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#### **UNIVERSITY OF OKLAHOMA**

#### **GRADUATE COLLEGE**

# SINGLE-WALL CARBON NANOTUBES PRODUCTION BY HETEROGENEOUS CATALYTIC REACTION

A Dissertation

#### SUBMITTED TO THE GRADUATE FACULTY

in partial fulfillment of the requirements for the

degree of

**Doctor of Philosophy** 

By

BOONYARACH KITIYANAN Norman, Oklahoma 2000 UMI Number: 9972510

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A Dissertation

#### **APPROVED FOR**

# THE SCHOOL OF CHEMICAL ENGINEERING AND MATERIALS SCIENCE





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#### ABSTRACT

Carbon nanotubes has shown their outstanding properties and potential applications. However the production of carbon nanotubes is still in the gram-scale that results in the very high cost, particularly single-wall type. The production of single-wall carbon nanotubes (SWNTs) by heterogeneous catalytic reaction is the most promising technique to manufacture this material. Among several catalysts tested in this study, a family of Co-Mo catalysts on silica support has been found to be able to produce SWNTs from carbon monoxide (CO) disproportionation with high selectivity, depending on the Co:Mo ratio, and the reaction condition. The catalyst composition and operating conditions for the synthesis of SWNTs from CO disproportionation have been systematically varied in order to maximize the selectivity towards SWNTs. A simple quantification method based on the standard Temperature Programmed Oxidation (TPO) technique has developed in order to determine the distribution of the different forms of carbonaceous deposits presenting on the catalysts after the CO decomposition reaction.

A synergistic effect between Co and Mo has been observed. When both metallic species are simultaneously present, particularly when Mo is in excess, the catalyst is very effective. However, when they are separated they are either inactive (Mo alone) or unselective (Co alone). To understand this synergistic effect, X-ray absorption spectroscopy (EXAFS and XANES) has been used to characterize the state of Co and Mo on the catalysts before and after the production of SWNT. Co species has found to alter from cobalt oxide in fresh catalyst to metallic cobalt after the reaction, with its particle size growing with reaction time. In the case of Mo species, the molybdenum carbide is identified in the catalyst after the reaction while molybdenum oxide is observed in the fresh catalyst.

# **CHAPTER 1**

## **INTRODUCTION TO CARBON NANOTUBES**

# 1.1 Introduction

Buckminsterfullerene, often called fullerene or buckyball, is a closed-cage spherical structure formed from hexagonal and pentagonal carbon rings as shown in Figure 1–1. Regularly, fullerene contains sixty carbon atoms in its molecule; however, this number of carbons can vary depending on its molecular size. No matter what size of fullerene, it must contain twelve pentagons to have a stable closed spherical structure.

Fullerene was first discovered in 1985 in the plume of helium from laser vaporization of carbon graphite [1]. Later in 1990, by a simple carbon arc technique to vaporize graphite in helium atmosphere, the macroscopic production of fullerene was successfully developed [2] and resulted in the systematic research of this new carbon structure. The variety of unusual physical and chemical properties of fullerene has lead to intense research on carbon, which was considered as a nothing-more-to-learn element prior to the fullerene discovery. In 1996, the Nobel Prize in Chemistry was awarded for the discovery of Buckminsterfullerene.



Figure 1–1  $C_{60}$ : Buckminsterfullerene; adopted from [3].

Besides carbon spherical structures, carbon pentagon and hexagon can form an elongated version of fullerene or carbon nanotubes, which has been speculated to exist and possess several unique properties as its fullerene cousin. Carbon nanotubes can be viewed as the seamless cylindrical tubes having walls made from role-up of hexagonal ring or graphite sheets and closed at each end with half sphere carbon caps or half of fullerenes, which contain six pentagonal carbon rings.

Generally carbon nanotubes can be categorized into two types: multi-wall carbon nanotubes (MWNTs) and single-wall carbon nanotubes (SWNTs). The transmission electron microscope (TEM) images of these two types are shown in Figure 1–2(a) and Figure 1–2(b) respectively. MWNT was first discovered in cathode deposit from carbon arc discharge experiment in 1991 [4]. The electron microscopic results revealed that these carbon nanotubes consist of concentric walls of graphitic layer and the spacing between the nanotubes walls closely match the spacing in between the carbon sheets in graphite (around 0.34 nm). Typically multi-wall nanotubes range in length from a few tens of nanometers to several micrometers, and in outer diameter from about 2.5 nm to 30 nm.



Figure 1–2 TEM images of (a) multi-wall carbon nanotube (b) single-wall carbon nanotube; [5].

In 1993, SWNT was simultaneously discovered by two research groups in carbon arc discharge experiments, using metals as catalysts [6,7]. Typically the diameter of SWNT is about 1 nm and can be up to a micron long. These tubes are curled and looped rather than straight, and can be alone or in groups as bundles or ropes. SWNT can be considered as one-dimension molecule due to its high aspect ratio (length to diameter). Due to its nanosize, this carbon material has recently become strongly associated with the emerging area of nanoscience and nanotechnology.

The advent of the carbon fullerenes and nanotubes has spread a wide net of attention in the sciences and engineering research due to the prominence of these new materials that will play a major role in coming years. This chapter will present the general aspects of carbon nanotubes. The structure of carbon nanotubes will be firstly reviewed. Then the properties and applications of carbon nanotubes will be introduced. Subsequently current production and purification methods of carbon nanotubes will be summarized. Finally carbon nanotubes characterization techniques will be discussed.

#### 1.2 Structure of Carbon Nanotubes

A carbon nanotube is a carbon macromolecule composed of hexagonal and pentagonal carbon rings. Certainly, carbon atoms in hexagon and pentagon are bound together by covalent bonds. In order to form covalent bonds, carbon, having the electronic configuration as  $(1s)^2(2s)^2(2p)^2$ , has to undergo hybridization by promoting one of its 2s electrons to 2p level resulting in three  $sp^2$  hybridized orbital. As mentioned earlier, a carbon nanotube is made from graphene sheets rolled up seamlessly as the walls and ideally capped by half of fullerenes at both ends. Therefore, it is worthwhile to consider first the structure of both graphite and fullerene, then the structure of carbon nanotubes.

Generally graphite has three of sp<sup>2</sup> electron orbitals, which are at 120° to each other in the same plane, while the remaining orbital having a  $p_z$  configuration is perpendicular to this plane. The sp<sup>2</sup> orbitals form the strong  $\sigma$  bonds between carbon atoms in the graphite planes, while the  $p_z$  or  $\pi$  orbital provides the weak van der Waals bonds between the planes. The overlap of  $\pi$  orbitals on adjacent atoms in a given plane provides the electron bond network, which gives graphite its relatively high electrical conductivity. In naturally occurring or high-quality synthetic graphite, the stacking sequence of the layers is generally ABAB, with an interlayer {0002} spacing of approximately 0.334 nm, as shown in Figure 1–3. This structure is often known as Bernal graphite. In less perfect graphite, the interplanar spacing is found to be significantly larger than the value for single crystal graphite (typically 0.344 nm), and the layer planes are randomly rotated with respect to each other about the c axis. These less perfect graphite are called "turbostratic".



Figure 1-3 Structure of hexagonal (Bernal) graphite and the unit cell; from [3].

In the  $C_{60}$  molecule, the carbon atoms are bonded in an icosahedral structure made up of 20 hexagons and 12 pentagons. Each of the carbon atoms in fullerene is joined to three neighbors, so the bonding is essentially sp<sup>2</sup>, although these three bonding are not in the same plane. However, the strain in  $C_{60}$  molecule is evenly distributed over the molecule since all sixty atoms of carbon are identical.

In a carbon nanotube, each carbon atom also bonds to its three neighboring carbon atoms through the sp<sup>2</sup> hybridization as in graphite and  $C_{60}$  molecule. Typically the sp<sup>2</sup>hybridized carbons form the hexagonal networks as the walls of carbon nanotubes, however, the pentagons are required at the caps to close themselves. Carbon nanotubes may consist of one or more cylindrical layers of graphitic sheets. If the carbon nanotube contains two or more concentric walls, it is referred as the multi-wall carbon nanotube, while the SWNT is certainly the one layer carbon nanotube.

In MWNTs, there appears to be no particular ordering between individual cylindrical planes forming the nanotube such as can be found in perfect graphite where the planes are stacked relative to each other in an ABAB configuration (Bernal stacking). In other words, a multi-wall carbon nanotubes will typically be composed of a mixture of cylindrical tubes having different helicity or even no helicity, thereby resembling turbostratic graphite.

SWNT can be chiral molecules due to their helical twist of the carbon lattice. This helicity should not be confused with the helicity of coiled nanotubes produced by the catalytic growth process. However, there are two types of non-helical tube or achiral nanotubes that are highly symmetrical and known as "zigzag" and "armchair" as shown in Figure 1–4. Zigzag type nanotube arranges the carbon lattice with the sides of parallel to the axis of the tube, whereas the sides of the hexagonal carbon rings of armchair type are perpendicular to the tube's axis.

The simplest way to specify the structure of an individual tube is in terms of a chiral vector, denoted as C. As shown in Figure 1–5, the vector C can be expressed as  $C = na_1 + ma_2$  where  $a_1$  and  $a_2$  are unit cell base vectors of the graphene sheet, and nand m are integer number which  $n \ge m$ . This vector joins two equivalent points on the original graphene lattice. The tube is produced by rolling up the sheet such that the two end-points of the vector C are superimposed. Each pair of integers (n,m) represents a possible tube structure [8]. From Figure 1-5, it can be concluded that m=0 for all zigzag tubes, while n = m for all armchair nanotubes. All other n and m will result in chiral nanotubes. In the particular chiral vector, nanotubes can be capped by one half of a  $C_{60}$  molecule, for instances, the (9,0) zigzag tube and the (5,5) armchair tube. Since the distance of unit cell vector,  $|\mathbf{a}_1| = |\mathbf{a}_2| = 0.246$  nm, therefore, the diameter  $d_t$  can be obtained from  $d_i = 0.246 \sqrt{(n^2 + n \cdot m + m^2)}/\pi$ . The magnitude of C (i.e. the tubes circumference) in nanometers be calculated from can  $|C| = 0.246 \sqrt{(n^2 + n \cdot m + m^2)}$ , and the chiral angle,  $\theta$ , can be known by  $\theta = \tan^{-1} \left[ \sqrt{3} \, m / (m+2n) \right].$ 



Figure 1-4 Single-wall carbon nanotubes (a) zigzag and (b) armchair; adapted from [3]



Figure 1-5 Unit vector  $\mathbf{a}_1$  and  $\mathbf{a}_2$  of the two dimensional lattice graphene sheet.

# **1.3 Carbon Nanotubes Properties and Applications**

Carbon nanotubes are often referred to as "super carbon fibers" thanks to their exceptional properties in a broad range of electronic, thermal, and structural properties. Intense research over the past few years has revealed that this new carbon material simultaneously possesses superb properties for many applications. Carbon nanotubes, having a diameter in nanometer scale, can conduct the electrical current as metal wire or as semi-conductors and yet can be a very strong material. These remarkable properties have been theoretically predicted, and gradually some of these predicted properties have been experimentally confirmed as these materials become available; especially the singlewall type. However, certain properties still cannot be tested due to limitation of technology that can manipulate nanoscale objects.

Originally the excitement around carbon nanotubes was greatly stimulated by the theoretical predictions of unusual electronic properties. Carbon nanotubes can be either conductor or semi-conductor, depending on their diameter and helicity. As mentioned in the previous section, the vector notation (n,m) can simply determine the chirality and diameter, therefore, implies the electronic behavior. Based on theoretical calculations, SWNT is anticipated to be metallic if the value n - m can be divided by three. If not, the nanotube is predicted to be semiconductor. Thus, with the random values of n and m, it is expected that two-thirds of nanotubes would be semi-conductor, while a third would behave as a metallic conductor.

This prediction has been confirmed by probing SWNT with scanning tunneling microscope probes, which can simultaneously measure the diameter, helicity and the density of electronic states (DOS) of SWNT [9,10]. In addition, sharp peaks in the DOS are observed, which are the characteristic signatures of the one-dimensional nature of conduction within a one-dimensional system. Furthermore SWNT can conduct electricity at room temperature with essentially no resistance, which is known as ballistic transport—where the electrons can be considered as moving freely through the structure, without any scattering from atoms or defects. Electrical conduction in finite-sized SWNT occurs through well-separated, discrete electron states that are quantum-mechanically coherent over long distances ( $\approx 3 \mu m$ ), with electron wave functions extending over the entire tube [11]. Semiconductor nanotubes connected to two metal electrodes can be made to function as a field-effect nanotransistor. By applying a voltage to a gate electrode, the nanotube can be switched from a conducting to an insulating state at room temperature [12]. Theoretically modeling also suggests the joining between a semiconducting nanotube and a metallic nanotube in order to create a nanosize diode [13].

MWNTs have demonstrated good field emission of high currents at low operating voltages as well [14]. Electron emission from arrays of tubes has been used to construct a cathode ray tube lighting element. Nanotube arrays now can be grown on glass substrates for field-emitting flat panel displays [15].

Nanotubes can also be used as a tip for atomic force microscopes (AFM) because nanotubes, particularly the single-wall type, have a very small diameter for high resolution, high aspect ratio for imaging deep structure, low tip-sample adhesion for gentle imaging and elastic ability to buckle rather than break when large forces are applied [16]. Initially, this was done by mounting MWNT to the ends of AFM by direct mechanical assembly [17]. Recent research has demonstrated that both MWNT and SWNT can be directly grown on the tip of AFM by chemical vapor deposition technique [18].

While carbon nanotubes have been predicted to be the strongest material, they are also highly flexible. As shown in Figure 1–6, the Young's modulus of a single graphite crystal highly depends on the orientation of graphite plane and shows the highest value when the force is applied to the direction parallel to the basal plane. Carbon nanotubes having graphitic basal plane parallel to the fiber axis are expected to have this exceptionally high tensile modulus. Even though several theoretical predictions range over a wide scope of nanotubes' modulus, they all at least semi-quantitatively indicate that carbon nanotubes are the strongest materials. The predicted mechanical properties are sensitive to details of nanotubes' structure and defects, therefore, real measurements on individual nanotubes are essential to study these properties. However, it is a challenge to find direct experimental mechanical properties of individual nanotube since the manipulation of nano-size materials is still in the early stage. In spite of this, certain MWNT mechanical properties can be estimated by indirect measurement from TEM.



Figure 1–6 Calculated tensile Young's modulus (E) as a function of  $\theta$  (angular displacement from the a-axis) for a single crystal of graphite; from [19].

The results suggest that MWNT has an average Yong's modulus of 1800 GPa [20] and compressive strengths in the range of 100-150 GPa [21]. The AFM technique also illustrates that MWNT can be repeatedly bent without breaking, which indicates how extraordinarily flexible and resilient MWNTs are [22]. Clearly, carbon nanotubes composites show outstanding promise for new structural materials [23]. And, with the high conductivity, nanotubes can be added into polymers in order to make conductive polymers [24].

Other unique applications of nanotubes have been demonstrated as well. Nanotubes are potentially useful for energy storage and delivery system due to their high capacity in hydrogen storage and their excellent electron transfer characteristics [25,26]. Molecular nanowires inside nanotubes are prepared by filling with metallic and inorganic compounds in MWNT [27] and in SWNT [28]. Carbon nanotubes have also demonstrated to be used as "nanotweezers" for manipulation of nanostructure [29]. Sheets of SWNT could be exploited as electromechanical actuators with possible applications as artificial muscles because this application requires low operating voltages with large actuator strains [30].Carbon nanotubes have shown a wide range of remarkable properties, which are not commonly found in other materials. Moreover the robust nanosize can lead to new physics of nanomaterial that probably provides insightful fundamental molecular behavior and new nanotechnology. Because of these features as mentioned above, carbon nanotubes could be a material that drastically change our way of living in the future. However, these will not happen if we cannot find the way to produce carbon nanotubes in economical way.

# 1.4 Carbon Nanotube Production Routes

Currently, there are three major ways to produce a tangible amount of carbon nanotubes for experimental test: the arc discharge of carbon electrode, the laser vaporization of carbon graphite, and the heterogeneous catalytic reaction of carboncontaining gases. In order to yield SWNT, it is necessary to have transition metals present in the system of carbon arc discharge and laser vaporization technique. However, depending upon the catalysts and reaction condition, transition metals can possibly generate multi-wall or single-wall carbon nanotubes in gas phase catalytic method. This section will briefly introduce the production of carbon nanotubes (both multi-wall and single-wall type) from the arc discharge, the laser vaporization techniques as well as the catalytic carbon deposition of carbon containing gas. The details of gas phase catalytic production of carbon nanotubes will be further reviewed in Chapter 2.

