



The effect of arylferrocene ring substituents on the synthesis of multi-walled carbon nanotubes

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ABSTRACT

The synthesis of shaped carbon nanomaterials (SCNMs) such as carbon nanotubes (CNTs), amorphous carbon, carbon fibres (CFs) and carbon spheres (CSs) was achieved using *para*-substituted arylferrocenes, FcPhX (X = H, OH, Br, COCH₃) or a mixture of ferrocene (Fch) and substituted benzenes (PhX; X = H, OH, Br, COCH₃). The reactions were carried out by an injection chemical vapour deposition (CVD) method using toluene solutions (carrier gas: 5% H₂ in Ar at a flow rate of 100 ml/min) in the temperature range of 800–1000 °C. In most instances multi-walled CNTs (MWCNTs) were produced. Variations in the concentrations of precursor catalysts, the injection rate and temperature affected the type, distribution and dimensions of the SCNMs produced. The overall finding is that the presence of Br and O in these studies significantly reduces CNT growth. A comparative study on the effect of FcPhX versus Fch/PhX mixtures was investigated. The SCNMs were characterized by transmission electron microscopy (TEM), Raman spectroscopy and thermal gravimetric analysis (TGA).

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1. Introduction

The synthesis of shaped carbon nanomaterials (SCNMs) such as carbon spheres (CSs), carbon fibres (CFs), nanohorns, nanocoils and in particular carbon nanotubes (CNTs) have become an increasingly important subject area in the field of nanostructured materials. Although the existence of filamentous carbon nanomaterials [1] has been known for decades, it is only since the 1990s that they have become a material type that has attracted considerable attention. This is due to their unique chemical and physical (electrical [2,3], magnetic [4,5] and mechanical [6,7]) properties. These properties have implications for industrial and technological applications [8–10], especially in nanoelectronics [11], energy storage [12] and in catalysis [13].

SCNMs have been synthesised using various vapour phase methods including laser vapourization [14,15], arc discharge [16,17] and chemical vapour deposition (CVD) [18,19]. The CVD method is one of the most promising methods for the large scale production of SCNMs and the method has in particular been shown to produce high yields of CNTs in good purity, as well as aligned CNTs, even at low temperatures [20,21]. More recently another type of CNT synthesis methodology which utilizes a closed container (e.g. sealed quartz tubes or autoclaves) has also been developed [22].

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Organometallic compounds such as ferrocene (Fe(C₅H₅)₂) [23] and Fe(CO)₅ [24] have been widely reported to produce good yields of CNTs and other SCNMs. These compounds do not have a counterion and they also contain both the metal and some carbon within their structure. Hence, they act both as a catalyst and as a carbon source in SCNM production. In general, a carbon source such as CH₄ [25], C₆H₆ [26], CO [27], etc. is also added to the catalyst to provide the major source of carbon to produce the SCNMs. The choice of this added carbon source also affects the kind and shape of SCNMs obtained. Toluene has proven to be a good carbon source for the synthesis of CNTs in the CVD reaction in the temperature range 800–1000 °C [28].

Currently only a limited number of studies have appeared in the literature describing the effect of ferrocene (Fch) substituents on SCNM product formation using the CVD floating catalyst method [29–31]. Furthermore, no information has been reported on the use of arylferrocenyl derivatives in the synthesis of SCNMs. A study of the effect of various *para*-substituted arylferrocenes, on the influence on SCNMs synthesis is thus reported in this study. A comparative study on the effect of mixing ferrocene with substituted benzenes, on SCNM synthesis relative to that of arylferrocenes, is also reported (Fig. 1).

