UNIVERSITI PUTRA MALAYSIA

EFFECTS OF MOLAR RATIO OF IRON CATALYST ON SYNTHESIS OF CARBON NANOTUBES VIA CATALYTIC CHEMICAL VAPOR DEPOSITION

SETAREH MONSHI TOUSSI

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By

SETAREH MONSHI TOUSSI

Thesis Submitted to the School of Graduate Studies, Universiti Putra Malaysia, in Fulfilment of the Requirements for the Degree of Master of Science

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Chairman: Fakhru'L-Razi B Ahmadun, PhD

Faculty: Institute of Advanced Technology (ITMA)

Research on the area of the synthesis of carbon nanotubes is fundamental and critical to the entire subject of carbon nanotubes. This dissertation describes an experiment to synthesize carbon nanotubes by the method of catalytic chemical vapor deposition (CCVD). It focuses on the relationship between the as-prepared catalyst and the synthesized carbon nanotubes. The effect of growth parameters for the synthesis of carbon nanotubes was also studied.

The Fe-Mo-MgO catalysts with five different molar ratios of iron (Fe) in this composite catalyst were prepared through the impregnation method. The goal of this work was to identify the suitable molar ratio of iron (Fe) in the composite catalyst of Fe-Mo-MgO on which carbon nanotubes (CNTs) can be grown with a higher yield and quality.

Scanning electron microscopy (SEM), transmission electron microscopy (TEM), x-ray diffraction (XRD), and thermogravimetric analysis (TGA) were used to characterize the as-prepared catalysts and as-grown carbon nanotube samples.

Among these catalysts with different molar ratio of iron, the main and obvious observation in the synthesis of carbon nanotubes was the yield of synthesized carbon nanotubes. That is, increasing the molar ratio of iron, the yield of produced carbon nanotubes increases strongly, but the quality did not improve. While by decreasing the Fe concentration, both the structural defects and yield were reduced. Therefore, based on the experimental results, the best catalyst was catalyst 3 (Fe: Mo: MgO = 0.5: 0.1: 10) with a moderate molar ratio of iron. This catalyst not only had good yield but also good quality.

The different parameters such as flow rate of argon (Ar) as a carrier gas, and temperature to improve the growth condition of CCVD method for the synthesis of CNTs by Fe-Mo-MgO catalyst were examined. It is found that the best flow rate for carrier gas is 100 ml/min. For the flow rate lower or higher than this, there were very few CNTs formed, since the low flow rate of Ar could not carry enough ethanol vapors through the reactor to be deposited on the catalyst. As for the high flow rate of Ar, most of the carbon source exited from the outlet of the reactor and again they could not be deposited on the catalyst, thus few carbon nanotubes were formed.

In the synthesis of carbon nanotubes by CCVD method, the temperature plays a key role. The results show that when the temperature is lower than 750˚C, few CNTs were formed, and when the temperature is higher than 900˚C, more and more amorphous carbons were formed in the CNTs. The best temperature for the growth of carbon nanotubes by these catalysts is between 800˚C and 900˚C.

The results showed that the growth of carbon nanotubes was significantly influenced by the reaction condition due to its sensitivity. The synthesis products were always a mixture of single-walled carbon nanotubes (SWCNTs) and multi-walled carbon nanotubes (MWCNTs).

Abstrak tesis yang dikemukakan kepada Senat Universiti Putra Malaysia sebagai memenuhi keperluan untukijazah Master Sains

KESAN NISBAH KEMOLARAN PEMANGKIN IRON TERHADAP SINTESIS NANOTIUB KARBON MELALUI PEMANGKINAN PEMENDAPAN WAP KIMIA

Oleh

SETAREH MONSHI TOUSSI

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Kajian penyelidikan dalam bidang sintesis nanotiub karbon adalah asas dan kritikal kepada seluruh bidang nanotiub karbon. Kajian disertasi ini menerangkan ujikaji untuk sintesis nanotiub karbon dengan menggunakan teknik pemangkinan pemendapan wap kimia. Ia menumpu kepada hubungan antara pemangkin sedia ada dan nanotiub karbon yang disintesis. Kesan parameter pertumbuhan untuk sintesis nanotiub karbon juga telah dikaji.

Pemangkin Fe-Mo-MgO bersama dengan lima nisbah kemolaran iron (Fe) yang berbeza dalam setiap pemangkin komposit telah disediakan melalui cara pengisitepuan atau impregnasi. Matlamat kajian ini adalah untuk mengenalpasti nisbah kemolaran iron (Fe) yang sesuai dalam pemangkinan komposit Fe-Mo-MgO dimana nanotiub karbon boleh dihasilkan dengan hasil dan kualiti yang tinggi.