#### 1.4.1 Arc discharge technique

The arcing of a graphite electrode is currently the most widespread method for carbon nanotube production. The arc can create high-temperature carbon plasma (up to 3700°C) in helium atmosphere [31]. This method has been effectively used to produce fullerene [2]. And, by adjusting the gas pressure in the arc chamber, the arc discharge
technique can generate MWNTs in high quantity sufficient for a detailed study of their physical and chemical properties [32].

The carbon arc discharge apparatus is schematically illustrated in Figure 1–7 [3]. Typically, arc plasma is generated between the two graphite electrodes in an inert helium atmosphere by applying voltage around 20 V and dc current around 150 A/cm<sup>2</sup>. Initially, the two rods are barely touching in order to heat up the tips and initiate the arc. Once the arc stabilizes, the electrode gap is maintained at about one millimeter and helium pressure around 500 torr. The carbon on positive electrode (anode) is vaporized into plasma and deposited on negative electrode (cathode). MWNTs are found only in the deposit on cathode, unlike the fullerene, which are found in the soot at the chamber wall.



Figure 1–7 A carbon arc discharge apparatus; from [3]

Several factors can affect the arc process for producing a good yield of high quality nanotubes. The most important factor is the pressure of the helium in the evaporation chamber [32]. As the pressure is increased, a remarkable increase in the number of nanotubes is noticed in the product, as observed by TEM. At pressures above 500 Torr, there is no obvious change in sample quality, but less in total yield. Thus, 500 Torr appears to be the optimum helium pressure for nanotubes production. It should be noted that these conditions are not suitable for fullerene production, which requires a pressure of below 100 Torr. Another important factor in the arc-evaporation method is the current [31]. Too high a current will result in a hard, sintered material with few free nanotubes. Therefore, the current should be kept as low as possible in order to produce good quality nanotubes samples and avoiding excessive sintering.

In 1993, single-wall carbon nanotubes, having an average diameter of 1 to 2 nm, were created by arcing the graphite rod together with catalytic metal such as iron or cobalt [6,7]. Typically, a carbon rod is drilled to create a hole at the center and this hole is then filled with metal powder [7]. The amount of catalyst necessary depends on the catalyst, but more tubes are formed in the presence of larger amounts of catalysts. The chamber can either be filled with helium or argon and good yields are obtained at pressures around 500 to 600 Torr [7].

SWNTs are found in a weblike structure deposited in the chamber, not on the cathode as MWNTs. The yield is still low and product contains a lot of amorphous

carbon. Later the high yields of single-wall nanotubes bundle were obtained by using bimetallic catalysts in the electric arc of graphite [33]. Unlike in the carbon fiber production method, no catalytic particles are found in the tips of these single-wall nanotubes. Actually, the catalytic particles are much larger than the diameter of the tubes, so the mechanism of formation of these tubes remains to be understood.

In order to make the arc-discharge process more economical, bituminous coal was used instead of more expensive graphite [34]. Raman scattering spectroscopy and electron microscopy results indicated that these SWNTs posses the same properties as those derived from graphite. The estimated yield of SWNTs is about 45% from the web-like soot. In this case, yield is defined as percent of carbon in the form of SWNT to the total carbon in raw product which is the web-like soot. Furthermore the arc discharge semi-continuous process was also introduced to produce the materials in large scale [35]. Hydrogen was used to replace the helium because hydrogen is cheaper and also has high thermal conductivity, enough to efficiently quench the plasma flow. In addition, sulfur (usually in the form of FeS) has been used as a promoter to keep the high yield of SWNTs.

#### 1.4.2 Laser evaporation technique

The synthesis of MWNTs by oven laser-vaporization was first reported in 1995 [36]. MWNTs were self-assembled under homogeneous gas phase conditions of carbon condensation in an oven heated to 1200°C filled with argon. The laser employed was the

532 nm of a Nd:YAG laser providing 10 ns, 250 mJ pulses at 10 Hz. A continuous laser pulse is aimed at the graphite target and scanned across the target surface in order to maintain a smooth and uniform target for vaporization. The self-assembled product is then swept out of the furnace zone by argon gas and deposited as soot on a conical water-cooled copper rod as shown in Figure 1–8.

Subsequently, by adding a small amount of transition metal catalyst into the carbon target, the laser vaporization technique was reported to produce SWNTs with high yield, particularly when bi-metals (e.g. Co/Ni or Co/Pt) were used as catalysts [37]. By using a dual pulsed laser vaporization technique, the single-wall nanotubes yield is higher and the tubes diameter is highly uniform with the diameter about 1.4 nm. [38]. The single-wall nanotubes were also found to be in bundles, often called nanotubes ropes. These nanotubes organized in hexagonal close-packed bundles with a lattice constant of 1.7 nm.

The oven temperature was reported to influence the diameter of SWNTs [39]. It was found that the tubes diameter could be varied from 0.8-1.5 nm by adjusting the oven temperature from 780-1050 °C. Moreover, the nanotubes diameter was also affected by the laser pulse power. The nanotubes diameters were shifted to smaller sizes when the laser pulse power was increased [40].



Figure 1-8 Laser vaporization apparatus; from [41]

#### 1.4.3 Gas phase catalytic production

It is believed that the gas phase catalytic production of carbon nanotubes will be the route for the commercial scale production of nanotubes as it is today in polymer production. Basically, this catalysis technique is implemented by passing carboncontaining gas (e.g. methane, ethylene or carbon monoxide etc.) or mixtures over small metal particles at elevated temperature for a period of time. Often an inert gas, such as helium or argon, and hydrogen are fed into the reactor as well. At sufficiently high temperature, these carbon-containing gases are catalytically decomposed, resulting in carbon formation on the metal surface. This deposited carbon can be in many structures, for instances, amorphous carbon, graphitic carbon, filamentous carbon. It is well known that many parameters, including the gas composition, the catalyst nature, the reaction temperature, flow rate etc., affect the morphology of deposited carbon. A detailed review of this technique will be present in Chapter 2.

#### 1.4.4 Other production techniques

Besides the previous three techniques, other methods been used to produce carbon nanotubes. Solar energy furnace can be used to evaporate carbon target together with metal catalysts, and results in carbon nanotubes [42]. Carbon nanotubes are also found after passing current through molten lithium chloride salt between two graphite electrodes [43]. By heating of polymer, carbon nanotubes can be synthesized due to the removal of other elements in polymer precursors [44]. Carbon nanotubes are also reported to form once metal carbide powders, such as  $Al_4C_3$ , are heated with catalytic metal e.g. Fe, Co or Ni, at temperature around 1000°C [45].

## 1.5 Purification of Carbon Nanotubes

To improve the nanotubes properties, the further purification of the raw material is necessary for carbon nanotubes application. The level of purity, however, depends upon the field of application. For examples, in the application as reinforcing filler, carbon nanotubes may not required in such high purity, while the high purity is very significant in electronic application.

The ideal way to obtain purified carbon nanotubes is to produce them without any side- or by-products. However, carbon nanotubes are typically produced along with a number of impurities in all the production processes currently known. The amount and type of impurities also depend on the production techniques. Laser vaporization and arc discharge methods create carbonaceous impurities, such as amorphous carbon, carbon nano-particles and fullerenes, as well as metal catalysts used in the producing SWNT. For gas phase catalytic method, catalysts supporting material (i.e. silica, zeolite, alumina) is often presented in the final product in addition to all impurities as in other production techniques. In this section, the physical and chemical purification techniques of carbon nanotubes from other materials will be summarized.

#### 1.5.1 Physical based purification of carbon nanotubes

A number of separation techniques, such as filtration, centrifugation and chromatography, have been attempted in order to purify carbon nanotubes. Physical separation techniques have advantages over chemical treated technique that the purified nanotubes will likely be in their original form or not be damaged, but it has a drawback that it is less efficient.

A micro-filtration process has been reported to purify SWNT [46]. In this report, the laser vaporization raw material was first extracted by CS<sub>2</sub> solvent to remove fullerenes and poly-aromatic carbon, then the remaining carbon material was sonicated in cationic surfactant solution and sent to micro-filter to filter out carbon nano-particles resulting in purified SWNT on the membrane filter. This technique can purify SWNT up to 90% by starting from the material containing SWNT about 76% [46]. The microfiltration is however very slow and inefficient if the process starts from large amounts of low-purity SWNTs. To facilitate the filtration step, Shelimov and colleagues employed the ultrasonic sonication to assist micro-filtration [47]. The ultrasonic sonication helps suspending SWNT in the solution and prevents the cake formation on the membrane. However, the ultrasonic sonication can damage SWNT by cutting it into smaller pieces, leading to the study of making "fullerene pipes" [48]. Bandow and co-workers demonstrated that centrifuge can purify an arc discharge soot having 3-5% SWNT to final product containing 40-70% of SWNT [49]. They started with the sonication of the low yield soot in cationic surfactant then centrifuge out the carbon nano-spheres leaving SWNT suspending in the aqueous solution.

Bonard and colleagues further demonstrated that filtration and flocculationsedimentation can be utilized in purifying MWNT. With the aid of surfactant, the nanotubes were allowed to flocculate and the nano-particles were left in suspension. The sediment was then removed and further controlled flocculation step was repeated in order to induce a size-dependent flocculation, resulting in nanotubes length selection [50]. Furthermore purification and length-selected carbon nanotubes, dispersed in surfactant solution, can be accomplished by using size exclusion chromatography [51]. In an attempt to align carbon nanotubes in the electric field, Yamamoto and co-workers showed that, especially at high frequency of ac electric field in the ac electrophoresis, only carbon nanotubes moved toward the electrodes, but the carbon particles did not move [52]. Therefore this technique is possible to purify carbon nanotubes.

#### 1.5.2 Chemical based purification of carbon nanotubes

Chemical purification of carbon nanotubes is mainly based on the oxidation of carbon. Carbon with different structures shows different rate of oxidation. The less stable carbon structure is the easier carbon to be oxidized. The oxidation purification of carbon nanotubes can be performed either in gas or liquid phase.

Ajayan and co-workers reported that oxidation for carbon nanotubes can open the tubes caps that have higher oxidation reactivity due to the curvature or the presence of pentagon carbon rings [53]. Subsequently, Ebbesen and colleagues showed that oxidation in air can remove carbon nano-particles with defect-rich structure from the relatively perfect MWNT, but the major portion of cabon nanotubes was removed as well [54]. In addition, the gas phase purification of SWNT was successfully carried out by using a chlorine, water and hydrogen chloride gas mixture [55].

Tohji and colleagues presented the hydrothermally initiated dynamic extraction method (HIDE) to aid the purification procedure of SWNTs produced from arc discharge [56]. Their technique started with refluxing of the raw soot in distilled water for 12 hours, and followed by filtering and drying. Then samples were washed by toluene in order to get rid of the fullerenes, and subsequently oxidized in air for 20 minutes at 470 °C for removing amorphous carbon and graphite coating on metal. These authors believed that, during the reflux, water molecules break the network between SWNT and amorphous carbon and metal particles, therefore, significantly contribute to overall oxidation performance. Intercalation of metal in between graphitic layers was also implemented in order to assist the subsequent oxidation of graphite and carbon nano-particles [57]. This technique started with soaking unpurified sample in CuCl<sub>2</sub>-KCl and then reducing copper compound to copper metal. After the oxidation stop, graphite and carbon nano-particles was cleaned up, but nanotubes still survived due to its closed cage structure.

The removal of carbon nano-particles and amorphous carbon in liquid phase has been implemented using several strong oxidants, for instances, nitric acid, sulfuric acid, potassium permanganate and mixtures [58]. The results show that the liquid phase oxidation tends to render higher yields than the gas phase oxidation, however, the purified nanotubes appears to be shortened in length and severely damaged. Dujardin and co-workers also demonstrated the simple purification technique of SWNT from carbonaceous material produced from Laser vaporization technique [59]. Only SWNT can sustain the 4 hours reflux in concentrated nitric acid at 120 °C. Subsequently this product is repeatedly centrifuged, decanted off the supernatant and re-dispersed in water until the pH of liquid is about 6, at which the suspension of SWNT starts to be stable. The overall yield of the purification steps ranges between 30 and 50%.

Furthermore, the large-scale purification of SWNT has been implemented by Rinzler and co-workers [60]. They started with carbon product produced from a "gramscale" pulse laser vaporization technique and containing approximately 70-90% of SWNT. This carbon is then purified as the following steps. First the as prepared product was treated by refluxing in 2-3 M of nitric acid. The authors reported weighs lost about 70 % after this acid refluxing step. Then the refluxed solution was centrifuged and washed by de-ionized water for a few times. After the centrifuge, the sediment containing mostly SWNT was re-dispersed in surfactant solution and filtered by hollowfiber, cross-flow filtration. In addition from nitric acid, the authors also suggested several higher reactive oxidizing acids in order to facilitate the reflux step. For examples, a three to one mixture of 98% sulfuric and 70% nitric acid or a four to one ratio of 98% sulfuric acid and 30% hydrogen peroxide are used to reduce the reflux time.

Carbon nanotubes produced by catalytic reaction usually contain catalystsupporting materials such as zeolite, silica or alumina. Fonseca and colleagues suggested two alternative ways to remove the supporting material from nanotubes [61]. One is the use of 50% HF acid solution to dissolve zeolite, followed by filtering and washing in order to get rid of the acid. For the case of silica support, diluted nitric acid are first used to dissolve the metals catalyst then the sample were sonicated in organic solvent. Silica, which is heavier than nanotubes, will settle down, then the sediment is removed and the process is repeated. Subsequently the KMnO<sub>4</sub>/H<sub>2</sub>SO<sub>4</sub> aqueous solution is employed in order to eliminate amorphous carbon.

### 1.6 Characterization of carbon nanotubes

Several techniques have been broadly studied for carbon nanotube characterization: electron microscopy, Raman spectroscopy, temperature programmed analysis, scanning probe microscopy, electron energy loss spectroscopy, x-ray diffraction and etc. This section will briefly discuss certain techniques that have been widely employed to characterize carbon nanotubes from various production processes. Definitely electron microscopy and Raman spectroscopy are two main methods that are widely utilized to study the nanotubes. But, these two techniques are still considered to be relatively elaborated and only suitable for qualitative characterization. It is necessary establish a rapid and economical method for monitoring and studying the production of carbon nanotubes. Temperature program analysis technique, which looks promising for carbon nanotubes quantitative analysis, therefore will be subsequently reviewed.

#### 1.6.1 Electron microscopy

Electron microscopy has been a major technique in characterization of carbon nanotubes. In fact, both MWNT and SWNT were first observed through electron microscopy [4-7]. Electrons having characteristic wavelengths of less than an angstrom render a high resolution of carbon nanotubes images. In transmission electron microscopy (TEM), the two dimensional images of carbon nanotubes are obtained from transmitted electron. TEM are able to give sub-nanometer resolution, therefore it is highly suitable for studying structure of nanotubes, for examples, diameter of both SWNT and MWNT, diameter of SWNT bundle, graphitic layer of MWNT as well as crystallinity of carbon sample.

For scanning electron microscopy (SEM), the electron beam scans over the sample surface causing backscattered electron. The three dimensional information are achieved from the contrast of images with the resolution in the scale of nanometer scale, thus, SEM is proper for obtaining overall structure of carbon nanotubes, but not for detailed structure.

#### 1.6.2 Raman spectroscopy

Raman spectroscopy is the fingerprint of vibrations in molecules or in solid lattices, which are excited by the inelastic scattering of photons. Raman scattering technique has proved to be very useful in characterizing graphite and diamond in the past [62,63]. Raman scattering provides information on the amount of ordering, the degree of sp<sup>2</sup> to sp<sup>3</sup> bonding, and the size of graphitic crystallites in the material. Fullerenes have vibrational characteristics reflecting their molecular nature, which is distinct from graphite and diamond. Carbon nanotubes have the physical dimensions of both large fullerenes and solid graphite should have their own vibrational properties.

