

https://dspace.org/

Organometallic iron complexes as catalysts for carbon nanotube synthesis

Mohlala, Matshwenyego Sarah

2008-03-19T10:12:33Z
http://hdl.handle.net/10539/4689

Downloaded from a DSpace repository. https://dspace.org/

Organometallic iron complexes as catalysts for carbon nanotube synthesis

By

Matshwenyego Sarah Mohlala

Submitted in partial fulfillment of the requirements for the degree of

Doctor of Philosophy in the Faculty of Science

Department of Chemistry

University of the Witwatersrand

Private Bag X03

WITS

2050

Supervisor: Professor Neil J. Coville

December 2006

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.

Name: Matshwenyego Sarah Mohlala (Ms) Date: 15 December 2006

Signature:_____

DEDICATION

TO MY DAUGHTER MOLOGADI MOHLALA

TABLE OF CONTENTS

	PAGE
ABSTRACT	viii
LIST OF FIGURES	xi
LIST OF TABLES	xv
ABBREVIATIONS	xvi
ACKNOWLEDGEMENTS	xvii
CHAPTER 1	1
LITERATURE REVIEW	
1.1 Structural features of carbon nanotubes (CNTs)	1
1.2 Synthesis of carbon nanotubes	2
1.2.1 Arc-discharge technique	3
1.2.2 Laser vaporization technique	5
1.2.3 Catalysis methods	6
1.2.3.1 Catalytic chemical vapour deposition (CCVD) technique	6
1.2.3.2 Unsupported/ Floating catalyst method	16
1.3 Synthesis of Nitrogen and Boron-doped CNTs	25
1.4 Catalysts used for CNT growth	27
1.5 Carbon sources used for CNTs growth	28
1.6 Growth mechanisms of CNTs	28
1.6.1 Growth stages of MWCNTs by floating catalyst method	29
1.6.2 Growth stages of CNTs by CVD supported catalyst method	30
1.7 Morphological and structural characterization of CNTs	31
1.7.1 Scanning electron microscopy (SEM)	31
1.7.2 Transmission electron microscopy (TEM)	31
1.7.3 X-ray diffraction (XRD)	32
1.7.4 Raman spectroscopy	32
1.8 Properties of CNTs	33

1.8.1 Electronic properties 33
1.8.2 Mechanical properties 34
1.8.3 Adsorption properties 35
1.8.4 Thermal Properties 35
1.8.5 The catalytic properties of CNTs 35
1.8.6 CNTs as catalysts supports 36
1.9 References 36

CHAPTER 2 53
EXPERIMENTAL SECTION
2.1 Introduction 53
2.2 Carbon nanotube preparation 53
2.3 TEM analysis 54
2.4 SEM analysis 55
2.5 TGA analysis 55
2.6 Raman analysis 55
2.7. References 56

CHAPTER 3 57
CARBON NANOTUBE SYNTHESIS FROM Fe-Mo BIMETALLIC CATALYSTS
3.1 Introduction 57
3.2 Experimental 59
3.3 Results 60
3.4 Discussion 68
3.5 Conclusion 70
3.6 References 70
3.7 Appendix 73

CHAPTER 4 74
CARBON NANOTUBE SYNTHESIS USING FERROCENE AND

FERROCENYL SULPHIDE: THE EFFECT OF SULPHUR
4.1 Introduction 74
4.2 Experimental 77
4.3 Results and discussion 78
4.4 Conclusion 86
4.5 References 87
4.6 Appendix 90

CHAPTER 5 91
SYNTHESIS OF MULTI-WALLED CARBON NANOTUBES
CATALYZED BY ALKYL SUBSTITUTED FERROCENES
5.1 Introduction 91
5.2 Experimental 94
5.3 Results and discussion 95
5.4 Conclusions 104
5.5 References 105
5.6 Appendix 107

CHAPTER 6 108
THE USE OF DIISOPROPYLAMIDE AND DIFLUOROBORATE
FERROCENE SUBSTITUTED COMPOUNDS AS CATALYSTS
FOR THE SYNTHESIS OF DOPED CARBON NANOTUBES
6.1 Introduction 108
6.2 Experimental 110
6.3 Results and discussion 112
6.3.1 CNTs synthesized by diisopropylamide catalyst 112
6.3.2 CNTs synthesized by difluoroborate-$CaCO_3$ supported catalyst 120
6.4 Conclusions 124
6.5 References 124
6.6 Appendix 127

