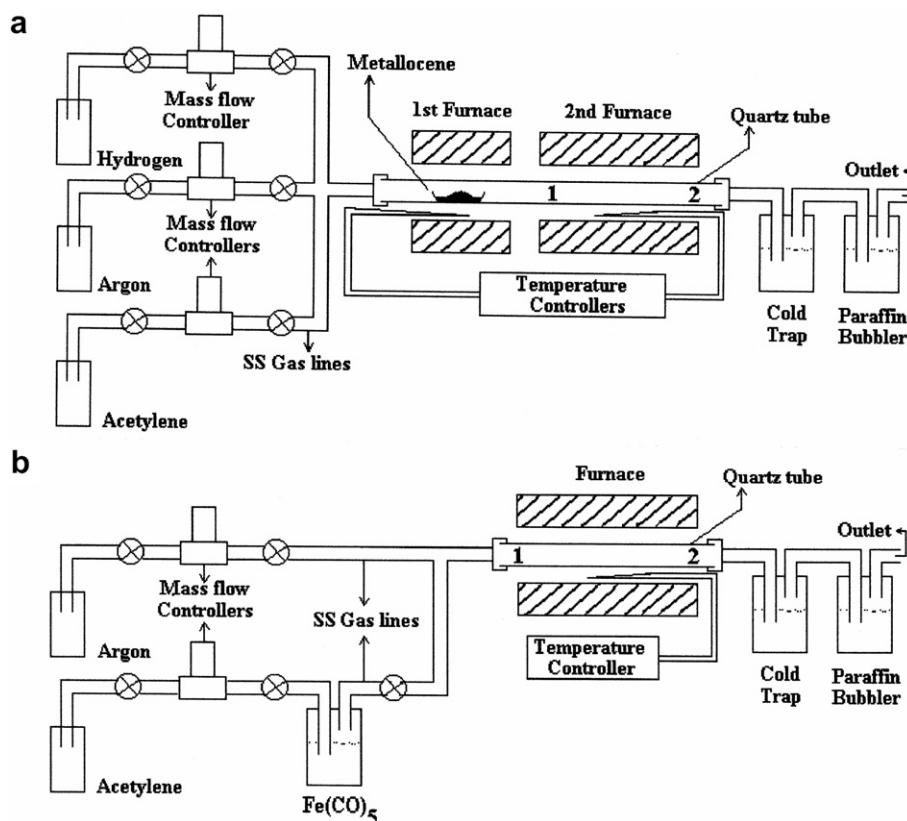
Fig. 6. Pyrolysis apparatus employed for the synthesis of SWCNTs by pyrolysis of (a) metallocenes and (b) Fe(CO)$_5$ along with acetylene [37].
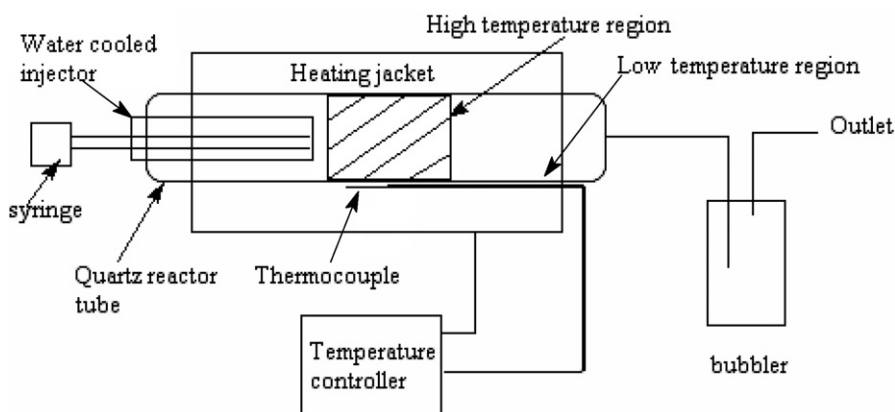

Fig. 7. Floating catalyst CVD reactor for the synthesis of CNTs [39].