2. Experimental

Ferrocene was purchased from Strem Chemicals while toluene (analytical grade) was obtained from Sigma Aldrich Chemical Company and was used as the carbon source. Both were used as

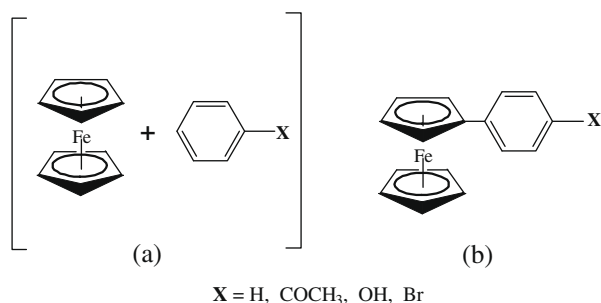


Fig. 1. The precursors used for synthesis of SCNMs in toluene: (a) ferrocene (FcH) and para-substituted benzenes; (b) arylferrocenes (FcPhX).

received. Phenylferrocene (FcPhH), 4-hydroxyphenylferrocene (FcPhOH), 4-bromophenylferrocene (FcPhBr) and 4-nitrophenylferrocene (FcPhNO₂) were prepared by the diazonium salt method [32] while 4-ferrocenylacetophenone (FcPhCOCH₃) was prepared by a modified Suzuki cross-coupling reaction [33]. 4-Ferrocenylaniline (FcPhNH₂) was obtained by the catalytic reduction of 4-nitrophenylferrocene (FcPhNO₂) [34].

A quartz tube reactor, 80 cm in length and 2.8 cm internal diameter, was inserted horizontally into an electrical furnace with the outlet of the tube connected to a gas bubbler (Supplementary material; Fig. S1). The temperature inside the quartz tube was determined by means of a thermocouple placed in the middle of the furnace. Synthesis of CNTs was carried out in the temperature range 800–1000 °C, under 5% H₂ in argon (v/v) at atmospheric pressure. The flow rate of H₂ in argon was kept constant at 100 ml/min. The substituted arylferrocenes were dissolved in toluene (2.5 wt.% or 5 wt.%); the catalyst loading in toluene was limited by solubility constraints. The solutions were placed in a 10 ml syringe and injected into the heated tube by means of a SAGE syringe pump (at 0.8 and 0.2 ml/min injection rate). The solutions were injected into the tube reactor via a specially designed quartz tube 0.2 cm internal diameter and 20 cm in length, cooled by water. The solutions were injected directly into the high temperature zone of the large quartz tube reactor. When solution injection was complete the electrical furnace temperature was allowed to cool down to room temperature under 5% H₂ in argon (v/v).

The carbon deposited materials that formed were scraped from the walls of the quartz tube. These materials were characterized by low resolution transmission electron microscopy (TEM; JEOL JEM 100 S). The samples for TEM analysis were prepared by sonication of the carbonaceous materials in methanol or ethanol. A few drops of the resulting dispersed suspension were placed onto a holey TEM copper grid for analysis at 80 kV and at varying magnifications. The distribution, number and size of the various nanoparticles materials were obtained from the TEM photographs by

counting procedures (counting at least 100 'carbon shaped objects' per sample). These were randomly chosen from different TEM images and represent average values.

Raman spectra were measured using the single spectrograph stage of a Jobin-Yvon T64000 Raman spectrometer. The excitation source was 636.4 nm from a tuneable Spectra-Physics dye laser. The laser beam was focused onto the sample using the 20× objective of an Olympus microscope. The backscattered light was dispersed using a 600 line/mm grating and detected using a liquid nitrogen cooled CCD detector. Thermal gravimetric analysis (TGA) measurements were performed under flowing air on a Perkin-Elmer TGA 7 at a heating rate of 10 °C/min.

3. Results and discussion

The SCNMs were synthesised from solutions of FcH, FcPhH, FcPhOH, FcPhBr, FcPhCOCH₃ and FcPhNH₂ in toluene. They were also synthesised from mixtures of solutions of FcH and substituted benzenes in toluene (2.5 wt.%). Toluene, *para*-substituted phenyl rings and the cyclopentadienyl ligands provided the carbon for the CNT growth. The catalysts used in this study are shown in Fig. 1.

3.1. Analysis of SCNMs

Generally four types of SCNMs were made using the above catalysts, namely; (i) CNTs, (ii) carbon fibres (CFs), (iii) carbon spheres (CSs) and (iv) amorphous carbon (a-C). Reactions with FcH and FcPhH were performed to provide reference data for the effect of the substituted benzenes and arylferrocenes on the reaction products formed.