CHAPTER 7 128
CARBON NANOTUBES OBTAINED BY INJECTION CVD METHOD USING CYCLOPENTADIENYLDICARBONYLMETHYL(IODO)IRON
7.1 Introduction 128
7.2 Experimental 129
7.3 Results and discussion 130
7.4 Conclusions 138
7.5 References 139
7.6 Appendix 140

CHAPTER 8 141
CONCLUSIONS

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 $M(CO)_5{}^tBuCN$ (M = Mo and W), (b) mixtures of ferrocene and ferrocenyl sulphide, (c) alkyl-ferrocenes, (d) ferrocenylacetanalides 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), $Mo(CO)_5L$ (L = CO, ^tBuNC) and bimetallic catalyst systems ($Fc/M(CO)_5{}^tBuNC$; M = W or Mo). Ferrocene yielded CNTs and CSs while the $M(CO)_5L$ 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 {(1Z)-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, $CpFe(CO)_2I$ was found to be inactive for CNT synthesis and active for carbon spheres and fibers formation. $CpFe(CO)_2Me$ 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.%).

LIST OF FIGURES

FIGURES	PAGE
Figure 1.1(a): Schematic diagram of an open carbon nanotube	2
Figure 1.1(b): Schematic diagram of a closed carbon nanotube	2
Figure 1.2: Arc discharge plasma experimental setup for production of CNTs	3
Figure 1.3: Schematic representation of the oven-laser vaporization apparatus	5
Figure 1.4: The horizontal furnace used for the catalytic CVD of nanofibers and nanotubes	7
Figure 1.5: Schematic diagram of two stage horizontal reactor	17
Figure 1.6: The vertical furnace used to synthesize CNTs and CNFs in CCVD method	18
Figure 1.7: Schematic diagram of growth stages of MWCNTs by floating catalyst method	29
Figure 1.8: Growth mechanism of the tip growth and base growth nanotube models by supported CVD method	30
Figure 2.1: Thermal pyrolysis apparatus used to synthesize CNTs	54
Figure 3.1: SEM image of CSs formed by toluene at 800 °C	61
Figure 3.2: SEM image of CSs and CNTs (800 °C, Fc:$Mo(CO)_5$ ^tBuNC (2:1) 7.5 wt.%)	65
Figure 3.3: TEM image of CNTs (700 °C, Fc:$Mo(CO)_5$$^tBuNC$ content: (10:1) 5 wt.%)	65
Figure 3.4: TEM image of CNT-fiber (900 °C, Fc:$Mo(CO)_5$$^tBuNC$ content: (10:1) 5 wt.%)	66
Figure 3.5: HMTEM of MWCNT showing metal particle in the middle of the tube	66
Figure 3.6: Raman spectra of MWCNTs synthesized from Fc:$Mo(CO)_5$$^tBuCN$(10:1); 5 wt%; at 800 °C	67
Figure 3.7: TGA of MWCNTs grown from Fc:$Mo(CO)_5$$^tBuCN$(10:1);	

5 wt%; at 800 °C 68

Figure 4.1: CNT/CNF yield versus Fc:FcS_2Me_2 (6:1-148:1) metal ratio, at 1000 °C and injection rate of 0.2 ml/min (- - -) and 0.8 ml/min (–) 80

Figure 4.2(a): TEM image of CNTs (1000 °C; Fc:FcS_2Me_2: (36:1); 0.8 ml/min; 5 wt.%) 81

Figure 4.2(b): TEM image of CNTs (1000°C; Fc:FcS_2Me_2: (36:1); 0.2 ml/min; 5 wt.%) 81

Figure 4.2(c): TEM image of CNTs (1000 °C; Fc:FcS_2Me_2: (73:1); 0.8 ml/min; 5 wt.%) 81

Figure 4.2(d): TEM image of CNTs (1000 °C; Fc:FcS_2Me_2: (73:1); 0.2 ml/min; 5 wt.%) 81

Figure 4.3: Mean diameter of the CNTs versus Fc:FcS_2Me_2 metal ratio (6:1-148:1), at 1000 °C and injection rate of 0.2 ml/min (- - -) and 0.8 ml/min (–) 82