Hiura and colleagues studied the Raman scattering of as prepared MWNTs produced from the arc discharge technique [64]. The first-order Raman spectra of these materials are illustrated in Figure 1–9. In comparison, the Raman spectra of highly oriented pyrolytic graphite (HOPG) and glassy carbon were included. The first-order Raman spectra were characterized by a strong band at approximately 1580 cm<sup>-1</sup> and another at approximately 1350 cm<sup>-1</sup>. The 1580 cm<sup>-1</sup> band corresponds to one of the vibration modes of two neighboring carbon atoms moving in opposite directions in a graphite sheet [63]. The spectrum of inner core of the deposited material, as shown in Figure 1–9 (b), has a strong resemblance to HOPG, Figure 1–9 (a), which has a perfect crystalline flat sheet graphitic structure. The 1580 cm<sup>-1</sup> but much narrower than the corresponding band of glassy carbon, shown in Figure 1–9 (d). This indicates the high

degree of crystallinity of the nanotubes and nanoparticles composing the sample. The small downshift of the 1574 cm<sup>-1</sup> peak for nanotubes sample, with respect to that 1580 cm<sup>-1</sup> of HOPG was initially attributed to the fact that the nanotubes are curved and closed structures. More recent studies by Bacsa and co-workers show that a significant downshift is only expected for nanotubes and nanoparticles with diameters less than a few nanometers, while the average diameter of multi-wall nanotubes is typically 10 nm [65].

The appearance of the 1350 cm<sup>-1</sup> band can be ascribed to the presence of graphitic particles and crystallites of finite size of nanometer order, as suggested by Huira and colleagues [64]. However, Bacsa and co-workers argued that, based on their interpretation of peak ratio with purified nanotubes sample, the 1350 cm<sup>-1</sup> peak is not because of the presence of nanoparticles, but due to defects in the curved graphene sheets and the tube ends [65].



Figure 1–9 Comparison of Raman spectra of (a) HOPG, (b) inner core of the cathodic deposit containing carbon nanotubes and nano-particles, (c) outer shell of the cathodic deposit, (d) glassy carbon; from [64].

As discussed above, the Raman spectra of MWNT from cathode deposit in arc discharge apparatus is not much different from the spectra obtained from graphite. However, the Raman spectra of SWNT show significantly different. The Raman spectra obtained from the Co-catalyzed nanotube, which believed to be SWNT, are shown in Figure 1-10(e) and compared with spectra from other carbon materials [66]. The distinctive features of spectrum in Figure 1-10(e) are two sharp first-order lines at 1566 and 1592 cm<sup>-1</sup>. Also prominent in the first-order Raman spectrum is a broad ban centered at 1341 cm<sup>-1</sup>. The weak Raman peaks near 1460 cm<sup>-1</sup> (Figure 1-10(e) and (d)) is identified with fullerene impurities in the nanotube samples. After washing the fullerene out by toluene, the authors noticed that the peaks near 1460 cm<sup>-1</sup> are disappeared while the overall strength and intensity ratio of the 1566 cm<sup>-1</sup> and 1592 cm<sup>-1</sup> lines in Figure 1-10(e) remains unaltered. In comparison, the Raman spectrum for the dc arc-derived carbons prepared in the same way as that studied in Figure 1-10(e), except for the absence of the cobalt catalyst, shows no evidence for the sharp 1566 cm<sup>-1</sup> and 1592 cm<sup>-1</sup> lines, although other broad features in both spectra are strikingly similar in shape and frequency.

To show that the sharp features in Figure 1–10(e) are not associated with ordinary amorphous soot, glassy carbon or graphitic carbons, several Raman spectra are included in Figure 1–10 for a variety of  $sp^2$  and  $sp^3$  solid forms of carbon. These include the Raman spectrum for diamond, Figure 1–10(g), showing its single sharp line at 1335 cm<sup>-1</sup>, and for HOPG, Figure 1–10(f), showing a sharp first-order line at 1582 cm<sup>-1</sup>. Another important benchmark spectrum shown in Figure 1-10(a) is that for a typical glassy carbon, showing a significantly broadened feature at 1600 cm<sup>-1</sup> and a broad band near 1359 cm<sup>-1</sup>.

Subsequently many new low and mid-frequency Raman peaks were studied [67]. The Raman spectrum of SWNT exhibits three main zones at low (140-200 cm<sup>-1</sup>), intermediate (300-1300 cm<sup>-1</sup>) and high (1500-1600 cm<sup>-1</sup>) frequencies, as shown in Figure 1–11. This spectrum is also compared with the theoretical results from several sizes of armchair type SWNT (Figure 1–11). Notably the sharp peaks at around 1567 cm<sup>-1</sup> as well as the sharp peaks at 1593 cm<sup>-1</sup> observed in the work mentioned in previous paragraph are consistent with the theoretical value. Moreover, theory suggests that peaks at low frequency range are strongly depend upon tube's diameter while the peak at high frequency (1592 cm<sup>-1</sup>) is not.



Figure 1–10 Room temperature Raman spectra of (a) glassy carbon; (b) nano-soot; (c) nano-soot after heat treatment at 2820 °C; (d) soot from the dc carbon arc method; (e) same as (d) but with Co added to anode; (f) HOPG; and (g) single crystal diamond; from [66]



Figure 1–11 Raman spectrum of SWNT samples (top) taken with 514.5 nm excitation. The \* in the spectrum indicates features that are tentatively assigned to second-order Raman scattering. The four bottom panels are the calculated Raman spectra for armchair (n,n) nanotubes, n = 8 to 11. The downward pointing arrows in the lower panels indicate the positions of the remaining weak, Raman-active mode; from [67].

#### 1.6.3 Temperature programmed analysis

Temperature programmed analysis is a technique which monitors the change in sample, e.g. weight or chemical reaction, while the temperature increases linearly in time. If the sample's weight is the monitored parameter, this technique is often called thermal gravitation analysis (TGA). For instance, carbon with different morphology is burnt at different temperature; therefore temperature program analysis is a technique that is suitable to study carbon structures. In addition TGA is a simple technique that provides a reliable result. However, it is necessary to keep in mind that the oxidation of carbon is sensitive to the presence of other materials, e.g. metals that can act as a catalyst to facilitate carbon burning.

In order to opening MWNTs' cap, Ajayan and co-workers compared the oxidation of fullerenes and MWNTs in air for 15 minutes and they found that the weight of fullerene started dropping dramatically when the temperature was at around 470 °C and completely disappeared at temperature around 630 °C [53]. The nanotubes samples started to show substantial loss of weight once they were heated above 700°C, and at about 850 °C the entire sample was burnt off. Despite the wide distribution in shapes and sizes of MWNTs, the oxidation curves are smooth over the temperature range. The authors proposed that the oxidation of carbon nanotubes first occurs at the caps of nanotubes and carbon are consumed layer by layer resulting in opening the tube's caps and thinning the nanotubes. Thermal gravitation analysis of laser produced SWNT is also reported by Rinzler and colleagues [60]. With air as an oxidizing agent, they found that the unpurified SWNTs start burning at temperature around 400°C with the maximum rate of burning at around 480°C. However, the purified SWNTs show the major weight loss at temperature almost 600°C with the high rate at about 650°C. Furthermore, the TGA of purified SWNTs with 0.1 % oxygen in argon does not show a major fraction loss until the temperature after 600°C. According from the authors, the major weight reduction of unpurified SWNT at lower temperature is due to the present of other forms of carbon that can be burnt at lower temperature. The oxidizing reaction at low temperature provides the heat for prematurely burning of more stable carbon. In general, it is accepted that SWNT will be oxidized at temperature higher than amorphous carbon and  $C_{60}$ , but lower than MWNT and graphitic carbon fiber.

In the case of a minute amount of carbon, e.g. deposited carbon on catalysts, TGA is not sufficiently effective due to its low sensitivity. Instead of sample weight monitoring, the carbon dioxide gas evolution is followed. This technique is well known in catalysis field as temperature programmed oxidation (TPO). Chapter 4 and 5 will introduce and utilize this technique for both qualitative and quantitative study of carbon nanotubes.

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# **CHAPTER 2**

# **REVIEW OF HETEROGENEOUS CATALYTICALLY PRODUCED CARBON NANOTUBES**

## 2.1 Introduction

Carbon nanotubes have revealed a number of potential applications and very promising commercialization as mentioned in Chapter 1. However the current production techniques can provide only gram-scale of carbon nanotube, particularly single wall carbon nanotubes (SWNT), at very high cost. A large-scale and economical production of carbon nanotubes is thus extremely necessary in order to commercialize carbon nanotubes and related products. The heterogeneous catalysis technique has the potential for making possible the large scale production of nanotubes. The key technology to develop in this method is the ability to produce carbon nanotubes in such a controlled fashion with regard to tubes quality and quantity.

Carbon nanofibers or carbon filaments possess structures and properties that can be analogous to carbon nanotubes obtained from arc-produced [1]. Generally the observed carbon filaments are hollow and consisting of graphitic carbon layers [2]. However, these graphite layers can be preferentially oriented at an angle with respect to the fiber axis (herring-bone arrangement) or aligned in a direction parallel to the fiber (tubular arrangement) as shown in Figure 2–1 [3]. The perfect concentric carbon nanofibers with their graphitic plane parallel to the tubes axis therefore can be considered as a catalytic grown carbon nanotubes.

Carbon nanofibers can be produced in a relative large scale by the catalytic decomposition of certain carbon-containing gases on metal particles. Promisingly carbon nanotubes could be generated in large scale by similar technique. Therefore understanding the catalytic growth of carbon filaments definitely facilitates the understanding carbon nanotubes growth mechanism.

In this chapter, the catalytic production of carbon filaments will be firstly reviewed. Then the gas phase catalytic production of multi wall carbon nanotubes (MWNTs), aligned carbon nanotubes and growth mechanism will be mentioned. Subsequently heterogeneous catalysis production SWNTs will be brought up as well.



Figure 2–1 Possible graphite layers arrangement in carbon nanofiber (a) herring-bone arrangement (b) tubular arrangement

# 2.2 Carbon filaments from catalytic reaction of carbon containing gases

The catalytic growth of graphitic carbon fibers from the decomposition of hydrocarbons on supported or unsupported metals has been widely studied in heterogeneous catalysis of hydrocarbons conversion. In earlier studies in 1970s, the main goal was to avoid or inhibit the formation of carbon filaments, which causes catalysts deactivation. Ironically, later in 1980s, study for this material production was more emphasized due to some interesting properties carbon filaments [4].

Commonly, the catalytic production of carbon nanofibers experiment is carried out in a flow reactor heated by electrical furnace at atmospheric pressure. The catalyst is placed in a ceramic boat and positioned at the hot zone of a quartz tube. Typically the catalyst sample is initially reduced in diluted hydrogen stream at temperature 500-600°C. Then, the temperature is adjusted to the desired temperatures and the feeding gases mixture is passed over the catalyst for a period of time. After the reaction, the system is cooled to room temperature under inert gas. A typical set up of reactor is shown in Figure 2–2. Using this approach, approximate 20 g of carbon fibers can be easily obtained from 100 mg of relatively active catalysts [1].



Figure 2-2 A typical reactor set up for catalytically growing carbon nanofibers

Carbon deposited from carbon containing gases on catalysts surface can form either amorphous or crystalline carbon. As observe by high-resolution transmission electron microscope (TEM), the deposited crystalline carbon possess several different structures, for example, lamellar graphite, graphite coated particle, fiber and tubes. The filaments can also be in helical, twisted or straight morphology. Their diameters range from 10 nm to 500 nm and can be up to 100 µm in length. It is known that temperature, catalyst composition, as well as type of gases are the main influences on the morphology and crystalline order. Audier and coworkers carried out an investigation intending to correlate the effect of temperature and nature of the catalyst on the morphology of carbon deposits following the decomposition of carbon monoxide (CO) and methane (CH<sub>4</sub>) [5]. These authors observed the presence of tubes, bi-tubes, solid and shell-like structures with catalyst particles enclosed. These extreme differences in carbon structures were found to be entirely dependent on the temperature, the metal composition and also the reacting gas. The particular temperature that yields specific carbon structure could generate the completely different carbon structure if the metals and/or the reaction gases were changed.

The effect of catalysts and reactions conditions was also found in the work done by Krishmankutty and co-workers [6]. From the study of ethylene decomposition over iron-copper powder, they confirmed that the structure and properties of the carbon filaments were depending upon the composition of the catalyst, the temperature as well as the percent of hydrogen in the reactant gas mixture. Adding hydrogen in carbon
containing feed gases has been suggested to be a crucial step in carbon fiber production. Hydrogen is believed not only to initiate the decomposition of carbon containing gases over certain metals system, but also influence on the structures of carbon filaments [7,8]. However this aspect is still controversial because not all metals require hydrogen in order to show activity for carbon filament formation [9].

A technique to mass-produce vapor-phase-grown carbon fiber (VGCF) from iron catalyst and benzene at 1100°C was also reported by Endo [10]. This VGCF can have diameter up to 10  $\mu$ m and several hundreds millimeters long. However this VGCF composes of two different structures. First structure is a hollow tube as the inner core of VGCF and it is composed of linearly extended carbon layer with diameter about 10 nm. The second structure is the carbons microcrystalline depositing on the outside of the inner core and causes thickening of the VGCF. Based on this observation, Endo suggested a two-step growth process for VGCF. Initial step is the fiber catalytic growing as a fine hollow tube and linearly extended. Then the radial direction fiber growth is followed due to the subsequent thermal decomposition of benzene.

### 2.3 Multi wall carbon nanotubes

Multi wall carbon nanotubes can virtually be categorized as one type of carbon filaments that have the graphitic layers parallel to the fiber axis and no secondary carbon depositing on outside wall. The MWNT derived from a catalytic production method are usually much longer but cost much less than those from an arc discharge process. Unfortunately, the tubes produced by catalytic process are rather thick and containing a high density of defects. To overcome these problems, novel catalysts and reactor design have been utilized, but still needed further development. The summary of the catalytic technique of MWNTs production will be presented in this section.

By using similar technique as carbon filaments production, carbon nanotubes can be found together with several structures of carbon, for example, amorphous carbon on catalysts surface, carbon graphite covering metal particles [11,12]. These carbon nanotubes are found to be concentric cylindrical hollow tubes with well-crystallized graphitic layer and can also be in several shapes such as straight, curved, planar-spiral, as well as helix. The nanotubes often have metal particles their tip and the tubes outside wall are coated with amorphous carbon. Early work on gas phase catalytic production of MWNT was the catalytic decomposition of acetylene over iron particles supported on graphite at 700°C and atmospheric pressure [11]. The transmission electron microscopy results revealed that multi-wall carbon nanotubes had formed with length up to 50 µm and diameter ranged from 5 to 50 nm. This work suggested that carbon nanotubes constantly grew with the reaction time as long as the deposited carbon did not cover the metal and the diameters of nanotubes were dictated by the size of metal particles that the tubes were generating from. The deposited carbon from acetylene was further discovered in the form of graphitic filament in Fe and Co supported on graphite catalysts, while it was amorphous in Cu catalyst [12]. Furthermore, the nanotubes from catalyst using silica (SiO<sub>2</sub>) as support were found thinner than the nanotubes from graphite supporting catalyst

[12]. Notably, reducing the reaction temperature from 700°C to 600°C successfully diminished the undesired amorphous carbon. However the degree of the graphitic layers crystalline in nanotubes was also poorer at lower temperature [12]. Additionally, Sun and colleagues studied the effects of temperature oscillation (800±30°C) during acetylene decomposition over cobalt supported on zeolite catalyst [13]. They reported that MWNT contained a number of incomplete carbon layers on both outer and inner shell, and also in the middle part of nanotubes wall (dislocations). These defect structures strongly relate to the frequency of the temperature oscillation. As the oscillation period longer, the defects are less and the overall structure is similar to that grown at constant temperature.

Similar to acetylene, methane decomposition over cobalt catalysts had been reported to be depending on the nature of a support and temperature as well [14]. The conversion of methane was found to be highest on Co supported on alumina (Al<sub>2</sub>O<sub>3</sub>) followed by silica (SiO<sub>2</sub>) and magnesia (MgO). By increasing the reaction temperature to 550-600°C, the stacking angle of graphitic layers was decreased and basal plane became rather parallel to the tubes axis. In addition, methane decomposition over nickel catalysts rendered a conical hollow shape of carbon fibers while the disproportionation of carbon monoxide was observed to contain carbon nanofiber in a cylindrical shape with the basal plane parallel to the tubes axis, [15]. Carbon nanotubes was also grown on Ni-MgO catalyst by decomposition of methane and carbon monoxide at 600°C [16]. A little portion of Ni<sup>2+</sup> in calcined catalysts was reduced to Ni<sub>0</sub> due to the Ni<sub>x</sub>Mg<sub>1-x</sub>O solid solution formation, thus the Ni-species were in high dispersion, causing less amount of

large  $Ni_0$  metal particles formation. Consequently the observed nanotubes were fairly small and uniform in diameter.

