SYNTHESIS AND CHARACTERISATION OF MULTI-WALLED CARBON NANOTUBES ON SUPPORTED CATALYSTS VIA CATALYTIC CHEMICAL VAPOUR DEPOSITION

TEE JIA CHEE

UNIVERSITI TEKNOLOGI MALAYSIA
Beloved mum and dad,

just for you.
ACKNOWLEDGEMENT

In this column of acknowledgements, I would particularly like to express my sincere appreciation and gratitude to both of my supervisors, Assoc. Prof. Dr. Nor Aziah Buang and Prof. Dr. Ahmad Fauzi Ismail for providing me noble guidance and valuable advices throughout the period of this master programme.

Besides that, I am also grateful to Mr. Azmi, Mr. Jaafar, Madam Noor Khaidawati (Faculty of Science) and Madam Suhaila Mohd. Sanip, Mr. Sohaimi, Mr. Ng Be Cheer (Membrane Research Unit, Faculty of Chemical Engineering and Natural Resources Engineering) as well as Mr. Jefri, Mr. Ayub and Mr. Zainal Abidin (Faculty of Mechanical Engineering). They had put considerable time and effort in assisting me doing my laboratory works. Without them, I might not be able to complete all the tests so successfully.

Appreciation is also acknowledged to my friends Norhuda, Zatur and Yusran for their moral support and concerns and to everyone who has contributing to the success of this study, either directly or indirectly.

Last but foremost, I wish to show my gratitude to my parents and my brother for their care and support. Without my parents’ love and encouragement throughout my life I will not able to be as present. Finally, I wish to thank my dear Jerry, for all the love and happiness he brought to me. I cannot remember how many times he came to be with me and sit by my side while I was doing my works. I thank God for bringing him into my life.
ABSTRACT

The main hindrance to employ carbon nanotubes (CNTs) commercially is the inability to control the growth of the nanotubes and to grow bulk amounts of carbon nanotubes. However, recently the Chemical Vapour Deposition (CVD) has been modified by applying various supported metals catalysts in the production of CNTs. Therefore, in this research we focus on the effects of supported catalysts in the synthesis of CNTs via Catalytic Chemical Vapour Deposition (CCVD) method. The CCVD method was used to synthesize high quality CNTs in high yield and economical cost with controlling of the CNTs characteristics and morphologies. A practical and high performance CCVD system has been designed and built. The fixed bed flow reactor in the CCVD system is specifically fabricated to carry out the pyrolysis of hydrocarbon to produce CNTs. The supported catalysts of cobalt (Co), iron (Fe) and mixture of these metals (Co/Fe) were prepared by using the alumina (Al₂O₃), molecular sieves (MS) and anodic aluminium oxide (AAO) template as supports. All supported catalysts were prepared by impregnation method. The as-prepared supported catalysts were subjected to calcination at 450 °C. The catalysts were characterised using X-Ray Diffraction (XRD) technique. Acetylene (C₂H₂) was selected as the carbon precursor and the reaction was performed at 700 °C for 30 minutes. The yields of the reaction collected as black depositions on the catalysts. The characterisations of the yield were carried out using Scanning Electron Microscopy (SEM), Field-Emission Scanning Electron Microscopy (FE-SEM) and Transmission Electron Microscopy (TEM) as well as Energy Dispersive X-Ray Analysis (EDAX) techniques. Catalysts prepared were active in the production of CNTs. The most active catalysts were identified as Al-Co/Fe(3.0)Cal, AAO-Co/Fe(1.0)Cal and MS-Co/Fe(3.0)Cal as they generated high carbon contents of 72.00, 64.03 and 48.50 wt.% respectively. The as-grown CNTs over various catalysts showed high degree of graphitisation, purity and density with configurations of bundles, arrays and coils. The CNTs yields were classified as multi-walled carbon nanotubes (MWNTs). The best MWNT consists of 11 layers of turbostratic graphene wall with inner diameter of 3.57 nm and outer diameter of 11.43 nm as well as distance between layers of 0.33 nm. The CNTs grown over Al₂O₃ supported catalysts followed the tip growth mechanism whereas the CNTs grown over MS supported catalysts followed the base growth mechanism.
Halangan utama dalam menggunakan nanotiub karbon (CNTs) secara komersial adalah ketidakupayaan untuk mengawal pertumbuhan nanotiub karbon dan tidak dapat menghasilkan nanotiub karbon dalam jumlah yang banyak. Walau bagaimanapun, kebelakangan ini kaedah Pemendapan Wap Kimia (CVD) telah diubahsuai dengan menggunakan pelbagai jenis mangkin logam berpenyokong dalam penghasilan CNTs. Oleh itu, kajian ini menfokuskan kepada kesan mangkin berpenyokong ke atas sintesis CNTs melalui teknik Pemendapan Wap Kimia Bermangkin (CCVD). Teknik CCVD ini digunakan untuk mensintesis CNTs berkualiti tinggi dengan hasil yang tinggi, kos yang ekonomik dan dapat mengawal ciri-ciri dan morfologi CNTs terhasil. Sistem CCVD yang praktikal dan berkeupayaan tinggi telah direka bentuk dan dibina. Reaktor pengaliran dasar tetap dalam CCVD sistem ini dibina khas untuk proses pirolisis hidrokarbon untuk menghasilkan CNTs. Mangkin berpenyokong jenis kobalt (Co), ferum (Fe) and campuran kedua-dua logam ini (Co/Fe) telah disediakan dengan menggunakan alumina (Al₂O₃), penapis molekul (MS) dan templat anodik aluminium oksida (AAO) sebagai penyokong. Kesemua mangkin berpenyokong telah disediakan dengan kaedah pengisitepuan. Mangkin berpenyokong tersedia telah dikalsinkan pada suhu 450 °C. Semua mangkin berpenyokong telah dicirikan dengan teknik Pembelauan Sinar-X (XRD). Asetilena (C₂H₂) telah dipilih sebagai bahan asas karbon. Tindak balas telah dijalankan pada suhu 700 °C selama 30 minit dan hasil daripada tindak balas dikumpul sebagai serbuk hitam yang termendap atas mangkin. Pencirian hasil ini telah dilakukan dengan menggunakan teknik Mikroskopi Imbasan Elektron (SEM), Mikroskopi Imbasan Elektron Pemancaran Medan (FE-SEM) dan Mikroskopi Transmisi Elektron (TEM) serta Analisis Penyerakan Tenaga Sinar-X (EDAX). Mangkin berpenyokong yang disediakan adalah aktif dalam penghasilan CNTs. Mangkin yang teraktif dikenalpasti sebagai Al-Co/Fe(3.0)Cal, AAO-Co/Fe(1.0)Cal dan MS-Co/Fe(3.0)Cal kerana ia menghasilkan kandungan karbon yang tinggi, iaitu masing-masing 72.00, 64.03 and 48.50 % berat. CNTs tersedia atas pelbagai jenis mangkin menunjukan darjah grafitasi, ketulin dan kepadatan yang tinggi dengan konfigurasi jenis gumpalan, teratur dan lingkaran. Hasil CNTs itu telah diklasifikasikan sebagai nanotiub karbon dinding berganda (MWNTs). MWNTs yang terbaik terdiri daripada 11 lapis dinding grafen turbostratik dengan diameter dalam 3.57 nm dan diameter luaran 11.43 nm serta jarak antara lapisan 0.33 nm. Pertumbuhan CNTs bagi mangkin berpenyokong Al₂O₃ adalah melalui mekanisma pertumbuhan hujung, manakala mangkin berpenyokong MS melalui mekanisma pertumbuhan pangkal.
# TABLE OF CONTENTS

