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Synthesis of multi-walled carbon nanotubes catalyzed by substituted ferrocenes

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Abstract

A range of substituted ferrocenes were used as catalysts for the synthesis of multi-walled carbon nanotubes (MWCNTs) and carbon fibers (CFs). These products were obtained in the temperature range 800–1000 °C, in a reducing atmosphere of 5% H_2 by pyrolysis of $(CpR)(CpR')Fe$ (R and R' = H, Me, Et and COMe) in toluene solution. The effect of pyrolysis temperature (800–1000 °C), catalyst concentration (5 and 10 wt.% in toluene) and solution injection rate (0.2 and 0.8 ml/min) on the type and yield of carbonaceous product synthesized was investigated. Carbonaceous products formed include graphite film (mostly at high temperature; 900–1000 °C), carbon nanotubes and carbon fibers. The carbonaceous materials were characterized by scanning electron microscopy (SEM), transmission electron microscopy (TEM) and Raman spectroscopy. The ferrocene ring substituents influenced both the CNT diameter and the carbon product formed.
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1. Introduction

Filamentous carbons [1] have been known for many decades but since the 1990s have become a material type that has attracted considerable attention because of their potential applications in nanoelectronics [2], energy storage [3], as catalyst supports [4], etc. One of the most important types of filamentous carbons is the carbon nanotube, reported by Iijima in 1991 [5]. CNTs can be viewed as graphitic sheets, rolled up so that the ends meet to form tubes, with typical diameters in the nano dimension range [6]. CNTs are classified according to the number of tubes formed: i.e. single walled (SWCNTs), double walled (DWCNTs), multi-walled (MWCNTs), etc.

Three main generic synthesis methods have been used to make CNTs and these are: arc-discharge [5,7], laser ablation [8] and chemical vapor deposition (CVD) [9]. All three methods can produce SWCNTs and MWCNTs. The CVD method requires the use of both a catalyst (typically Fe, Co or Ni) and a carbon source to produce CNTs and other novel carbon 'shaped' materials. A variant of this method is the so called floating catalyst CVD method (or gas phase CVD or injection CVD method) [10]. In this method a volatile metal catalyst and a carbon source are passed through a quartz reactor (temp. between 700 °C and 1100 °C) to generate the new carbon materials.

Organometallic compounds such as ferrocene [11] and $Fe(CO)_5$ [12] have been widely reported to produce good yields of CNTs since both compounds contain both the metal and a carbon source within their structure. Indeed the current commercial method to make CNTs, is the HiPCO process [13] which uses $Fe(CO)_5$ as catalyst and CO as carbon source.

Surprisingly, other than studies on the organometallic complexes listed above there have been very few studies on the use of other volatile organometallic precursors as possible catalysts in the synthesis of tubular carbon materials.

Some early work reported on the use of Cp_2Co as a catalyst but few studies have been reported to follow up on this study [14]. Pyrolysis of iron phthalocyanine (FPc), cobalt phthalocyanine (CoPc), and nickel phthalocyanine (NiPc) have also been found to be efficient catalysts for the synthesis of CNTs [15]. More recently the use of organometallic Mo [16] and Fe [17] catalyst precursors for CNT synthesis have also been reported by others.

We have commenced a systematic study of the use of organometallic complexes in the synthesis of tubular and other 'shaped' carbons by the floating catalyst method [12b,18]. Recently we reported on the use of Cp_2Fe/$Mo(CO)_5(^tBuCN)$ mixtures and found that MWCNTs were produced from the Fe/Mo catalysts. A study on the effect of S attached to the ferrocene ring has also been reported [19]. In this paper we report on the use of substituted ferrocenes as catalysts to evaluate the role of the ring substituent on filamentous carbon formation.

2. Experimental

Ferrocene (Fc) was purchased from Strem Chemicals; acetylferrocene was purchased from Sigma–Aldrich and used as received. Dimethylferrocene [20] and diethylferrocene [21] were synthesized as reported in the literature. A quartz tube reactor (800×28 mm i.d.) was inserted horizontally into an electrical furnace with the outlet of the tube connected to a gas bubbler similar to studies reported by other workers [22]. The temperature inside the quartz tube was determined by means of a thermocouple placed in the middle of the furnace. As previously reported, a second moveable thermocouple was used to establish the profile of the temperature in the reactor.

