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Organometallic Precursors for Use as Catalysts in Carbon Nanotube Synthesis

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The synthesis of multiwalled carbon nanotubes (MWCNTs) and carbon balls (CBs) catalyzed by ferrocene (Fc), $Mo(CO)_5L$ (L = CO, ^tBuNC), and bimetallic catalyst systems ($Fc/M(CO)_5{}^tBuNC$; M = W or Mo) was investigated. These reactions were carried out in flowing 5% H_2 in Ar in the temperature range 700−900 °C. Under the reaction conditions, Fc yielded CNTs and CBs, while the $M(CO)_5L$ complexes yielded little carbonaceous material. Depending on the temperature and weight ratio of the metals used, mixtures of Fc and $M(CO)_5L$ generated varying amounts of CNTs and CBs. EDS and TEM analysis revealed the formation of large particles of Mo/Fe alloys. It was observed that the diameters of the CNTs catalyzed by Fc are smaller while the diameters of CBs are larger relative to the diameters of CNTs and CBs produced by the bimetallic catalyst systems. In all instances MWCNTs were produced, which contrasts with the single-walled CNTs produced by Fe/Mo-supported heterogeneous catalyst systems.

1. Introduction

The area of carbon nanotube science and engineering has grown dramatically since the pivotal paper of Iijima in 1991.[1−3] Since then, many synthetic strategies have been developed to make both SWCNTs (single-walled carbon nanotubes) and MWCNTs (multiwalled carbon nanotubes), and numerous reviews have appeared outlining these approaches as well as the properties and uses of the CNTs produced.[4] However, control of the shape, length, width, number of walls, and chirality of CNTs produced by the various synthetic strategies has still to be achieved, especially if the unique properties of the CNTs are to be exploited.

Many methods used to make CNTs employ metals, typically deposited on a suitable support using CVD, incipient wetness, deposition−precipitation, and other procedures.[5]

The metal source can be an organometallic complex, and a wide range of metals have been deposited by this procedure.[6] The use of polymers containing organometallic complexes to provide a metal source for nanotube synthesis has been reported to yield controlled production of nanotubes.[7] An unusual synthesis has entailed the decomposition of volatile organometallic carbonyl precursors with Mg under pressure in a closed system.[8] In this reaction the CO released from the precursor is the carbon source used in the CNT synthesis. An alternative method to the above, described by Vollhardt and co-workers, is to use an organometallic complex as both the catalyst and the carbon source i.e., to use the *bound* ligand to make the CNT.[9] In this process cobalt-containing organometallic complexes are heated to high temperature to cleanly produce CNTs.

However, the most successful method for using organometallic precursors in CNT synthesis is the so-called "floating catalyst" method.[10] In this process an organometallic complex, together with a carbon source, (e.g., ethane, CO, ethyne, etc.), is sprayed into a hot tube where the metal reacts with the carbon source, in the gas phase or on a solid support, to generate carbon

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nanotubes. Surprisingly, very few organometallic complexes have been used to generate the catalyst by this procedure, with ferrocene and $Fe(CO)_5$ being the most studied complexes studied to date.[10a,b,11] Notwithstanding the paucity of studies reported, the methodology (using $Fe(CO)_5$ at pressure) is used in the Hyperion (HiPco) process to commercially synthesize CNTs.[12]

Part of the reason for the limited investigations into the use of alternative organometallic complexes as gas phase catalysts in CNT synthesis relates to the poor solubility and low vapor pressure of many potential organometallic catalysts.

Recently we commenced a study to systematically explore the use of organometallic complexes in CNT synthesis,[5a,13] and herein we report our studies on the use of mixed ferrocene/$Mo(CO)_6$ and ferrocene/$M(CO)_5(^tBuNC)$ (M = Mo, W) mixtures, together with a carbon source, to make CNTs. The $M(CO)_5(^tBuNC)$ catalysts were chosen so as to enhance the solubility, and hence the gas phase concentration of the Mo and W precursors. The Fe/M (M = Mo, W) mixture has been chosen since reports on supported Fe/Mo catalysts have revealed that the Mo enhances the activity and selectivity of the Fe catalyst and the process selectively produces SWCNTs in good yield.[14] The results from our study have been compared with literature reports on supported Fe/Mo catalysts.