Based on the same technique employed in vapor grown carbon fiber (VPGF) production, Endo and co-workers [17,18] were able to produce MWNTs from benzene at 1000-1100°C from ultra fine Fe catalyst. By reducing the pressure of benzene fed into the reactor, they observed hollow carbon tubes having structure similar to arc discharge produced carbon nanotubes. However, these tubes were not well crystallized and coated with amorphous carbon on the tubes' outside wall. These as-formed nanotubes were further treated at 2500-3000°C under argon atmosphere for 15 minutes. After the heat treatment, the remaining are very thin hollow tube and possess a better graphitic crystalline than the product before the heat treatment. Benito and colleagues also reported carbon nanotubes generated from benzene, but with Ni catalyst [19]. They observed different forms of carbon; amorphous carbon layers, graphitic polyhedral nanoparticles with metal particles inside, and MWNTs. At low reaction temperature (650 °C), they reported that the nanotubes were short and curved with more defects in the graphitic layers and graphitic polyhedral nanoparticles were presented at high ratio. As the reaction temperature increased, the tubes were longer and rather straight, exhibiting a better degree of graphitization.

In addition, MWNTs together with metal-filled onion like carbon structure are observed after pyrolysis of benzene at 1140 °C in argon and hydrogen flow with metallocenes, e.g. ferrocene, cobaltocene and nickelocene [20]. Mixture of  $H_2$ -CH<sub>4</sub> gas also produces MWNTs at 750 °C by feeding with ferrocene [21]. Moreover aligned nanotubes film can be achieved at the reactor wall by pyrolysis of ferrocene along with methane, acetylene or butane at 1100°C [22].

# 2.4 Preparation of self-aligned multi wall carbon nanotubes

Generally there are two techniques that can render aligned carbon nanotubes. The first technique is applying a shear force on randomly oriented carbon nanotubes in order to align nanotubes in one direction [23,24]. However, only a moderate degree of orientation and uniformity in length of the MWNT was achieved by this method. The other technique is the direct growth of aligned carbon nanotubes on substrates by using catalytic method. This later approach is particularly in widely interest because it connects with nano-electronic applications of carbon nanotubes.

The direct growth of aligned carbon nanotubes can be achieved by depositing carbon onto a pattern template. Li and co-workers embedded iron particles in mesoporous silica to obtain a catalysts template, then this template catalytically decomposed acetylene at 700°C. After the reaction, aligned MWNT perpendicular to the mesoporous silica surface were obtained [25]. Terrones and colleagues utilized the patterned cobalt on silica substrate, prepared by laser etching of cobalt thin film, to catalytically decompose 2-amino-4,6-dichloro-s-triazine at 950 °C and generating aligned

MWNT growing fairly parallel to the substrate [26]. Ren and his research group employed nickel deposited on glass substrate to grow aligned MWNT at relatively low temperature (660 °C) [27]. The remarkable "forests" of aligned MWNT with nickel particles at the tip were achieved after growing carbon nanotubes by plasma-enhanced hot filament CVD, with acetylene as the carbon source. Furthermore high-purity aligned MWNTs were successfully produced by using mixture of ferrocene and xylene as a source of iron catalyst and a carbon feed stock at 675 °C [28]. By using electron microscope, the aligned MWNT array was observed and grows perpendicularly from the quartz substrates at an average growth rate of 25  $\mu$ m/h. Moreover, the regularly spaced arrays of aligned MWNT were grown from decomposition of ethylene at 700°C on top of patterned iron squares on porous silicon substrates, prepared by evaporating iron film through a shadow mask [29]. Consequently Lee and co-workers also reported that the vertically aligned of MWNT on a large area of silicon substrate could be synthesized by the thermal chemical vapor deposition of acetylene gas with cobalt and nickel catalyst [30]. This research group pointed out that the domain density of metals on substrate is a key to get vertically aligned carbon nanotubes due to the steric hindrance. Thev controlled the domain density of Co-Ni alloy by dipping the substrate in HF and then etching with ammonia gas prior to reaction.

A significant advance in patterned and aligned MWNT was demonstrated by employing microcontact printing and micromolding techniques [31]. In microcontact printing, the self-assembling monolayers of alkylsiloxane were stamped on a quartz substrate in order to mask the lateral adsorption of polymer chains, and then the siloxane was removed by carbonization in argon atmosphere. This will result in patterned mask quartz substrate. For micromolding technique, the polymerizable material was spread out over the quartz plate, and the patterned stamp was then pressed on the top. After that, the materials were polymerized so the pattern of polymer was left on quartz substrate after removing the stamper. After carbonization step in both techniques, the growth of MWNT was initiated by pyrolysis of iron(II) phthalocyanine (FePc) under argon and hydrogen at temperature 800-1000°C, which result in pattern of aligned carbon nanotubes on substrates.

# 2.5 Growth mechanism of carbon nanofibers and nanotubes

The large and economical production scale of carbon nanotubes will become more feasible only when the growth mechanisms are better understood. Although carbon nanotubes just have been recently discovered, the carbon nanofibers and their growth mechanism have been studied for years. Since MWNTs and carbon nanofibers, particularly the type that the graphitic plane parallel to the axis, are very similar, it is reasonable to critically compare these two carbon materials and their production model. This section will start with the review of carbon nanofibers growth mechanism. The more detailed report can be found in the article by Rodriguez [1]. Subsequently the recently proposed model of carbon nanotubes growth by catalytic method will be reviewed as well.

#### 2.5.1 Carbon nanofiber growth mechanism

The first detailed study of growth mechanism of catalytic grown carbon fiber was based on the observation of carbon filament growth by controlled atmosphere electron microscopy (CAEM) by Baker and his co-workers [32-34]. They proposed that, initially, the carbon-containing molecules are adsorbed at the front faces of a metal particle and decomposed which generate carbon in contact with the surface. After that, the carbon specie dissolves in the bulk of metals and diffuses to the rear face of metal where carbon eventually precipitates and forms a filamentous structure. The growth is ceased when significant amount of carbon overcoat the active metal faces and effectively prevent further carbon-containing molecules decomposition. Remarkably the activation energy for filament growth obtained from CAEM experiment exhibits a good correlation with the activation energy for bulk carbon diffusion in metals. This implies that the diffusion of carbon through the catalyst particle is the rate-determining step [32].

The potential that drives carbon to diffuse through the metal particle is still in debate. Originally, it was suggested that the driving force was a temperature gradient created in the particle due to exothermic decomposition at the front face and endothermic precipitation of solid carbon at the trailing faces [33]. Later it was proposed that carbon concentration gradient between the front face and the rear face of metal particle is in fact

a driving force for carbon diffusion step [35]. This argument based on the fact that heat conduction is very fast in the catalyst metals and, also the fact that methane decomposition is endothermic reaction. Sacco and colleagues claimed that the driving force for diffusion of carbon was established between a metal carbide phase formed at the gas-metal interface and the metal-solid carbon interface [36]. Alstrup then modeled that the saturated carbon just below the carbide layer at the front face creates the carbon concentration gradient with the rear face [37]. Safvi and co-workers argued that it is not necessary to assume the presence of surface carbide, but more importantly, it should be recognized that the gas phase carbon activity affect the diffusion coefficient and mass fraction of carbon in the metal, especially at low gas phase activity range [38]. Yang and Chen argued that not all the metal producing nanofibers contain carbon supersaturation and the large amount of heat transfer via radiation can compensate for the endothermic heat of reaction at the front face and the precipitation of carbon at rear face is highly endothermic (40.5 kJ/mol), therefore, they believed that the temperature-driven hypothesis still cannot be ruled out [39].

From the overall mechanism mentioned above, the growth of carbon nanofibers from the catalyst particle is generally related to 3 major region; (i) the gas-metal interface where the adsorption and decomposition of carbon containing molecules take place; (ii) the bulk metal catalysts which determine the amount of dissolved carbon and the rate of carbon diffusion and (iii) the metal-carbon nanofiber interface, whose orientation is responsible for determining the structural characteristics of the material. In order to develop a comprehensive understanding of the growth and control of this form of carbon, it is essential to consider the events occurring at each of these regions.

#### Metal-gas interface

Prior to carbon diffusion, the carbon containing molecules must be adsorbed and decomposed on metal surface. Iron, cobalt and nickel are found to be very active for dissociative adsorption of carbon containing molecules. However different metals or even same metal species but different crystallographic face can behave differently on catalyzing decomposition reaction. Furthermore, by adding the other metals, the metals activity can be greatly enhanced. As an example, tin was added into cobalt and resulted in significantly higher in the catalytic activity for decomposition of ethylene at 600°C [40].

Carbon deposition from hydrocarbon can be greatly improved by the presence of hydrogen [41] or carbon monoxide [42] and this has been interpreted as the result of either reconstruction of the metal surface or the existence of an electron-transfer process between the two components. The minute amounts of sulfur can greatly enhance the activity by promoting the reconstruction of metal surface and lower the structure perfection of the carbon nanofibers as well [43].

Kim and co-workers proposed two possible configurations of adsorbed C2 molecules of hydrocarbon (e.g. ethylene and acetylene) on metal surfaces, "parallel" configuration and "end-on" configuration [44]. Parallel configuration that the carbon-

carbon bond is parallel to the surface, would favor the polymerization-condensation reaction, while "end-on" configuration would transform to "ethylidyne" and eventually decompose to produce solid carbon and methane. Pure metals appear to adsorb ethylene preferably in parallel conformation whereas systems and metal surfaces containing adatoms tend to promote the existence of both conformations. Typically the decomposition of the hydrocarbon in the "end-on" case is much higher since the catalyst can tolerate deactivation via reducing the formation of overcoating graphite.

#### Bulk chemical state of catalyst

The state of the metal catalyst has been debated for years, particularly in the case whether the chemical state of the bulk of the particle could either be metallic or metal carbide. By electron diffraction technique, Oberlin and co-workers revealed the existence of cementite (iron carbide,  $Fe_3C$ ) after the reaction of benzene and hydrogen over iron [45]. Subsequently Audier and colleagues reported the presence of metallic iron together with several iron carbide species, including  $Fe_2C_5$  and  $Fe_3C$ , after the reaction with carbon monoxide [46]. Baker and colleagues then pointed out that the cementite was not the active phase for carbon nanofiber formation from the fact that there is no carbon nanofibers when high purity cementite was used as a catalyst. Yang and Yang demonstrated that the surface of  $Fe_3C$  was essentially inactive for benzene decomposition [41]. However, they suggested that the metallic phase was generated in the presence of hydrogen and the activity toward carbon nanofiber growth was attained. Rodriguez and co-worker reported that Cu-Ni alloys exhibited a high activity toward the production of

carbon nanofibers during reaction in ethylene/hydrogen mixtures [47]. With the in situ electron diffraction techniques, they also demonstrated that the active metal catalyst was the copper-nickel alloy and no evidence for the existence of bulk carbide was found.

From the kinetics study of carbon nanofiber formation as mentioned earlier, the activation energy of carbon nanofiber formation is found to correlate to activation energy for carbon diffusion through the metals, not the metals carbide. However, when carbon-containing molecules interact with metal surfaces, the intermediate states can be formed. Decomposition of these intermediates leads to the formation of the so-called carbidic carbon, which proceeds to dissolve in the bulk and eventually precipitates, thus contributing to the formation nanofiber. Carbidic carbon is defined as surface metal carbide that possesses extraordinarily high activity compared to activity of bulk carbide [48,49].

#### Metal-carbon nanofiber Interface

After diffusion from the front face, dissolved carbon will precipitate in the form of graphite at certain faces of metals that are favorable toward an epitaxial fit between the two components. Yang and Chen showed that, for methane decomposition on nickel with a fcc structure, the (111) and (311) faces of nickel provide the strongest epitaxial covalent bonds with the basal plane of graphite, while the (100) and (110) faces of nickel are the most active for decomposition [39]. Audier and coworkers reported that in the case of Fe

containing alloys with a bcc structure, the catalyst particle was single crystal, which was oriented with its  $\overline{100}$  direction parallel to the carbon fiber axis [50].

## 2.5.2 Catalytic growth of multi wall carbon nanotubes from gas phase reaction

Based on carbon filaments growth mechanism, it has been recognized that the catalyst particle size determines the size of the filament. Sinnott and co-workers suggested that the filament curvature is increased as the metal is smaller, which will result in an increasing strain on the basal planes of the "herring-bone" crystallites [51]. Eventually, a continuous surface of carbon is energetically more favorable and carbon tubes are formed. The authors also logically predicted that the SWNTs would be formed if the metal particle were small enough. Furthermore the authors calculated the energy potential of carbon systems, based on reactive empirical bond-order model, and found that the smaller nanotubes diameter is more stable than the larger tubes and graphene sheet in the case of small number of carbon atom in the system. However, as the number of carbon atoms increased, the bigger nanotubes is more stable. The less stability of graphene sheet is explained by the presence of dangling bond at the edge. Furthermore, the calculation also suggested that double wall carbon nanotube is more stable than SWNT as the number of carbon atoms increase. The authors explained that it is due to the Van der Waals interaction between the tubes layer helps increase the stability.

Dai and his colleagues suggested that a graphene cap from deposited carbon is formed on the nano-size metal particles and, as results, the metal surface energy is lowered and the carbon dangling bonds are stabilized [52]. Then, the later deposited carbon can either add to the cap, resulting in the cap growing away from the particle, or form a following layer of carbon under the former layer leading to MWNTs formation. These researchers called the graphene cap mechanism as "yarmulke" mechanism.

Amelinckx and co-workers proposed that the different carbon morphologies (e.g. helical, twisted nanotubes) stem from the growth rate differences of carbon around the metal particle [53]. The differences in growth rate possibly arise from the rate differences in the catalytic activity and the carbon diffusion rate through the metal particle, on which the nanotubes were nucleated. This growth mechanism totally relies on an assumption that the different crystallographic facets of metal determine the geometry of the carbon nanotubes. However Gao and co-workers proposed a kinetically controlled growth model for helical and zigzag MWNTs [54]. They disputed that the shape of helical nanotubes was indeed controlled by a pairing of pentagon-heptagon carbon rings. They proposed that the hexagonal carbon rings are the basic structure units and the presence of pentagonal carbon ring curve a hexagonal network inward, while the heptagonal carbon ring turns the hexagonal carbon nanotubes can be formed with various morphologies.

## 2.5.3 Catalytic growth of single wall carbon nanotubes from gas phase reaction

For commercialization of the application of SWNTs, the crucial technology is obviously the method for mass production that can produce high quality SWNTs at low cost. It is believed that heterogeneous catalytic reaction will be the leading process for large-scale production of SWNTs. Unlike laser and arc technique, carbon vapor deposition over transition metal catalysts tends to create MWNT as a main product instead of SWNTs. However there are few successful experiments have been reported on producing SWNTs from catalytic hydrocarbon cracking process.

The first observation of SWNT derived from heterogeneous catalysis technique was reported in the work done by the research group at Rice University [52]. They demonstrated the growth of SWNT and a small amount of double-wall carbon nanotubes (DWNTs) by disproportionation of carbon monoxide (CO) at 1200°C with molybdenum (Mo) supported on alumina as a catalyst. From the electron microscope images, SWNT were isolated instead of forming bundles as in laser or arc technique, and mostly attached with metals particle at individual tip. The reported diameter of SWNT varied from 1-5 nm and seemed to be control by the Mo particle size. Subsequently the same research group improved the yield of SWNT by decomposition of ethylene over molybdenum and iron-molybdenum on alumina catalysts [55]. They claimed that SWNT could be produced with no MWNT containing by limiting the carbon supplied to the reaction. To limit the carbon supply, the partial pressure of ethylene was lowered to 0.5 torr (0.06 %)

so that the rate-limiting step was shifted from a diffusion of carbon control to a carbon supply control. As a result, the carbon would be slowly precipitated, allowing it to form the lowest energetic configuration, in this case, the SWNTs. Recently the same research group has produced SWNT by thermal decomposition of iron pentacarbonyl [Fe(CO),] in a flow of CO at elevated pressure (1-10 atm) and at temperature 800-1200°C. The yield of SWNT was increased with temperature and pressure of the system, while the diameter of SWNT was decreased as the pressure is increased. The diameter as small as 0.7 nm, which is the same as diameter of fullerene ( $C_{60}$ ), was achieved at the system pressure of 10 atm. These researchers also discover that, by adding a little amount of methane  $(CH_4)$ in the feed stream, the amount of deposited carbon was significantly enhanced. However the considerably amount of amorphous carbon would overcoat SWNT when the concentration of methane was increased more than 1.4%, unless the reaction temperature was decreased from 1200°C to 1100°C. In addition, they proposed the growth mechanism of SWNT as following. Initially Fe(CO), is decomposed and formed a cluster to the size of 0.7-1.4 nm, and then carbon from the feed gas is deposited on the cluster and formed a hemisphere carbon cap on the cluster, resulting in the nucleation for SWNT growth. Subsequently the lateral deposited carbon will prolong SWNT from the iron cluster and combine into the bundle by Van der Waals force.