Good yields of well structured MWCNTs were obtained at 800 °C (Fig. 2) and 900 °C with 2.5 wt.% of FcH in toluene, while no CNTs were found at 1000 °C (Table 1). Generally, the pyrolysis of hydrocarbons at high temperatures (e.g. 1000 °C) favours the productions of CSs and amorphous carbon. Transmission electron microscopy (TEM) studies revealed that the mean internal diameter of the CNTs produced at 800 °C was 35 nm with a mean external diameter of 55 nm while at 900 °C the CNT diameters were found to be 30 nm and 40 nm, respectively. This observation of narrower tube formation as the temperature is increased is not unexpected. The average tube length (obtained from TEM pictures) at 800 °C and 900 °C were 5.5 μm and 6.0 μm, respectively. The mean diameter of the nanofibres was found to be 125 nm at 900 °C and 100 nm at 1000 °C.

FcPhH in toluene (2.5 wt.% and 5 wt.%, Table 1) was used as a catalyst to synthesise the CNTs at 800 °C, 900 °C and 1000 °C. At all the temperatures used, MWCNTs were formed with *T* = 1000 °C providing very low percentages of CNTs at both catalyst concentrations. The 2.5 wt.% catalyst concentration gave CNTs with

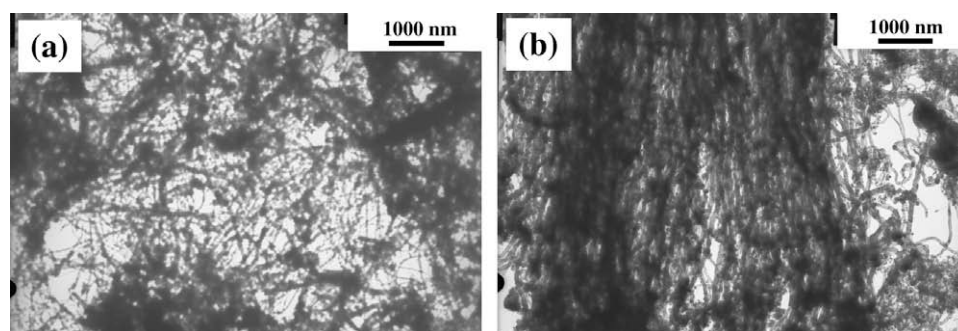


Fig. 2. CNTs formed from pyrolysis of (a) 2.5 wt.% FcH and (b) 2.5 wt.% FcPhH in toluene with a flow rate of 0.8 ml/min and at temperature of 800 °C.

Table 1
Summary of the yield and size distribution of SCNMs produced from different catalysts under a constant flow rate of 100 ml/min of 5% H₂ in argon (v/v) at different temperatures.

Catalyst	Temperature (°C)	Injection flow rate (ml/min)	Yield (g)	SCNMs formed (%)	Mean CNTs and CFs diameters (nm)
FcH (2.5 wt.%)	800	0.8	0.210	80T, 20a-C	35 T(ID), 55T(OD)
	900	0.8	0.375	70T, 10F, 20a-C	30T(ID), 40T(OD), 125F
	1000	0.8	4.200	25F, 5S, 70a-C	100F
FcPhH (2.5 wt.%)	800	0.8	0.300	85T, 10F, 5a-C	20T(ID), 50T(OD), 120F
	900	0.8	1.254	40T, 50F, 10a-C	15T(ID), 60T(OD), 160F
	1000	0.8	2.605	5T, 5F, 10S, 80a-C	55T(ID), 85T(OD), 170F
FcPhH (5.0 wt.%)	800	0.8	0.305	80T, 20a-C	25T(ID), 45T(OD)
	900	0.8	1.264	30T, 50F, 20a-C	10T(ID), 40T(OD), 120F
	1000	0.8	2.701	5T, 5F, 5S, 85a-C	10T(ID), 35T(OD), 110F
FcPhOH (2.5 wt.%)	800	0.8	0.050	70T, 10F, 10S, 10a-C	20T(ID), 40T(OD), 125F
		0.2	0.210	20T, 50F, 30a-C	15T(ID), 50T(OD), 135F
		0.8	0.250	50T, 50a-C	25T(ID), 35T(OD)
	900	0.2	1.300	15T, 50F, 5S, 30a-C	15T(ID), 40T(OD), 140F
		0.8	0.260	40F, 40S, 20a-C	135F
		0.2	1.670	20F, 30S, 50a-C	140F
FcPhCOCH ₃ (2.5 wt.%)	800	0.8	0.015	10T, 40F, 30S, 20a-C	15T(ID), 65T(OD), 100F
	900	0.8	0.926	20F, 30S, 50a-C	110F
	1000	0.8	3.065	10F, 10S, 80a-C	120F
FcPhBr (2.5 wt.%)	900	0.8	0.260	10T, 5F, 80S, 5a-C	15T(ID), 30(OD), 60F
	800	0.8	0.390	2T, 5F, 90S, 2T	20T(ID), 45(OD), 80F