2. Experimental Section

Ferrocene and $M(CO)_6$ (M = Mo, W) were purchased from Strem Chemicals and used as received. The preparation of $M(CO)_5(^tBuNC)$ catalysts was carried out as described elsewhere.[15] Reactions were performed in the apparatus shown in Figure 1.

A large 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 (Figure 1) similar to studies reported elsewhere.[16] The temperature of the quartz tube was determined by means of a thermocouple placed in the middle of the furnace. As previously, a second movable thermocouple was used to establish the profile of the temperature in the reactor.

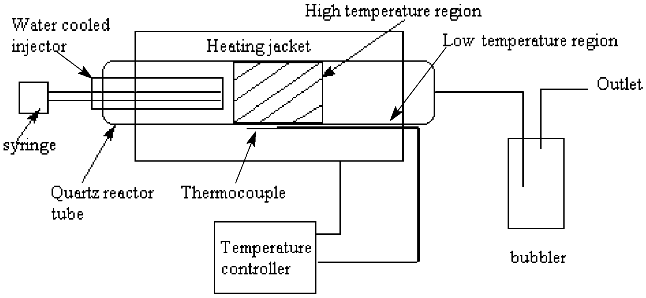

Figure 1. Thermal pyrolysis apparatus used to synthesize carbon nanotubes.

Synthesis of CNTs was carried out in the temperature range 700−900 °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. Mixtures of ferrocene and $M(CO)_5RNC$ or $Mo(CO)_6$ at different weight ratios were dissolved in toluene (Merck Chemicals). The catalyst solutions were placed in a 10 mL syringe driven by a SAGE syringe pump at ~0.80 mL/min rate. The solutions were injected into the quartz 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.[13,17] This specially designed tube enabled the solution to be injected into the high-temperature region of the large quartz tube reactor.

The method used in this study differed from our earlier procedure[13] in that the solution was sprayed from the temperature reported into a "hot" zone (about 1.5 cm from the spray nozzle) that was ca. 100 °C hotter than that reported. 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) of the tube (see Figure 1). The carbon materials were characterized by scanning electron microscopy (SEM) (Joel JSM 840), low-resolution transmission electron microscopy (TEM) (Joel JEM 100S), and high-resolution transmission electron microscopy (HRTEM) (Phillips CM200). Samples for SEM analysis were prepared by placing the carbonaceous material on conductive tape. Samples for TEM analysis were prepared by sonication of the carbonaceous material in methanol, and a few drops of the resulting suspension were placed onto a holey carbon TEM grid for analysis. The number and size of the carbon tubes and balls were obtained from the SEM/TEM photographs by counting procedures and represent average values.

The nanotube yield was calculated from the wt % of the products obtained relative to the mass of solvent injected into the system.

3. Results

All CNT synthesis reactions were carried out in the apparatus shown in Figure 1. In these reactions the carbon source and the catalysts were injected into the hot quartz tube, where the organometallic precursors instantly decomposed to form metal particles. These zero oxidation state metal particles condense either in the gas phase or on the quartz reactor walls to generate the small active metal particles used to synthesize the CNTs.

Reactions were performed under a standard set of conditions, so that the effect of the metals on the carbonaceous material produced in the reaction could be made. Variables that were investigated in the reaction were toluene injection rate, metal ratios, metal

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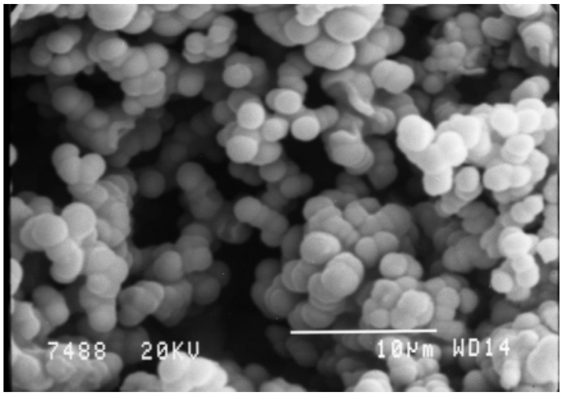

Figure 2. SEM image of CBs (800 °C, toluene).