<table>
<thead>
<tr>
<th>CHAPTER</th>
<th>TITLE</th>
<th>PAGE</th>
</tr>
</thead>
<tbody>
<tr>
<td>TITLE PAGE</td>
<td></td>
<td>i</td>
</tr>
<tr>
<td>DECLARATION</td>
<td></td>
<td>ii</td>
</tr>
<tr>
<td>DEDICATION</td>
<td></td>
<td>iii</td>
</tr>
<tr>
<td>ACKNOWLEDGEMENT</td>
<td></td>
<td>iv</td>
</tr>
<tr>
<td>ABSTRACT</td>
<td></td>
<td>v</td>
</tr>
<tr>
<td>ABSTRAK</td>
<td></td>
<td>vi</td>
</tr>
<tr>
<td>TABLE OF CONTENTS</td>
<td></td>
<td>vii</td>
</tr>
<tr>
<td>LIST OF TABLES</td>
<td></td>
<td>xiii</td>
</tr>
<tr>
<td>LIST OF FIGURES</td>
<td></td>
<td>xv</td>
</tr>
<tr>
<td>LIST OF ABBREVIATIONS</td>
<td></td>
<td>xxi</td>
</tr>
<tr>
<td>LIST OF APPENDICES</td>
<td></td>
<td>xxii</td>
</tr>
</tbody>
</table>

1 **INTRODUCTION** 1

1.1 Research Background 1

1.2 Problem Statement 2

1.3 Research Objectives 3

1.4 Scopes of Study 4

2 **CARBON AND CARBON NANOTUBES** 5

2.1 Carbon and Carbon Structures 5

2.1.1 Carbon and Bonding between Carbon Atoms 5

2.1.2 Graphite 7
3 CATALYTIC CHEMICAL VAPOUR DEPOSITION (CCVD) 26

3.1 An Overview of Catalytic Chemical Vapour Deposition (CCVD) Method 26

3.2 Metal Oxides Supported Catalysts 27

3.3 Anodic Aluminium Oxide (AAO) Template Supported Catalysts 37

3.4 Types of Carbon Precursor 40

3.5 Reaction Temperature 40

3.6 Modified Catalytic Chemical Vapour Deposition (CCVD) 42

4 RESEARCH METHODOLOGY 44

4.1 Preparation of Supported Catalysts 44

4.1.1 Preparation of Alumina and Molecular Supported Catalysts 44

4.1.2 Preparation of Anodic Aluminium Oxide (AAO) Template Supported Catalysts 45

4.2 Synthesis of Carbon Nanotubes 47

4.2.1 Design and Fabrication of Custom Built Catalytic Chemical Vapour Deposition (CCVD) System 47
4.2.2 Production of Carbon Nanotubes 49

