ROLE OF METAL SUPPORTED CATALYSTS AND THEIR CHARACTERIZATION IN THE CATALYTIC DECOMPOSITION OF METHANE FOR THE FORMATION OF UNIFORM CARBON NANOTUBES IN A SINGLE STEP PROCESS

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by

CHAI SIANG PIAO

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LIST OF ABBREVIATIONS

BEI	Back-scattering electron imaging
BET	Brunauer-Emmett-Teller
BJH	Barrett, Joyner and Halenda
BOC	British Oxygen Company
CDM	Catalytic decomposition of methane
CNFs	Carbon nanofibers
CNTs	Carbon nanotubes
Conv.	Conversion
Co-P	Co-precipitation
CO_2RM	Carbon dioxide reforming of methane
COST	Change one separate factor at a time
CVD	Chemical vapor deposition
D	Dimension
DWNTs	Double-walled carbon nanotubes
EAD	Electric-arc-discharge
GC	Gas chromatography
FCs	Filamentous carbons
FID	Flame ionization detector
FT	Fischer-Tropsch (FT)
FWHM	Full width half maximum
HRTEM	High-resolution transmission electron microscopy
GHSV	Gas-hourly-space velocity
GTL	Gas to liquid
IMP	Impregnation
LA	Laser ablation
MOX	Malaysian Oxygen Berhad
MSI	Metal-support interaction
MTG	Methanol to gasoline
MWNTs	Multi-walled carbon nanotubes
OCM	Oxidative coupling of methane
POM	Partial oxidation of methane

RBM	Radial breathing mode
RDS	Rate-determining step
RSM	Response surface methodology
SEI	Secondary electron imaging
SEM	Scanning electron microscopy
SG	Sol-gel
SMSI	Strong metal-support interaction
SRM	Steam reforming of methane
SWNTs	Single-walled carbon nanotubes
Syngas	Synthesis gas
TCD	Thermal conductivity detector
TDM	Thermal decomposition of methane
TEM	Transmission electron microscopy
Temp.	Temperature
TGA	Thermogravimetric analysis
TPR	Temperature programmed reduction
VLS	Vapor-liquid-solid
WMSI	Weak metal-support interaction
XRD	X-ray diffraction
ZSM-5	Zeolite Socony Mobil-five

LIST OF SYMBOLS

CS	Surface carbon
$C_{Co,f}$	Concentration of carbon dissolved in at the front side of cobalt particle
$C_{Co,r}$	Concentration of carbon dissolved in at the rear side of cobalt particle
C_T	Total concentration of active sites
C_V	Concentration of vacant sites
D	Diameter (nm)
E_a	Activation energy (kJ/mol)
k	Rate constant (g_C/g_{metal}.min.atm)
k_{+1}, k_{-1}, k_{+2}, k_{-2}, k_{+3}, k_{-3}, k_{+4}, k_{-4}, k_{+5}, k_{-5}, k_{+6}, k_{-6}	Rate coefficients of the forward and reverse reactions
K_1, K_2, K_3, K_4, K_5, K_6	Equilibrium coefficients
P_{CH_4}	Partial pressure of methane (atm)
P_{H_2}	Partial pressure of hydrogen (atm)
R	Ideal gas law constant (8.314 J/mol.K)
r_0	Initial reaction rate (g_C/g_{metal}.min)
S	Surface active site
T	Reaction temperature (^oC)
X_{CH_4}	Conversion of methane (%)
W	Catalyst weight (g)

Greek symbols

θ	Diffraction angle (rad)
ω	Raman shift (cm^{-1})
β	Full width half maximum (FWHM) (rad)
λ	X-ray wavelength (Å)
τ	Thickness of nanotube wall (nm)
α	Frequency factor in Arrhenius equation
α-Al_2O_3	Alpha alumina
γ-Al_2O_3	Gamma alumina

PERANAN MANGKIN LOGAM TERSOKONG DAN PENCIRIAN MANGKIN DALAM PENGURAIAN METANA BERMANGKIN BAGI PEMBENTUKAN NANOTIUB KARBON SERAGAM DALAM PROSES SATU LANGKAH

ABSTRAK

Nanotiub karbon (CNTs) menarik perhatian para saintis di seluruh dunia kerana dimensi, kekuatan dan sifat-sifat fizikal yang istimewa membuatkannya satu bahan yang unik dengan banyak aplikasi. Pelbagai kaedah sintesis CNTs telah dibangunkan dan di antaranya kaedah tumbesaran bermangkin muncul sebagai satu kaedah terjamin dalam penghasilan CNTs yang tinggi. Walaubagaimanapun, kaedah tumbersaran bermangkin masih menghadapi banyak cabaran dan usaha-usaha mengatasi cabaran tersebut merupakan tumpuan utama projek ini. Dalam penyelidikan ini, penguraian metana bermangkin telah digunakan untuk menghasilkan CNTs. Mangkin-mangkin monologam dan dwilogam turut disediakan daripada logam peralihan seperti Cr, Mn, Fe, Co, Ni, Cu, Mo dan Ag, dan disokong pada Al_2O_3, CeO_2, CaO, H-ZSM-5, La_2O_3, MgO, TiO_2 dan SiO_2. Sifat-sifat mangkin yang dibangunkan ini diuji di dalam reaktor lapisan tetap tahan karat pada tekanan atmosfera. Pelbagai ujikaji pencirian termasuklah kaedah penurunan berprogramkan suhu (TPR), mikroskop elektron imbasan (SEM), mikroskop elektron transmisi (TEM), analisis pemetaan graviti haba (TGA), analisis permukaan dan kespektroskopan Raman telah dijalankan pada mangkin baru dan mangkin terpakai untuk mengetahui ciri-ciri CNTs yang dihasilkan dan kriteria yang diperlukan untuk membentuk CNTs yang berkualiti tinggi. Beberapa penemuan penting telah dikenalpasti di dalam penyelidikan ini. Di antaranya morfologi filamen karbon boleh disediakan secara khusus dengan menetapkan komponen mangkin dan menjalankan

tindakbalas dalam keadaan yang bersesuaian. Penemuan ini juga menunjukkan bahawa mangkin 8NiO-2CuO/SiO_2 dengan kandungan 80 wt% NiO-CuO menghasilkan nanofiber karbon (CNFs) dan hidrogen dalam kuantiti yang tinggi, iaitu dengan hasil karbon sebanyak 143 $g_C/g_{(NiO+CuO)}$ dan hasil hidrogen 2344 mol H_2/mol (NiO+CuO). Nanotiub karbon berdinding tunggal (SWNTs) dengan kememilihan yang tinggi juga dihasilkan oleh mangkin NiO/Al_2O_3 pada suhu tindakbalas serendah 700^oC dan CNTs berstruktur Y ditemui pada mangkin 7NiO-2CuO-1MoO_x/SiO_2. Penyelidikan ini juga menunjukkan bahawa suhu pengkalsinan bagi mangkin adalah faktor penting dalam penentuan hasil dan morfologi CNTs terbentuk. Mangkin 8CoO_x-2MoO_x/Al_2O_3 yang dikalsinkan pada 700^oC telah dikenalpasti berupaya menghasilkan nanotiub karbon berdinding lapisan (MWNTs) dengan kawalan baik dari segi taburan diameternya, iaitu 9.0 ± 1.4 nm. Kajian rawatan awal mangkin juga menunjukkan bahawa mangkin selepas diturunkan oleh hidrogen adalah lebih aktif dan suhu penurunan yang optimum adalah pada 550^oC. Suhu tindakbalas dan tekanan separa metana juga dikenalpasti mempengaruhi hasil karbon bagi mangkin 8Co-2Mo/Al_2O_3 dengan ketara, sebaliknya faktor kuantiti mangkin yang digunakan adalah tidak ketara. Program rekabentuk eksperimen (DoE) menunjukkan proses yang optimum bagi penguraian metana bermangkin adalah pada suhu 761^oC, tekanan separa metana 0.75 atm dan kuantiti mangkin 0.4 g dengan hasil karbon sebanyak 607%. Kajian kinetik juga menunjukkan bahawa penguraian metana bermangkin oleh mangkin 8Co-2Mo/Al_2O_3 adalah tertib pertama dengan tenaga pengaktifan 87 kJ/mol. Analisi seterusnya mendedahkan bahawa penjerapan terurai merupakan langkah penentuan kadar bagi penguraian metana oleh mangkin 8Co-2Mo/Al_2O_3.