T = CNTs, F = CFs, S = CSs, a-C = amorphous carbon; T(ID) = mean tube inner diameter; T(OD) = mean tube outer diameter.

a mean length of 13.0 μm while that of 5.0 wt.% catalyst was found to give slightly shorter tubes (11.0 μm). At higher concentration (5.0 wt.%) and higher temperature (>1000 °C) a significant increase in amorphous material (85%) was noted.

In general, the phenyl ring appears to have a very modest effect on the SCNM yield and morphology when compared to ferrocene. Even the addition of more catalyst (compare 2.5% and 5% results) has only a minor effect on the product yield/dimensions.

Due to solubility constraints 2.5 wt.% catalyst concentrations were used in all studies involving the *para*-substituted arylferrocenes, FcPhX (X = OH, COCH₃, Br). For comparative purposes, the experiments were conducted at three different temperatures (800 °C, 900 °C and 1000 °C). These conditions allowed for a comparison with the FcPhX (X = H) catalyst described above.

The reactions with FcPhX (X = OH) at 800 °C were performed at two different flow rates, 0.8 and 0.2 ml/min (Table 1). Although higher yields of SCNMs were formed at the lower flow rate (0.2 ml/min) the product was mainly comprised of amorphous carbon. Again at the highest temperature, CNT formation was at a minimum (both flow rates). A comparison of the morphological data with X = H indicates that the tubes prepared with X = OH tend to have narrower outer diameters. The outer tube diameter was larger at the lower flow rate. The CFs showed a larger mean diameter than those observed using ferrocene (Table 1). The tube lengths could not be easily measured since they were not well aligned but were estimated to be in the micro length range of 2.0–2.2 μm.

The use of FcPhCOCH₃ (2.5 wt.%) as catalyst gave MWCNTs at 800 °C in very low yield (Table 1). The mean internal diameter of 15 nm and outer diameter of 65 nm were similar to those found when FcH was used as catalyst. Fig. 3a depicts TEM micrographs of the MWCNTs observed. The mean length of the tubes was observed to be 2.5–3.0 μm. A large amount of amorphous carbon and fused CSs with typical diameters in the range of 0.8 μm to 1.50 μm were obtained at 1000 °C (Fig. 3b).

The use of FcPhBr (2.5 wt.%) in the synthesis of CNTs resulted in the production of 90% spheres and <2% small diameter tubes even at a temperature of 800 °C. Thus the presence of the Br leads to sphere formation rather than CNT or amorphous carbon production.

Reactions were also attempted in which FcH and PhX (X = OH, OMe, Br) were used in a 1:1 molar ratio (Table 2). A comparison of the data in Table 1 with this data (Table 2) permits an evaluation of the effect of proximity of the Fe catalyst to the heteroatom substituent to be established [35]. Comparative reactions were carried out at 900 °C at a flow rate of 0.8 ml/min. In every instance, yields for the FcH/PhX mixture were lower. However, the type of SCNM formed varied—more tubes were formed using the FcH/PhX mixture than with FcPhX (see Fig. 4).