to the formation of filamentous carbon. This was suggested to be due to the formation of a eutectic Fe–P melt that increased the fluidity of the liquid particles. Phosphorus was also suggested to enhance the diffusion of carbon atoms in catalyst particles and hence the growth of carbon filaments. No phosphorus was incorporated into the CNTs [86]. More recently reaction of W(CO)$_6$ with PPh$_3$ in an autoclave was reported [87]. It is also possible that the presence of PF$_6$ ions in the synthesis of SCNMs from [CpFe(arene)]$^+$[PF$_6$]$^-$ may have impacted on the type of SCNM products formed [10b].

2.4.7. Halides

The role of halogens in SCNM formation is not clear. Halogen atoms have been added to reaction mixtures as part of a carbon reactant, as the element, or as part of a catalyst. Numerous reac-

tions entailing the use of halogen atoms/radicals have been performed in an autoclave. For example, the reaction of Cl$_2$ with ferrocene gives rise to several different carbon forms, such as amorphous nanotubes, nanobags and elliptical hollow particles at $T < 300$ °C, whereas hollow carbon nanospheres were observed at $T = 900$ °C [88]. Spherical carbon nanoparticles have also been produced by direct chlorination of cobaltocene [89]. Many reactions have also been performed with chlorinated carbon reactants, e.g. C$_2$Cl$_4$ [90] and the products obtained have included hollow carbon nanospheres [91]. Lv et al. have reported on the effect of using chlorine-containing precursors to synthesize micrometer-long continuous FeNi nanowires inside thin-walled CNTs [92]. The degree of 'hollowness' of the CNTs increases with the increase of Cl content in carbon precursors, hence providing a convenient way to control the morphology of CNTs.

In all the above cases, the presence of the halogen has assisted in forming CNTs and SCNMs. In contrast, the presence of I in an Fe catalyst (CpFe(CO)₂I) killed the ability of the Fe to catalyse the formation of CNTs [30].

2.4.8. Other elements

The effect of numerous other elements has also been investigated in the CVD syntheses of CNTs. However, very few elements have been incorporated into the CN*T* (or other SCNM) products. One element that has potential is silicon as Si–C bonds are known to be stable. Indeed, templating of carbons using porous silica(s) has been extensively studied [93a–c] and volatile Si complexes have been used to make CNTs [93d,e].

2.5. Physical parameters

Variation in the type of SCNM produced using an organometallic catalyst and a carbon source is strongly influenced by the temperature and pressure conditions. In a flow system, the reaction is influenced by the decomposition temperatures of the catalyst and the carbon source. At atmospheric pressure, this typically requires temperatures above 450 °C for ferrocene but the maximum temperature is limited by the physical characteristics of the quartz reactor (<1200 °C).

The kind and size of SCNMs produced are temperature dependent. Chaisitsak et al. observed that the diameter of SWCNTs that were produced when $T > 650$ °C increased with temperature [54]. This was confirmed by the appearance of narrow radial breathing mode (RBM) peaks in the Raman spectra (ca 200 cm^{-1}) of the SWCNTs. The report is also supported by Singh et al. [44d], Zhan et al. [94a] and Moisala et al. [94b]. The assumption is that under the high temperature conditions used the frequency of metal particle collision increases resulting in an increase in the particle diameter [95]. As a consequence, the diameter of the CNTs becomes larger.

Studies to date suggest that the catalyst must be in a reduced state and this can be achieved by (i) using a reducing carbon source, e.g. CO, (ii) by adding H₂ to the reactants, (iii) by using the H generated from the carbon source, e.g. CH₄, or (iv) by using

a catalyst with the metal in the zero oxidation state, e.g. Fe(CO)₅. Reactions with ferrocene require a reductant.