ROLE OF METAL SUPPORTED CATALYSTS AND THEIR CHARACTERIZATION IN THE CATALYTIC DECOMPOSITION OF METHANE FOR THE FORMATION OF UNIFORM CARBON NANOTUBES IN A SINGLE STEP PROCESS

ABSTRACT

Carbon nanotubes (CNTs) have attracted the fancy of many scientists worldwide due to their small dimensions, strength and remarkable properties that make them a very unique material of a whole range of promising applications. Many methods have been proposed to synthesize CNTs of which the catalytic growth method appears to be the most promising method for high yield synthesis of CNTs. However, there still lie many challenges in the catalytic growth method which is the main concern of this project. In this study, catalytic decomposition of methane was employed for producing CNTs. A number of monometallic and bimetallic catalysts were developed from transition metals, such as Cr, Mn, Fe, Co, Ni, Cu, Mo and Ag, on different supports of Al_2O_3, CeO_2, CaO, H-ZSM-5, La_2O_3, MgO, TiO_2 and SiO_2. The varied catalytic properties of these materials were examined in a vertical fixed-bed tubular reactor for methane decomposition. Various characterization tests, including surface characteristics, temperature-programmed reduction (TPR), X-ray diffraction (XRD), scanning electron microscopy (SEM), transmission electron microscopy (TEM), thermogravimetry analysis (TGA) and Raman spectroscopy, were carried out on the fresh and used catalysts in order to comprehend the properties of the produced CNTs and the criteria required to grow higher quality CNTs in high yield. Many illustrious findings were obtained in this study, one of which showed that various types of filamentous carbons could be tailor-made through proper designing of the catalyst components at the suitable reaction

conditions. It was also found in this study that 8NiO-2CuO/SiO_2 catalyst with 80 wt% of NiO-CuO loading produced carbon nanofibers (CNFs) and hydrogen of the highest yields, representing the yields of 143 $g_C/g_{(NiO+CuO)}$ and 2344 mol H_2/mol (NiO+CuO), respectively. Single-walled CNTs (SWNTs) were produced in high selectivity over NiO/Al_2O_3 catalyst at a temperature as low as 700^oC and Y-junction CNTs were found grown on 7NiO-2CuO-1MoO_x/SiO_2 catalyst. The study also demonstrated that the effect of catalyst calcination temperature on the yield and the morphology of the produced CNTs was momentous. In this regard, 8CoO_x-2MoO_x/Al_2O_3 catalyst, calcined at 700^oC, grew multi-walled CNTs (MWNTs) with the best control of diameter distribution, i.e. 9.0 ± 1.4 nm. The catalyst pretreatment study disclosed that the catalyst was more active for the growth of CNTs after being reduced by hydrogen and the optimum reduction temperature was found to be 550^oC. An examination of the process parameters for methane decomposition over reduced 8Co-2Mo/Al_2O_3 catalyst showed that reaction temperature and methane partial pressure affected significantly the yield of carbon formation, whereas the effect of catalyst weight was insignificant. As predicted by Design of Experiment (DoE), the optimum process conditions for methane decomposition were found to be a temperature of 761^oC, methane partial pressure of 0.75 atm and catalyst weight of 0.4 g, which give the highest carbon yield of 607%. Kinetic studies showed that methane decomposition reaction is first order with activation energy of 87 kJ/mol over 8Co-2Mo/Al_2O_3 catalyst. An analysis of possible mechanisms showed that dissociative adsorption of methane is the rate-determining step for methane decomposition over 8Co-2Mo/Al_2O_3 catalyst.

CHAPTER 1
INTRODUCTION

1.1 Catalysis

Catalysis involves the modification of the rate of a chemical reaction, usually a speeding up of the reaction rate, by addition of a substance, known as “catalyst”. According to the definition of Berzelius, a catalyst is a substance that accelerates the establishment of a chemical equilibrium without itself being consumed (Berzelius, 1836; Fogler, 1999). In general, catalysts can be categorized into three major groups, representing homogeneous catalysts, heterogeneous catalysts and biocatalysts (enzyme).

Heterogeneous catalysts, in particular supported catalysts, are important both from an industrial and a scientific point of view. These catalysts are widely used in many chemical processes such as catalytic reforming, hydrotreatment, polymerization reaction, hydrocracking, decomposition reaction and hydrogenation. Although most production processes using supported catalysts are carried out in a large-scale reactor, the reactions that actually take place in the catalysts occur on the surface of highly dispersed metal particles. The typical dimensions of these particles range from 1 nm to 100 nm (Figure 1.1), which by today’s standard are nanomaterials. Knowing that most of the catalysts have nanosized metal components, catalysis research and catalyst-based technologies have perhaps been at the heart of nanotechnology for many years. Nowadays, nanostructured catalysts receive a great demand in the petroleum and chemical processing industries. It is estimated that nanostructured catalysts will have an annual impact of USD 100 billion by 2015 (Roco and Bainbridge, 2001).

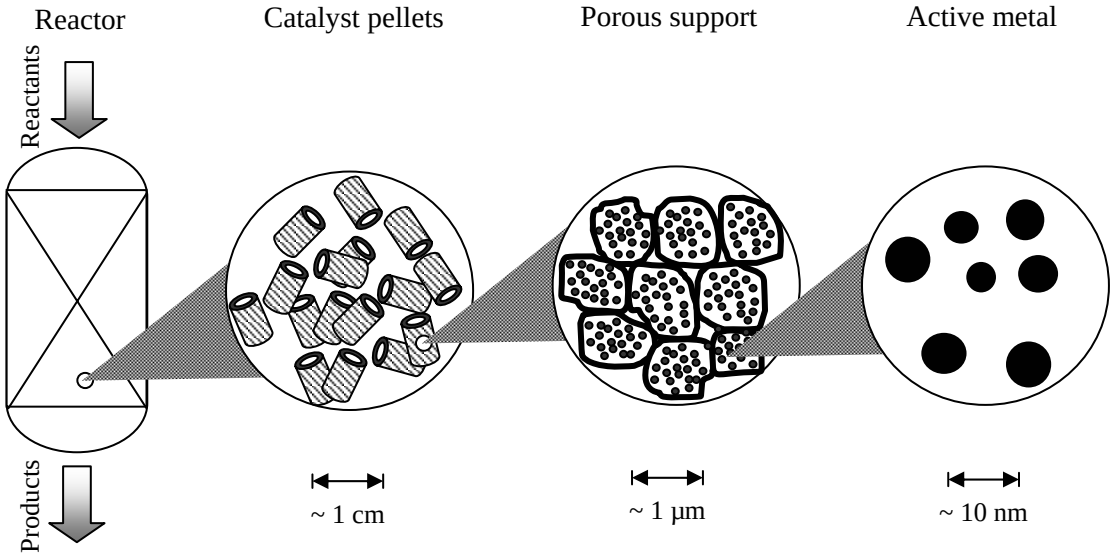

Figure 1.1. Schematic diagram showing the typical catalyst structure used in a chemical reactor (Inano, 2007).