Synthesis of CNTs was carried out in the temperature range 800–1000 °C, under 5% H_2 in Argon (v/v) (AFROX) at atmospheric pressure. The flow rate of H_2 in argon was kept constant at 100 ml/min. Dimethylferrocene and diethylferrocene were dissolved in toluene at weight percentages of 5 wt.% and 10 wt.%. The catalyst 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 (2 mm i.d., 200 mm in length), cooled by water, similar to that described in the literature [12b,18]. This specially designed tube enabled the solution to be injected directly into the high temperature zone of the large quartz tube reactor.

The carbon deposited materials formed were scraped from the walls of the quartz tube in both the high temperature region and low temperature region (temperature <300 °C) in the tube. Carbon products were also collected at the rear end of the quartz tube; these products were carried away from the hot zone of the furnace by the gas stream. The carbon materials were characterized by scanning electron microscopy (SEM; JEOL JSM 840), low resolution transmission electron microscopy (TEM; JEOL JEM 100 S) and Raman spectroscopy (J-Y T64000). The number and size of the carbon materials were obtained from the TEM photographs by counting procedures and represent average values.

3. Results and discussion

A range of ring substituted ferrocenes have been evaluated for making filamentous carbons (CNTs, CFs). In particular ferrocenes, $(CpR)(CpR')Fe$, with R and $R' = H$, Me, Et and COMe have been evaluated for MWCNT synthesis in the reaction. The carbon source chosen for the study was toluene, as it has been shown to be a good carbon source in the temperature range 800–1000 °C [12b]. In the reaction the iron catalyst and toluene (5 and 10 wt.% Fe conc.) were injected into the high temperature quartz reactor at two different flow rates (0.8 and 0.2 ml/min).

Ferrocene, which is currently regarded as a standard Fe catalyst source in CNT synthesis, was also tested for CNT synthesis capabilities to provide a standard to compare with the substituted ferrocene complexes.

The carbonaceous materials produced from all the reactions were weighed (yields given in Table 1) and analyzed by SEM and TEM. The composition of the materials are also given in Table 1. In general amorphous carbon, carbon fibers (tubular material which does not show an internal hollow region), MWCNTs and carbon microspheres were produced in different amounts in the reactions. These products are identical to those reported in earlier studies using ferrocene [23]. The average dimensions of the materials produced are also given in Table 1.

Ferrocene. Consistent with our earlier study, the reaction produced tubes with micron lengths and diameters of 30–50 nm as well as fibers with larger diameters (100–140 nm) (Fig. 1). No carbon microspheres were noted, even at 1000 °C.

Dimethylferrocene. The data reveal that tubes, fibers and amorphous carbons are produced in the reactions (Fig. 2, Table 1).

(i) The fibers have the same diameter as those produced from ferrocene (100–140 nm). In general the fiber content increased with temperature and with lower Fe content but the flow rate had little effect on the relative fiber yield. The fibers were amorphous rather than graphitic in structure.

(ii) The MWCNTs were, in general, narrower than those produced by ferrocene (typically about 20–25 nm in diameter). The yield decreased with increasing temperature, with lowered Fe content and appeared to be independent of flow rate.

(iii) The overall yields were generally lower than obtained from ferrocene.

Diethylferrocene. A wide range of conditions were studied but no CNTs or fibers were produced in the reaction. Carbon microspheres were obtained in the temperature range of 900–1000 °C with a diameter of about 210 nm.