Table 1. Effect of Toluene and Single-Metal Catalysts on the Synthesis of CNTs and CBs

metal	temp (°C)	notes	mean diameter (nm), T = tubes, B = balls
toluene	700	no carbon deposit	
	800	balls (50%)	625
	900	balls	750
ferrocene 5 wt %	700	balls (40%) and tubes (10%)	500B, 167T
	800	balls (20%) and tubes (60%)	750B, 50T
	900	balls (30%) and tubes (50%)	800B, 160T
Mo(CO)$_5{}^{t}$BuCN 5 wt %	700	balls (60%)	1 μm
	800	balls (70%)	625
	900	balls (80%)	600
W(CO)$_5{}^{t}$BuCN 5 wt %	700	balls (50%)	670
	800	balls (40%)	690
	900	balls (60%)	625

concentrations, and reaction temperature. No attempt was made to optimize product yields. The yields of the carbonaceous materials relative to the carbon source (toluene) were found to range between 0.1 and 2%.

Thermal pyrolysis of toluene in the absence of a catalyst was first investigated. It was observed that at 700 °C no carbon deposit was observed, but at 800 °C (and higher) small amounts of CBs were observed (Figure 2). These were similar to the CBs previously observed by ourselves and others[18] with the diameters of the balls formed by pyrolysis of toluene (no metal present) in the range 250−750 nm.

Attempts were then made to use Mo(CO)$_6$/toluene to synthesize CNTs and CBs. The poor solubility of Mo(CO)$_6$ in toluene resulted in only low concentrations of Mo(CO)$_6$ being used in our studies. Consequently little carbon deposit due to the presence of the pure metal could be detected. To overcome this limitation, soluble Mo complexes were used in further studies. When single metal catalysts containing Mo(CO)$_5{}^{t}$BuCN or W(CO)$_5{}^{t}$BuCN in a weight ratio of 5.0 wt % (700−900 °C) were used, CBs and amorphous carbon were formed (see Table 1). The amount and diameters of these CBs (diameter between 625 nm and 1 μm) were generally found to be larger than those formed using only toluene.

Ferrocene has been reported to be a catalyst for the synthesis of CNTs,[13a,19] and blank runs were performed to determine the conditions for CNT synthesis in our apparatus. Conditions were chosen to limit tube formation such that the effect of the second metal (Mo, W) could be evaluated. It was established that ferrocene (5.0 wt %) generated a maximum of 60% CNTs (as well as CBs) under our reaction conditions.

Table 2. Effect of Fc/Mo Bimetallic Catalyst on the Synthesis of CNTs and CBs

metal	temp (°C)	notes	mean diameter (nm), T = tubes, B = balls
Fc:Mo(CO)$_6$ (9:1) 10 wt %	800	tubes (60%)	525
	900	graphite	
Fc:Mo(CO)$_5{}^{t}$BuCN (1:1) 5.0 wt %	700	balls (30%)	600
	800	balls (40%)	625
	900	balls (50%) and tubes (10%)	750B, 300T
Fc:Mo(CO)$_5{}^{t}$BuCN (1:2) 7.5 wt %	700	no carbon deposit	
	800	balls (50%) and tubes (10%)	1.2 μmB,
	900	balls (50%) and tubes (20%)	700B, 200T
Fc:Mo(CO)$_5{}^{t}$BuCN (2:1) 7.5 wt %	700	no carbon deposit	
	800	balls (40%) and tubes (20%)	750B, 250T
	900	balls (50%) and tubes (30%)	475B, 250T
Fc:Mo(CO)$_5{}^{t}$BuCN (10:1) 5.0 wt %	700	tubes (60%?) (very low yield)	50
	800	balls (30%) and tubes (50%)	500B, 300T
	900	balls (70%) and tubes (20%)	700B, 200T
Fc:Mo(CO)$_5{}^{t}$BuCN (50:1) 5.0 wt %	700	balls (20%) and tubes (40%)	500B,
	800	balls (60%) and tubes (30%)	600B
	900	balls (50%) and tubes (40%)	500B, 250T