3.2. TGA analysis

TGA studies were carried out to study the thermal stability of the *unpurified* SCNM mixtures produced by heating the samples

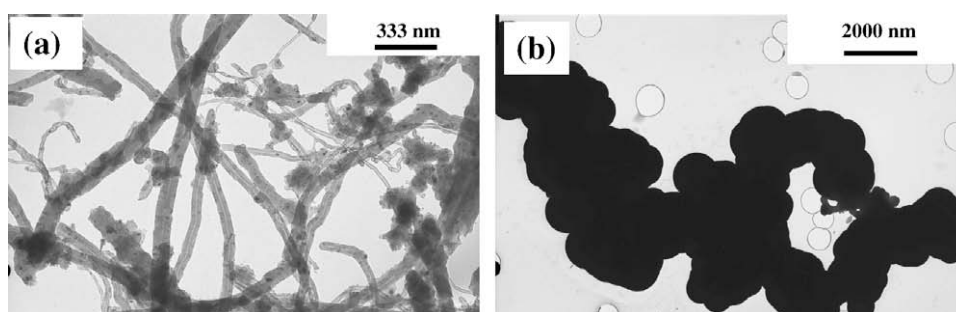


Fig. 3. (a) CNTs produced from the pyrolysis of 2.5 wt.% FcPhCOCH₃ and (b) fused CSs from 2.5 wt.% 4 FcPhCOCH₃ in toluene with a flow rate of 0.8 ml/min at 800 °C and 900 °C, respectively.

Table 2

Summary of the yield and size distribution of SCNMs produced from mixtures of ferrocene and *para*-substituted phenyls in toluene under a constant flow rate of 100 ml/min of 5% H₂ in argon (v/v) at 900 °C.

Catalyst	Temperature (°C)	Injection flow rate (ml/min)	Yield (g)	SCNMs formed (%)	Mean CNTs and CFs diameters (nm)
FcH (2.5 wt.%)	900	0.8	0.375	70T, 10F, 20a-C	30T(ID), 40T(OD), 125F
FcH/Ph (2.5 wt.%)	900	0.8	0.125	98S, 2T	30T(ID), 50(OD)
FcH/PhCOCH ₃ (2.5 wt.%)	900	0.8	0.315	70T, 25F, 5a-C	35T(ID), 50T(OD), 110F
FcH/PhBr (2.5 wt.%)	800	0.8	0.295	95S, 5a-C	–

T = CNTs, F = CFs, S = CSs, a-C = amorphous carbon; T(ID) = mean tube inner diameter; T(OD) = mean tube outer diameter. Fc/PhX molar ratio = 1:1.

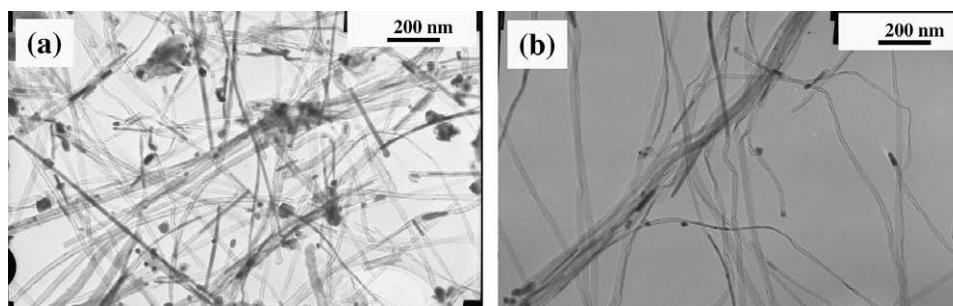


Fig. 4. TEM pictures of CNTs produced from the pyrolysis of FcPhBr (2.5 wt.%) at 900 °C.

at elevated temperatures in air at a constant rate. In all cases the TGA profiles showed that the products commenced decomposition at $T > 500$ °C. In every instance about 5–10% residue was observed in the TGA profile at $T > 700$ °C; due to the presence of iron oxide (Fig. 5). The TGA data for reactions performed at 900 °C are shown in Fig. 5. The TGA curves (Fig. 5) reveal that SCNMs grown from FcPhCOCH₃ are thermally more stable than those grown from all the other organometallic complexes (FcH, FcPhOH, FcPhNH₂) decomposing at 590 °C (e.g. compared to 550 °C for SCNMs produced from FcH). The SCNMs obtained from FcPhOH gave the thermally least stable materials that commenced decomposing at lower temperatures (500 °C). This effect is attributed to the nature of the carbon products in the mixture. Generally, samples containing more amorphous carbon and CSs tend to lose weight at much lower temperatures than those containing more CNTs and CFs.