Table 1
Effect of substituted ferrocene on CNTs growth

Metal content[a]	Temperature (°C)	Injection rate (ml/min)	Notes[b]	Mean diameter[c] (nm)	Yield (g)
FcMe$_2$, 5.0 wt.%	800	0.8	A-C (50%), tubes (50%)	22T	0.087
		0.2	A-C (30%), tubes (60%), fibers (10%)	21T, 100F	0.165
	900	0.8	A-C (80%), tubes (10%), fibers (10%)	25T, 100F	0.197
		0.2	A-C (95%), fibers (5%)	120F	0.256
	1000	0.8	A-C (70%), fibers (30%)	140F	0.848
		0.2	A-C (70%), fibers (30%)	120F	1.302
FcMe$_2$, 10 wt.%	800	0.8	A-C (60%), tubes (40%)	17T	0.529
		0.2	A-C (40%), tubes (30%)	22T	0.585
	900	0.8	A-C (95%), tubes (5%)		0.413
		0.2	A-C (40%), tubes (60%)	25T	0.467
	1000	0.8	A-C (70%), tubes (10%), fibers (15%)	50T, 120F	1.150
		0.2	A-C (65%), tubes (5%), fibers (30%)	46T, 120F	1.987
Fc, 5.0 wt.%	800	0.8	A-C (10%), tubes (70%), fibers (20%)	45T, 100F	0.008
		0.2	A-C (30%), tubes (50%), fibers (20%)	43T, 120F	0.012
	900	0.8	A-C (80%), fibers (20%)	120F	0.359
		0.2	A-C (80%), tubes (10%), fibers (10%)	37T, 130F	0.394
	1000	0.8	A-C (80%), fibers (20%)	140F	1.235
		0.2	A-C (60%), tubes (5%), fibers (35%)	60T, 120F	1.152
Fc,10 wt.%	800	0.8	A-C (20%), tubes (70%), fibers (10%)	42T,120F	0.504
		0.2	A-C (40%), tubes (60%)	33T	0.572
	900	0.8	A-C (10%), tubes (80%), fibers (10%)	38T, 120F	0.906
		0.2	A-C (40%), tubes (50%), fibers (10%)	33T, 140F	0.924
	1000	0.8	A-C (90%), fibers (10%)	120F	1.818
		0.2	A-C (60%), fibers (40%)	140F	0.996
FcAc, 10 wt.%	800	0.8	A-C (60%), spheres (40%)	210S	0.081
	900	0.8	A-C (30%), fibers (30%), spheres (40%)	100F, 180S	0.631
	1000	0.8	A-C (20%), fibers (20%), spheres (60%)	120F, 200S	0.861

[a] Fc = ferrocene, FcMe$_2$ = dimethylferrocene, FcEt$_2$ = diethylferrocene, FcAc = acetylferrocene.
[b] A-C = amorphous carbon.
[c] F = fibers, T = tubes, S = spheres.

Acetylferrocene. No CNTs were produced in these reactions. The fibers produced had the same dimensions as those described above (100–140 nm). Carbon microspheres were produced at all temperatures (diameter typically about 200 nm), but the yield increased with temperature. This is consistent with other reports on carbon microsphere formation. The sphere formation does not require an iron catalyst [12b,24].

Low resolution TEM analysis was performed on samples from all the reactions. Representative TEM pictures are shown in Figs. 1–3. After dispersion in solvent for TEM analysis the products show a mat like appearance, independent of reaction conditions and catalyst used. The lengths of CNTs could not be easily measured since they were not well aligned. As mentioned above, the CNTs produced from ferrocene have much wider diameters than those produced from dimethylferrocene (see Figs. 1–3).

Raman spectra can be used to establish the graphitic nature of the CNTs [25]. Thus, a G-peak at about 1590 cm^{-1}, originating mainly from the graphite in plane E$_{2g}$ vibration mode and a D-peak (at about 1350 cm^{-1}) is attributed to a finite particle size effect and/or structural disorder within the carbon sheet G peak. The D-peak of the CNTs synthesized from both dimethylferrocene and ferrocene, shown in Fig. 4, occur at similar positions
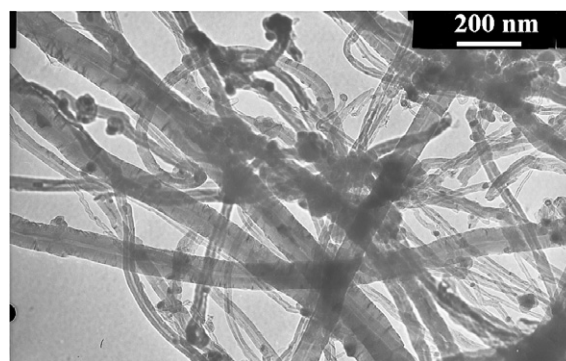

Fig. 1. TEM image of CNTs at 800 °C [ferrocene content: 5 wt.%; 0.2 ml/min injection rate].