Reactions performed in a confined space permit the effect of pressure on SCNM formation to be explored. Most reactions have been carried out at autogeneous pressures but in some studies reactions at high pressures have been reported [52,96]. The addition of a solid reductant (Na, Ca, K, etc.) to ferrocene and a carbon source is possible using this approach. This has resulted in the formation of CNTs at low temperatures (<210 °C). These CNTs tend to be amorphous [97]. Luo et al. used an autoclave reactor which was filled with benzene to 90% of total volume and a mixture of ferrocene/sulfur to synthesize amorphous CNTs at 200 °C [98a]. They investigated the effect of sulfur on the growth of amorphous CNTs and it was found that an optimal amount of sulfur (molar ratio ferrocene:sulfur (1:2); near the stoichiometric proportion of FeS₂) is needed to obtain the amorphous CNTs.

The gas flow rates for introduction of the catalyst/carbon source in the CVD process also influence the type, quality and quantity of SCNMs produced. Barreiro and co-workers showed that a decrease in the SWCNT mean diameter distribution can be obtained by increasing the total gas flow [50]. With a high flow rate they were also able to synthesize very long SWCNTs. Tapasztó et al. have also made a similar observation and they suggested that the strong effect of flow rate on the average tube diameter must be related to the size of liquid droplets produced in the gas phase and hence to a larger number of catalyst particles formed in the reaction [76]. The shorter duration time of the growth cycle for larger flow rates may also make a contribution to the uncatalysed thermal decomposition of benzene at high temperatures. This process can lead to the formation of a pyrolytic carbon overcoat on the nanotubes. An increase in gas flow rate beyond the optimum also leads to an increase in the amount of amorphous carbon formed [34]. The alignment of tubes can be improved by increasing the flow rate of the active solution.

2.6. Reactor design

Numerous procedures have been developed to ensure that a volatile organometallic catalyst can be transferred into a reactor
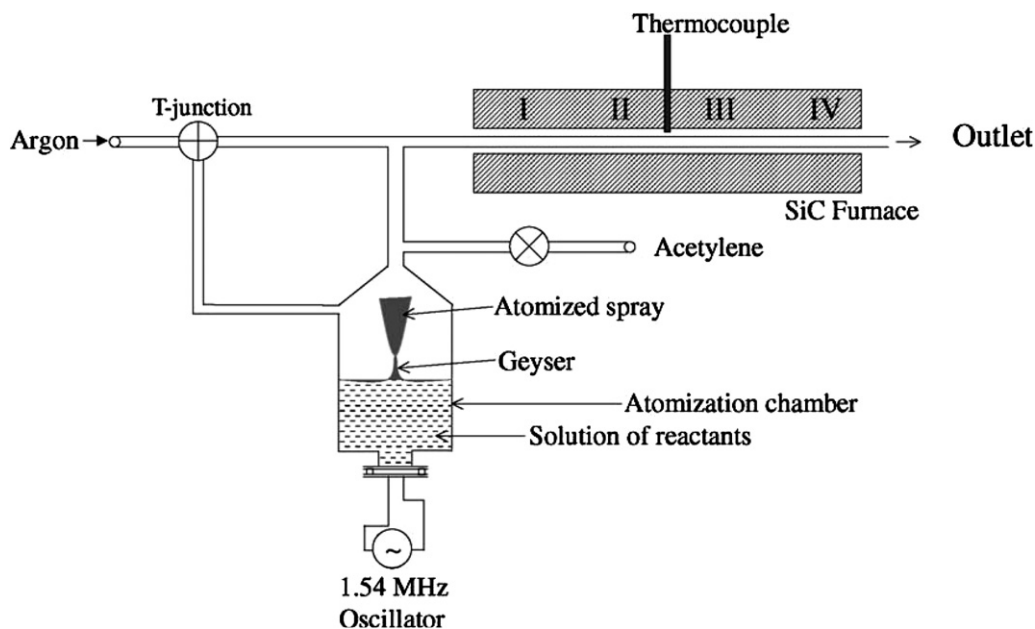

Fig. 8. Schematic representation of a CVD furnace with an atomizer [23].

to generate the SCNMs. In the simplest system an inert gas is bubbled through a liquid organometallic complex (e.g. $Fe(CO)_5$) and the vapour is passed through an oven held typically between 700 and 1100 °C. In this temperature range, a quartz reactor tube can be used; use of a metal reactor leads to the possibility of the reactor wall playing a part in the reaction [98b].