Table 3. Effect of Fc/W Bimetallic Catalyst on the Synthesis of CNTs and CBs

metal	temp (°C)	notes	mean diameter (nm), T = tubes, B = balls
Fc:W(CO)$_5{}^{t}$BuCN (1:1) 5.0 wt %	700	balls (40%)	800
	800	balls (40%)	500
	900	balls (50%)	750
Fc:W(CO)$_5{}^{t}$BuCN (1:2) 7.5 wt %	700	no carbon deposit	
	800	balls (50%)	500
	900	balls (40%) and tubes (10%)	650B, 500T
Fc:W(CO)$_5{}^{t}$BuCN (2:1) 7.5 wt %	700	no carbon deposit	
	800	balls (30%) and tubes (20%)	500B, 167T
	900	balls (50%) and tubes (10%)	667B, 467T
Fc:W(CO)$_5{}^{t}$BuCN (10:1) 5.0 wt %	700	balls (30%)	500
	800	balls (30%) and tubes (50%)	500B, 200T
	900	balls (60%) and tubes (30%)	625B, 333T
Fc:W(CO)$_5{}^{t}$BuCN (50:1) 5.0 wt %	700	balls (50%) and tubes (20%)	700B, 300T
	800	balls (60%) and tubes (30%)	333B, 300T
	900	balls (70%) and tubes (30%)	375B, 250T

Reactions were then performed at different metal ratios, flow rates, and temperatures to evaluate the effect of Fe/Mo and Fe/W mixed metals on CNT and CB synthesis (Tables 2 and 3). Figure 3 shows an SEM image of a product revealing both CNTs and CBs. All the CNTs produced were MWCNTs (see below). While the ratio and size of the CNTs/CBs varied, all reactions

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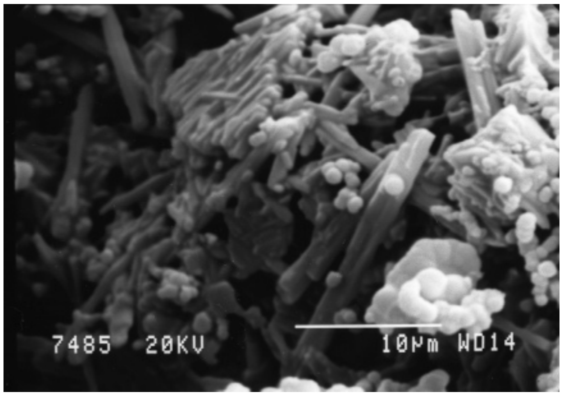

Figure 3. SEM image of CBs and CNTs (800 °C, Fc:Mo$(CO)_5{}^t$BuNC (2:1; 7.5 wt % in toluene).

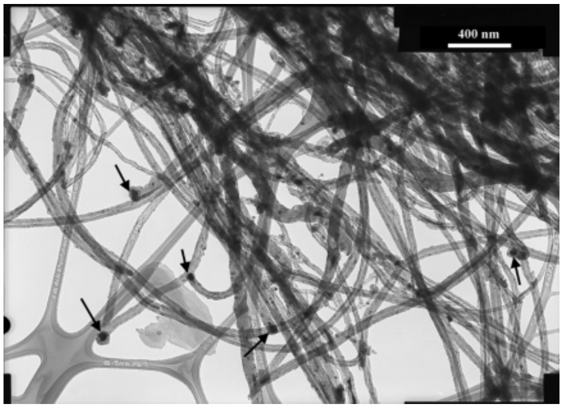

Figure 4. TEM image of CNTs (700 °C, Fc:Mo$(CO)_5{}^t$BuNC content: (10:1) 5 wt %).

gave similar shaped products. The diameters of CNTs are widely distributed compared with the CNTs that have been reported using different heterogeneous Fe−Mo bimetallic catalysts and other synthetic techniques.[14b,20] Further, the diameters of the CNTs and CBs have changed relative to the diameters of CNTs and CBs formed from Fc alone (800 and 900 °C, Tables 1 and 3). The inner diameters of these tubes ranged from 8 to 12 nm.