4.3 Characterisation Techniques 50

4.3.1 X-Ray Diffraction (XRD) 50

4.3.1.1 Particle Size Measurement 51

4.3.2 Electron Microscopy 53

4.3.2.1 Scanning Electron Microscopy (SEM) 53

4.3.2.2 Field-Emission Scanning Electron Microscopy (FE-SEM) 55

4.3.2.3 Transmission Electron Microscopy (TEM) 55

4.3.3 Energy Dispersive X-Ray Analysis (EDAX) 57

5 PRODUCTION OF CARBON NANOTUBES (CNTs) OVER ALUMINA AND ANODIC ALUMINIUM OXIDE (AAO) SUPPORTED CATALYSTS 60

5.1 Alumina Supported Catalysts 60

5.1.1 Physical Appearance of Alumina Supported Catalysts 61

5.1.2 X-Ray Diffraction (XRD) Analysis 62

5.1.2.1 XRD Analysis of Alumina Supported Cobalt Catalysts 62

5.1.2.2 XRD Analysis of Alumina Supported Ferrum Catalysts 67

5.1.2.3 XRD Analysis of Alumina Supported Cobalt/Ferrum Catalysts 71

5.1.2.4 Particle Size of Alumina Supported Catalysts 73

5.1.2.5 Conclusion of XRD Analysis 75

5.1.3 As-Grown Carbon Deposition Yield and Physical Appearance 75
5.1.4 Scanning Electron Microscopy (SEM) Analysis
  5.1.4.1 SEM Analysis of Alumina Supported Cobalt Catalysts and the CNTs Yield 78
  5.1.4.2 SEM Analysis of Alumina Supported Ferrum Catalysts and the CNTs Yield 81
  5.1.4.3 SEM Analysis of Alumina Supported Cobalt/Ferrum Catalysts and the CNTs Yield 84
  5.1.4.4 Conclusion of SEM Analysis 88
5.1.5 Field Emission-Scanning Electron Microscopy (FE-SEM) Analysis 89
5.1.6 Transmission Electron Microscopy (TEM) Analysis 81
5.1.7 Energy Dispersive X-Ray Analysis (EDX) 95
5.2 Anodic Aluminium Oxide (AAO) Supported Catalysts 98
  5.2.1 Physical Appearance of AAO Supported Catalysts 98
  5.2.2 X-Ray Diffraction (XRD) Analysis 99
  5.2.3 As-Grown Carbon Deposition Yield and Physical Appearance 99
  5.2.4 Scanning Electron Microscopy (SEM) Analysis 101
    5.2.4.1 SEM Analysis of AAO Supported Cobalt Catalysts and the CNTs Yield 101
    5.2.4.2 SEM Analysis of AAO Supported Ferrum Catalysts and the CNTs Yield 105
5.2.4.3 SEM Analysis of AAO Supported Cobalt/Ferrum Catalysts and the CNTs Yield 106
5.2.4.4 Conclusion of SEM Analysis 109
5.2.5 Energy Dispersive X-Ray Analysis (EDX) 110

6 PRODUCTION OF CARBON NANOTUBES (CNTs) OVER MOLECULAR SIEVES SUPPORTED CATALYSTS 113

6.1 Molecular Sieves Supported Catalysts 113
6.2 Physical Appearance of Molecular Sieves Supported Catalysts 114
6.3 X-Ray Diffraction (XRD) Analysis 115
6.3.1 XRD Analysis of Molecular Sieves Supported Cobalt Catalysts 115
6.3.2 XRD Analysis of Molecular Sieves Supported Ferrum Catalysts 120
6.3.3 XRD Analysis of Molecular Sieves Supported Cobalt/Ferrum Catalysts 125
6.3.4 Particle Size of Alumina Supported Catalysts 126
6.3.5 Conclusion of XRD Analysis 128
6.4 As-Grown Carbon Deposition Yield and Physical Appearance 129
6.5 Scanning Electron Microscopy (SEM) Analysis 131
6.5.1 SEM Analysis of Molecular Sieves Supported Cobalt Catalysts and the CNTs Yield 131
6.5.2 SEM Analysis of Molecular Sieves Supported Ferrum Catalysts and the CNTs Yield 134
6.5.3 SEM Analysis of Molecular Sieves Supported Cobalt/Ferrum Catalysts and the CNTs Yield 137
6.5.4 Conclusion of SEM Analysis 140
6.6 Field Emission-Scanning Electron Microscopy (FE-SEM) Analysis 141
6.7 Transmission Electron Microscopy (TEM) Analysis 142
6.8 Energy Dispersive X-Ray Analysis (EDAX) 146