1.2 Nanotechnology

Nanotechnology has emerged as one of the most exciting fields recently resulted from an integration of basic sciences like chemistry, physics, biology and mathematics with engineering sciences. The prefix *"nano"* in the world nanotechnology means a billionth (1×10^{-9}). According to Roco (2001), nanotechnology covenants with materials and systems having the following key properties:

- they have at least one dimension of about 1 – 100 nm
- they are designed through processes that exhibit fundamental control over the physical and chemical attributes of molecular-scale structure
- they can be combined to form larger structures

Nanotechnology is an important tool to control the processes in which materials are made and the manner devices function at the atomic and molecular

level. This level of control enables unlimited creation of new materials and new devices. In addition, the properties of traditional materials change at the nanoscale level, where the behavior of the surface starts to dominate over the behavior of the bulk phase. Thus, nanomaterials possess excellent and unique properties which cannot be found in any traditional materials in the bulk phase. Figure 1.2 presents a diagram showing the region that belongs to nanotechnology.

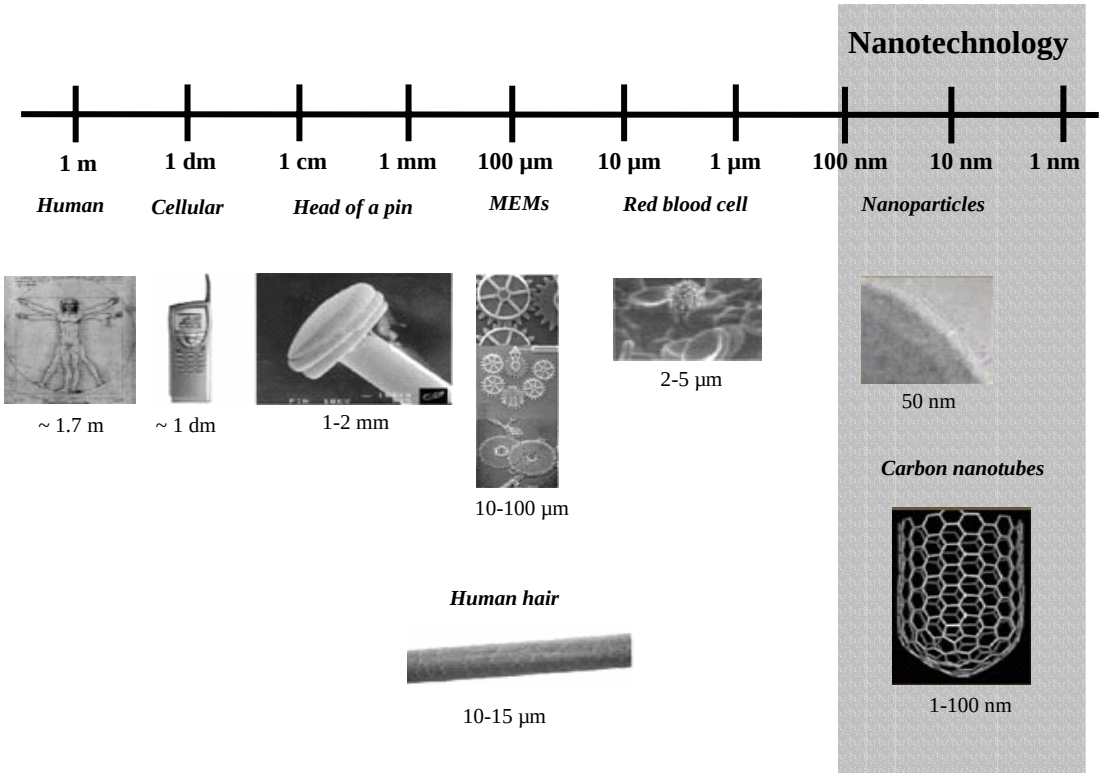

Figure 1.2. The diagram shows the nanotechnology region (Nanodimension, 2005).

The 21st century will undoubtedly be a period of substantial progress for nanotechnology. It is strongly believed that nanotechnology will complement and change life science, pharma, diagnostic, medicine technology, food, environmental technology, water, energy, electronics, mechanical engineering and so on to a new dimension in a near future. As reported by Roco and Bainbridge (2001), the market value of nano products and services will reach USD 1 trillion by 2015.

1.3 Allotropes of Carbon

Advances in nanotechnology have led to the discovery of a growing number of new materials. Carbon nanotubes (CNTs), the newly-discovered carbon allotrope, have emerged as one of the most important components of the nanotechnology.

It is widely known that carbon is an important element of unique properties with each carbon atom has six electrons, which occupy $1s^2$, $2s^2$ and $2p^2$ atomic orbitals. These atomic orbitals give three possible hybridizations in carbon bonding, representing sp, sp^2 and sp^3 configurations. Bonding of carbon atoms with neighbor atoms via sp configuration gives rise to chain structures, sp^2 bonding to planar structures and sp^3 bonding to tetrahedral structures. These hybridizations in carbon bonding are responsible for the formation of different carbon allotropes, including diamond (3-D form), graphite (2-D form), fullerene (0-D form) and recently CNTs (1-D form). The structures of these carbon allotropes are shown in Figure 1.3.

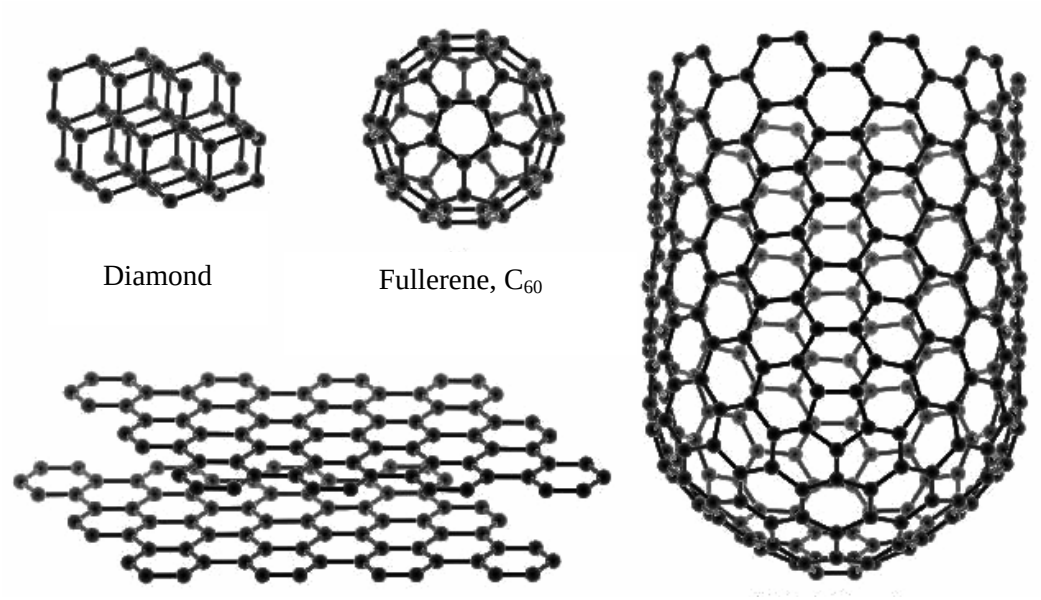

Figure 1.3. The allotropes of carbon (Lau and Hui, 2002).

Before 1985, it is commonly believed that carbon only exists in the forms of diamond and graphite. In 1985, the discovery of fullerene by Kroto and coworkers (Kroto *et al*., 1985) has changed the perception of scientists that very small dimension of carbon or perhaps a new carbon allotrope could be synthesized in a laboratory. This discovery has since stimulated researchers to study carbon of very small dimension more seriously. The real breakthrough on CNTs research came with Iijima's report of experimental observation of CNTs using transmission electron microscope (TEM) in 1991 (Iijima, 1991).