Cheng and co-workers demonstrated the rope-like bundles of SWNT derived from the thermal cracking of benzene with ferrocene catalyst and sulfur additive (thiophene) at temperature between 1100-1200°C [56,57]. The synthesized SWNT were roughly aligned in bundles and woven together. Both quality and quantity of SWNT were strongly depending upon the amount of thiophene presented in the system. The optimal amount of thiophene was suggested to be between 0.5 and 5 wt%. The SWNT product was cleaner as the lesser amount of thiophene was added. However, the yield of SWNT was reduced with the amount of thiophene. There were no SWNT observed with out thiophene. On the other hand, MWNT was the main product if thiophene is more than 5 wt%.

Flahaut and colleagues employed the oxide spinels containing binary transition metals of iron, cobalt and nickel catalyst, particularly with iron and cobalt, can fabricate high quality SWNT by catalyzing mixture of hydrogen and methane gases at 1070 °C [58]. They believed that the reduction of oxide spinels renders relatively small metal nanoparticles with narrow size distribution leading to good quality SWNT product in term of yield, size distribution and cleanness.

Recently the research group led by Hongjie Dai at Stanford University has demonstrated the growth of SWNT from methane (CH<sub>4</sub>) with supported catalyst at  $1000^{\circ}$ C [59]. The high temperature was required in growing SWNT in order to overcome high strain energy of small diameter SWNT and to obtain defect-free SWNT. They believe that methane is a critical choice for feeding gas to prevent the amorphous carbon formation because of high temperature stability methane so that methane will not go self-pyrolysis. As expected, they noticed that the nature of catalysts and the support have an

appreciable influence on SWNT production. They observed that iron oxide (Fe<sub>2</sub>O<sub>3</sub>) on alumina or silica support yielded abundant of SWNT, while cobalt oxide (CoO) on alumina or nickel oxide/cobalt oxide (NiO/CoO) on silica delivered moderate amount of SWNT, however, nickel oxide (NiO) did not generate SWNT in their report [59]. Furthermore they discovered that the yield of SWNT could be varied by preparing iron oxide from different precursors or by using bimetallic catalysts [60]. They reported that the catalyst prepared from Fe<sub>2</sub>(SO<sub>4</sub>) aqueous solution provided a better yield of SWNT than catalysts from Fe(NO<sub>3</sub>) solution, and also the bimetallic catalyst Fe/Mo and Fe/Ru considerably improved the growth of SWNT when compare with Fe alone catalyst. Moreover, by using Fe<sub>2</sub>O<sub>3</sub> supported on alumina, this research group observes mainly individual SWNT with some bundle SWNT or double-wall carbon nanotubes but, by using silica as a support, they observed bundles of SWNT, whereas the hybrid aluminasilica (Al<sub>2</sub>O<sub>3</sub>-SiO<sub>2</sub>) support offered the highest yield of synthesized SWNT among investigated support materials.

Furthermore Dai and his colleagues proposed a base growth mechanism of SWNT from methane deposition process since they often observed one closed end of SWNT without any attached or encapsulated metal particles and the other end embedded in the catalyst support [61]. The proposed mechanism begins with the absorption and decomposition of methane on the catalysts surface, which is similar to carbon nanofibers growth mechanism. Afterward the deposited carbon atoms dissolve and diffuse into the metal particle and form a metal-carbon solid solution. Consequently the carbon atoms precipitate out and form the SWNT while the metals particle is still on the substrate surface. Therefore this model suggests that the tubes diameter is determined by the size of metal particles. And the base growth model implies the strong interaction of metal and support so that the metal is attached to the support, resulting in the nanotubes growing out from the metal particles with the closed ends.

## 2.6 Conclusion

Several parameters, such as type of carbon containing gases, type and size of active metal, the nature of the support, the reaction conditions on the formation of nanotubes, etc, can influence the morphology of deposited carbon from catalytic decomposition process. The structure of deposited carbon is also depending upon combination effect of these parameters. This possibly lead to many contradict results and proposed models. However, for carbon nanofiber, it is generally accepted that carbon diffuses from the front face of catalyst, where it deposits, to the rear face of catalyst, where it forms filaments. In the case of SWNT, the understanding of growth mechanism is still in confusion because there is a few successful experiments have been reported and not many of them pays attention to catalysts characterization. Therefore the production of SWNT via catalytic decomposition of carbon containing gases still has a lot more to explore.

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## **CHAPTER 3**

## PRELIMINARY STUDY OF CATALYTIC CARBON NANOTUBES PRODUCTIONS FROM CARBON CONTAINING GASES

### 3.1 Introduction

As mentioned in the previous chapter, many hydrocarbon gases and carbon monoxide can generate several deposited carbon structures over supported metal catalysts. These deposited carbons, including carbon nanofibers and carbon nanotubes, highly depend on reacting gases, reaction conditions and definitely the catalysts.

Recently several researches groups have reported the generation of single-wall carbon nanotubes (SWNT) from decomposition of carbon monoxide [1,2], methane [3], ethylene [4], and benzene [5,6]. Group VIII metal, especially Fe, is a major metallic catalyst, which is widely studied [2-6]. More recently bimetallic catalysts are reported to more efficiently produce SWNTs [7,8].

In this chapter, a large number of preliminary attempts have been made to generate carbon nanotubes, particularly SWNTs, via heterogeneous catalysis technique. Various gases (acetylene, carbon monoxide and methane), catalyst metals (nickel, cobalt, iron, molybdenum, and tungsten), supports (silica, titania, and alumina) as well as reaction conditions have been experimentally implemented and therein summarized.

### 3.2 Experimental

#### 3.2.1 Catalyst preparation

Many catalyst supports has been used for preparing catalysts. They are MCM-41, silica gel (SiO<sub>2</sub>), titanium dioxide (TiO<sub>2</sub>),  $\gamma$ -alumina (Al<sub>2</sub>O<sub>2</sub>) and magnesium-aluminum oxide (MgAlO). Some support materials are commercially available and some are prepared in the laboratory. For instances, titanium dioxide P-25 was obtained from Degusssa Corp, alumina was obtained from Mark V laboratory, and silica gel was purchased from Aldrich.

MCM-41 type mesoporous silica support was prepared as in work done by Ioneva [9]. A 233 g of 25 wt% hexadecyltrimethylammonium bromide (CTAB) aqueous solution was first mixed with solution containing: 25 g of precipitated silica (HiSil-915 from PPG Industries), 100 g of tetramethylammonium silicate (10 wt% silica and ratio of tetramethulammonium/silica = 1/2 from SACHEM) and 30 g of 25 wt% tetramethylammonium hydroxide aqueous solution (Aldrich). The mixture was then loaded in a 1000 ml Teflon-lined stainless steel autoclave (PARR reactor), and left to be stirred overnight. After that, the reactor temperature was raised to 150°C and kept at this temperature for 24 hours with continuously stirring and under autogeneous pressure. The

reactor was then cooled down to room temperature and the solid product was obtained by filtering and washing with water. The recovered solid product was then dried at ambient condition and later calcined in static air at 500°C for 7 hours.

All catalysts were prepared by incipient wetness impregnation technique. The metals precursors were nickel nitrate, cobalt nitrate, iron sulfate, ammonium heptamolybdate and ammonium metatungstate. As an example, the Co:Mo/Silica gel was prepare as following. First, the aqueous solutions of cobalt nitrate and ammonium heptamolybdate were prepared by dissolving the metals salt in deionized water. The amount of water was kept at incipient-wetness conditions, which is 0.63 cm<sup>3</sup> of water to a gram of silica gel. The metals aqueous solution was then dropwise introduced to the support with continuously stirring by mortar and pestle. Then catalysts were left to dry in ambient air at room temperature for a few hours, and then in oven at 80°C for 12 hours, and finally calcined in flowing air at 500°C for 3 hours.

#### 3.2.2 Reaction

Catalytic reactions were carried out in both a fixed bed and a floating boat reactor. In fixed bed reactor, the quartz tube was set vertically and the gases was fed from the top of the reactor and the catalysts were placed at the middle of reactor supporting by quartz wools and quartz rod. In the case of floating boat reactor, the catalysts were put in a ceramic boat and then inserted into the middle of reactor, which was set in horizontal configuration. In order to get rid of the quartz wools contamination, the floating boat reactor was prefer and used as a major reactor in subsequent chapters. Electric oven equipped with temperature control was used as a heating source in both reactor types. Temperature of the reaction was measured by a thermocouple. The tip of thermocouple was positioned, with out touching, close to the catalyst. The thermocouple's tip was hung above the catalyst in the case of floating boat reactor and located in the quartz wools in the case of fixed bed reactor. All the gases, e.g. helium, hydrogen, acetylene, ethylene, methane and carbon monoxide, were fed into the reactor with the mass flow controllers (Porter instrument). All the mass flow controllers were calibrated with the particular gases prior to the experiments.

Typically 0.1-0.5 g of the calcined catalyst was placed in the middle of the quartz reactor. First the catalysts were reduced in hydrogen flow with the hydrogen flowrate of 100 sccm—standard cubic centimeter per minute. The temperature was raised from room temperature to 500°C in one hour and kept constant at this temperature under hydrogen flow for 30 more minutes. Then the hydrogen flow was shut off and helium flow was introduced at the flowrate of 100 sccm. The temperature was then set to linearly increase to the desired reaction temperature, typically at 700°C, under the helium flow. Once the temperature reached the setting point, the reacting gases were introduced and the flow of both helium and reacting gases were adjust to the preferred ratio with the total flowrate of 100 sccm. The reaction time has reached, the reacting gases were turned off and the samples were cooled down to room temperature with the helium flow.

The spent catalysts with deposited carbon were studied by transmission electron microscope (TEM) model JEOL 2000FX. For TEM observations, the catalysts sample were first dispersed in methanol by sonication for about 10 minutes. Then these samples were dropped on carbon coated copper grids and left to dry prior to TEM observation.

### 3.3 Results and discussions

Table 3-1 is the summary of all preliminary study in this chapter. First the 2% nickel catalyst was prepared on the MCM-41 materials. The idea to use MCM-41 as a support material was that it could be used as a template to grow aligned carbon nanotubes, similar to the work done by Li and co-workers [10]. The MCM-41 was chosen because it has a constant pore diameter and arrange in a hexagonal pattern, as illustrated in TEM results (Figure 3-1). The 2% Ni/MCM-41 catalyst was then reacted with 10% acetylene gas at 500, 600 and 700°C. There were not carbon nanotubes in TEM observation from the samples that perform the reaction at 500 and 600°C. However, as shown in TEM image (Figure 3-2), the multi-wall carbon nanotubes (MWNTs) were obtained from 2% Ni/MCM-41 at 700°C with acetylene gas and were not aligned. The observed MWNTs were found to be abundant and mostly were about 10 nm in diameter and possibly up to several microns in length. These MWNTs were partially covered with amorphous carbon. The similar MWNTs were resulted when repeated the experiments with the same Ni/MCM-41 catalysts, but without hydrogen treatment before the reaction.

Catalyst	Gases	Temperature	ТЕМ
2% Ni/MCM41	10% C <sub>2</sub> H <sub>2</sub> in He	500 °C	No nanotube
2% Ni/MCM41	10% C <sub>2</sub> H <sub>2</sub> in He	600 °C	No nanotube
2% Ni/MCM41	10% C <sub>2</sub> H <sub>2</sub> in He	700 °C	MWNTs
2% Ni/MCM41 (no reduction)	10% C <sub>2</sub> H <sub>2</sub> in He	700 °C	MWNTs
2% Ni/MCM41	100% CO	1000 °C	No deposited carbon
2% Mo/MCM41	100% CO	700 °C	No nanotube
10% Mo/MCM41	100% CO	700 °C	No nanotube
Co-Mo HDS catalyst	100% CO	700 °C	Carbon nanofiber and bundles of SWNTs
Co-Mo HDS catalyst	100% CO	1000 °C	No nanotubes
2% Co-Mo (2:1 by mole)/MCM41	100% CO	700 °C	Small amount of SWNTs
10% Co-Mo (2:1 by mole)/MCM41	100% CO	700 °C	Carbon nanofiber and bundles of SWNT
Co-Mo HDS catalyst	10% C <sub>2</sub> H <sub>2</sub> in He	700 °C	MWNTs
Ni-Mo HDS catalyst	10% C <sub>2</sub> H <sub>2</sub> in He	700 °C	MWNTs
10% Co-Mo (2:1 by mole)/MCM41	Mix 50% CO and 50% H <sub>2</sub>	700 °C	SWNT
10% Co-Mo (2:1 by mole)/MCM41	10% $C_2H_2$ in He	700 °C	MWNT

Table 3-1 Summary of TEM observation from certain experiments of different gases and catalysts

rable 3-1 (communed)	Table	3-1	(continu	ied)
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Catalyst	Gases	Temperature	ТЕМ
10% Co-Mo (2:1 by mole)/MCM41	100% CH₄	700 °C	Mix MWNTs and SWNTs
10% Co-Mo (2:1 by mole)/Silica gel	100% CO	700 °C	Bundles of SWNTs
10% Co-W (2:1 by mole)/silica gel	100% CO	700 °C	Bundles of SWNTs and carbon nanofibers
10% Co-Mo (2:1 by mole)/TiO <sub>2</sub>	100% CO	700 °C	Graphite
10% Co-Mo (2:1 by mole)/MgAlO	100% CO	700 °C	No nanotubes
10% Co-Mo (2:1 by mole)/Alumina	100% CH₄	900 °C	SWNTs and majority of carbon nanofibers
10% Co-Mo (2:1 by mole)/Silica gel	100% CH₄	900 °C	carbon nanofibers with a little of SWNTs



Figure 3-1 TEM image of synthesized MCM-41



Figure 3–2 TEM images of carbon nanotubes obtained from 2% Ni/MCM-41 catalyst with 10% acetylene in helium at 700°C

The Ni/MCM-41 catalyst was next tested with carbon monoxide at 1000°C and the result was virtually no deposited carbon. It is important to note here that, when contact with carbon monoxide at temperature below 150°C, nickel can form nickel carbonyl that is a highly poisonous, odorless and stable gas [11]. Therefore the reactor containing nickel in a catalyst should be purged with inert gas while it is cooling down.

Further study on CO gas with Mo/MCM-41 catalyst at 500 and 700°C showed no formation of carbon nanotubes. Then the idea of binary metal catalyst was quickly tested by using a commercial hydrodesulfurization (HDS) catalyst containing Co and Mo on alumina. The Co-Mo HDS catalyst was put in the reactor and performed the reaction at 700 and 1000°C. Strikingly this catalyst at 700°C showed some SWNT in the TEM (Figure 3–3), but there was no carbon deposits at 1000°C.

The Co-Mo/MCM-41 with the molar ratio of Co:Mo = 2:1 and total metal of 2 and 10% by weight was then prepared and studied for carbon nanotubes production. Interestingly this catalyst was found to generate SWNT when carbon monoxide was used as a carbon source. The reaction temperature was 700°C, which is lower than the temperature reported by other research groups [1–6]. As shown in Figure 3–4, the observed SWNTs were in bundles or ropes with the individual tube's diameter of about 1 nm.



Figure 3-3 TEM of SWNT produced from Co-Mo/HDS catalyst with CO at 700°C


Figure 3-4 SWNTs from Co-Mo/MCM-41 with CO at 700°C

However, when using the acetylene gas instead of carbon monoxide, MWNTs was observed as a major product in Co-Mo/HDS, Ni-Mo/HDS and 10% Co-Mo/MCM-41, while the fairly equal amount of SWNTs and MWNTs were achieved when methane was fed.