In most instances however the organometallic reagent is a solid at room temperature (e.g. ferrocene) and a number of methods can be used to introduce the catalyst into a reactor. These include the use of a two furnace system in which the catalyst is placed in a low temperature furnace under a flow of an inert gas (and/or carbon source). The volatile catalyst is transferred to a second higher temperature furnace where product formation occurs. A horizontal reactor is generally used in the reaction (Fig. 6).

If the organometallic complex is soluble in some carbon source then the dissolved catalyst can be added directly to the reactor hot zone. This will permit the use of both horizontal and vertical reactor designs. The dissolved material can be added by means of a syringe (Fig. 7) or by bubbling an inert gas through the reactant solution.

Alternatively, a catalyst/carbon source can be sonicated and the sonicated mist (aerosol) transferred to the reactor in an inert gas (Fig. 8).

Recently, SCNMs have been prepared under static conditions, i.e. in a confined reactor. This includes reaction in an autoclave or in a sealed glass reactor [10]. In both instances, the organometallic complex is placed in the reactor and the reaction carried out under autogeneous (or higher) pressures. This approach allows for the use of solid carbon and/or solid organometallic complex reactants.

2.7. Mechanism

2.7.1. CNT growth mechanism on supported catalysts

Many studies have been reported that have attempted to rationalize the catalytic synthesis of SCNMs, and in particular CNTs. Indeed a consensus has arisen as to the mechanism involved in the synthesis of CNTs over *supported catalysts* [17,99]. In this process small (metal) catalyst particles are deposited on a support and the carbon from the gas phase deposits on or dissolves in the catalyst particle. For metals like Fe and Co growth of the CNT then arises from precipitation of the carbon out of the metal. If the catalyst-support interaction is strong the carbon tubes grow away from the support surface (base-growth mechanism) but if the catalyst–support interaction is weak, the metal particle is displaced from the surface by the carbon (tip-growth mechanism). These two processes are shown schematically in Fig. 9.

Use of a floating catalyst methodology eliminates the need for a support and although concepts of carbon deposition/crystallisation/growth are assumed to be similar the mechanism becomes simplified (tip-growth and base-growth lose their meaning).

The metal catalyst particles are still believed to act as nuclei for the growth of CNTs in the gas phase and a mechanism for gas-phase CNT growth is shown in Fig. 10. Control of the catalytic growth of SCNMs is achieved by control of the catalyst nanoparticle size and distribution during the high temperature reaction. Indeed, control of the catalyst diameter determines whether SWCNTs, DWCNTs, or MWCNTs among other SCNMs will be formed in the reaction. The control of the diameter also controls the helicity and hence the conducting properties, the mechanical properties, and the magnetic properties of the product CNTs [17c].

2.7.2. The role of the metal-floating catalysts

The role of an organometallic complex is to provide a metal in the zero oxidation state that will catalyse the condensation of carbon. The general picture that has emerged can be summarized as follows.

The volatile organometallic complex decomposes at high temperature into metal ions/radicals/neutrals and these can coalesce to form larger particles in the gas phase. Depending on the reactants used, these metal clusters may contain carbon as well as heteroatoms. The clusters can then react with more carbon atoms or metal atoms either in the gas phase or after deposition on the reactor walls. It appears that the metal cluster catalyst will be in the
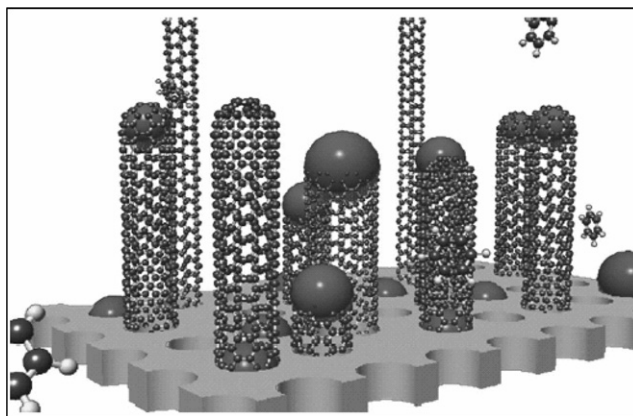