1.4 Carbon Nanotubes

CNTs have been called the most innovative materials of the 21st century due to their extraordinary properties and their enormous potential applications. Perhaps, CNTs are the most interesting carbon allotrope with large application potential. The structure of a nanotube is similar to that of graphite, which is like a cylinder of rolled graphene sheet with its body contains hexagonal rings and end cap with certain number of pentagonal rings. The end cap and body each has a structure similar to that of fullerene and graphite, respectively (Figure 1.4). Therefore, CNTs are also referred to at times as a hybrid structure of fullerene and graphite.

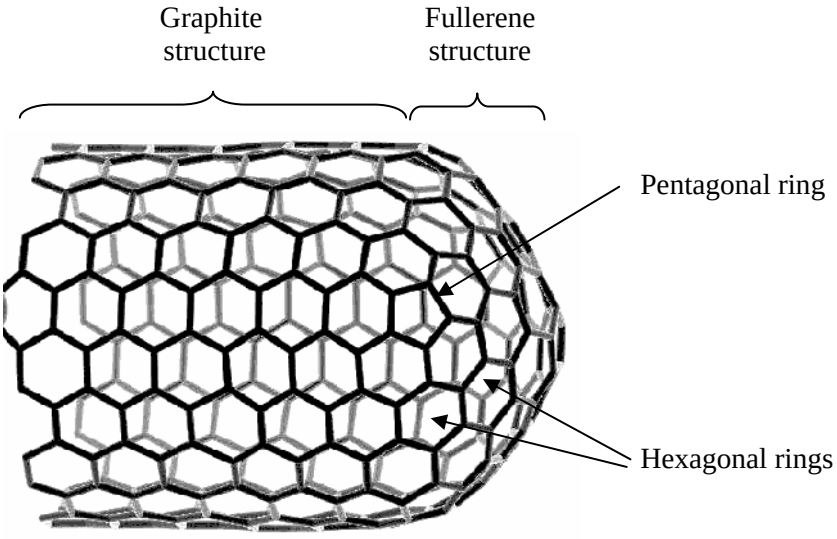

Figure 1.4. The structure of CNT with enclosed tip (Nanodimension, 2005).

CNTs can be categorized into two major groups based on the number of graphene sheets that forms their walls. A nanotube consisting of a single graphene sheet is referred to as single-walled CNT (SWNT). The nanotube that consists of two or more graphene sheets is named multi-walled CNT (MWNT). MWNT has an interlayer spacing of 0.34 – 0.36 nm, that is close to the typical atomic spacing of graphite, which is 0.335 nm. The C-C bonds that building up of CNTs have a length of 0.14 nm, which are shorter than the bonds in diamond. This indicates that CNTs are stronger than diamond (Bonard *et al*., 2001). The diagram shown in Figure 1.5 represents: (a) a model of SWNTs bundle and (b) a model of MWNT with five graphene sheets. SWNTs are less stable as to stand alone due to their ultra-small size. Thus, most of the observed SWNTs appear in the bundle form, where the SWNTs are held by the weak *van der Waals* force.

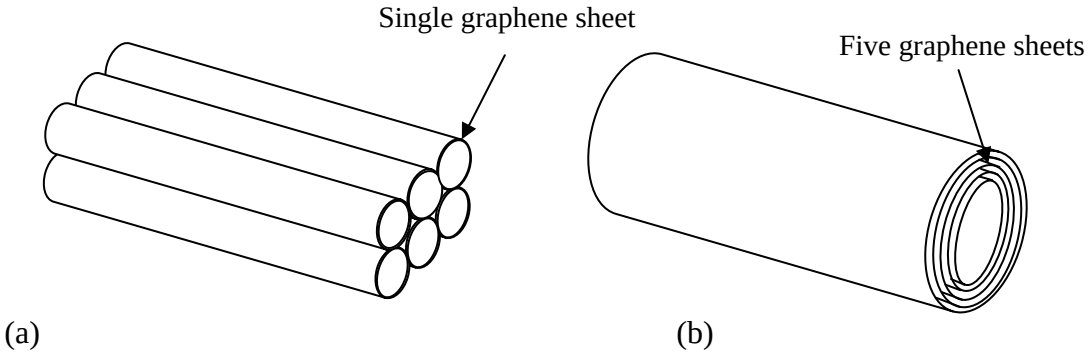

Figure 1.5. Schematic diagrams for (a) SWNTs in bundle form and (b) MWNT with five graphene sheets.

It is important to differentiate the following terms i.e. “filamentous carbons”, “carbon nanotubes (CNTs)” and “carbon nanofibers (CNFs)”. “Filamentous carbons” is a general term used to represent all carbon nanostructures with needle-like morphology. Filamentous carbons can be classified into two main categories on the basis of their structures, i.e. CNTs and CNFs. The nomenclature of CNTs and CNFs is ambiguous as no standardization on the terms used has been implemented so far. According to Vander Wal *et al.* (2001), CNTs are referred to as a highly graphitic structure with the orientation of the basal carbon planes parallel to the tube axis whereas CNFs are the structures with the other orientations of the graphitic lamella that will leave a smaller or no central channel (Figure 1.6). According to Pan *et al.* (2004) and Pérez-Cabero *et al.* (2003), the term “CNTs” is used to refer to the filamentous carbons with a significant center channel or hollow core. Filamentous carbons without or with insignificant central channel are denoted as “CNFs”, regardless of their graphitic structure (Figure 1.7). The terms used in this thesis for these carbon structures are defined according to those given by Pan *et al.* and Pérez-Cabero *et al.* as they are easily comprehended in explaining the types of filamentous carbons synthesized in the present study.

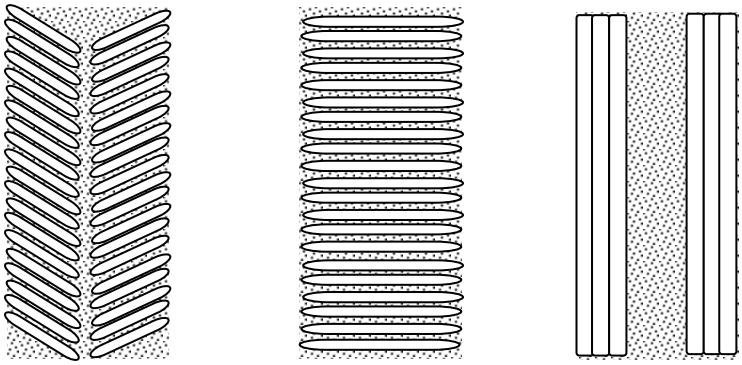

Figure 1.6. Schematic diagram presentation of the cross sections of (a,b) CNFs and (c) CNTs, with regard to their graphitic structures.

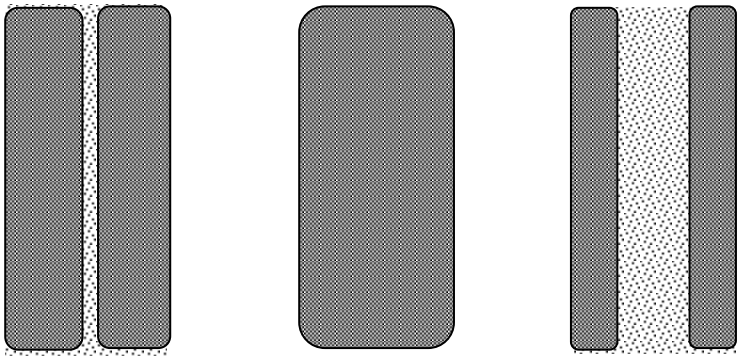

Figure 1.7. Schematic diagram presentation of the cross sections of (a,b) CNFs and (c) CNTs, with regardless to their graphitic structures.

1.5 Hydrogen

Hydrogen is an ultimate clean energy carrier. When it is combusted, heat and water are the only products. Therefore, the use of hydrogen as fuel can greatly reduce green house gas emissions. Moreover, development of affordable hydrogen fuel will help reducing our nation's dependence on oil, leading to an increased national energy security. Thus, hydrogen offers a potentially non-polluting, inexhaustible, efficient and cost attractive fuel for today's rising energy demands.