In order to test the effect of the support, 10% wt of Co-Mo on silica gel were prepared and tested with the same reaction condition. TEM results showed that SWNTs from Co-Mo catalyst on Co-Mo/silica gel support (Figure 3–5) was virtually not different from catalyst using MCM-41 as a support. Therefore later study used silica gel as support instead of MCM-41, which is a time consuming during the preparation.

Interestingly, tungsten (W), which is in the same group with Mo on the periodic table, showed similar results when Co-W/silica gel was utilized with CO at 700°C. The TEM image of SWNTs obtained from Co-W/silica gel catalyst is showed Figure 3–6.



Figure 3-5 SWNTs from Co-Mo/silica gel with CO at 700°C



Figure 3-6 TEM of SWNTs with some graphitic nanofibers from Co-W/silica gel catalyst with CO at 700°C

The titanium dioxide or titania  $(TiO_2)$  as a support was then tested. The CO decomposition over Co-Mo/titania at 700°C yields graphitic carbon as shown in Figure 3–7. However there was no carbon nanotubes observed in TEM when MgAlO was used as a support on Co-Mo and react with CO at 700°C.

The catalysts, Co-Mo/Alumina and Co-Mo/silica gel, were also tested with methane at 900°C. As shown in Figure 3–8, carbon nanofibers or MWNTs were observed together with SWNTs. It is worth to note here that, at 900°C, only alumina or silica alone can generate deposited carbon from methane.



Figure 3–7 TEM image of carbon deposited on Co-Mo/titania reacted with CO at 700°C



Figure 3-8 TEM images of carbon deposited from methane decomposition at 900°C (a) Co-Mo/Alumina (b) Co-Mo/Silica gel

#### 3.4 Conclusion

From this preliminary study, Co and Mo or Co and W on silica with carbon monoxide as a carbon source at temperature 700°C have shown to be the most promising catalysts for SWNTs production. Methane also shows ability to produce SWNTs, but the product also contains high amount of MWNT. Furthermore, acetylene, the most reactive gas in this study, has demonstrated to generate MWNTs with various catalysts.

However, due to the limitation of TEM, further characterization on both nanotubes' quality and quantity is needed. In chapter 4 and 5, the temperature program oxidation technique and the Raman spectroscopy will be employed and more systematic study on catalysts and reaction conditions for SWNTs will be presented.

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## **CHAPTER 4**

# CONTROLLED PRODUCTION OF SINGLE-WALL CARBON NANOTUBES BY CATALYTIC DECOMPOSITION OF CARBON MONOXIDE ON BIMETALLIC CO-MO CATALYSTS

### 4.1 Introduction

Single-wall carbon nanotubes (SWNT) have shown unmatched electrical and mechanical properties [1], which might lead to a variety of new applications. However, the low availability of high-quality nanotubes and the high costs associated with the current synthesis methods would be a serious impediment for large-scale production in any commercial endeavor. The production of multi-wall nanotubes (MWNT) by catalytic hydrocarbon cracking on supported metals is now on a commercial scale [2] but the production of SWNT by laser [3] and arc [4] techniques is still in the gram scale. A cost effective process for the production of SWNT will only emerge when today's gram-scale technology advances to a ton-scale technology, in a way similar to the production of chemical commodities. In fact, it is conceivable to design a continuous fluidized-bed catalytic reactor that could produce carbon nanotubes in a gas-phase process. To reach

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this point however, an excellent control over the activity, selectivity, and catalyst life is necessary.

In many catalytic processes found in the chemical industry, the separation steps that precede or follow the chemical reactor represent the largest portion of the capital and operating costs. On the other hand, while the cost of the catalyst is usually minimal in comparison to the overall cost of the plant, the catalyst is the key factor that determines how much should be spent in the separation steps. For example, a catalyst with high tolerance to the presence of impurities may reduce the costs of feed pretreatment. At the same time, a very selective catalyst can greatly reduce the separation costs involved in the purification of the product. Selectivity is in many cases the most important property that an efficient catalyst should exhibit. The same concepts will apply to the production of nanotubes in industrial scale, i.e. a catalyst should be designed with selectivity high enough to minimize the subsequent purification steps. This is particularly important for the catalytic production of SWNT, which in most cases produces MWNT, amorphous, and graphitic forms of carbon as by-products.

In comparison to most of the other methods currently used for the synthesis of SWNT, the potential advantage of using a gas-phase catalytic method is that the solid catalyst can be tailored to maximize selectivity. Until now, however, in most attempts to produce nanotubes by the catalytic method, little attention has been paid to the optimization of the selectivity towards SWNT. In fact, the majority of the reports found

in the literature disclose formation of MWNT or a combination of amorphous carbon, MWNT, and graphitic carbon [5,6]. Only a few papers [7-11] have reported the formation of SWNT by catalytic decomposition. One of the greatest limitations in the current technology is the inability to obtain a simple and direct quantification of the different forms of carbon obtained in a particular synthesis. Nowadays, electron microscopy is the characterization technique most widely employed to determine the fraction of SWNT present in a particular sample. However, transmission electron microscopy (TEM) can only provide a qualitative description of the type of carbon species produced. Obtaining semi-quantitative determinations of the distribution of the different carbon species in a sample, with any statistical significance is time consuming and the method could not be applied as a routine quality control to large-scale operations.

In this chapter, a breakthrough in the controlled synthesis of SWNT is described. Controlled production is defined as the ability to modify the selectivity of a catalyst by changing catalyst parameters, such as composition and support, combined with the ability to obtain a reliable quantitative measurement of the yield and selectivity of SWNT produced. This measurement should be direct and easy to conduct, so changes in selectivity during catalyst selection or steady-state production can be readily detected, facilitating the reproducibility and quality control.

#### 4.2 Experimental Results

Several transition metal catalysts have been shown to be active for generation of carbon nanotubes [12,13]. Among the various formulations that we have investigated, a Co-Mo/SiO<sub>2</sub> catalyst, containing 6 wt % total metals and a Co:Mo molar ratio of 1:2, exhibited the highest selectivity towards SWNT. This catalyst was prepared by incipient wetness impregnation of aqueous solutions of Cobalt Nitrate and Ammonium Heptamolybdate, followed by drying in oven at 80 °C and calcination in flowing air at 500 °C. For the production of nanotubes, 100-500 mg of calcined catalyst was placed in a horizontal quartz tubular reactor, heated in  $H_2$  up to 500 °C, and then in He to 700 °C. Subsequently, CO was introduced at this temperature and at a flowrate of 100 cm<sup>3</sup>/min for the production of nanotubes. The product was inspected in a TEM, model JEOL JEM-2000FX at 200 kV. As shown in Figure 4-1, SWNTs were observed in large quantities, most of them aligned as bundles. From the TEM pictures, it was observed that the diameter of the individual tubes was about 1 nm. While small quantities of amorphous carbon were observed covering the bundles of SWNT, no evidence of MWNT or graphitic carbon was observed on this sample. The presence of SWNT on this sample was further confirmed by Raman spectroscopy, conducted at room temperature and using 532 nm excitation. The spectrum exhibited a strong line in the range 1580-1590 cm<sup>-1</sup>, normally observed in SWNT [14].

It is important to note here that not all Co-Mo formulations investigated were equally effective in producing SWNT. For example, while Mo samples produced no SWNT at 700 °C, when Mo was added to Co, the selectivity towards SWNT greatly increased, which indicates that some sort of synergism between Co and Mo makes the combination of the two metals effective. As illustrated in Figure 4–2, the TEM image shows that the catalyst with a Co:Mo molar ratio of 2:1 resulted in a significant fraction of carbon nanofiber, as opposed to the catalyst with a molar ratio of 1:2, which mainly produced SWNT.

As commonly employed to characterize carbonaceous deposits on heterogeneous catalysts, the standard Temperature Programmed Oxidation (TPO) technique have been developed for quantifying the amount of SWNT produced on the Co-Mo catalyst [15,16]. In order to conduct the TPO, a continuous flow of 5 %  $O_2$ /He is passed over the catalyst containing the carbon deposits while the temperature is linearly increased (11°C/min). The evolution of CO<sub>2</sub> produced by the oxidation of the carbon species is monitored by a mass spectrometer. Quantification of the evolved CO<sub>2</sub>, calibrated with 100 µl pulses of pure CO<sub>2</sub> and oxidation of known amounts of graphite, gives a direct measurement of the amount of carbon that gets oxidized at each temperature. This method appears particularly suitable for the quantitative characterization of SWNT because SWNT are oxidized in a relatively narrow temperature range, which lies above the temperature of oxidation of amorphous carbon and below the oxidation of MWNT and graphitic carbon. In agreement with our results, previous TGA studies [3,17] have shown that, in the

absence of a catalyst, the ignition temperature of SWNT is 100 °C higher than that of  $C_{60}$  fullerenes and 100 °C lower than that of MWNT.



Figure 4-1 TEM images showing SWNT produced by decomposition of 50% CO/He at 700 °C on a CO-Mo/SiO2 catalyst, 6 wt% total metals, Co:Mo molar ratio of 1:2. Inset shows the detail of a front view of a SWNT bundle.



Figure 4-2 TEM images showing mixture of SWNT and carbon nanofiber produced by 50% CO/He at 700 °C on a Co-Mo/SiO2 catalyst, 6 wt% total metals, Co:Mo molar ratio of 2:1.

Figure 4-3 illustrates the TPO profiles of the carbon species produced on the Co:Mo/SiO, catalyst, which, as described above, exhibited the highest selectivity towards SWNT. This sample presented a small oxidation peak centered at around 330°C, which is assigned to amorphous carbon, and a major peak marked in the figure with an arrow, centered at about 510°C, which is ascribed to the oxidation of SWNT. Two important reference samples were investigated by TPO and their profiles are included in Figure 4-3. The first reference was a graphite powder physically mixed with the bare Co:Mo catalyst. The oxidation of this form of carbon occurred at very high temperatures, starting at about 700°C, and completed after holding 30 minutes at 800°C. The second important reference sample investigated was a commercial sample of purified SWNT, obtained from Tubes@Rice (Rice University). This sample comes in a liquid suspension of 5.9 grams/liter, containing a non-ionic surfactant Triton X-100. To conduct the TPO experiment, this suspension was impregnated on the Co:Mo/SiO, catalyst to get 0.6 wt % SWNT on the sample. As shown in Figure 4–3, the TPO of this impregnated sample exhibited two peaks, a low-temperature one that corresponds to the oxidation of the surfactant and a second one centered at 510°C, which corresponds exactly to the position that we ascribed to the oxidation of SWNT. To corroborate that the first peak was indeed due to the oxidation of Triton, an identical sample was prepared with a blank solution containing only the surfactant in the same concentration. The TPO shows that indeed that was the case. The quantification of the amount of SWNT in the sample from the  $CO_2$  produced gave a value of 0.64 wt %, in good agreement with the amount of SWNT loaded in the sample (0.6 wt %).

With varying Co:Mo ratios and type of catalyst supports, different catalyst formulations leading to different SWNT selectivities has been tested by using TPO. For example, Figure 4-4 shows the clear synergistic effect exhibited by Co and Mo. In the first place, Mo alone does not produce carbon nanotubes, and only exhibits a small lowtemperature peak corresponding to amorphous carbon. Similarly, Co alone is not selective for the production of SWNT, and generates mainly graphitic carbon and MWNT. By contrast, the combination of the two metals in appropriate ratio results in high selectivity for SWNT. By using TPO we have been able to investigate the effect of varying the Co:Mo molar ratio in the Co-Mo/SiO<sub>2</sub> catalysts. Figure 4-5 shows that, in agreement with the TEM characterization, the TPO of the Co:Mo = 1:2 sample indicates that this sample produced mostly SWNT, with a small amount of amorphous carbon. An increase in the Co:Mo ratio did not enhance the production of SWNT, but it did accelerate the formation of MWNT and graphitic carbon, as shown by the increasing size of the peaks in the region 600-700°C. From the TPO data, selectivity values were estimated by curve fitting. They were 57 % SWNT and 31 % MWNT for the Co:Mo (2:1), 80 % SWNT and 4 % MWNT for the Co:Mo (1:1), and 88 % SWNT and 4 % MWNT for the Co:Mo (1:2). It is important to note that, in all cases, the quantitative data agreed very well with the qualitative observations made by TEM.



Figure 4–3 Temperature programmed oxidation (TPO) of all the carbonaceous species present in the Co-Mo/SiO<sub>2</sub> catalyst (Co:Mo = 1:2) after decomposition of 50% CO/He at 700 °C, compared to similar TPOs of a graphite reference and commercial SWNT obtained from Tubes@Rice. Also included is the TPO of the blank solution, containing a surfactant, in which the commercial SWNT are dispersed. All the references were physically mixed with bare Co-Mo/SiO<sub>2</sub> catalyst. The temperature ramp was 11 °C/min.



Figure 4-4 Temperature programmed oxidation (TPO) of all the carbonaceous species present in the Co-Mo/SiO<sub>2</sub> catalyst (Co:Mo = 1:2) after decomposition of 50% CO/He at 700 °C for 1 h, compared to monometallic Co/SiO<sub>2</sub> and Mo/SiO<sub>2</sub> catalysts, treated in identical way.



Figure 4-5 Effect of Co:Mo ratio in the distribution of different carbonaceous species produced by decomposition of 50% CO/He at 700  $^{\circ}$ C for 1 h, as measured by TPO, using a temperature ramp of 11  $^{\circ}$ C/min. The arrow indicates the center of the peak corresponding to the oxidation of SWNT.

The use of TPO also allows for a systematic screening of operating conditions. For example, the TPO profiles from products run at different reaction temperatures showed that the selectivity to SWNT had a maximum at about 700°C. Similar analysis was done to investigate the effects of gas phase concentration and reaction time at a given temperature.

Even though the results presented in this chapter demonstrate that the TPO method is a very efficient way of quantifying the production of carbon nanotubes, it is important to be aware of some limitations of the method. The TPO is a catalytic process in which the metals present in the sample catalyze the oxidation of the carbon species. Therefore, if the nature of the catalyst is significantly changed, the position of the oxidation peaks may appear shifted even when the carbon structures are the same. Therefore, in order to use this method properly, a complete analysis of the family of catalysts and the operating conditions needs to be done together with known references, as it has been done in the present chapter.

By a proper quantification of the amount of SWNT produced as a function of time at varying temperatures and gas phase concentrations, the reliable kinetic parameters will be able to obtained, which will lead to the mechanism of SWNT formation. Several interesting trends are already apparent in the present data. For example, the clear synergism shown by Co and Mo illustrates the complexity of the SWNT growth mechanism, which is today much less understood than the growth of MWNT. Previous studies [10] have shown that the decomposition of CO on Mo catalysts yield SWNT at 1200°C. However, at the much lower temperatures employed in this study, 700°C, Mo alone was unable to form any carbon nanotube. By contrast, Co alone formed significant amounts of MWNT, some graphite, and relatively small amounts of SWNT. Interestingly, when Mo and Co were simultaneously present in the catalyst, the production of MWNT was drastically suppressed while the production of SWNT was enhanced.

To understand the suppression of MWNT by addition of Mo, one needs to refer to the well-established mechanism of MWNT formation. In that case, the formation of nanotubes occurs by the formation of metal carbide followed by diffusion and precipitation of carbon at the other end of the particle [18,19]. Baker and co-workers [5] have proposed that the precipitation step and formation of filamentous structures is a structure-sensitive process that only occurs on certain crystallographic planes. In our case, it appears possible that the interaction between Co and Mo results in an inhibition of this structure-sensitive step, leading to a decrease in the formation of MWNT. By contrast, the formation of SWNT may need the contribution of both Co and Mo. Recent studies [20] have reported the appearance of SWNT during the decomposition of hydrocarbons on multi-metallic Ni-Co-Fe catalysts. Unfortunately, in that report TEM was the only characterization technique employed and it was not indicated whether a large fraction of MWNT was also present.

## 4.3 Conclusions

In summary, this chapter has demonstrated a methodology called "controlled production" of SWNT, based on a simple quantification method that allows us to conduct systematic screening of catalyst formulations and operating conditions. By this methodology, a Co-Mo catalyst formulation that yields high selectivity towards SWNT has been identified. Also, through the application of this quantitative analysis kinetics studies can be carried out, which will provide relevant mechanistic information about the growth of SWNT.