7 CONCLUSION 148
7.1 Overall Conclusion 148
7.2 Future Works 152

REFERENCES 153

APPENDICES 165
# LIST OF TABLES

<table>
<thead>
<tr>
<th>TABLE NO.</th>
<th>TITLE</th>
<th>PAGE</th>
</tr>
</thead>
<tbody>
<tr>
<td>2.1</td>
<td>Shape of cross section for three types of carbon nanotubes.</td>
<td>15</td>
</tr>
<tr>
<td>2.2</td>
<td>A summery of the major production methods and their efficiency.</td>
<td>21</td>
</tr>
<tr>
<td>4.1</td>
<td>Denotation for the alumina, molecular sieves (MS) and Anodic Aluminium Oxide (AAO) template supported metal catalysts.</td>
<td>46</td>
</tr>
<tr>
<td>5.1</td>
<td>Phases, peak position ($2\theta$) and d values (Å) in the X-ray diffractogram patterns of the Al$_2$O$_3$ support, Al-Co(2.5) and Al-Co(2.5)Cal catalysts.</td>
<td>64</td>
</tr>
<tr>
<td>5.2</td>
<td>Phase, peak position ($2\theta$) and d values (Å) in the X-ray diffractogram patterns of Al-Co(40.0)Cal catalyst calcined at 450 °C / 17 h and 750 °C / 17 h.</td>
<td>66</td>
</tr>
<tr>
<td>5.3</td>
<td>Phases, peak position ($2\theta$) and d values (Å) in the X-ray diffractogram patterns of the Al$_2$O$_3$ support, Al-Fe(2.5) and Al-Fe(2.5)Cal catalysts.</td>
<td>69</td>
</tr>
<tr>
<td>5.4</td>
<td>Phase, peak position ($2\theta$) and d values (Å) in the X-ray diffractogram patterns of Al-Fe(30.0)Cal catalyst calcined at 450 °C / 17 h and 750 °C / 17 h.</td>
<td>70</td>
</tr>
<tr>
<td>5.5</td>
<td>Phases, peak position ($2\theta$) and d values (Å) in the X-ray diffractogram patterns of the Al$_2$O$_3$ support, Al-Co/Fe and Al-Co/Fe(2.5)Cal catalysts.</td>
<td>73</td>
</tr>
<tr>
<td>5.6</td>
<td>The particle size ($d$) of Co$_3$O$_4$ face-centred cubic and Fe$_2$O$_3$ rhombohedral particles in Al$_2$O$_3$ supported Co/Fe catalysts.</td>
<td>74</td>
</tr>
</tbody>
</table>
5.7 The Al$_2$O$_3$ supported catalysts and the yield (%), the physical appearance and density of the as-synthesized carbon deposit in CCVD of C$_2$H$_2$.

5.8 EDX analysis data of surface compositions of various Al$_2$O$_3$ supported catalysts before and after decomposition of C$_2$H$_2$.

5.9 The AAO template supported catalysts and the yield (%), the physical appearance and density of the as-synthesized carbon deposit in CCVD of C$_2$H$_2$.

5.10 EDX analysis data of surface compositions of various AAO supported catalysts before and after decomposition of C$_2$H$_2$.

6.1 Phases, peak position (2$\theta$) and d values (Å) in the X-ray diffractogram patterns of the MS support, MS-Co(2.5) and MS-Co(2.5)Cal catalysts.

6.2 Phase, peak position (2$\theta$) and d values (Å) in the X-ray diffractogram patterns of MS-Co(40.0)Cal catalyst calcined at 450 °C / 17 h and 750 °C / 17 h.

6.3 Phases, peak position (2$\theta$) and d values (Å) in the X-ray diffractogram patterns of the MS support, MS-Fe(2.5) and MS-Fe(2.5)Cal catalysts.

6.4 Phase, peak position (2$\theta$) and d values (Å) in the X-ray diffractogram patterns of MS-Fe(30.0)Cal catalyst calcined at 750 and 1000 °C for 5 hours.

6.5 Phases, peak position (2$\theta$) and d values (Å) in the X-ray diffractograms of the MS support, MS-Co/Fe(2.5) and MS-Co/Fe(2.5)Cal catalysts.

6.6 The particle size ($d$) of Co$_{333}$Na$_{333}$(AlSiO$_4$)(H$_2$O)$_{2.92}$ cubic and Fe$_{2.7}$Na$_{2.0}$(Si$_{12}$Al$_{12}$O$_{48}$)(H$_2$O)$_{14.8}$ cubic phase in MS supported bimetallic catalysts.

6.7 The MS supported catalysts and the carbon deposition yield (%), the physical appearance and density of the as-synthesized carbon deposit.
6.8 EDAX analysis data of surface compositions of various MS supported catalysts before and after decomposition of $\text{C}_2\text{H}_2$. 147

7.1 Comparison of purity, density and configurations of as-grown CNTs and CNFs over various supported catalysts. 150
# LIST OF FIGURES