Figure 4 shows a TEM image of the “spaghetti”-like arrangement of the CNTs produced from Fc/Mo (10:1; 5%) at 700 °C. The metal particles (diameter range 40−80 nm) are clearly seen both at the ends and in the tubes[21] (indicated by arrows). Similar TEM images are observed for the products produced at 800 °C (similar reaction conditions).

Toluene conversion catalyzed by Fc:W$(CO)_5{}^t$BuNC gave a very low yield of tubes (700−900 °C; all ratios) and CBs. These results indicate that W metal is not a good catalyst for nanotube synthesis.

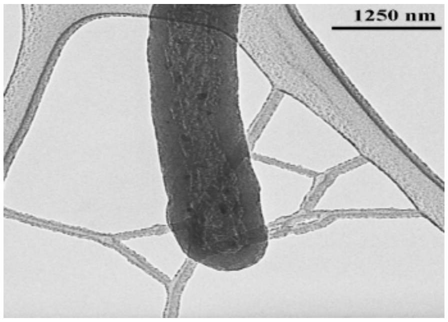

Figure 5. TEM image of CNT-fiber (900 °C, Fc:Mo$(CO)_5{}^t$-BuNC content: (10:1) 5 wt %).

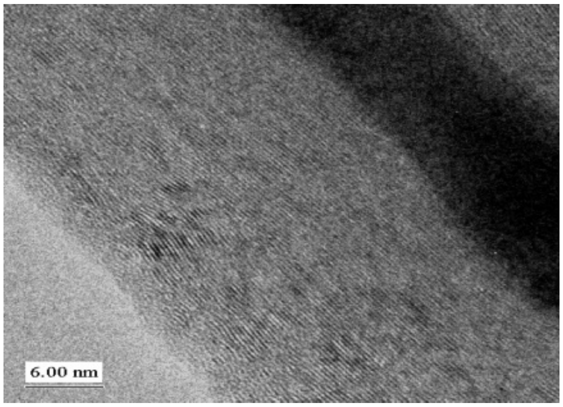

Figure 6. HRTEM of MWCNT showing a metal particle in the middle of the tube (tube contains about 70 layers; metal completely fills the center of the tube).

In the Fe/Mo-catalyzed reaction, variation of the product distribution was found as a function of position in the reactor. The products collected in the low-temperature region of the reactor (Figure 1) indicated the presence of more CNTs than CBs. The diameter of the CBs found in the high-temperature region were found to be widely distributed compared to the diameter of the carbon balls formed in the low-temperature region. CBs in the high-temperature region have diameters in the range 250−3000 nm, while CBs collected in the low-temperature region have a diameter range of 250−700 nm. The diameters of CNTs collected from the high-temperature region (17−500 nm) and the low-temperature region (17−400 nm) are similar.

The yield of the carbon materials increased with increasing temperature. It was found that at 800 and 900 °C amorphous carbon and graphite were also formed in 20 and 40% relative yield, respectively.

Figure 5 shows a TEM image of a single, closed, MWCNT (low resolution). The image clearly reveals an inner region (in this case not filled with metal catalyst) surrounded by a layered tube arrangement. A high-resolution TEM image of a similar (filled) tube is shown in Figure 6, and the inner portion of the tube (dark coloration) was shown by EDS to correspond to the metal catalyst. The tube is made up of about 70 carbon layers.

The identity of the metal particles was confirmed by EDS analysis performed by focusing the electron beam onto the individual metal particles. Most metal particles were identified to be Fe, and no pure Mo metal particles were observed. However, many particles were shown by EDS to be Fe−Mo metal alloys. The elemental percentage ratio of Fe and Mo (by EDS) varied from 100:0 to 95:5 for the mixed catalyst systems (10:1; 50:1), indicat-

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ing that the Mo and Fe did indeed interact in the gas phase in a ratio close to that used in the reaction.