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## **CHAPTER 5**

# SYNERGISM OF COBALT AND MOLYBDENUM IN THE CATALYTIC PRODUCTION OF SINGLE WALL CARBON NANOTUBES BY DECOMPOSITION OF CARBON MONOXIDE

#### 5.1 Introduction

The fascinating properties of single-wall carbon nanotubes (SWNT) have opened a great number of potential applications for these unique materials. However, the high costs of the current production methods and the difficulty in making them available for large-scale manufacture have slowed down the process of bringing nanotube-based technologies to commercial practice. Following the original arc-discharge method [1,2], other synthesis methods have been investigated, including laser ablation [3,4] and plasma discharge. To develop a cost-effective operation for the manufacture of SWNT a drastic change in the production scale is necessary. The catalytic method for production of nanotubes has been known for a long time, but this method typically results in production of multi-wall carbon nanotubes (MWNT) or carbon nanofibers [5]. In recent years, several researchers have focused their attention to the production of SWNT by catalytic decomposition of carbon-containing molecules [6–11]. This method is sometimes referred to as chemical vapor deposition [12]. We have recently pointed out that the catalytic decomposition method is suitable for scaling up and for achieving a "controlled" *production*" of single-wall carbon nanotubes (SWNT) [13]. By this term we imply the ability to control the selectivity towards SWNT by changing catalyst parameters and operating conditions, combined with the ability to obtain a reliable quantitative measurement of the amount of SWNT produced.

In the previous chapter, a simple quantification method of the SWNT produced by catalytic decomposition of CO was described and directed to conduct a systematic screening of catalyst formulations. This quantification method was based on the standard Temperature Programmed Oxidation (TPO) technique commonly employed in catalysis research to quantify and investigate the nature of carbonaceous deposits on spent catalysts. In this method, a continuous flow of an oxygen-containing gas is passed over the catalyst containing the carbon deposits while the temperature is linearly increased. Quantification of the CO<sub>2</sub> evolved gives a direct measurement of the amount of carbon that gets oxidized at each temperature. This method appears particularly suitable for the quantification of SWNT in a set of samples of similar composition and comparable carbon contents. In such set of samples, SWNT are oxidized in a relatively narrow temperature range, which lies above the temperature of oxidation of amorphous carbon and below the oxidation of MWNT and graphitic carbon. The position of the oxidation peak corresponding to the SWNT produced on the catalyst was exactly matched with that of pure SWNT obtained from Tubes@Rice (Rice University), mechanically mixed with the same catalyst powder used in the production of nanotubes.

By using this methodology, it can be demonstrated that Co is not selective for the production of SWNT and Mo is inactive in the temperature range investigated, i.e., 600-800°C. However, bimetallic Co-Mo catalysts with low Co:Mo ratios exhibited a real synergism that resulted in high selectivity towards SWNT. Previous reports [14] have shown improved performances of bimetallic catalysts in comparison to monometallic, but none of the previously investigated systems showed the dramatic synergism exhibited by Co and Mo in the decomposition of CO.

In that case, the reaction temperature, CO concentration, and reaction time were kept constant at 700°C, 50 % CO in He, and 30 min, respectively. In this contribution, we have employed the same methodology to investigate the effects of varying the operating parameters in order to optimize the production of SWNT. In addition, we have characterized the state of Co and Mo on the catalysts before and after the production of SWNT by X-ray absorption spectroscopy (EXAFS and XANES) in an effort to understand the synergism exhibited by these two metals.

### 5.2 Experimental

The Co, Mo, and Co-Mo catalysts were prepared by impregnating a silica gel support (SiO<sub>2</sub>, from Aldrich, 70-230 mesh, average pore diamter 6 nm, BET area 480  $m^2/g$ , pore volume 0.75 cm<sup>3</sup>/g), with aqueous solutions of Cobalt Nitrate and/or Ammonium Heptamolybdate to obtain the bi- or monometallic catalysts. The liquid/solid ratio was kept at incipient-wetness conditions, which for this support corresponds to 0.63

cm<sup>3</sup>/g. In all cases, the total metal content was kept at 6 wt %. The bimetallic catalyst was prepared with a Co:Mo molar ratio from 1:4 to 2:1. The catalysts were first dried in air at room temperature, then in oven at 80°C for 12 hours, and finally calcined in flowing air at 500°C. A Micromeritics ASAP 2010 adsorption apparatus was used to obtain the BET surface area, pore volume and pore size of the supports and catalysts.

For the production of nanotubes, 100-500 mg of calcined catalyst was placed in a horizontal quartz tubular reactor, heated in H<sub>2</sub> up to 500°C, and then in He up to 700°C. Subsequently, CO was introduced at the same temperature, at a flow rate of 100 cm<sup>3</sup>/min and kept under these conditions for a given period of time, which ranged from 3 to 60 min. A combination of transmission electron microscopy (TEM), Raman spectroscopy and temperature programmed oxidation (TPO) techniques was used to characterize the carbon species produced during the reaction period. The TEM images were obtained in a JEOL 2000FX-TEM. For these observations, the samples were prepared by sonicating in methanol for 10 min followed by deposition of a few drops of the resulting suspension on the TEM grid. The laser Raman spectra were obtained in a JASCO TRS-600SZ-P single monochromator spectrophotometer, equipped with a CCD (charge-couple device) with the detector cooled to about 153 K with liquid nitrogen. The excitation source was the 514.5 nm Spectra 9000 Photometrics Ar ion laser. All the spectra were recorded with the samples under ambient conditions. TPO measurements were conducted by passing a continuous flow of 5 % O<sub>2</sub> in He over the catalyst containing the carbon deposits, while the temperature was linearly increased at a rate of 12°C/min. The evolution of CO,

produced by the oxidation of the carbon species was monitored by a MKS mass spectrometer. Quantification of the evolved  $CO_2$  was achieved by calibrating with 100 µl pulses of pure  $CO_2$  and oxidation of known amounts of graphite. No CO was observed during any of the TPO experiments

X-ray absorption (EXAFS/XANES) data were obtained at the National Synchrotron Light Source (NSLS) at Brookhaven National Laboratory, Upton, New York using beam line X-18b equipped with a Si (111) crystal monochromator. The X-ray ring at the NSLS has an energy of 2.5 GeV and a ring current of 80-220 mA. The samples were investigated as fresh samples after the initial treatment in H<sub>2</sub> (500°C)/He (700°C) and as spent samples after different reaction periods for the growth of carbon nanotubes. In both cases, the samples were not exposed to the air, but directly transferred from the reaction chamber to a He glove bag, where they were wrapped in Kapton tape and stored in He-purged sealed vessels. The EXAFS experiments were conducted in a stainless steel sample cell at liquid nitrogen temperature. Six scans were recorded for each sample. The average spectrum was obtained by adding the six scans. The pre-edge background was subtracted by using power series curves. Subsequently, the post-edge background was removed using a cubic spline routine. The spectra were normalized by dividing by the height of the absorption edge. To obtain structural parameters, theoretical references for Co-Co, Co-O, Mo-O, Mo-C and Mo-Mo bonds were obtained by using the FEFF and FEFFIT fitting programs from the University of Washington [15-17]. In this routine, the Debye Waller factors for each bond type ( $\sigma$ ), the edge energy difference ( $\Delta E_{o}$ ), the

coordination number N, and the difference in bond distances ( $\Delta R$ ) with respect to the theoretical reference, were used as fitting parameters. The quality of the fit was determined using the r-factor, which gives a sum-of-squares measure of the fractional misfit. Therefore, the smaller the r-factor, the better the fit is. For good fits, the r-factor is always less than or about 3%.

#### 5.3 Results

One of the objectives of this work was to investigate the influence of the various operating parameters on the carbon yield and selectivity to SWNT. Here we must point out the way that yield is defined in the gas phase catalytic method, which is different from that normally employed in the other methods of producing carbon nanotubes. We define yield as the ratio of the weight of SWNT deposited per total catalyst weight. Similarly, selectivity is defined as the fraction of carbon products deposited on the catalyst that is in the form of SWNT.

Table 5–1 summarizes some of the data, as calculated from the TPO profiles. The quantification of the different forms of carbon was done by fitting the entire profiles with gaussian-lorentzian mixtures. The peak centered at 500-530°C represents the carbon in the form of SWNT. It must be noted that the shape and position of a TPO peak may vary when the catalyst composition changes, and may also vary depending on the kinetics of the oxidation process and the amount of carbon on the surface. However, in this case, all the samples were analogous and the amounts of carbon were also similar. Therefore, the

position of the TPO peaks for each carbon species did not greatly vary. For samples containing larger amounts of carbon, a kinetic analysis of the TPO, such as that reported by Fung and Querini [18] must be conducted.

The data in Table 5–1 shows that the monometallic Co catalyst was unselective, while the monometallic Mo was almost inactive in the temperature range investigated. Similarly, an unsupported  $Mo_2C$  sample was also shown to be inactive. Physical mixtures of a Co catalyst with monometallic Mo catalyst or an unsupported  $Mo_2C$  resulted in the same production as the Co catalyst alone.

Table 5–1 Yield and Selectivities to SWNT obtained by decomposition of CO on Co:Mo catalysts as calculated by TPO. Yield is defined as the percent weight of carbon deposited per total catalyst weight. Similarly, selectivity is defined as the percent of carbon products deposited on the catalyst that is in the form of SWNT.

Catalyst	Operating Temperature	Reaction Conditions	Total Carbon Yield (%)	Selectivity To SWNT (%)
Со	700°C	1 h, 50 % CO	1.8	7
Мо	700°C	1 h, 50 % CO	0.6	0
Co:Mo (1:1)	600°C	1 h, 50 % CO	2.7	25.8
	700°C	1 h, 50 % CO	1.7	62.5
	800°C	1 h, 50 % CO	1.0	86.6
Co:Mo (1:1)	600°C	30', 20 % CO	1.38	43
	700°C	30', 20 % CO	0.55	61
	800°C	30', 20 % CO	0.33	39
Co:Mo (1:2)	700°C	1 h, 50 % CO	1.5	88
Co:Mo (2:1)	700°C	1 h, 50 % CO	2.2	57
Co:Mo (1:4)	700°C	1 h, 50 % CO	1.6	96
### 5.3.1 Effect of reaction temperature on the production of nanotubes

To study the effect of varying the operating temperature on the yield and selectivity to SWNT, we conducted the decomposition of CO over two Co-Mo/SiO<sub>2</sub> catalysts for 60 min at temperatures ranging from 600°C to 800°C. Figure 5–1 illustrates the TPO profiles obtained on the Co:Mo (1:1) at 600, 700, and 80 °C and on the Co:Mo (1:2) at 700°C. As described in the previous chapter, the oxidation of SWNT on this type of catalysts under the particular TPO conditions used in this work has a maximum around 510°C. The position of maximum rate of oxidation of SWNT was confirmed using purified SWNT from Tubes@Rice and it is indicated in the figure with a dashed line. When compared at 700 °C, the Co:Mo (1:2) catalyst was more selective than the Co:Mo (1:1), exhibiting lower contributions in the area of amorphous carbon (centered at around 330°C) as well as MWNT and graphite (centered at around 590 and 620°C, respectively).



Figure 5–1 Temperature programmed oxidation (TPO) of the carbonaceous species present in Co:Mo/SiO2 (Co:Mo = 1:1) catalysts after decomposition of 50 % CO/He at for 60 min at reactions temperatures  $600^{\circ}$ C, 700°C, and 800°C

As shown in the Figure 5–1 and summarized in Table 5–1, the amount of carbon deposited on the Co:Mo (1:1) catalyst over the 60-min period increased with decreasing operating temperature. This counterintuitive trend can be ascribed as due to the complex temperature dependence of both the rate of carbon deposition, which increases with temperature, and the rate of catalyst deactivation, which also increases with temperature. Therefore, the low carbon yield observed at 800°C is most probably due to a rapid deactivation of the catalyst, which counterbalances the rapid rate of CO decomposition. At 600°C, the amount of carbon deposited is significantly higher than at higher temperatures. However, the selectivity towards SWNT is much lower. It is clearly seen that the TPO of the sample reacted at 600°C exhibited a significant amount of amorphous carbon (centered at around 330°C) as well as MWNT, and perhaps some graphitic carbon, represented by the intense peak and shoulder at 556 and 610°C, respectively. The TEM observations of these samples are shown in Figure 5-2, and agree very well with the TPO results. The Co:Mo (1:1) sample reacted at 600 °C showed the presence of MWNT with external diameters of about 18 nm and wall thickness of around 6 nm. By contrast, the samples reacted at 700°C and 800°C showed mostly SWNT. The high-magnification TEM pictures of these two samples exhibited the presence of the typical rope-like bundles, which are similar to the structures grown by other methods [19]. A thin layer of amorphous carbon covers the SWNT bundles, which exhibited very uniform individual diameters of about 1 nm. The presence of SWNT on the sample treated at 700°C was further confirmed by Raman spectroscopy, conducted at room temperature and using

514.5 nm excitation. The spectra for the reference and the sample after reaction at 700°C are shown in Figure 5–3. They both exhibit the typical sharp doublet lines due to the "graphite-like" tangential modes in the range 1580-1590 cm<sup>-1</sup>, previously observed for purified SWNT [20]. In addition, a broad D-band it is observed in the region of 1300-1350 cm<sup>-1</sup>. This band is due to disordered carbon and has been previously observed with MWNT and polycrystalline graphite [21]. The sample reacted at 600°C is also included in Figure 5–3. In good agreement with the TEM observations and the TPO profiles, the presence of disordered carbon is clearly seen by the intense D-band appearing in the region of 1300-1350 cm<sup>-1</sup>. Clearly, the TPO cannot differentiate between MWNT and carbon nanofibers, because they all burn in the same temperature range. However, the TEM clearly shows that the tubes produced at 600°C are hollow in their core and their walls are multilayer having the basal plane parallel to the tube axis, which are characteristic features of MWNT.



Figure 5–2 TEM images showing SWNT and MWNT produced by decomposition of 50 % CO/He on a  $Co:Mo/SiO_2$  (Co:Mo = 1:1) catalyst for 60 min at various temperatures. (a) 600°C; (b) 700°C; (c) 800°C



Figure 5–2 (continued)



Figure 5-3 The Raman spectra of SWNT reference (from Carbolex Inc.), deposited carbon on Co:Mo/SiO2 catalyst (Co:Mo = 1:1) after CO decomposition at 700°C, and deposited carbon on Co:Mo/SiO2 catalyst (Co:Mo = 1:1) after CO decomposition at 600°C.

### 5.3.2 Effect of CO concentration on the production of nanotubes

It was observed that not only the temperature, but also the concentration of CO in the gas phase has a profound effect on the rate of formation of SWNT. Figure 5–4 shows the TPO of samples treated for 60 min at 700 °C on the Co:Mo (1:1) catalyst with varying CO concentration in the gas phase. From the position of the TPO peak, it can be concluded that at low CO concentrations, the main form of carbon deposited at 700°C was amorphous. Only when the CO concentration increased, the SWNT began to dominate. The weak shoulders observed at 550°C and 600°C correspond to small amounts of MWNT, which were also observed by TEM.

When the measurements at various temperatures were conducted under a CO concentration in the gas phase of only 20 %, clear differences in selectivity were again observed. Table 5–1 shows that at the lower reaction temperature a larger amount of carbon was observed, but as shown before, a lower selectivity towards SWNT was obtained. At the other end, when the reaction was conducted at 800°C at this low concentration, this catalyst deactivated very quickly and only formed amorphous carbon.



Figure 5-4 Temperature programmed oxidation (TPO) of the carbonaceous species present in a  $Co:Mo/SiO_2$  catalyst (Co:Mo = 1:1) after CO decomposition at 700°C for 60 min with varying CO concentrations.