<table>
<thead>
<tr>
<th>FIGURE NO.</th>
<th>TITLE</th>
<th>PAGE</th>
</tr>
</thead>
<tbody>
<tr>
<td>2.1</td>
<td>The graphite hexagonal single crystal structure (Dresselhaus et al., 1995). The planes of carbon (graphene layers) are stacked in an ABAB sequence. The A and B carbon sites are denoted by open circles and the A’ and B’ sites by black circles. The in-plane lattice constant is denoted by $a_0$ and the vectors of the unit cell in the directions $a_1$, $a_2$ and $c$ are indicated.</td>
<td>7</td>
</tr>
<tr>
<td>2.2</td>
<td>Diamond crystal structure consisting of the FCC lattice positions and the tetrahedral atom positions.</td>
<td>9</td>
</tr>
<tr>
<td>2.3</td>
<td>The $C_{60}$ molecule showing single bond ($a_3$) and double bond ($a_6$).</td>
<td>10</td>
</tr>
<tr>
<td>2.4</td>
<td>Carbon fiber morphologies for (a) as-deposited at 1100 °C and (b) after heat treatment at 3000 °C (Dresselhaus et al., 1995).</td>
<td>12</td>
</tr>
<tr>
<td>2.5</td>
<td>Classification of carbon nanotubes: (a) armchair, (b) zig-zag, and (c) chiral nanotubes (Saito et al., 1998).</td>
<td>14</td>
</tr>
<tr>
<td>2.6</td>
<td>The unfolded nanotube on a 2-dimensional graphene lattice (Kong, 2002).</td>
<td>16</td>
</tr>
<tr>
<td>2.7</td>
<td>Schematic experimental set-ups for carbon nanotubes growth methods; (a) arc-discharge, (b) laser ablation and (c) chemical vapour deposition (CVD) (Dresselhaus and Avouris, 2001).</td>
<td>20</td>
</tr>
<tr>
<td>2.8</td>
<td>Visualization of a possible carbon nanotube growth mechanism (Daenen et al., 2003).</td>
<td>22</td>
</tr>
</tbody>
</table>
3.1 The schematic diagram of an anodic aluminium oxide (AAO) template. 38
4.1 Schematic diagram of the Catalytic Chemical Vapour Deposition (CCVD) system (fixed bed flow reactor). 48
4.2 Photograph of the fixed bed flow reactor. 48
4.3 Photograph of the gas mixing component in the CCVD system. 49
4.4 The diffraction of X-rays by crystal lattices. 51
4.5 The components of a Scanning Electron Microscope (SEM) (Reimer, 1984). 54
4.6 Schematic ray path for a Transmission Electron Microscope (TEM). 56
4.7 The interaction of an electron beam with an atom. 58
5.1 XRD patterns of Al$_2$O$_3$ support, Al–Co(2.5), Al–Co(2.5)Cal, Al–Co(3.0) and Al–Co(3.0)Cal catalysts. 
   ■: Al$_2$O$_3$ tetragonal and ○: Co$_3$O$_4$ face-centred cubic. 63
5.2 XRD patterns of Al-Co(40.0)Cal catalyst calcined at 450 °C / 17 h and 750 °C / 17 h. ○: Co$_3$O$_4$ face-centred cubic. 66
5.3 X-ray diffractogram patterns of various Al-Fe catalysts together with Al$_2$O$_3$ support. ■: Al$_2$O$_3$ tetragonal and ▲: Fe$_2$O$_3$ rhombohedral. 68
5.4 XRD patterns of Al-Fe(30.0)Cal catalyst calcined at 450 °C / 17 h and 750 °C / 17 h. ▲: Fe$_2$O$_3$ rhombohedral. 70
5.5 XRD diffractogram patterns of Al-Co/Fe catalysts and Al$_2$O$_3$ support. ■: Al$_2$O$_3$ tetragonal, ○: Co$_3$O$_4$ face-centred cubic and ▲: Fe$_2$O$_3$ rhombohedral. 72
5.6 SEM micrograph of dried Al$_2$O$_3$ support (500×). 78
5.7 SEM micrographs of Al$_2$O$_3$ supported Co catalysts: (a) Al-Co(3.0) (1000×) and (b) Al-Co(3.0)Cal (1000×). 79
5.8 SEM micrographs of as-grown CNTs over various Al$_2$O$_3$ supported Co catalysts, (a) Al-Co(2.5) (10000×), (b) Al-Co(2.5)Cal (10000×), (c) and (d) Al-Co(3.0) (5000× and 10000×) and (e) Al-Co(3.0)Cal (10000×).

5.9 SEM micrographs of Al$_2$O$_3$ supported Fe catalysts: (a) Al-Fe(2.5)Cal catalyst (1000×) and (b) Al-Fe(3.0) catalyst (1000×).

5.10 SEM micrographs of as-grown CNTs over different Al$_2$O$_3$-Fe catalyst, (a) Al-Fe(2.5) (10000×), (b) Al-Fe(2.5)Cal (10000×), (c) Al-Fe(3.0) (10000×), (d) and (e) Al-Fe(3.0)Cal (5000× and 10000×).

5.11 SEM micrographs of various Al$_2$O$_3$-Co/Fe catalysts: (a) Al-Co/Fe(2.5) (1000×), Al-Co/Fe(2.5)Cal (1000×) and (c) Al-Co/Fe(3.0) (1000×).

5.12 SEM micrographs of CNTs grown over various of Al-Co/Fe catalysts: (a) Al-Co/Fe(2.5) (10000×), (b) Al-Co/Fe(2.5)Cal (10000×), (c) and (d) Al-Co/Fe(3.0) (10000×), (e) to (h) Al-Co/Fe(3.0)Cal (2500×, 5000× and 10000×).

5.13 FE-SEM micrographs of as-grown CNTs over Al-Co/Fe(3.0)Cal catalyst, (a) 60000× magnification and (b) 250000× magnification.