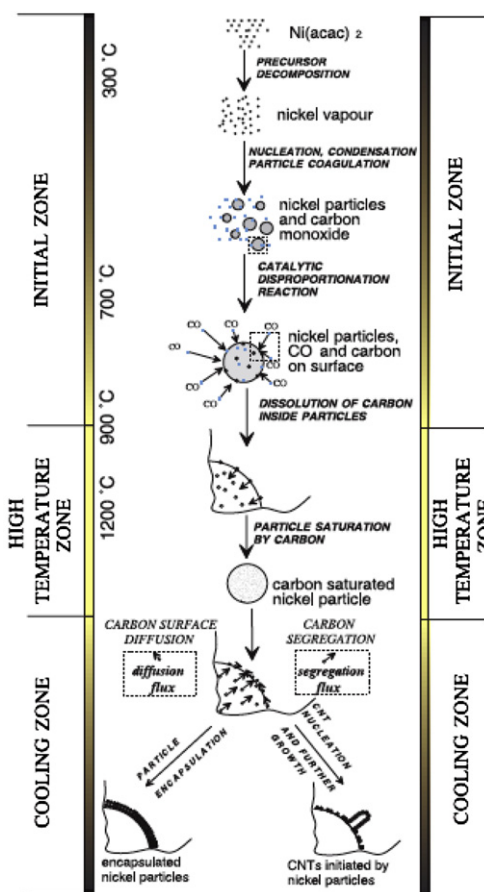**Fig. 9.** Cartoon showing growth of CNTs by both tip-growth and base-growth mechanisms [99].

Fig. 10. SWCNT formation mechanism during aerosol synthesis with nickel acetylacetonate as the catalyst precursor [131].
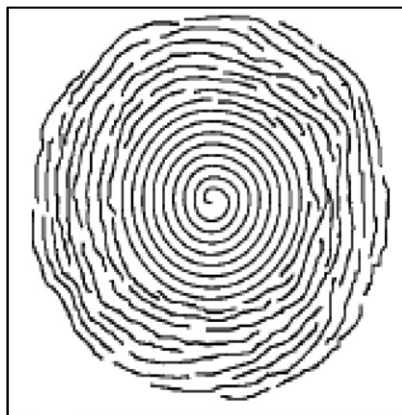
Fig. 11. A patchwork of aromatic rings that make up a carbon sphere synthesized in the absence of a catalyst [127].

gas or liquid phase under typical reaction conditions used. Reaction with carbon then leads to dissolution of the carbon into the metal cluster or deposition onto the metal cluster surface. This appears to be metal dependant.

Fe in particular has the ability to dissolve carbon. Beyond a certain C/Fe ratio, precipitation of carbon occurs. Depending on the cluster size and composition, SCNMs with different shapes and sizes are formed. If the particles are small SWCNTs form and if larger, MWCNTS or even fibrous materials appear. If the carbon forms without the intervention of the Fe, carbon spheres and amorphous carbon are preferably formed.

Studies on Cu suggest that the carbon does not dissolve in the Cu clusters [100]. The carbon rather precipitates on the Cu surface and carbon condensation takes place on the Cu catalyst particle surface.

2.7.3. The carbon growth species

Many different types of carbon ions/radicals/neutrals are formed by decomposition of the carbon source in the gas phase. The metal will also catalyse bond making/breaking in the reaction chamber. The species formed include C_1 radicals/ions, large structures such as PAHs (polyaromatic hydrocarbons) and all intermediate size radicals/ions. These species will be determined by C/H ratios, bond strengths, temperature, metal, pressure, flow rates, etc. Clearly, the type of ligand used in the organometallic catalyst precursor will impact on the gas phase species.