Discussion

The choice of reagents used in this study was determined by the following considerations: (i) the solubility of the organometallic complexes in appropriate solvents, (ii) the use of low oxidation state metals, as CNT formation is known to be generated by zerovalent metals (or metal carbides), (iii) the use of a reactive carbon source, e.g., toluene, to minimize the reaction temperature, and (iv) the well-known behavior of the Mo/Fe system, produced by classical deposition methods, to produce SWCNTs.

When ferrocene was used as a catalyst, CNTs as expected were produced. However, no CNTs were produced by pure $M(CO)_5(^tBuNC)$, and indeed high concentrations of Mo (or W) in ferrocene (1:1, 1:2) resulted in reduced CNT formation. However, when lower Fe/M ratios are used (1:10; 1:50), an increase in CNT production was noted. CBs were also produced in the catalyzed reaction but presumably not via a metal-catalyzed route.

The results for the reactions carried out in this study have been collected in Tables 1−3. The data indicate that a small temperature range is available for the maximization of tube formation, with maximum relative tube production generally occurring at 800−900 °C. No correlation between the size (diameter) of the CNBs or the CNTs with temperature is obvious from our data set.

The data do however indicate that a synergic effect exists when the two metals are in close contact with each other. This interaction is confirmed by the detection of Fe/Mo alloys by EDS.

A key difference between the CNTs produced in this study and those produced when heterogeneous supported Mo/Fe complexes are used as catalysts for CNT synthesis is that only MWCNTs were observed in this study. This may relate to the metal particle size produced in the reactor since it is well known that the metal particle size will influence both the internal tube diameter and the type of CNT produced (multiwall, single wall, etc.). Large metal particles generate large tubes that tend to be multiwalled, and in the extreme, generate amorphous carbon materials.[22] It appears that alloy formation in the gas phase results in the formation of larger metal particles than produced from ferrocene alone. This is substantiated by the smaller diameters of the CNTs produced from pure ferrocene (average diameter 50−167 nm) relative to those produced from Fe/Mo or Fe/W mixtures (>150 nm).

The mechanism for CNT production is known in some detail, and in the case of CVD Fe catalysts tube growth is anticipated to occur by both tip and base growth mechanisms.[23,24]

While the effect of an alloy of Fe on the CNT formation mechanism is not known, the following is to be noted: (i) most metal particles were found at the tip of a tube and inside a tube (Figure 4); this implies that the mechanism to produce CNTs from alloys is substantially the same as that to produce CNTs from Fe, and (ii) fewer tubes were formed from Fe−Mo metal alloys than produced from Fe metal particles. This must relate to an inhibiting effect that Mo has on CNT growth, an effect indicated by use of the pure metal.

Our results thus reveal the impact that a Mo/Fe alloy has on CNT production. The Mo modifies the behavior of the Fe to generate larger metal particles and hence larger tubes. The key to high CNT production with this system will thus entail better control of the particle sizes and metal content ratios produced in the gas phase. This suggests that the use of gas phase organometallic metal clusters may be more appropriate catalysts for controlled CNT synthesis, and studies in this direction have commenced.

Conclusion

A series of experiments were performed in which mixtures of ferrocene and $M(CO)_5{}^tBuNC$ (M = Mo, W) were decomposed in the presence of toluene at high temperature (700−900 °C). From the experiments the following conclusions can be drawn: (i) in the absence of metal, CBs were formed from toluene, (ii) the low solubility of $Mo(CO)_6$ prevented formation of any carbonaceous materials from this metal source in the temperature range 700−900 °C, (iii) the single metal catalysts, $M(CO)_5{}^tBuNC$, produced only CBs, and (iv) CNTs were mainly synthesized by Fc or Fc-Mo bimetallic mixtures. TEM results revealed that metal particles, comprising Fe or Fe-Mo alloys, were present in the MWCNTs produced. The large size of the particles produced in this study is believed to be responsible for the limited formation of CNTs produced in the reaction.

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