Future shortage of petroleum supply and surging prices of petroleum-based fuels, coupled with the increasing awareness of green house gas emissions increase the shift towards the alternative fuels sector. From Figure 1.8, it can be observed that over the decades hydrogen will increase its energy share dramatically, accounting for approximately 49% of the global final energy consumption by the end of the 21st century.

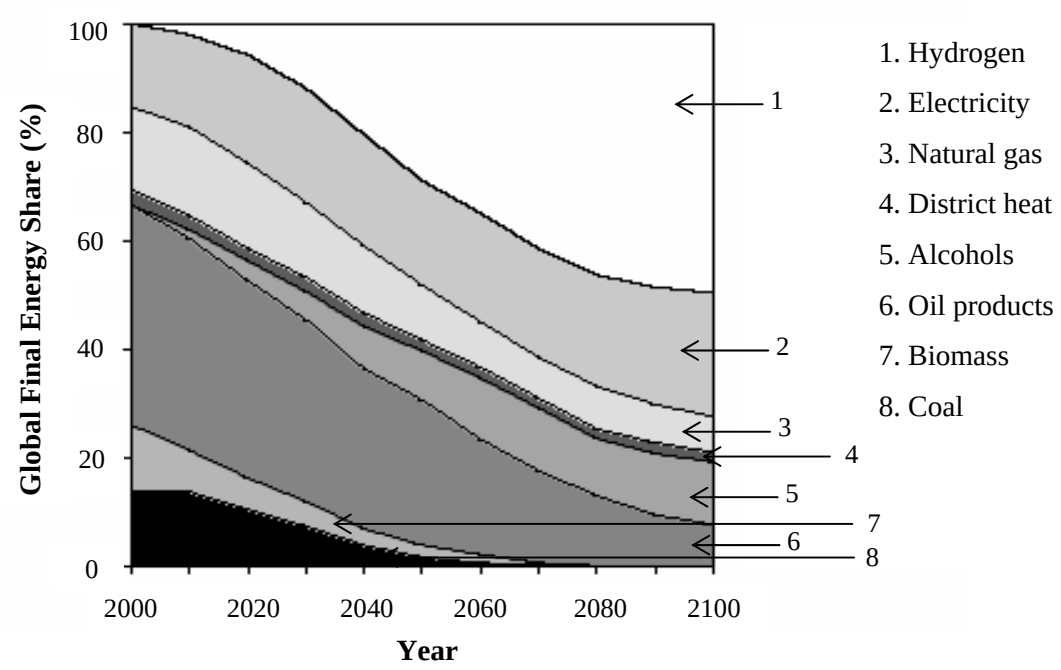

Figure 1.8. Evolution of global market shares of different energy carriers for the period 2000 – 2100. The alcohol category includes methanol and ethanol (Barreto *et al.*, 2003).

1.6 Natural Gas

Natural gas is a gaseous fossil fuel consisting primarily of methane and significant quantities of ethane, butane, propane, carbon dioxide, nitrogen, helium and hydrogen sulfide. Natural gas occurs in great abundance in some parts of the world, making a potential hydrocarbon feedstock and energy source that should not be underestimated. According to the recent Energy Information Administration (EIA)

report (EIA, 2007), Malaysia's natural gas reserve ranks 16th in the world with a total reserve of 75 trillion ft^3. The total world's natural gas reserve records 6,183 trillion ft^3 in 2007. There will be a tremendous market for natural gas if more valued products can be obtained from it. Coupled with the current worldwide crude oil shortage, the role played by natural gas as a fuel and raw material is of increasing importance.

Table 1.1 shows the typical composition of natural gas and the composition of Malaysia natural gas. The composition of natural gas falls in a range for each of its component as the composition of natural gas from different reservoirs worldwide varies. Effective utilization of natural gas remains a challenge from the economic point of view. Natural gas itself can serve as fuel. However, for diversity, various routes have been considered for its conversion to value-added products, such as higher hydrocarbons, hydrogen and recently CNTs. Since methane is the major component of natural gas (70 – 90%), conversion of natural gas is always expressed scientifically as methane conversion.

Table 1.1. Composition of natural gas (NaturalGas, 2007; GasMalaysia, 2008).

Components		**Typical**	**Malaysia**
Methane	CH_4	70-90%	92.73%
Ethane	C_2H_6		4.07%
Propane	C_3H_8	0-20%	0.77%
Butane	C_4H_{10}		0.14%
Carbon Dioxide	CO_2	0-8%	1.83%
Oxygen	O_2	0-0.2%	N.A.
Nitrogen	N_2	0-5%	0.45%
Hydrogen sulphide	H_2S	0-5%	N.A.
Rare gases	Ar, He, Ne, Xe	trace	N.A.
Other hydrocarbon		N.A.	0.01

1.7 Methane Activation

Figure 1.9 shows various paths of methane activation to other value-added products. Keller and Bhasin (1982) were the first to report the direct conversion of methane to ethylene. Following their work, oxidative coupling of methane (OCM) became one of the most pursued topics of research in methane activation. This is because hydrocarbon production via synthesis gas (syngas) is expensive and rather circuitous, and OCM prepares a simpler and cheaper route for the production of higher hydrocarbon from natural gas, using intermediate product, ethylene, as feedstock. Another process, known as steam reforming of methane (SRM), can be used for syngas production. Owing to SRM produces higher H_2 to CO ratio, being 3:1 (Figure 1.9), this process is widely applied in the gas industry for producing hydrogen on a large scale. Another alternative way to make syngas from methane is through partial oxidation of methane (POM). This reaction produces H_2 and CO in the ratio of 2:1. Carbon dioxide reforming of methane (CO_2RM) is another way to produce syngas. This process produces H_2 and CO in the ratio of 1:1. It is noteworthy that the ratios of 2:1 and 1:1 are desirable H_2 to CO ratio for the downstream process. The syngas produced from the mentioned routes can be further converted into methanol, an important feedstock for the methanol to gasoline (MTG) process meant for producing gasoline (Chang, 1998). Alternatively, syngas can be directly processed into hydrocarbons via the Fischer-Tropsch (FT) process (Vannice, 1976).

Direct decomposition of methane has been proposed as an economical process to produce hydrogen. Unlike SRM, POM and CO_2RM, methane decomposition process produces only H_2 and solid carbon, thereby eliminating the necessity for separation of CO_x from H_2 product. The carbon product produced from methane decomposition has an additional advantage as various valuable types of

carbon, including carbon black, CNFs and CNTs, can be obtained as by-products from this process.