Figure 4.4: Wall thickness of the CNTs versus Fc:FcS_2Me_2 (6:1-148:1) metal ratio, at 1000 °C and injection rate of 0.2 ml/min (- - -) and 0.8 ml/min (–) 83

Figure 4.5: HMTEM image of a MWCNT (1000 °C; Fc:FcS_2Me_2: (73:1); 0.8 ml/min; 5 wt.%) 84

Figure 4.6(a): TEM image of CNTs (1000 °C; Fc:thiophene: (4:1); 0.2 ml/min; 5 wt.%) 84

Figure 4.6(b): TEM image of CNTs (1000 °C; Fc:sulphur: (2:1); 0.2 ml/min; 5 wt.%) 84

Figure 4.7: Raman spectra of CNTs grown using Fc:FcS_2Me_2: (73:1); 5 wt% , 0.8 ml/min; at 1000 °C 85

Figure 4.8: TGA of CNTs grown using Fc:FcS_2Me_2: (73:1); 5 wt% , 0.8 ml/min; at 1000 °C. 86

Figure 5.1(a): TEM image of CNTs at 800 °C (ferrocene content: 5 wt.%; 0.2 ml/min injection rate). 98

Figure 5.1(b): TEM image of CNTs at 800 °C, (ferrocene content:

5 wt.%; 0.8 ml/min injection rate). 98
Figure 5.2(a): TEM image of CNTs at 800 °C, (ferrocene content:
10 wt.%; 0.2 ml/min injection rate) 99
Figure 5.2(b): TEM image of CNTs at 800 °C, (ferrocene content:
10 wt.%; 0.8 ml/min injection rate) 99
Figure 5.3(a): TEM image of CNTs at 800 °C, (dimethylferrocene content:
5 wt.%; 0.2 ml/min injection rate) 99
Figure 5.3(b): TEM image of CNTs at 800 °C, (dimethylferrocene content:
5 wt.%; 0.8 ml/min injection rate) 99
Figure 5.4(a): TEM image of CNTs at 800 °C, (dimethylferrocene content:
10.0 wt.%; 0.2 ml/min injection rate) 100
Figure 5.4(b): TEM image of CNTs at 800 °C, (dimethylferrocene content:
10.0 wt.%; 0.8 ml/min injection rate) 100
Figure 5.5: TGA of CNTs grown using dimethylferrocene (10 wt%, 0.8 ml/min;
at 800 °C) 101
Figure 5.6: Raman spectra of CNTs using (a) dimethylferrocene (10 wt.%),
(b) ferrocene (10 wt.%) at 800 °C and 0.8 ml/min injection rate 102

Figure 6.1: TEM image of N-doped MWCNTs formed using
diisopropylamide catalyst (800 °C, 0.8 ml/min 2.0 wt%) 113
Figure 6.2: TEM image of N-doped MWCNTs formed using
diisopropylamide catalyst (800 °C, 0.4 ml/min, 2.0 wt.%) 114
Figure 6.3: TEM image of N-doped MWCNTs formed using
diisopropylamide catalyst (800 °C, 0.2 ml/min, 2.0 wt.%) 114
Figure 6.4: TEM image of MWCNT using ferrocene (800 °C,
0.2 ml/min, 2.0 wt.%) 114
Figure 6.5: TEM image of MWCNT using ferrocene (800 °C,
0.2 ml/min, 1.0 wt.%) 114
Figure 6.6: TEM image of MWCNT using ferrocene (800 °C,
0.8 ml/min, 2.0 wt.%) 115

Figure 6.7: TEM image of MWCNT using ferrocene (800 °C, 0.3 ml/min, 2.0 wt.%) 115
Figure 6.8: TGA of MWCNTs grown from (a) diisopropyl amide complex and (b) ferrocene (800 °C, 0.2 ml/min, 2.0 wt.%) 118
Figure 6.9: Raman spectra of MWCNTs grown using (a) diisopropylamide catalyst and (b) ferrocene (800 °C, 0.2 ml/min, 2.0 wt.%) 119
Figure 6.10: Proposed growth mechanism for N-doped MWCNT bamboo or "nanobell" structures. 120
Figure 6.11: TEM image of MWCNTs formed at 700 °C (difluoroborate catalyst, 240 ml/min N_2 flow rate, 90 ml/min C_2H_2 flow rate) 122
Figure 6.12: TGA of MWCNTs synthesized by (a) difluoroborate catalyst and (b) Fe/$CaCO_3$, without the boron element (700 °C, 240 ml/min N_2 flow rate, 90 ml/min C_2H_2 flow rate) 122
Figure 6.13: Raman spectra of MWCNTs grown using difluoroborate catalyst (700 °C, 240 ml/min N_2 flow rate, 90 ml/min C_2H_2 flow rate) 123