3.3. Raman spectroscopy studies

The Raman spectra for all the *unpurified* samples showed the presence of two major peaks: a G-band at approximately

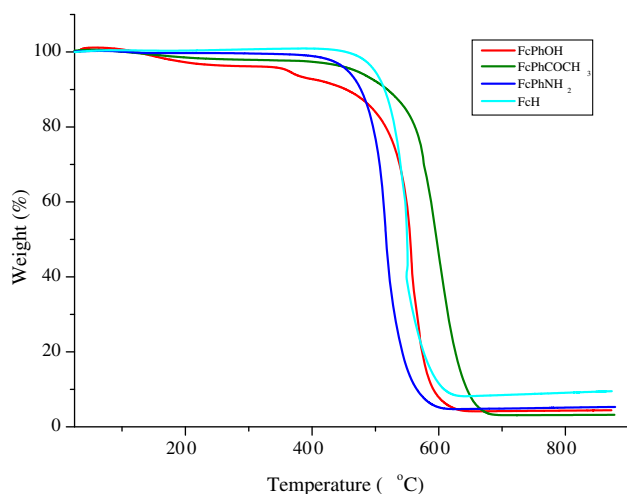


Fig. 5. TGA curves of CNTs grown from different arylferrocenes (2.5 wt.%) at 900 °C.

1590 cm⁻¹ originating from the Raman active E_{2g} mode and a D-band at around 1350 cm⁻¹ known as the disorder-induced band. The Raman spectra of SCNMs produced from a range of catalysts at 900 °C is depicted in Fig. 6. The I_D/I_G ratio gives a measure of the extent of disorder in the nanomaterials. For example, a higher I_D/I_G ratio implies more disorder within the CNTs, while lower ratios imply less disorder.

The SCNMs grown from both FcH and FcPhCOCH₃ demonstrate low I_D/I_G ratios (0.63 and 0.69, respectively) while FcPhOH synthesised SCNMs show more disorder (0.83; Table 3). This data corresponds with the TGA data since CNTs derived from FcH and FcPhCOCH₃ are more stable (i.e. graphitic) than those produced from FcPhOH. Interestingly the Raman data obtained for SCNMs produced from FcPhX with X = NH₂ [35] gave an even higher I_D/I_G ratio; this is readily explained by the doping of C by N in the SCNMs.

3.4. Mechanism of catalyst deactivation

The mechanism by which CFs, CNTs and CSs are produced in the presence of ferrocene has been well documented [30]. The Fe acts

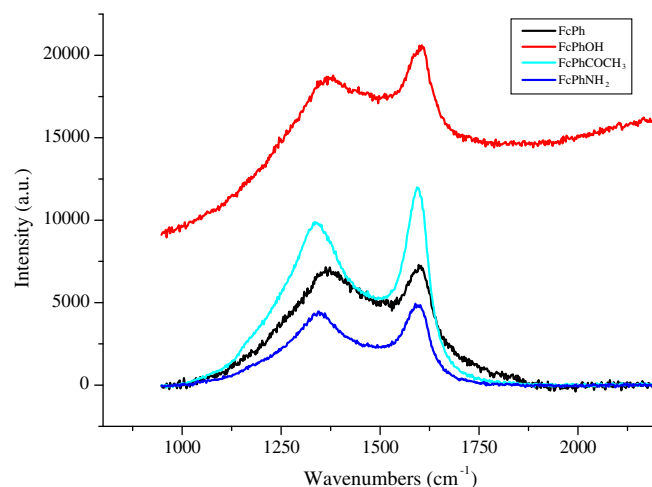


Fig. 6. Raman spectra of CNTs grown from different arylferrocenes (2.5 wt.%) at 900 °C.

Table 3

D- and G-band positions and I_D/I_G ratios of SCNMs grown from different aryl ferrocenes.