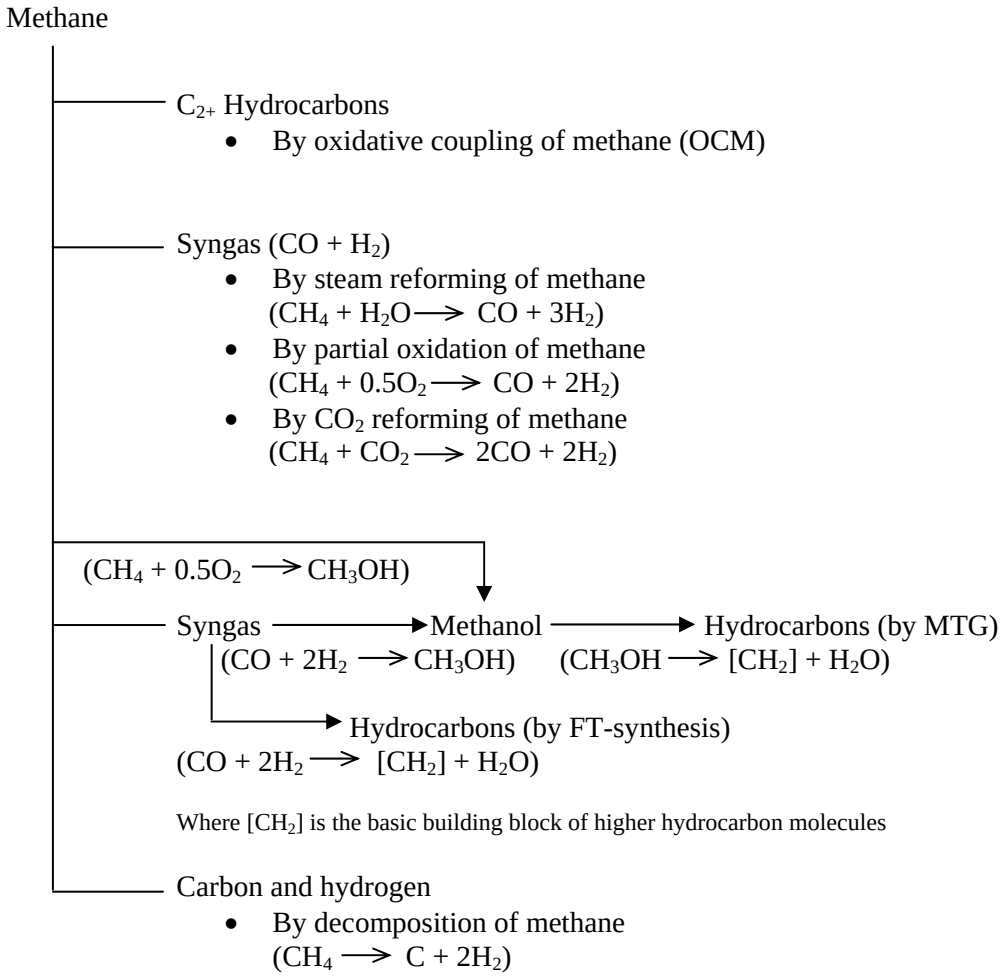

Figure 1.9. Various paths of methane activation to more value-added products (Choudhary *et al*., 2003).

1.8 Methane Decomposition

Decomposition of methane can be categorized into two major types, representing thermal decomposition and catalytic decomposition. Thermal decomposition of methane (TDM) (equation 1.1) occurs at elevated temperatures, above 1200°C, in a thermal reactor without the presence of a catalyst (Shpilrain *et al*., 1999; Muradov, 2001). This process produces hydrogen as the major product and clean carbon black as by-product. Carbon black is an important feedstock for rubber industry (Zuev and Michailov, 1970).

$$\underset{\text{Methane}}{CH_4} \xrightarrow{>1200^{o}C} \underset{\text{Carbon black}}{C} + \underset{\text{Hydrogen}}{2H_2} \qquad (1.1)$$

The reasons for not employing catalyst in the decomposition of methane is mainly due to the carbon formation will deactivate the catalyst and thus, decreasing the hydrogen yield. However, the TDM process is not economical for commercial hydrogen production as it requires very high operating temperatures. To overcome this drawback, specially designed catalyst is used, and it allows reducing the reaction temperature of the decomposition process. Methane decomposition with the presence of catalyst is widely known as catalytic decomposition of methane (CDM) (equation 1.2).

$$\underset{\text{Methane}}{CH_4} \xrightarrow[CATALYST]{500\text{-}900^{o}C} \underset{\text{Filamentous carbon}}{C} + \underset{\text{Hydrogen}}{2H_2} \qquad (1.2)$$

The types of catalysts used and the reaction conditions employed are the two important factors to be considered for a CDM process. Transition metals, especially

metals from group VIII (Fe, Co and Ni) in the periodic table, are normally used as catalytic materials. (Bethune *et al*., 1993; Fan *et al*., 1999; Takenaka *et al*., 2003b; Zein *et al*., 2006). The typical reaction temperatures for CDM are in a range of 500 - 900^{o}C, a temperature which is much lower than that required by the TDM process. As a consequence of this, more attentions are focused on the CDM process by industrialist, researchers, scientists, etc. Also, not only hydrogen gas is produced, filamentous carbons can be produced as one of the valued products from the CDM process (Figure 1.10). It should be noted that filamentous carbons are more valuable than carbon black due to their excellent properties and their many promising applications. By proper designing of a catalyst and performing the CDM process at suitable reaction conditions, one can tailor-make the specific types of filamentous carbons for the needs of the market and this is one of the major researches that has attracted the great interest of many researchers around the world.

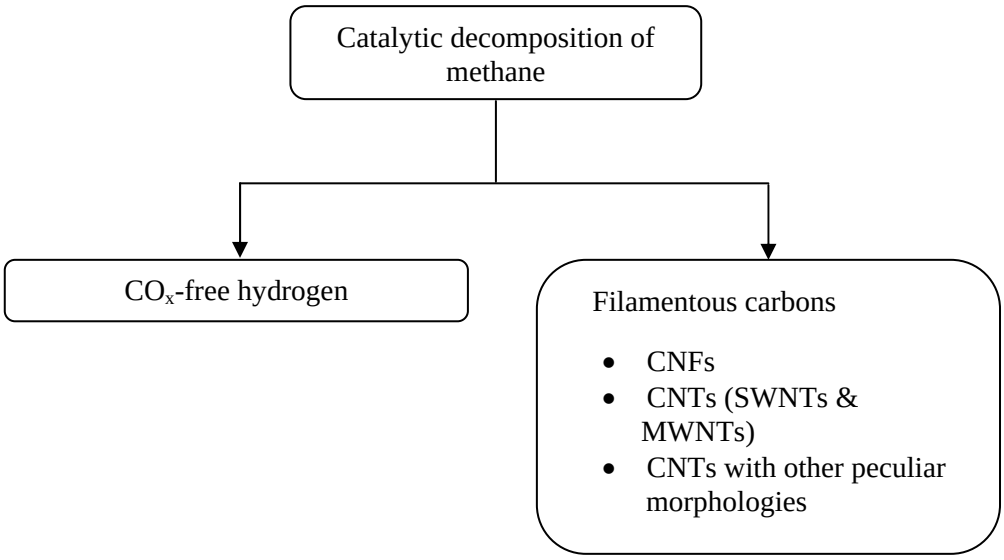

Figure 1.10. Flowchart showing the possible products obtained from CDM process.

1.9 Problem Statement

The discovery of CNTs using various technologies in the past 17 years has witnessed significant progress in their synthesis and applications. Even though CNTs have been successfully synthesized via various approaches, there are still technical challenges that must be investigated and overcome. To date, no one has successfully achieved controlled synthesis and cost effectively growing CNTs on a large scale. Controlled synthesis means one can tailor-make CNTs with the desirable structures and morphologies, such as MWNTs, SWNTs, Y-junction, specific diameter, etc., through designing the catalyst and optimizing the process conditions. Production of cost effectively growing CNTs can only be achieved when one can grow CNTs in high selectivity to the desired structures and morphologies at high yield and with minimum cost. Since CNTs are very new materials, the problems arising especially in their synthesis part need further investigation and research.

As most commonly known, electric arc-discharge (EAD), laser ablation (LA) and chemical vapor deposition (CVD) are prominent methods for CNTs synthesis. The said methods have both advantages and disadvantages. As an example, EAD and LA methods, which require very high temperature ($\geq$ 3000 ^{o}C), are not economical for scaling up the production of CNTs although both are efficient in producing SWNTs and MWNTs with fewer defects (Dai, 2001). CVD has been appreciated as the most promising method for producing CNTs on a large scale. Unfortunately, the CNTs produced by the said method are usually MWNTs and often riddled with defects.