5.14 TEM micrographs of as-grown MWNTs produced by Al-Co(3.0) catalyst, (a) scale bar: 100 nm and (b) scale bar: 20 nm.

5.15 TEM micrographs of MWNTs formed by Al-Fe(3.0) catalyst, (a) scale bar: 100 nm and (b) scale bar: 10 nm.

5.16 TEM micrographs of as-synthesized MWNTs over Al-Co/Fe catalysts: (a) and (b) Al-Co/Fe(2.5)Cal (scale bar: 50 nm and 10 nm) as well as (c) and (d) Al-Co/Fe(3.0) (scale bar: 100 nm and 10 nm).

5.17 TEM micrographs of MWNTs grown over Al-Co/Fe(3.0)Cal catalyst: (a) scale bar: 100 nm, (b) scale bar: 5 nm and (c) scale bar: 10 nm.
5.18 X-ray diffractogram patterns of AAO template and AAO-Co(0.5) catalyst. 99
5.19 SEM micrograph of anodic aluminium oxide (AAO) template (20000 ×). 101
5.20 SEM micrographs of AAO template supported Co catalysts: (a) AAO-Co(0.5)Cal (20000 ×) and (b) AAO-Co(1.0)Cal (20000 ×). 102
5.21 SEM micrographs of carbon deposit over various Co catalysts: (a) and (b) AAO-Co(0.5) (10000× and 2000×), (c) and (d) AAO-Co(0.5)Cal (10000×), (e) and (f) AAO-Co(1.0) (20000× and 10000×), (g) and (h) AAO-Co(1.0)Cal (10000×). 103
5.22 SEM micrographs of different AAO-Fe catalysts: (a) AAO-Fe(0.5)Cal catalyst (20000×) and (b) AAO-Fe(0.5) (10000×), (b) AAO-Fe(0.5)Cal (10000×), (c) AAO-Fe(1.0) (10000×), (d) and (e) AAO-Fe(1.0)Cal (10000×). 105
5.23 SEM micrographs of as-grown CNTs over various AAO-Fe catalysts: (a) AAO-Fe(0.5) (10000×), (b) AAO-Fe(0.5)Cal (10000×), (c) AAO-Fe(1.0) (10000×), (d) and (e) AAO-Fe(1.0)Cal (10000×). 106
5.24 Micrographs from SEM analysis of AAO supported bimetallic catalysts: (a) AAO-Co/Fe(0.5) (10000×) and (b) AAO-Co/Fe(1.0) (5000×). 107
5.25 SEM micrographs of CNTs grown over: (a) AAO-Co/Fe(0.5) (10000×), (b) and (c) AAO-Co/Fe(0.5)Cal (10000× and 5000×), (d) and (e) AAO-Co/Fe(1.0) (10000× and 5000×), (f) and (g) AAO-Co/Fe(1.0)Cal (5000× and 10000×). 108
6.1 XRD diffractogram patterns of MS support, MS-Co(2.5), MS-Co(2.5)Cal, MS-Co(3.0) and MS-Co(3.0)Cal catalysts. ◆: NaSiAlO4 face-centred cubic and ▼: Co,333Na,333(AlSiO4)(H2O)2,92 cubic phase. 109
6.2 XRD patterns of MS-Co(40.0)Cal catalyst calcined at 450 °C / 17 h and 750 °C / 17 h. ▼: Co₃O₄ face-centred cubic.

6.3 XRD patterns of various MS-Fe catalysts together with MS support. ◆: NaSiAlO₄ face-centred cubic and ✷: Fe₂.₇Na₂.₀(Si₁₂Al₁₂O₄₈)(H₂O)₁₄.₈ cubic phase.

6.4 XRD patterns of MS-Fe(30.0)Cal catalyst calcined at 750 °C and 1000 °C for 5 hours. ✷: Fe₂O₃ rhombohedral.

6.5 X-ray diffractogram patterns of MS support and series of MS-Co/Fe catalysts. ◆: NaSiAlO₄ face-centred cubic, ▼: Co₀.₃₃Na₀.₃₃(AlSiO₄)(H₂O)₂.₉₂ cubic and ✷: Fe₂.₇Na₂.₀(Si₁₂Al₁₂O₄₈)(H₂O)₁₄.₈ cubic phase.

6.6 SEM micrograph of dried molecular sieves (MS) support (1000×).

6.7 SEM micrographs of MS supported Co catalysts: (a) MS-Co(2.5)Cal (1000×) and (b) MS-Co(3.0) (1000×).

6.8 SEM micrographs of as-grown CNTs over various MS supported Co catalysts: (a) and (b) MS-Co(2.5) (5000× and 10000×), (c) MS-Co(2.5)Cal (5000×), (d) MS-Co(3.0) (10000×), (e) and (f) MS-Co(3.0)Cal (10000×).

6.9 SEM micrographs of MS supported Fe catalysts: (a) MS-Fe(3.0) (1000×) and (b) MS-Fe(3.0)Cal (1000×).

6.10 SEM micrographs of as-grown CNTs over series of MS-Fe catalysts: (a) and (b) MS-Fe(2.5) (10000×), (c) and (d) MS-Fe(2.5)Cal (10000×), (e) and (f) MS-Fe(3.0) (10000×), (g) and (h) MS-Fe(3.0)Cal (10000×).

