

**Organometallic iron complexes as catalysts for carbon nanotube
synthesis**

By

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DECLARATION

I declare that “Organometallic iron complexes as catalysts for carbon nanotube synthesis” is my own, unaided work submitted for the degree of Doctor of Philosophy in the University of Witwatersrand, Johannesburg. It has not been submitted for any degree or examination in any other university, and all sources I have used or quoted have been indicated and acknowledged by means of complete references.

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DEDICATION

TO MY DAUGHTER MOLOGADI MOHLALA

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ABSTRACT

In this study, CNTs were produced using the floating catalyst CVD method by injection of a catalyst solution into a high temperature zone of a furnace. The catalysts, organometallic iron complexes, were dissolved in a hydrocarbon source (toluene) and injected into the furnace to form CNTs. Various organometallic iron complexes were used as catalysts for CNT synthesis. The catalysts used included: (a) mixtures of ferrocene and $M(\text{CO})_5^t\text{BuCN}$ ($M = \text{Mo}$ and W), (b) mixtures of ferrocene and ferrocenyl sulphide, (c) alkyl-ferrocenes, (d) ferrocenylacetanilides and (e) cyclopentadienyl carbonyl iron complexes.

The reactions were carried out in flowing 5% H_2 in Ar (100 ml/min) in the temperature range of 700-1000 °C and at injection rates of between 0.2 and 3.3 ml/min, using various catalyst concentrations (1-10 wt%).

The synthesis of multi-walled carbon nanotubes (MWCNTs) and carbon spheres (CSs) was achieved with ferrocene (Fc), $\text{Mo}(\text{CO})_5\text{L}$ ($\text{L} = \text{CO}$, $^t\text{BuNC}$) and bimetallic catalyst systems ($\text{Fc}/\text{M}(\text{CO})_5^t\text{BuNC}$; $M = \text{W}$ or Mo). Ferrocene yielded CNTs and CSs while the $\text{M}(\text{CO})_5\text{L}$ complexes yielded little carbonaceous material. EDS and TEM analysis revealed the formation of large particles of Mo/Fe alloys inside the tubes. It was observed that the diameters of the CNTs catalyzed by Fc are smaller while the diameters of CSs are larger relative to the diameters of CNTs and CSs 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.

MWCNTs were synthesised using toluene solutions of ferrocene and 1,1'-bis(methylthio)ferrocene (ferrocenyl sulphide). It was found that the presence of large amounts of sulphur in the reactant mixture deactivated the catalyst, therefore generating only amorphous carbon while lower amounts of sulphur led to mixtures of MWCNTs and carbon fibres. The product distribution and yield varied with the sulphur content. Thus,

when the sulphur content was high the yield was higher than when a low sulphur content was used. More CNTs were formed when a low sulphur content was used with more carbon spheres and amorphous carbon formed at a high sulphur content. HMTEM analysis revealed that the MWCNTs were poorly graphitised. Comparison with data using other sulphur sources (S_8 , thiophene) suggested that the proximity of the sulphur to the Fe catalyst in the gas phase did play a role in the CNT formation.

Pyrolysis of $(CpR)(CpR')Fe$ (R and $R' = H, Me, Et$ and $COMe$) in toluene solution gave multi-walled carbon nanotubes (MWCNTs) and carbon fibers (CFs). 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 synthesised was investigated. Carbonaceous products formed included graphite film (mostly at high temperature; 900-1000 °C), carbon nanotubes and carbon fibers. The yield of carbonaceous materials increased with temperature and concentration. The ferrocene ring substituents influenced both the CNT diameter and the carbon product formed. The outer diameters of CNTs formed by dimethylferrocene were found to be smaller (17-46 nm) than the diameters of CNTs formed by ferrocene (33-60 nm). Diethylferrocene produced carbon spheres and amorphous carbon with no success in forming CNTs.

Toluene solutions of 3-ferrocenyl-*N,N*-diisopropyl-3-oxo-propionamide (diisopropylamide catalyst) were used to synthesize nitrogen containing MWCNTs. The effect of pyrolysis temperature and solution feeding rate on the yield and morphology of carbonaceous products were investigated. CNTs with bamboo structures were formed by the diisopropyl catalyst at 800 °C, with outer tube diameters in the range of 28-74 nm. Carbonaceous products formed include graphite film, which was formed mostly at high temperatures, carbon nanotubes, carbon fibers and carbon spheres. A boron containing iron catalyst {(1*Z*)-3-(diisopropylamino)-3-oxo-1-ferrocenylprop-1-ene-1-yl difluoroborate} was used in an attempt to synthesize boron-doped CNTs. MWCNTs which are not boron-doped were produced.

The organometallic complexes, $\text{CpFe(CO)}_2\text{I}$ was found to be inactive for CNT synthesis and active for carbon spheres and fibers formation. $\text{CpFe(CO)}_2\text{Me}$ produced MWCNTs with narrow diameter range (19-41 nm). The influence of temperature and catalysts concentration was studied. High temperatures (900-1000 °C) produced more amorphous carbon while low temperatures produced more CNTs. A low catalyst concentrations (5 wt.%) was used to form more CNTs than a high catalyst concentrations (10 wt.%).

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ABBREVIATIONS

CFs = carbon fibers

CNTs = carbon nanotubes

CSs = carbon spheres

DWCNTs = double-walled carbon nanotubes

Fc = ferrocene

HMTEM = high magnification transmission electron microscopy

MWCNTs = multi-walled carbon nanotubes

SEM = scanning electron microscopy

SWCNTs = single-walled carbon nanotubes

TEM = transmission electron microscopy

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