CNTs of high quality and uniform diameter are essential to put the potential applications of CNTs into practice. This is attributable to the properties of CNTs: their metallic, semiconducting and mechanical properties depend strongly on their

diameter (Saito *et al.*, 1992; Odom *et al.*, 1998; Reich *et al.*, 2004). To date, many groups of researchers have successfully produced CNTs of good quality and nearly uniform diameters (Nikolaev *et al*., 1999; Cheung *et al*., 2002; Huh *et al*., 2005; Kumar and Ando, 2005; Ren *et al*., 2006). However, most of them involved with complicated catalyst preparation procedures and sophisticated equipment that resulted in rising catalyst and production costs. In addition, the CVD method favors very high reaction temperatures (900 – 1200^{o}C) for producing SWNTs (Hu *et al*., 2003; Liu *et al*., 2003; Ando *et al*., 2004). This is a major shortcoming as higher reaction temperature increases the cost of production as well as enhances the deposition of undesirable carbonaceous materials resulted from thermal-pyrolysis of methane. Furthermore, synthesizing SWNTs at a lower reaction temperature such as at 700^{o}C is very difficult and truly a challenge. Therefore, it is necessary to develop a method that can produce various types of CNTs with the capability in controlling their growth to the desired structures, morphologies and uniformity at a lower temperature.

It cannot be denied that process and kinetic studies are also essential for successful design and application of CVD in producing CNTs. Unfortunately, the information pertaining to these studies is very limited in the literature. In addition, the growth mechanism of CNTs is still controversial. Therefore, it is imperative to conduct the process and the kinetic studies for investigating various process parameters that may influence and affect the yield and the growth mechanism of CNTs. The vital parts of the present work are to search and study the criteria for growing CNTs and achieving the controlled production by means of a simpler and cheaper approach.

1.10 Objectives

The present study has the following objectives:

1) To study the effects of catalyst components, including active metal, promoter and support, the effect of active metal to promoter ratio as well as the effect of metal amount loading, on methane decomposition into CNTs and CO_x-free hydrogen.
2) To develop a relationship for the catalytic activity, the morphology of the produced CNTs and the CNTs growth mechanism with the nature of the catalyst used by performing various focal characterizations on both produced CNTs and developed catalysts.
3) To examine the effects of catalyst preparations, including the effect of catalyst calcination temperature, the effect of catalyst preparation methods, the effect of metal amount loading and the effect of catalyst reduction temperature on carbon yield and morphology of produced CNTs.
4) To evaluate the catalytic performance of the best catalyst in various process parameters, including reaction temperature, partial pressure of methane and catalyst weight. This is followed by analyzing, modeling and optimizing this process with respect to the simultaneous effects of these three process parameters on carbon yield and morphology of produced CNTs.
5) To perform kinetic study, including the determination of reaction rate, reaction order, rate constant and activation energy as well as rate-determining step (RDS) of methane decomposition over the best catalyst developed in this work.

1.11 Scope of the Study

The present study mainly focuses on catalyst development, process analysis as well as kinetic study for CNTs and CO_x-free hydrogen production via CDM process. Catalytic activity test of the developed catalysts is carried out at atmospheric pressure in a vertical fixed-bed micro-reactor. The product gases are analyzed using an online gas chromatography (GC). The freshly prepared catalysts and used catalysts are characterized using surface area analyzer, scanning electron microscope (SEM), transmission electron microscope (TEM), thermal gravimetric analyzer (TGA), temperature-programmed reduction (TPR) apparatus, X-ray diffractometer (XRD) and Raman spectroscopy.

The aim of the catalyst development is to identify the most suitable supported catalysts used in the CDM that exhibit higher activity, selectivity and stability. In this regard, various active metals, promoters and catalyst supports are tested for CDM into CNTs and hydrogen. In this study, the selection of the active metals and promoters is limited to those only from Groups VIB, VIIB, VIII and IB in Row 4; and from Groups VIB and IB in Row 5 of the periodic table, respectively. These metals are chosen because they belong to the same group of metals, which are either active or effective as promoter for a catalyst in the CDM process. Noble metals that are in the same groups as those aforementioned metals are not considered in this study. This is because the non-noble metals are preferred commercially over noble metals, owing to the inherent availability and low costs of the former. The selection of catalyst supports covers Al_2O_3, MgO, CeO_2, TiO_2, La_2O_3, SiO_2 (Cab-osil) and zeolites. These supports are chosen because they are widely reported in the literature as promising catalyst supports used in many chemical reactions, especially in the

CDM reaction. It is essential to choose the most suitable support which compatible with the metal used and the reaction condition employed in this study.

Besides monometallic catalysts, bimetallic and trimetallic catalysts are also developed and tested in the present study. It is expected that addition of second and third metals component, such as CuO, CoO_x, FeO_x, MnO_x, MoO_x, NiO and etc., will further improve the overall performance of the catalysts. The suitability of the final developed catalyst in the CDM will be demonstrated. The effect of these catalyst components, namely active metals, promoters and catalyst supports on CNTs formation are also examined. In this regard, the yield and the morphology of the produced CNTs are characterized using surface area analyzer, Raman spectroscopy, SEM, TGA, TEM and XRD. The relationship between the catalytic activity and the morphologies of the produced CNTs with the nature of the catalyst material is developed. The possible growth mechanism for those structures with respect to the catalyst used is proposed.

In the process analysis, the effects of reaction temperature, partial pressure of methane and catalyst weight on methane decomposition are investigated using COST (change one separate factor at a time) approach. These factors are selected because they are reported to have influence either on the carbon yield or on the morphology of the produced CNTs. Data analysis is further studied using factorial design of response surface methodology (RSM) approach as to analyze the influences of each process variable and their interaction effects on carbon yield. This is followed by the determination of the optimum reaction condition from the set of experimental data collected. Lastly, kinetic study is carried out to obtain the reaction rate, reaction order, rate constant, activation energy and rate-determining step (RDS) of methane decomposition over the best catalyst developed in this work.

1.12 Organization of the Thesis

This thesis consists of six chapters. Chapter 1 (Introduction) provides a brief description of catalysis, nanotechnology, allotropes of carbon, carbon nanotubes, hydrogen, natural gas as well as catalytic decomposition of methane process. This chapter also includes the problem statement that provides some basis and rationale to identify the research directions and objectives. The objectives and scopes of the study are then elucidated. This is followed by the organization of the thesis.

Chapter 2 (Literature Review) summarizes the past research works in the fields related to CNTs, including the properties and the potential applications of CNTs as well as their synthesis approaches. Synthesizing CNTs via CDM over supported catalysts is then being highlighted in this chapter. Possible growth mechanism of CNTs on supported catalysts is also reviewed and discussed. This serves as the background information about the specific problems that have to be addressed in this research work.

Chapter 3 (Materials and Methods) presents the details of the materials and chemicals used and the research methodology conducted in the present study. Detailed experimental setup is elaborated and shown in this chapter. This is followed by the discussion on the detailed experimental procedures, including catalyst preparations, CNTs synthesis procedures, process conditions and kinetic study. Finally, the analytical techniques and the conditions set for the equipment used for various characterizations of both CNTs and catalysts are presented.

Chapter 4 (Results and Discussion) presents and discusses all important findings obtained in this study. This chapter is the main part of the thesis and it comprises of six main sections based on the present experimental work. The main topics in this chapter include preliminary study on CDM process, CDM over

supported-nickel and -cobalt catalysts, effect of catalyst preparation, process analysis and kinetic study.

Chapter 5 (Conclusions) summarizes the results reported in the previous chapters and some concluding remarks are also made. The conclusions are obtained from each individual study carried out in the present research.

Chapter 6 (Recommendations) suggests the ways to improve the present studies and recommend the possible future studies in this field. These recommendations and suggestions are given after taking into consideration the significant findings, the conclusions obtained as well as the limitations and difficulties encountered in the present work.