6.11 SEM micrographs of MS supported Fe catalysts: (a) MS-Fe(3.0) (1000×) and (b) MS-Fe(3.0)Cal (1000×).

6.12 SEM micrographs of CNTs grown over the bimetallic catalysts: (a) and (b) MS-Co/Fe(2.5) (10000×), (c) and (d) MS-Co/Fe(2.5)Cal (5000× and 2000×), (e) and (f) MS-Co/Fe(3.0) (10000× and 300×), (g) and (h) MS-Co/Fe(3.0)Cal (5000×).
6.13 FE-SEM micrographs of as-grown CNTs over MS-Co/Fe(3.0)Cal catalyst, (a) 60000× magnification and (b) 250000× magnification. 141

6.14 TEM micrographs of the as-grown MWNTs over MS-Co(3.0)Cal catalyst, (a) and (b) scale bar: 10 nm. 142

6.15 TEM micrographs of as-grown MWNTs from: (a) and (b) MS-Fe(2.5)Cal catalyst, (c) and (d) MS-Fe(3.0) catalyst (for all images scale bar: 10nm). 143

6.16 TEM micrographs of as-grown MWNTs from MS-Co/Fe(2.5) catalyst, (a) scale bar: 100 nm, (b) scale bar: 10 nm and (c) scale bar: 10 nm. 144

6.17 TEM micrographs of as-synthesized MWNT over MS-Co/Fe(3.0)Cal catalyst, both of the micrographs have scale bar of 5 nm. 145
### LIST OF ABBREVIATIONS

<table>
<thead>
<tr>
<th>Abbreviation</th>
<th>Description</th>
</tr>
</thead>
<tbody>
<tr>
<td>AAO</td>
<td>Anodic Aluminium Oxide template</td>
</tr>
<tr>
<td>Al₂O₃</td>
<td>Alumina support</td>
</tr>
<tr>
<td>C</td>
<td>Carbon</td>
</tr>
<tr>
<td>Cal</td>
<td>Calcination</td>
</tr>
<tr>
<td>CVD</td>
<td>Chemical Vapour Deposition</td>
</tr>
<tr>
<td>CCVD</td>
<td>Catalytic Chemical Vapour Deposition</td>
</tr>
<tr>
<td>C₂H₂</td>
<td>Acetylene</td>
</tr>
<tr>
<td>CNFs</td>
<td>Carbon Nanofibers</td>
</tr>
<tr>
<td>CNTs</td>
<td>Carbon Nanotubes</td>
</tr>
<tr>
<td>Co</td>
<td>Cobalt</td>
</tr>
<tr>
<td>Cu</td>
<td>Copper</td>
</tr>
<tr>
<td>EDX</td>
<td>Energy Dispersive X-Ray Analysis</td>
</tr>
<tr>
<td>FE-SEM</td>
<td>Field Emission-Scanning Electron Microscopy</td>
</tr>
<tr>
<td>Fe</td>
<td>Iron</td>
</tr>
<tr>
<td>MgO</td>
<td>Magnesium Oxide</td>
</tr>
<tr>
<td>Mo</td>
<td>Molibdenum</td>
</tr>
<tr>
<td>MS</td>
<td>Molecular Sieves support</td>
</tr>
<tr>
<td>MWNTs</td>
<td>Multi-Walled Carbon Nanotubes</td>
</tr>
<tr>
<td>Ni</td>
<td>Nickel</td>
</tr>
<tr>
<td>sccm</td>
<td>Standard cubic centimetres per minute</td>
</tr>
<tr>
<td>SEM</td>
<td>Scanning Electron Microscopy</td>
</tr>
<tr>
<td>SiO₂</td>
<td>Silica</td>
</tr>
<tr>
<td>SMSI</td>
<td>Strong Metal-Support Interaction</td>
</tr>
<tr>
<td>SWNTs</td>
<td>Single-Walled Carbon Nanotubes</td>
</tr>
<tr>
<td>TEM</td>
<td>Transmission Electron Microscopy</td>
</tr>
<tr>
<td>V</td>
<td>Vanadium</td>
</tr>
<tr>
<td>XRD</td>
<td>X-Ray Diffraction</td>
</tr>
</tbody>
</table>
# LIST OF APPENDICES

<table>
<thead>
<tr>
<th>APPENDIX</th>
<th>TITLE</th>
<th>PAGE</th>
</tr>
</thead>
<tbody>
<tr>
<td>A</td>
<td>Mathematical Expressions for Stoichiometric Amount of Metal Salt Used in Wet Impregnation</td>
<td>165</td>
</tr>
<tr>
<td>B</td>
<td>Mathematical Expressions for Stoichiometric Amount of Metal Salt Used in Dip Coating</td>
<td>168</td>
</tr>
<tr>
<td>C</td>
<td>Mathematical Expressions for Crystallite Size of Co$_3$O$_4$ Cubic Crystal Using Scherrer Equation</td>
<td>171</td>
</tr>
<tr>
<td>D</td>
<td>Mathematical Expressions for Particle Size, Length and Diameter from the SEM Micrograph</td>
<td>173</td>
</tr>
<tr>
<td>E</td>
<td>Publications</td>
<td>174</td>
</tr>
</tbody>
</table>
CHAPTER 1

INTRODUCTION

1.1 Research Background

The past decade has witnessed tremendous effort and progress in the field of carbon nanotubes. Ever since the discovery of carbon nanotubes by Iijima (1991), it has captured the attention of researchers worldwide. Understanding their unique properties and exploring their potential applications have been a main driving force for this area.