Mikroskop pengimbas elektron (SEM), mikroskop pancaran elektron (TEM), pembelauan x-ray (XRD), dan analisis termogravimetri (TGA) digunakan untuk mengkaji sifat pemangkin sedia ada dan sampel pemangkin nanotiub karbon yang dihasilkan.

Antara pemangkin ini dengan nisbah kemolaran iron (Fe) yang berbeza, pemerhatian jelas dalam sintesis nanotiub karbon adalah nanotiub karbon yang terhasil. Dengan meningkatkan nisbah kemolaran Fe, hasil nanotiub karbon telah meningkat dengan banyak, tetapi kualiti tidak meningkat. Apabila menurunkan konsentrasi Fe, kedua-dua kecatatan struktur dan hasil berkurangan. Oleh itu, berdasarkan kepada keputusan eksperimen, pemangkin yang terbaik adalah pemangkin 3 (Fe: Mo: MgO = 0.5: 0.1: 10) dengan kemolaran iron yang sederhana. Pemangkin ini bukan sahaja mempunyai hasil yang baik bahkan juga kualiti yang baik.

Parameter yang berbeza seperti kadar pengaliran gas argon (Ar) sebagai gas pembawa, dan suhu digunakan untuk meningkatkan keadaan pertumbuhan dalam pemangkinan pemendapan wap kimia untuk sintesis nanotiub karbon (CNTs) dengan pemangkin Fe-Mo-MgO telah dikaji. Didapati kadar pengaliran terbaik untuk gas pembawa adalah 100 ml/min. Untuk kadar pengaliran lebih rendah atau lebih tinggi daripada ini, CNTs yang dihasilkan adalah sangat sedikit, kerana kadar pengaliran argon yang rendah tidak dapat membawa wap etanol yang mencukupi melalui reaktor untuk dimendapkan keatas pemangkin. Apabila kadar pengaliran argon tinggi, kebanyakkan sumber karbon mengalir keluar daripada reaktor dan ia tidak dapat dimendapkan keatas pemangkin, maka sedikit nanotiub karbon yang terbentuk.

Dalam sintesis nanotiub karbon melalui cara pemangkinan pemendapan wap kimia, suhu memainkan peranan utama. Keputusan menunjukkan apabila suhu lebih rendah daripada 750˚C, hanya sedikit CNTs terbentuk, dan apabila suhu melebihi 900˚C, semakin banyak karbon amorfus terbentuk dalam CNTs. Suhu yang terbaik untuk pertumbuhan nanotiub karbon dengan pemangkin ini adalah antara suhu 800˚C hingga 900˚C.

Keputusan menunjukkan bahawa tumbesaran nanotiub karbon dipengaruhi oleh keadaan reaksi disebabkan oleh sensitivitinya. Sintesis produk merupakan gabungan daripada nanotiub karbon dinding tunggal dan nanotiub karbon dinding banyak.

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In the name of God

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And last but not least, I would like to express my deepest appreciation to my dear parents who provided me with encouragement, love, and support in various ways.

DEDICATION

I dedicate this work to my parents who gave me this opportunity to experience life in its fullest. I would like to express my deepest gratitude for all their unconditional love, patient, understanding, and support throughout my life, which made this journey possible, and this educational achievement become a reality.

I certify that a Thesis Examination Committee has met on 25 June 2010 to conduct the final examination of Setareh Monshi Toussi on her thesis entitled "Effects of Molar Ratio of Iron Catalyst on Synthesis of Carbon Nanotubes via Catalytic Chemical Vapor Deposition" in accordance with the Universities and University Colleges Act 1971 and the Constitution of Universiti Putra Malaysia [P.U. (A) 106] 15 March 1998. The Committee recommends that the student be awarded the Master of Science.

Members of the Examination Committee were as follows:

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This thesis was submitted to the Senate of Universiti Putra Malaysia and has been accepted as fulfilment of the requirement for the degree of the Master of Science. The members of Supervisory Committee were as follows:

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Date: 12 August 2010

DECLARATION

I declare that this thesis is my original work except for quotations and citations which have been duly acknowledged. I also declare that it has not been previously, and is not concurrently, submitted for any other degree at Universiti Putra Malaysia or at any other institution.