It appears that small carbon species will dissolve in the metal catalyst particle and precipitate out to give CNTs in which the carbon forms graphitic layers. The layer formation is independent of the carbon source and provided there is a constant source of carbon the CNT will grow in length. However, studies have indicated that while the inner diameter may remain the same as a function of time the outer diameter can grow with time [57]. This indicates that carbon can also deposit on the outer layers of the CNTs. This growth generates carbon that appears as 'flakes' of aromatic fragments. A similar growth process occurs when carbon spheres, once nucleated, grow. In this instance NO catalyst is required and the surface appears as a patchwork of aromatic rings (Fig. 11). These spheres grow in diameter with time [101].

This secondary material that grows on CNTs is sometimes referred to as debris [57] and has been observed by TEM in most (if not all) studies that have been reported on the synthesis of MWCNTs. This will impact on the functionalization reactions that occur on the 'walls' of CNTs. The implication from the above is that PAHs are formed in the gas phase and can provide a source of material for SCNM growth.

2.7.4. The role of the heteroatoms

The hydrogen from a hydrocarbon is expelled at some point from the hydrocarbon reactant. This could occur in the gas phase or after reaction with a metal atom/cluster. The SCNMs are hence expected to be predominantly formed of C atoms. After condensation 'dangling bonds' will be saturated with heteroatoms (typically H and O atoms).

Radicals containing H atoms will certainly influence the final carbon deposits. Reilly et al. [102] have recently summarised the possible role of hydrocarbon species in CNT formation and implicated the importance of 'free radical condensates' [103] in the formation of CNTs. His proposal would apply to the formation of all SCNMs. The importance of this work is that it shifts the thinking on a carbon growth mechanism back onto the carbon precursors and this will again relate to the structure of carbons and volatile organometallic catalysts used as SCNM reactants. In particular, Reilly states that 'models built on the notion of elemental carbon diffusing on or through a metal lack completeness' [102].

The role of oxygen is to remove or saturate 'dangling carbon atoms' and remove amorphous carbon that would poison the metal sites. TGA studies have revealed that amorphous carbon is more readily oxidized than is aromatic carbon (i.e. sp^2 versus sp^3 carbon). Again, the role of oxygen radicals/ions/neutrals in the gas phase are important as has been shown by sonication studies with ferrocene/oxygenate mixtures [58].

3. A case study – ferrocene and SCNMs

Remarkably, ferrocene has been implicated in the synthesis of SWCNTs, DWCNTs, MWCNTs, amorphous CNTs, branched CNTs, spheres, etc. An evaluation of the literature allows for an understanding of how such a wide range of shaped carbons can be synthesized from one catalyst system. An analysis of the literature reveals that the control of reaction parameters permits control (partial) of the morphology of the final polymerized carbon material. The morphology of the SCNMs is also influenced by the choice of reactor and reactants.

SWCNTs: Produced in a flow system at high temperature (>1000 °C) [63c]; very high flow rate (1500 ml/min) [64]; argon/hydrogen carrier mixture with a ratio of Ar:H_2 of 2:1 [50]; numerous carbon sources used including acetylene [37,51,67], hexane [63] benzene [63c–e], xylene [50], carbon monoxide [61,96]; thiophene [63] or solid sulfur [64], as an additional promoter. High-pressure CVD reactor at 1–5 bar at high temperature of 900 °C [52]. Apart from the above conditions, the synthesis of SWCNTs is favoured by a high iron to carbon ratio, e.g. ferrocene/benzene mole ratio is above 7 [43b].

DWCNTs: Produced in a flow system at high temperature (>1000 °C) [104]; lower flow rate used (800 ml/min) [104]; numerous carbon sources used including acetylene [65,66], methane [70], xylene [71] and an additional sulfur promoter in the optimal ratio range of S:FcH at 1:8–1:64 [65]. The conditions for synthesis of SWCNTs are similar to those used to produce DWCNTs but in many instances a decrease in flow rate favours the formation of DWCNTs.