CHAPTER 2

LITERATURE REVIEW

2.1 Carbon Nanotubes

2.1.1 History of filamentous carbons

The history of filamentous carbons goes back to more than a century. The first filamentous carbons were synthesized by Thomas A. Edison in the 19th century to be used in an electric bulb (Dresselhaus and Endo, 2001). However, the study on filamentous carbons after Edison proceeded slowly due to the fact that most of the filamentous carbons had been replaced by more sturdy tungsten filaments. In 1975, Endo had reported the synthesis of carbon nanofilaments through catalyzed cracking of hydrocarbons in his PhD thesis (Endo, 1975; Dresselhaus and Avouris, 2001; Dresselhaus and Endo, 2001). At almost the same time, Obelin and coworkers reported carbon filaments of very small diameter (less than 10 nm) had been produced from decomposition of benzene at high temperatures (Oberlin *et al*., 1976a; Oberlin *et al*., 1976b). However, the studies of such very thin filaments were not systematically reported in those early years due to the limitation of the characterization equipment. The real breakthrough in the studies of carbon nanostructures was in 1985 when fullerenes were discovered by Kroto, Curl and Smalley (Kroto *et al*., 1985). This discovery since then had stimulated the systematical study on the very small diameter carbon structures.

It is widely known that fullerene is a zero-dimensional carbon allotrope, whereas graphite and diamond are generally considered as two- and three-dimensional structures, respectively. For this reason, scientists predicted that carbon allotrope of one-dimensional structure should be stable enough to exist

independently. In 1991, this speculation became a reality when the one-dimensional carbon structure was first discovered by a Japanese microscopist, Sumio Iijima (Iijima, 1991) in the Nippon Electric Company (NEC) Laboratory in Tsukuba, Japan. Under the transmission electron microscope (TEM) observation, this carbon structure appeared in the form of thread with significant hollow center core. Owing to its emplacement on the nano-scale and its thread-like structure, this carbon structure was named “carbon nanotubes (CNTs)”. Nowadays, CNTs are universally accepted as the fourth carbon allotrope. Figure 2.1 shows the structures of carbon allotropes including graphite, diamond, fullerene and CNTs. The first CNTs observed by Iijima were multi-wall carbon nanotubes (MWNTs). In 1993, single-walled carbon nanotubes (SWNTs) were discovered at almost the same time by Iijima and coworkers (Iijima and Ichihashi, 1993) in the NEC laboratory and by Bethune and coworkers (Bethune *et al*., 1993) in the IBM Almaden laboratory.

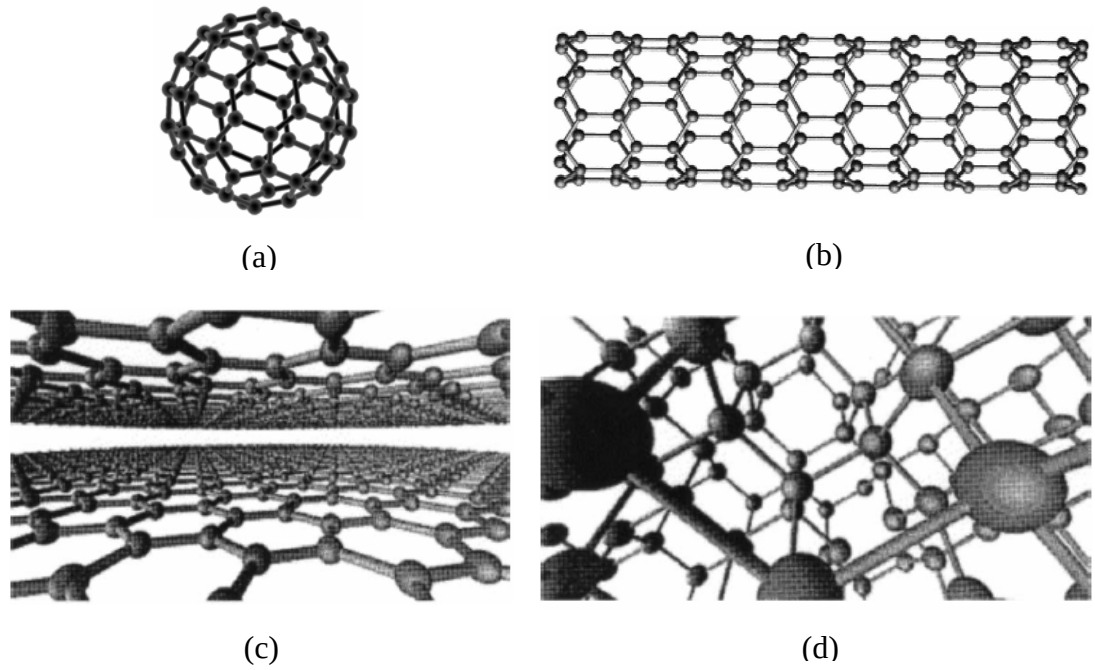

Figure 2.1. The different structures of carbon allotropes: (a) fullerene (0-D), (b) carbon nanotubes (1-D), (c) graphite (2-D) and (d) diamond (3-D) (Cohen, 2001).

2.1.2 Structure of carbon nanotubes

To have a basic understanding of the structure of CNTs is to visualize the folding of a graphene sheet into a tube. The folding can be done in many different angles to form armchair, zigzag or chiral nanotubes. Referring to Figure 2.2, the chiral vector C_h is defined as a line connecting two cystallographically equivalent sites O and C on a two-dimensional graphene structure. The chiral vector can be defined in terms of the lattice translation indices (n, m) (Dresselhaus *et al.*, 1992). The chiral angle (θ) is an angle measured between the chiral vector C_h with respect to the zigzag direction (n, 0). The armchair nanotube is defined as $\theta = 30^o$ and the translation indices is (n, n). A general θ direction, with $0 < \theta < 30^o$, gives the formation of chiral (n, m) nanotubes. The structures of zigzag, armchair and chiral nanotube are shown in Figure 2.3.

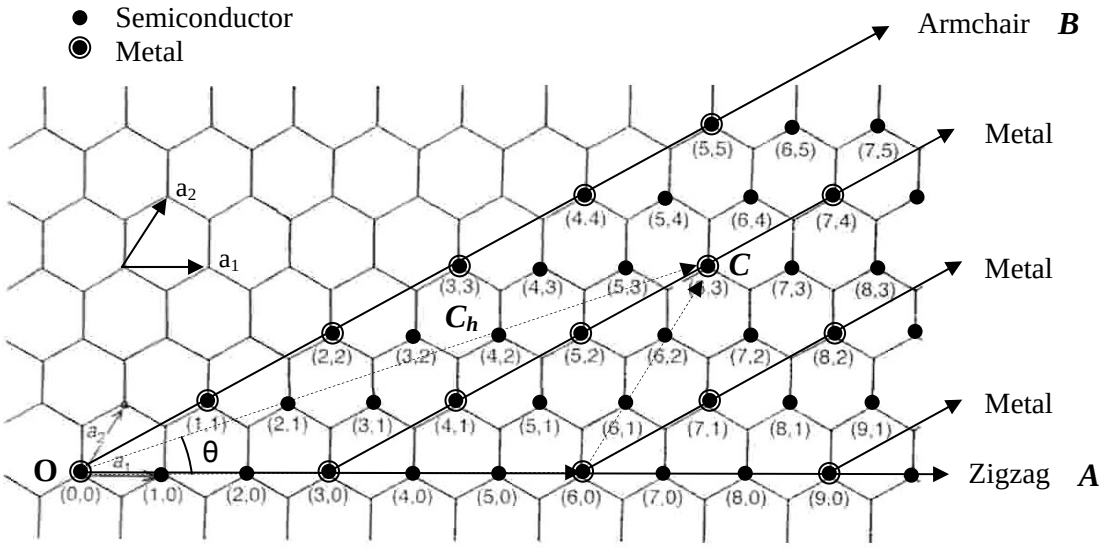

Figure 2.2. The two-dimensional graphene sheet given chiralities (n, m) (Dresselhaus and Avouris, 2001).