Figure 7.1: TEM image of CFs formed at 800 °C, ($CpFe(CO)_2I$: 5 wt.%; 0.8 ml/min injection rate) 130
Figure 7.2: TEM image of CSs formed at 800 °C, ($CpFe(CO)_2I$: 10 wt.%; 0.8 ml/min injection rate) 130
Figure 7.3: TEM image of CNTs formed at 800 °C, ($CpFe(CO)_2Me$: 5 wt.%; 0.8 ml/min injection rate) 133
Figure 7.4: TEM image of CFs formed at 900 °C, ($CpFe(CO)_2Me$: 5 wt.%; 0.8 ml/min injection rate) 133
Figure 7.5: TEM image of CNTs formed at 800 °C, ($CpFe(CO)_2Me$: 10 wt.%; 0.8 ml/min injection rate) 134
Figure 7.6: TEM image of CNTs formed at 900 °C, ($CpFe(CO)_2Me$: 10 wt.%; 0.8 ml/min injection rate) 134
Figure 7.7: TEM image of CNTs formed at 800 °C, (Fc:I = 50:1

(5 wt.%); 0.8 ml/min injection rate) 134
Figure 7.8: TEM image of MWCNTs formed at 800 °C
([CpFe(CO)$_2$]$_2$: 5 wt.%; 0.8 ml/min injection rate) 135
Figure 7.9: TGA of carbon nanotubes grown using CpFe(CO)$_2$Me
(5 wt.%, at 800 °C, 0.8 ml/min injection rate) 137
Figure 7.10: Raman spectra of MWCNTs grown from (a) CpFe(CO)$_2$Me
(5 wt.%, at 800 °C, 0.8 ml/min injection rate) and (b) ferrocene
(5 wt.%, at 800°C, 0.8 ml/min injection rate) 138

LIST OF TABLES

TABLES PAGE
Table 3.1: Effect of toluene and single metal catalysts on the synthesis
of CNTs and CSs 61
Table 3.2: Effect of Fc/Mo bimetallic catalyst on the synthesis
of CNTs and CSs 62
Table 3.3: Effect of Fc/W bimetallic catalyst on the synthesis of
CNTs and CSs 64
Table 4.1: Effect of sulphur containing compounds on CNTs growth 79
Table 5.1: Effect of substituted ferrocene on CNTs growth 96
Table 6.1: Effect of diisopropylamide catalyst on CNT synthesis 116
Table 6.2: Effect of difluoroborate on CNTs synthesis 122
Table 7.1: Effect of CpFe(CO)$_2$Me and CpFe(CO)$_2$I on CNTs growth 131

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

ACKNOWLEDGEMENTS

I would like to thank my supervisor, Professor Neil J. Coville and Dr X.Y. Liu for their advice and guidance in this research. I also thank Professor Mike Witcomb for HMTEM analysis, Mr R. Erasmus for Raman analysis and Mr R. M. Mampa for NMR analysis. I am very grateful to Council of Science and Industrial Research, National Research Foundation for paying my fees/accommodation and Centre of Excellence in strong materials for funding the project. I would also like to thank my co-researchers: Dr C. N. Mbileni, Mr S. D. Mhlanga, Mr A. Munyaneza, Mr M. A. Mamo, Mr M. Sithosa, Mr M. W. Ngobeni and Ms A. Budai for their support during the project. Special thanks to the department of chemistry, University of the Witwatersrand for giving me the opportunity to conduct this research at their premises, and staff members: Mr E. Valoyi, Mr. D Moloto, Mrs K. Banda, Mr Z. Gagopane and Ms M. M. Modise for making me feel at home. Finally if it was not for the will of GOD I would not be where I am today, thank you the almighty for guiding me through the challenges of my studies.