Journal of Organometallic Chemistry 694 (2009) 2222–2227

Contents lists available at ScienceDirect

Journal of Organometallic Chemistry

journal homepage: www.elsevier.com/locate/jorganchem

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

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ARTICLE INFO

Article history:
Received 16 January 2009
Accepted 24 February 2009
Available online 6 March 2009

Keywords:
Arylferrocene
Carbon nanotube
Chemical vapour deposition
Poison

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, $COCH_3$) or a mixture of ferrocene (FcH) and substituted benzenes (PhX; X = H, OH, Br, $COCH_3$). The reactions were carried out by an injection chemical vapour deposition (CVD) method using toluene solutions (carrier gas: 5% H_2 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).

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].

Organometallic compounds such as ferrocene ($Fe(C_5H_5)_2$) [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 CH_4 [25], C_6H_6 [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

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doi:10.1016/j.jorganchem.2009.02.031

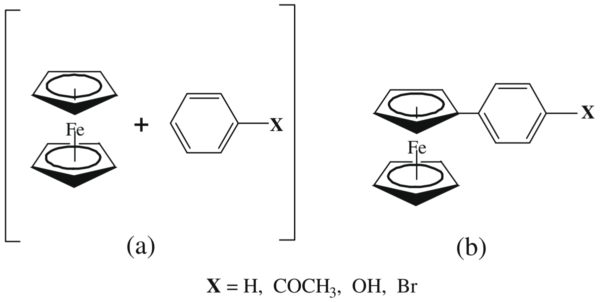

Fig. 1. The precursors used for synthesis of SCNMs in toluene: (a) ferrocene (FcH) and para-substituted benzenes; (b) arylferrocenes (FcPhX).

received. Phenylferrocene (FcPhH), 4-hydroxyphenylferrocene (FcPhOH), 4-bromophenylferrocene (FcH) and 4-nitrophenylferrocene ($FcNO_2$) were prepared by the diazonium salt method [32] while 4-ferrocenylacetophenone ($FcPhCOCH_3$) was prepared by a modified Suzuki cross-coupling reaction [33]. 4-Ferrocenylaniline ($FcPhNH_2$) was obtained by the catalytic reduction of 4-nitrophenylferrocene ($FcPhNO_2$) [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% H_2 in argon (v/v) at atmospheric pressure. The flow rate of H_2 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% H_2 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, $FcPhCOCH_3$ and $FcPhNH_2$ 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

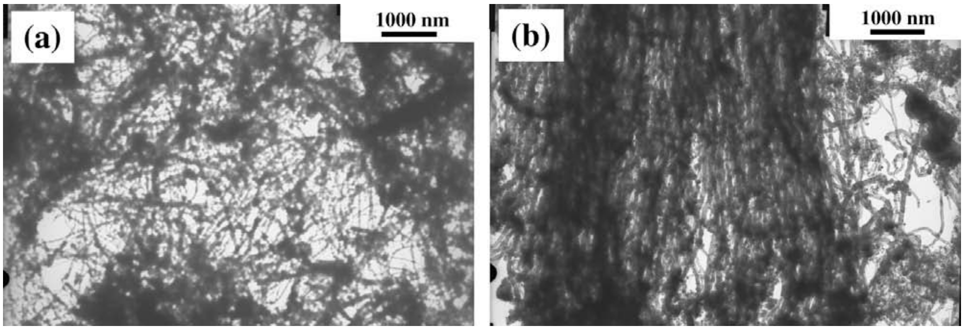

Fig. 2. CNTs formed from pyrolysis of (a) 2.5 wt.% FcH and (b) 2.5 wt.% FcPhH in toluene with a flow rate of 0.8 ml/min and at temperature of 800 °C.