Entry	Catalyst (2.5 wt.%)	D-band (cm^{-1})	G-band (cm^{-1})	I_D/I_G ratio
1	FcH	1356	1587	0.63
2	FcPhCOCH ₃	1334	1590	0.69
3	FcPhOH	1367	1602	0.83
4	FcPhBr	1349	1600	0.89
5	FcPhNH ₂ ^a	1364	1587	0.97

^a Ref. [35].

as a catalyst for C growth to form CNTs (or CFs if the Fe particles are big) while the FcH plays little or no role in CS growth [28]. This information provides the basis for establishing the impact of ferrocene ring substituents on SCNM yield and morphology.

The effect of varying the arylferrocenes on the production of SCNMs in this study revealed the following:

- (i) The total yield of carbonaceous material for all catalysts increased with temperature.
- (ii) As the temperature increased the CNT product yield decreased while either the CS or amorphous carbon content increased.
- (iii) The presence of 'O' containing *para*-substituents (OH, COCH₃) gave lower yields of all SCNMs compared to the other arylferrocenes.
- (iv) The presence of Br generates more spheres than are generated from the other aryl substituted ferrocene catalysts. The CNTs produced from the X = Br catalyst had very narrow diameters.
- (v) The proximity of the heteroatom substituent to the iron catalyst impacts on the SCNMs produced (compare results in Tables 1 and 2).

Points (i) and (ii) are expected results and are consistent with the behaviour of Fe catalyst systems. Points (iii) and (iv) reveal that the ability of Fe to act as a catalyst is modified by the presence of O and Br.

3.4.1. Effect of 'O'

In both studies the yield of SCNMs is reduced, relative to FcH. This indicates that the O poisons the catalyst. This is unexpected as there are many studies that indicate that O assists in cleaning CNTs. This is achieved by reaction of reactive (non graphitic) carbon with oxygen [36]. It is also clear that the experiments using FcPhX (X = OH and COCH₃) give different results. The presence of the OH results in the production of very low yields of all SCNMS at all temperatures. Further, much less amorphous carbon is produced when OH is present (relative to the other catalysts).

3.4.2. Effect of 'Br'

The Br has a dramatic effect on the formation of SCNMs. Poor yields are noted and a predominance of spheres are to be seen. This is reminiscent of studies with ferrocene at high temperatures. The data suggest that the Br destroys the catalytic activity of the Fe. Similar effects have been observed when CpFe(CO)₂I was used as a catalyst [37]. In these reactions the I poisoned the catalyst.

Point (v) is consistent with some related studies from our group [35]. In this study the influence of NH₂ groups was investigated – FcPhX and FcH/PhX mixtures were compared. It was observed that the Fe catalyst atoms interacted with both carbon and heteroatoms in the gas phase. Further, the closer the Fe and the heteroatom were to each other in the gas phase, the larger the impact of the heteroatom. A similar result was observed here for both O and Br atoms.

This information can be explained by the following mechanism. At the high temperatures used the catalysts and reagents decompose into radicals, atoms and ions. The type and concentration of these gas phase species will vary depending on the catalysts used. The Fe catalyst interacts with these species to generate the SCNMs that are produced. The data suggest that Br ions/radicals react with Fe to form 'FeBr' species that are not catalytically active and thus CSs are preferentially produced. In contrast Fe reacts with O containing ions/radicals to form 'FeO' species. These species react differently to the 'FeBr' species and generate more amorphous carbon. Both the 'Br' and 'O' produced in this study poison CNT growth.

4. Conclusions

In this study we have shown that the role of *para*-substituted ferrocene complexes is to provide a source of metal, carbon and heteroatom (O or Br) radicals/atoms/ions. The toluene also provides an extra source of carbon. This mixture of radicals/atoms/ions can act as a precursor for the production of SCNMs. Not unexpectedly, the heteroatoms impact on the catalyst activity and selectivity and thus influence the yields and morphologies of the resulting SCNMs. The overall finding is that the presence of Br and O in these studies significantly reduces CNT growth.

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Appendix A. Supplementary material

Supplementary data associated with this article can be found, in the online version, at doi:10.1016/j.jorgchem.2009.02.031.

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