(about 1350 cm^{-1}). The G-line peak for CNTs synthesized by both dimethylferrocene and ferrocene appeared at 1585 cm^{-1} and the D/G ratio is similar for both materials. Thus, there is no apparent change in the disorder structure of the two materials.

3.1. Mechanism of carbon structure formation

The TEM analysis (and other data) also permits for an interpretation of the synthesis data.
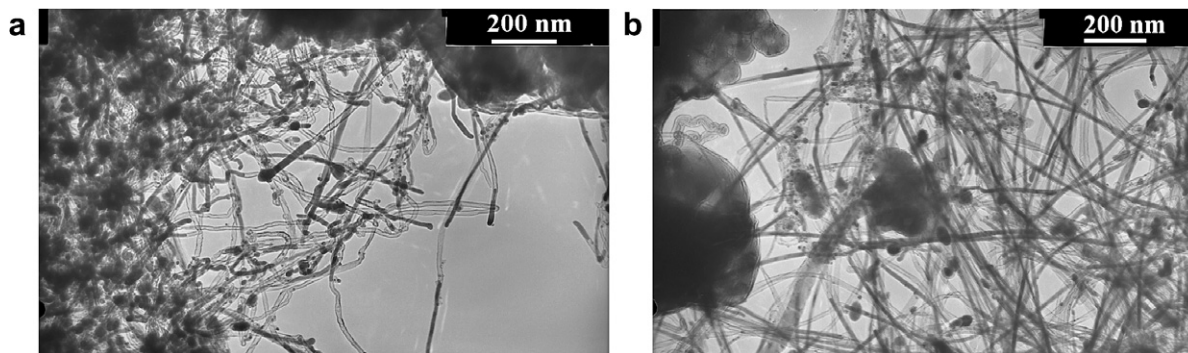
Fig. 2. TEM image of CNTs at 800 °C: (a) dimethylferrocene content: 5 wt.%; 0.8 ml/min injection rate and (b) dimethylferrocene content: 5 wt.%; 0.2 ml/min injection rate.
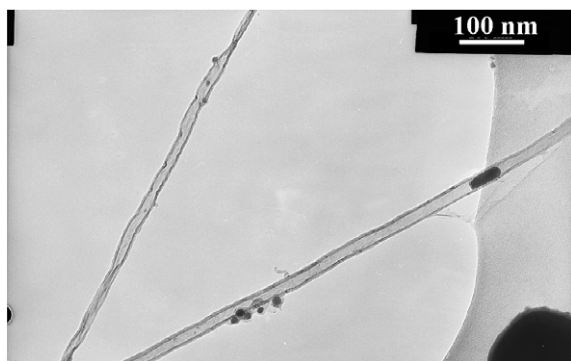

Fig. 3. TEM image of CNTs at 800 °C [dimethylferrocene content: 10.0 wt.%; 0.2 ml/min injection rate].
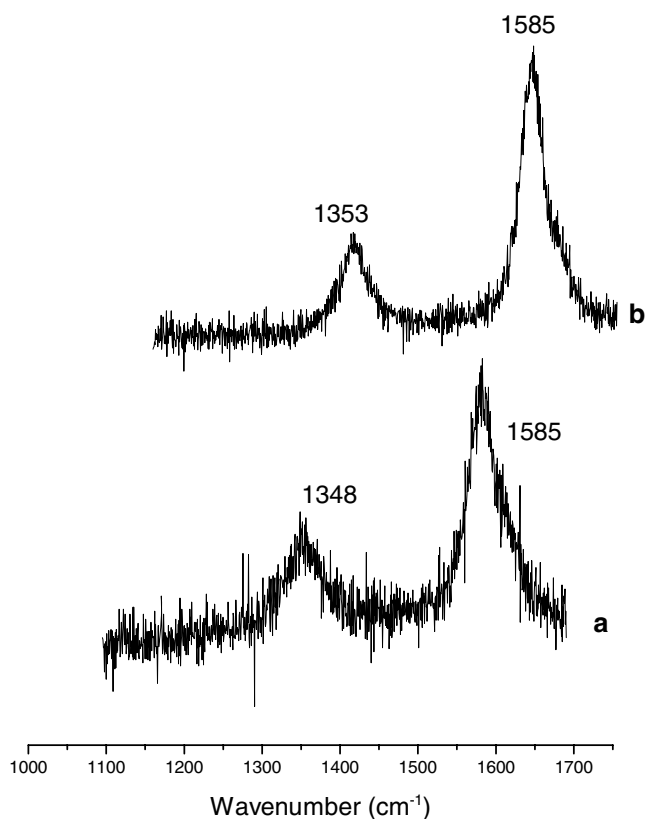