MWCNTs: Produced in a flow system at moderate temperature (~875 °C) [33b]; moderate carrier flow rate (~1000 ml/min) [45b]; numerous carbon sources used including benzene [43b], xylene [33b,45a–c], toluene [44b]; the use of sulfur (thiophene) as a promoter is not very common [43b]. Produced in a confined space under autogenic pressure and temperature in the range 700–800 °C [10a,13b,c] carbon sources used include anthracene [10a] and tetrachloroethene [13c].

Amorphous CNTs: Produced in a confined space at autogenic pressure and at a low temperature of ~200 °C [97,98]; carbon

sources used include benzene [97,98]. Additives include sodium [97] or sulfur [98]. Materials are produced in a flow system at high temperature 1100–1200 °C with benzene as carbon source, thiophene as additive and under a H_2 flow rate of 100 ml/min [63b].

HCSs: Produced in a confined space under nitrogen at pressure of 2.2 MPa and at moderate temperature of 700 °C [13b] or at a pressure of 8 MPa at 550 °C with C_2Cl_4 [90]. Materials are produced in a flow system at high temperature (1000 °C) with camphor as carbon source, thiophene as additive and under an Ar flow with a feedstock input rate of 12.5 g/h [101a]. Alternatively they are produced in a flow system at high temperature 900 °C with no external carbon source but under the flow of pure Cl_2 gas for 30 min [13a].

Filled spheres: Produced in a confined space at autogenic pressure and at a temperature of 800 °C when the Fe/C ratio is less than 0.033 using anthracene as carbon source [10a]. Materials are produced in a flow system in a moderate temperature range of 580–700 °C with anthracene as carbon source under H_2 with a flow rate of 300–400 ml/min. The key issue is the use of a low iron content; typically the ratio of ferrocene: anthracene is 1:7.

Carbon onions: Produced in a flow system at a high temperature of 900 °C with Fe_3CO_{12} as additional carbon source under an Ar gas (flow rate of 260 ml/min) containing 0.5% and 1.0% of O_2 [14].

Fe-filled CNTs: Produced in a confined space at autogenic pressure and at high temperature 1000 °C with thiophene as a carbon source [14]. CNTs are produced in a flow system at a high temperature of 900 °C in Ar/H_2 mixture (3:1) as the carrier gas with a total flow rate of 50 ml/min [5b].

Core shells: Produced in a confined space at autogenic pressure and at high temperature 1000 °C with picric acid as carbon source with low C/Fe ratio (<34:1) [16c].

CNTs Y-Juctions: Produced in flow system at a high temperature of 1000 °C with thiophene as an additive and an Ar/H_2 mixture as carrier gas with flow rates of 225 ml/min and 25 ml/min, respectively [75].

4. Conclusions

From the above discussions it can be seen that organometallic reagents have played a key role in both the synthesis of SCNMs and in providing mechanistic information on the synthesis reactions. The role of the organometallic complex is to provide a source of both metal and ligand (carbon, heteroatoms) for SCNM growth. Currently temperatures of above 700 °C are required in flow systems to generate graphitic CNTs but lower temperatures can produce other shaped carbons. Clearly, the role of the organometallic complex is to provide a source of carbon and metal fragments for the reaction. These fragments are determined by the actual complexes used. As lower temperatures become possible for the synthesis of SCNMs the role of the specific organometallic catalyst used will become more important.

In the pioneering days in organometallic chemistry the 'black' decomposition residues formed in many synthetic reactions that did not produce the required product from a synthesis were always discarded. It is possible that many of these residues may have contained unique shaped carbon nanomaterials. The ready accessibility of electron microscopes now permits a re-evaluation of some of these materials. Systematic studies could be revealing! [87,105].

Acknowledgements

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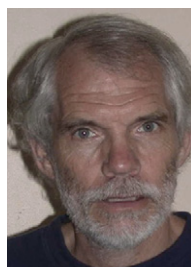
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