Throughout history, the allotropes of carbon have played a number of important roles in technology. In ancient times, diamond was celebrated for its hardness and beauty, and carbon black was used as a colorant. The industrial age brought greater interest in graphite and related carbon materials as a source of carbon vapour in arc-lamps and as clean-burning fuels. Graphite-like carbon materials are now widely used for their unique mechanical, electrical and thermal properties.

Very small diameter (less than 10nm) carbon filaments were prepared in the 1970’s and 1980’s by the decomposition of hydrocarbons at high temperatures (Dresselhaus and Avouris, 2001). Direct stimulus to study carbon filaments of very small diameters more systematically came from the discovery of fullerenes by Kroto and Smalley.
In December 1990 at a carbon-carbon composites workshop, papers were given on the status of fullerene research by Smalley, the discovery of a new synthesis method for the efficient production of fullerenes and a review of carbon fibers research by M.S. Dresselhaus. Discussions at the workshop stimulated Smalley to speculate about the existence of carbon nanotubes of dimensions comparable to C$_{60}$. These conjectures were later followed up in August by an oral presentation at a fullerene workshop by Dresselhaus on the symmetry proposed for carbon nanotubes capped at either end by fullerene hemispheres (Saito et al., 1998).

However, the real breakthrough on carbon nanotube research came with the experimental observation of carbon nanotubes in 1991 by Iijima of the NEC Laboratory in Tsukuba, Japan using High-Resolution Transmission Electron Microscopy (HRTEM) (Iijima, 1991). It was this work which bridged the gap between experimental observation and the theoretical framework of carbon nanotubes in relation to fullerenes and as theoretical examples of 1D system. Since the pioneering work by Iijima, the study of carbon nanotubes has progressed rapidly.

1.2 Problem Statement

The main hindrance to employing carbon nanotubes (CNTs) in real world is the inability to control the growth of the nanotubes and to grow bulk amounts of carbon nanotubes. There are three main techniques to grow carbon nanotubes: arc-discharge, laser ablation and chemical vapour deposition (CVD). The first two methods are high temperature processes that produce high quality CNTs, but they cannot grow mass quantities of nanotubes within a reasonable amount of time. The CVD technique is able to grow bulk amounts of nanotubes and arrays of multi-walled carbon nanotubes (MWNTs). However, these nanotubes contain a vast amount of defects along the length of the tubes due to the relatively low synthesis temperature of 600 – 1200 °C.
Nevertheless, some progress has been recently obtained, the chemical vapour deposition (CVD) has been modified by applying various supported metals catalysts in the production of CNTs. The catalytic chemical vapour deposition (CVD) method supplies CNTs in high yield and low costs, but also at controlling the CNTs characteristics and morphologies. Being a catalytic process, the combinations of transition metals and support can be changed depending on the characteristics required, such as the alignment and diameter of the nanotubes. The CCVD synthesis of CNTs can be carried out at low temperature and ambient pressure.

1.3 Research Objectives

This research is intended to synthesize carbon nanotubes (CNTs) of high yield and purity at economical cost. Therefore, this research is conducted to achieve the following primary objectives:

1. To produce carbon nanotubes (CNTs) using Catalytic Chemical Vapour Deposition (CCVD) method.

2. To study the effects of supported catalysts in the synthesis of carbon nanotubes (CNTs).

3. To characterise the supported catalysts and carbon nanotube yields chemically and physically.

4. To identify the best catalyst-support combination to catalyze the carbon nanotubes growth.
1.4 Scopes of Study

In order to achieve the objectives, this research is focusing on the following scopes:

(i) Designing and fabricating an effective Catalytic Chemical Vapour Deposition (CCVD) system contains a fixed bed flow reactor which facilitates the production of CNTs.

(ii) Preparing supported catalysts by using alumina (Al₂O₃) beads, molecular sieves (MS) beads and anodic aluminium oxide (AAO) template as catalyst supports and cobalt (Co) or ferrum (Fe) as metal catalysts with impregnation or dip coat techniques. Applying calcination treatment to enhance the activity of the catalysts.

(iii) Producing CNTs through catalyze pyrolysis of acetylene (C₂H₂) at optimum temperature, reaction time and gas flow rate.

(iv) Characterising the supported catalysts and CNT yields using X-ray Diffraction (XRD) technique to reveal the active catalyst sites and effects of calcination.

(v) Investigating the morphologies and topologies of the supported catalysts and the CNT yields through Scanning Electron Microscopy (SEM), Field-Emission Scanning Electron Microscopy (FE-SEM) and Transmission Electron Microscopy (TEM) techniques.

(vi) Determining the surface composition of a sample (metal catalyst and carbon content) using Energy Dispersive X-Ray Analysis (EDAX) technique.

(vii) Comparing the performance of supported catalysts in the production of CNTs to figure out the best combination of support, catalyst, loading and treatment for the supported catalysts.