Fig. 4. Raman spectra of MWCNTs using (a) dimethylferrocene (10 wt.%), (b) ferrocene (10 wt.%) at 800 °C and 0.8 ml/min injection rate.

(i) Fe particles are found in many of the CNTs. They are generally found in the middle of the tube (Fig. 3) and the type and shape of iron particles are not affected by the ferrocene complexes used. This, as expected, implies that a common mechanism exists for all the catalysts used.

(ii) The iron atoms generated at the high temperatures used, coalesce in the gas phase or on the quartz reactor wall. Once they reach a certain size MWCNTs and fibers commence forming. Control of the metal particle size determines the size of the inner diameter of the tubes and also the number of tubes-within-tubes (MWCNTs) that form. In this case it is apparent that the Fe particles formed from dimethylferrocene are *smaller* than those formed from ferrocene at 800 and 900 °C. At the higher temperature (1000 °C) the particle sizes generated from both catalysts are the same.

(iii) Fiber formation is assumed to be associated with the formation of large iron particles. The data indicate that the synthesis procedure generates particles with a large range of Fe particle sizes. Notwithstanding this, the study still provides *relative* data to assess the effect of ring effects on carbon tubular behaviour.

(iv) The reactions with acetylferrocene lead to the formation of only fibers (no tubes). This implicates the influence of oxygen in the process. The 'OMe' group is thus poisoning CNT formation. Reports have, however, shown that CNTs can be grown from alcohols [26] as carbon source (e.g. ethanol) suggesting that the mere presence of oxygen atoms in a carbon source is not in itself detrimental to CNT synthesis.

(v) The observation that amorphous carbon and spheres were observed with diethylferrocene as catalyst was unexpected. Indeed, the order for amorphous carbon production follows the sequence: ferrocene < dimethylferrocene < diethylferrocene. This would suggest that ring substituents play a decisive role it tubular carbon formation. However, further studies will be needed to assess whether the observed results are not due to some secondary effect. For example, the volatility of the catalyst sources is quite different - dimethyl-

ferrocene has a lower melting point (39–41 °C) than ferrocene (174–176 °C), and therefore it will decompose at lower temperature relative to ferrocene.

(vi) The role of the ring carbon atoms in the CNT synthesis is not known although our data shows that carbon atoms from the Cp ring influences the diameter size of the MWCNTs produced. Isotopic studies have not been performed (by ourselves or others) to evaluate the incorporation of the ring carbon atoms in the tubes using the ferrocene catalysts. However, it is known that the toluene breaks down into smaller carbon fragments/atoms at the high temperatures used. These atoms are proposed to dissolve in the catalyst and precipitate out with formation of the tubular materials [10,27].

4. Conclusions

The effect of ring substitution on the role of ferrocene as catalyst in the formation of tubular carbons has revealed that the substituent can affect the type of carbonaceous material formed. Further, the data show that the ring substituent impacts on the CNT diameter, but does not have an effect on the morphology of the tubes.

This result suggests that the morphology of CNTs can be influenced by ligand atoms attached to the catalyst. This has implications for the future design of CNT catalysts and the control that may be achieved via this approach to CNT synthesis.

Acknowledgements

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