SETAREH MONSHI TOUSSI

Date: 7 July 2010

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LIST OF ABBREVIATIONS

BSE	Backscattered Electrons
CD	Carbon Deposits
CNTs	Carbon Nanotubes
CCVD	Catalytic Chemical Vapor Deposition
CVD	Chemical Vapor Deposition
MWCNTs	Multi-Walled Carbon Nanotubes
SEM	Scanning Electron Microscope
SE	Secondary Electrons
SWCNTs	Single-Walled Carbon Nanotubes
TEM	Transmission Electron Microscope
TGA	Thermogravimetric Analysis
XRD	X-Ray Diffraction

CHAPTER 1

INTRODUCTION

1.1 Background

Carbon nanotubes (CNTs), one of the allotropes of carbon, are molecular scale tube of graphite sheet. Depending on the ways in which the sheets are rolled into a cylinder, carbon nanotubes, take different diameters, chiralities, and structures. carbon nanotubes (CNTs) are generally of two types: single-walled carbon nanotubes (SWCNTs) and multi-walled carbon nanotubes (MWCNTs) (Henrich *et al.*, 2006).

In 1985, a group of researchers at Rice University discovered buckminsterfullerene molecule. Since this molecule consists of 60 carbon atoms in sp^2 hybridized bonds, it is called C_{60} and is arranged in a symmetric fashion (Kroto *et al.*, 1985). This discovery stimulated researchers to search new forms of carbon. In 1991, the Japanese scientist Sumio Iijima discovered fullerene-related carbon nanotubes. He initially observed only multi-walled carbon nanotubes (MWCNTs) with 2 to 20 layers, using transmission electron microscopy (Iijima, 1991). In 1993 in a subsequent publication, he confirmed the existence of single-walled carbon nanotubes (SWCNTs) and explained their structure (Iijima and Ichihashi, 1993).

1.2 Statement of the Problem

In recent years, there has been an increasing interest in the field of carbon nanotubes (CNTs). The extraordinary properties of CNTs, such as chemical, physical, electrical (Saito, 1997), mechanical (Wong *et al.*, 1997) and thermal properties (Berber *et al.*, 2000; Kim *et al.*, 2001) made them potentially useful in a wide variety of applications in nanotechnology, electronics, and other fields of material science. These unique properties have attracted the researchers for low-cost synthetic production, large-scale production, control of diameter and walls, and their chiralities. Single-walled carbon nanotubes (SWCNTs) have especially created an active area of current research, because they show unique chirality-dependent electronic structures, mechanical strength, and high electrical and thermal conductivity (Kang *et al.*, 2008)

Based on our existing knowledge and literature review, catalyst is the most important key factor to control the single-walled carbon nanotubes (SWCNTs) growth. Hence, the focus of this study is on the nature of catalyst for the growth of SWCNTs. Therefore, the study deals with different molar ratios of iron (Fe) in the catalysts for synthesizing carbon nanotubes.

1.3 Objective of the Study

This study aims at determining the effects of the iron concentration in the Fe-Mo-MgO catalyst on the synthesis of carbon nanotubes via catalytic chemical vapor deposition (CCVD) technique. It is worthwhile to investigate whether single-walled carbon nanotubes (SWCNTs) can be synthesized when Fe-Mo-MgO is used as a catalyst, while argon is utilized as a carrier gas and ethanol as a carbon source by CCVD method. Accordingly, the objectives of the study are as the followings:

1. To study the relationship between different molar ratios of iron (Fe) in the as-prepared Fe-Mo-MgO catalyst and the yield and quality of the synthesized SWCNTs via catalytic chemical vapor deposition (CCVD) method.

2. To examine the effect of different flow rates of carrier gas (Ar) and also temperature on the yield and quality of synthesized SWCNTs with the as-prepared catalysts.

To be more specific, the purpose of this research is to prepare Fe-Mo-MgO catalyst with different molar ratios of iron (Fe) and examine the effects of as-prepared Fe-Mo-MgO catalyst on the synthesis of carbon nanotubes (CNTs) by using ethanol decomposition and argon as a carrier gas in order to obtain single-walled carbon nanotubes (SWCNTs) with high yield and quality.

1.4 Scope of the Study

Within the scope of our investigation lies the preparation of the catalyst with different molar ratios of iron by impregnation method. The catalysts were characterized with x-ray diffraction (XRD) to see the structural changes in catalysts before and after heat treatment in order to see the material composition in the catalysts.

The as-prepared catalysts with different molar ratio of iron were used to synthesize single-walled carbon nanotubes (SWCNTs), and to examine their effects on the yield and quality of synthesized CNTs. The effect of different flow rate of carrier gas (Ar) and temperature on the growth of carbon nanotubes were also tested. To study the relationship between these factors and synthesized CNTs, different characterization methods were used. Scanning electron microscopy (SEM), x-ray diffraction (XRD), thermogravimetric analysis (TGA), and transmission electron microscopy (TEM) are the characterization methods that were used for the synthesized CNTs in this study.