### 5.3.3 Effect of reaction time on the production of nanotubes

One of the important considerations in the design of a large-scale process for the selective production of SWNT will be the optimum time of reaction to maximize yield and selectivity. The amount of SWNT produced on the Co:Mo (1:1) catalyst by passing 50 % CO/He at 700°C during 3-, 10-, and 60-min reaction periods are measured by TPO. As shown in the TPOs of Figure 5–5, during the initial 3 min there was a rapid formation of amorphous carbon while the amount of SWNT formed was very small. At longer reaction times, the growth of SWNT became dominant. It is interesting to note that after about 10 min, the growth of carbon nanotube was much slower. To investigate whether the slowdown in growth was due to pore plugging, changes in textural properties of the catalysts were characterized by nitrogen adsorption experiments. Table 5-2 summarizes the BET surface area, pore volume, and average pore size obtained on the silica support pretreated at 500 °C and 800 °C and on the Co:Mo (1:2) catalyst before and after reaction at 700 °C for 3 min and 30 min. In the first place, it was observed that the structure of the silica support alone does not greatly vary by effect of temperature. At the same time, no significant loss in surface area or pore volume was observed during the growth of carbon nanotubes.



Figure 5-5 Temperature programmed oxidation (TPO) of the carbonaceous species present in a  $Co:Mo/SiO_2$  catalyst (Co:Mo = 1:1) after decomposition of 50 % CO/He at 700°C during different periods of time.

Sample	BET area (m²/g)	Single Point Total Pore Volume (cm <sup>3</sup> /g)	Average pore radius by BET (nm)	
SiO <sub>2</sub> support Calcined 500°C	480	0.75	3.1	
SiO <sub>2</sub> support Calcined 800°C	450	0.71	3.1	
Co:Mo (1:2) on SiO <sub>2</sub> Fresh catalyst Pretreated at 700°C, in He	427	0.67	3.1	
Co:Mo (1:2) on SiO <sub>2</sub> Spent catalyst, 3 min 700°C, 50 % CO	427	0.67	3.1	
Co:Mo (1:2) on SiO <sub>2</sub> Spent catalyst, 30 min 700°C, 50 % CO	421	0.67	3.1	

Table 5–2 Surface area, pore volume, and pore size of various catalysts and supports as determined by nitrogen adsorption at liquid nitrogen temperature.

#### 5.3.4 Characterization of the state of Co during the production of SWNT

X-ray absorption is an excellent technique to study the state of the catalyst ingredients during the reaction. As shown in Figure 5–6, the near-edge (XANES) spectra of the K edge of Co (Eo = 7709 eV) for the Co:Mo (1:2) catalyst show that after the pretreatment and before the reaction with CO, a significant fraction of Co is oxidized. However, as the reaction proceeds, metallic Co begins to form and after 30 min the XANES is almost identical to that of a Co foil. The trend observed in the Fourier transforms of the EXAFS data in Figure 5–7 agrees very well with the conclusion drawn from the XANES data. Both of them reveal that during the formation of carbon nanotubes, Co gets gradually reduced to the metallic state. The detailed structural analysis of the Co EXAFS data indicated that as the reaction preceded the Co reduction process was accompanied by an increase in metal particle size. Evidence for this process is presented in Table 5–3. The Co-Co coordination number increases as a function of reaction time and the Co-O coordination remains relatively high until 30 min.



Figure 5-6 Near edge spectra XANES obtained at the K edge of Co (Eo = 7,709 eV) on a fresh Co:Mo/SiO<sub>2</sub> catalyst (Co:Mo = 1:2), pretreated in  $H_2(500^{\circ}C)/He(700^{\circ}C)$ , and after the growth of carbon nanotubes by decomposition of 50 % CO/He at 700°C for reaction periods of 10 and 30 min. The XANES of a Co foil is included for comparison.



Figure 5–7 Fourier transforms of the  $k^3$  EXAFS data obtained at the K edge of Co for a fresh Co:Mo/SiO<sub>2</sub> catalyst (Co:Mo = 1:2), pretreated in H<sub>2</sub>(500°C)/He(700°C), and after the growth of carbon nanotubes by decomposition of 50 % CO/He at 700°C for reaction periods of 10 and 30 min. The EXAFS data of a Co foil is included for comparison.

Table 5–3 Structural parameters of the Co-Mo/SiO<sub>2</sub> catalyst (Co:Mo = 1:2) after different reaction periods, as obtained from the EXAFS data analysis. In the table,  $E_0$  represents the energy shift,  $\sigma$  is the Debye-Waller factor,  $N_{M-M}$ ,  $N_{M-O}$  and  $N_{M-C}$  are the coordination numbers between the metals (Co or Mo) with another metal atom, oxygen atom, and carbon atom respectively. R (Å) is the coordination distance for each respective bond, and the r factor is a measurement of the fit quality.

Sample	Sample Treatment	Edge (M)	E <sub>0</sub>	σ	N <sub>M-M</sub>	N <sub>M-0</sub>	N <sub>M-C</sub>	R (Å)	r factor
Co:Mo (1:2)	Spent 3 min	Со	4.2	0.0068 0.0025	5.8 -	- 2.2	-	2.470 2.050	0.043
Co:Mo (1:2)	Spent 10 min	Со	8.0	0.0075 0.004	8.2	- 2.6	-	2.490 2.075	0.034
Co:Mo (1:2)	Spent 30 min	Со	9.4	0.0065 0.0003	9.2 -	- 1.1	-	2.498 2.070	0.020
Mo <sub>2</sub> C	Reference (as received)	Мо	6.6	0.0063 0.0106	11.6 -	-	- 5.8	2.97 2.08	0.022
Co:Mo (1:2)	Spent 30 min	Мо	7.1	0.0075 0.0075 0.0039	6.7 - -	- - 0.9	- 0.33 -	2.98 2.09 1.68	0.038

#### 5.3.5 Characterization of the state of Mo during the production of SWNT

The characterization of the state of Mo was conducted on the K edge of Mo (Eo = 20,000 eV) both, on the fresh pretreated catalyst and after reaction. The near-edge spectra and EXAFS data are respectively shown in Figure 5-8 and Figure 5-9. The XANES of the fresh Co:Mo (1:2) catalyst pretreated at 700 °C can be compared to that of bulk MoO<sub>3</sub>, which is the Mo species that one would expect if large Mo oxide aggregates were present [22]. In fact, the near-edge spectrum of the fresh catalyst is similar, but not exactly identical to that of MoO<sub>3</sub>. It is well established that supported Mo oxide can exhibit different structures and states of aggregation depending on the Mo loading, thermal treatment, and type of support investigated. An investigation of Co-Mo catalysts supported on silica [23] has shown that, depending on the Co: Mo ratio, the form of preparation, and the thermal treatment, oxide species such as MoO<sub>3</sub>, Co<sub>3</sub>O<sub>4</sub> and CoMoO<sub>4</sub> can coexist on the samples. Some features in these XANES spectra can be used to describe the state of Mo in the catalyst. For example, the pre-edge feature clearly observed for MoO<sub>3</sub> is due to a  $1s \rightarrow 4d$  bound state transition [24], which is formally forbidden. However, it can become allowed by mixing of d-states with p-orbitals of the ligand. This mixing is very effective in compounds with tetrahedral geometry, such as  $Na_2MoO_4$ , and in those cases a strong pre-edge feature appears. When the geometry is octahedral, the transition is not allowed, but in MoO<sub>3</sub>, the octahedral is distorted, and as a result, a small pre-edge feature is observed. In the fresh catalyst pretreated at 700 °C, the pre-edge feature is very small, indicating a less distorted octahedral configuration. The

EXAFS data show that the coordination of Mo in the fresh catalyst involves Mo-O bonds, but it is not the same as that of  $MoO_3$  reference. At the same time, it does not exhibit coordination distances in the second shell region, which would indicate the presence of large aggregates. The results indicate that the fresh catalyst contains well-dispersed oxidized Mo species. As mentioned above, these oxidized species may in fact be a combination of oxides and molybdates [23]. Since the pretreatment involves a reduction step, it is possible that in the pretreated catalyst Mo may be in a partially reduced state e.g. Mo(IV).



Figure 5-8 Near edge spectra XANES obtained at the K edge of Mo (Eo = 20,000 eV) on a fresh Co:Mo/SiO<sub>2</sub> catalyst (Co:Mo = 1:2), pretreated in H<sub>2</sub>(500°C)/He(700°C), and after the growth of carbon nanotubes by decomposition of 50 % CO/He at 700°C for 30 min. The XANES of MoO<sub>3</sub> and Mo<sub>2</sub>C are included for comparison.



Figure 5–9 Fourier transforms of the  $k^3$  EXAFS data obtained at the K edge of Mo for a fresh Co:Mo/SiO<sub>2</sub> catalyst (Co:Mo = 1:2), pretreated in H<sub>2</sub>(500°C)/He(700°C) compared to a MoO<sub>3</sub> reference.

As illustrated in Figure 5–8, after a 30-min reaction period, the near-edge spectrum of Mo showed a drastic change in appearance and became very similar to that of molybdenum carbide,  $Mo_2C$ . At the same time, the EXAFS of the used catalyst, shown in Figure 5–10, exhibited peaks in the Fourier transform that exactly corresponded with those of the  $Mo_2C$  reference. The transformation of oxidized Mo species into Mo carbide during the reaction was indeed very clear, with only a small fraction of unconverted Mo remaining in the catalyst. This conversion can be clearly seen from the EXAFS analysis data of the spent catalyst summarized in Table 5–3. The best fit of the experimental data was obtained when the coordination sphere of the Mo was described as composed as Mo-C, Mo-Mo, and Mo-O. This indicates that the conversion to Mo carbide is not complete and a fraction of Mo remains as an oxidized species.

In contrast to the Mo carbide formation observed in the bimetallic sample, the XANES spectra of a catalyst containing only Mo, without Co, did not exhibit after 10 min reaction a transformation into the carbide form. As illustrated in Figure 5–11, the shape of the near-edge for the spent Mo catalyst resembles that of the fresh Mo catalyst rather than that of the spent Mo:Co catalyst, which is clearly representative of Mo carbide. This result would indicate that, when Co is not present, the supported Mo oxide is not as easily converted into Mo carbide.



Figure 5–10 Fourier transforms of the  $k^3$  EXAFS data obtained at the K edge of Mo for a Co:Mo/SiO<sub>2</sub> catalyst (Co:Mo = 1:2) after the growth of carbon nanotubes by decomposition of 50% CO/He at 700°C for 30 min compared to a Mo<sub>2</sub>C reference.



Figure 5-11 Near edge spectra XANES obtained at the K edge of Mo (Eo = 20,000 eV) on a fresh Mo/SiO<sub>2</sub> catalyst, pretreated in H<sub>2</sub> (500°C)/He(700°C), and after the growth of carbon nanotubes by decomposition of 50 % CO/He at 700°C for 10 min. The XANES of the 30 min spent Co:Mo=1:2 catalyst is included for comparison.

# 5.4 Discussion

In the first place, it is interesting to note that the growth of carbon nanotubes occurs for a limited period of time, after which the catalyst deactivates and the growth slows down. This was clearly observed when the growth was monitored by TPO as a function of time. During the first few minutes, the amount of carbon deposited on the catalyst increased very rapidly, but after about 10 min, the growth was much slower. This deactivation phenomenon may explain the inverse relationship between carbon deposits and temperature. At higher temperatures, the initial growth of nanotubes may be faster than at lower temperatures, but at the same time, the rate of catalyst deactivation is very fast. As a result, at 800°C, the total carbon yield is much lower than at 600 or 700°C. At the low temperature end, the catalyst deactivation seems to have a smaller influence. However, at lower temperatures, the selectivity to SWNT decreases. For example at 600 °C, the formation of MWNT is favored, as seen by TEM and TPO.

This competition between carbon growth and catalyst deactivation seems to play a very important role in determining the resulting structure of the nanotubes. Cassell and colleagues have observed similar decreases in growth rate at relatively short periods of time [25]. One of the explanations proposed by these authors for growth abatement was the plugging of the catalyst pores by the nanotubes themselves. That may indeed be a factor when there is a large amount of carbon formed. However, in the case of the reaction at 800 °C, the amount of carbon formed was very small and as shown by the N,

adsorption data, pore plugging is not significant. Also, the comparison of heat treatment of the silica at 500 °C and 800 °C showed no difference, indicating that support sintering due to thermal collapse does not occur. Therefore, deactivation by carbon encapsulation of the metal particles or carbon deposition on the surface appears more likely in this case. It is worth noting that the maximum amount of amorphous carbon by varying the reaction time or CO concentration was quickly reached, in contrast with the formation of SWNT, which was predominant only at longer times and at high CO concentrations. An important observation that may be linked to the deactivation process is the parallel trend observed in the oxidation state of Co with the rate of SWNT growth. XANES/EXAFS showed that oxidized Co was present while the growth rate of SWNT was high. After 30 min in reaction, when the SWNT growth slowed down, all Co became metallic.

The simultaneous presence of Co and Mo results in a more efficient catalyst for the production of SWNT from CO decomposition. Without Mo, Co is active for carbon growth but very unselective. Both TPO and TEM measurements showed the presence of large amounts of MWNT and amorphous carbon. Conversely, without Co, Mo is almost inactive in the temperature range investigated. Other investigators have reported the formation of SWNT by decomposition of CO on Mo catalysts [8]. However, those studies were conducted at 1200°C and an important difference of results of this study with those is that the bundles of SWNT are formed as opposed to the study conducted at 1200°C, in which the absence of bundles or "ropes" was reported [8]. Another important difference is that, at 1200°C with Mo catalyst, there was a wide distribution of tube diameters, ranging from 1 to 5 nm. The TEM observations in this chapter show a more uniform distribution of diameters at around 1 nm.

The EXAFS/XANES results on the Co:Mo (1:2) may shed some light in the combined action of Co and Mo. These results show that Co suffers a drastic transformation under reaction conditions. Before reaction, but after pretreatment in  $H_2$  at 500°C and then in He at 700°C, a large fraction of Co is in the oxidic state. After 10 min under reaction conditions, a significant growth in metallic Co was observed, although some oxidized Co was still present. After 30 min, the particles were even larger and essentially all the Co became metallic. The pronounced particle growth observed during the reaction was not observed during the treatment in He at the same temperature. It is well known that Co carbide is unstable at 700°C, but it is also known that CO greatly affects the surface of Co causing severe reconstruction [26]. This reconstruction can be associated to the rapid formation and decomposition of unstable carbides.

An important experimental observation to point out is that the formation of Mo carbide under reaction conditions only occurs in the presence of Co. That is, Co may be acting as an activator of CO, thus generating active carbon that would react with Mo and generate the carbide. After this finding, the possibility that Mo carbide is the active species is then tested. It has been recently proposed that intermediate aromatic species generated on Mo may be the growing units in the production of SWNT [25]. This proposal was based on the idea that Mo carbide is supposedly the active species in the newly discovered aromatization of methane to benzene [27]. However, in that case, the reaction is thought to proceed via C2 species, which are produced at the Mo carbide and subsequently oligomerize to benzene on the acid sites of the zeolite [28]. Therefore, it is unlikely that such mechanism operates in the growth of SWNT, but it is not unreasonable to consider that Mo carbide may play an important role in the reaction. For example, it is possible that Mo alone is not active for growing SWNT because in the absence of Co it cannot form the carbide, which in turn would be responsible for the formation of SWNT. However, the carbon growth measurement conducted on the pre-formed  $Mo_2C$  sample showed no SWNT formation. Therefore, the role of Mo may be that of a moderator of the Co activity rather than as an active species itself.

Likewise, no additional effect was observed when physical mixtures of Mo<sub>2</sub>C and Co/SiO<sub>2</sub> or Mo/SiO<sub>2</sub> and Co/SiO<sub>2</sub> were tested. In both cases, the physical mixtures behaved as the sum of the individual parts. Therefore, it is shown that Co and Mo are simultaneously needed and in rather intimate contact. The question that remains is how can Mo inhibit the activity of Co towards the formation of MWNT, which are formed in large quantities in the absence of Mo. As shown Figure 5–7, the cobalt species in the fresh catalyst are in an oxidized state and very highly dispersed. At the same time, Figure 5–9 demonstrates that only Mo-O are present with essentially no Mo-Mo contributions. This results indicates that molybdenum oxides species are present in small domains in comparison to bulk MoO<sub>3</sub>. In addition, as shown in Figure 5–6 and Figure 5–8, the oxidized cobalt species become metallic Co while the Mo species are converted to Mo

carbide during the reaction with CO. It is reasonable to speculate that one of the roles of molybdenum in the catalyst is the stabilization of small particles of oxidized cobalt species, which are highly selective to the production of SWNT. Without this stabilization, Co species would tend to agglomerate, to get reduced more easily, and to form MWNT and graphite, as it is seen on  $Co/SiO_2$  catalysts.

The formation of Mo carbide during reaction deserves some further discussion. It is certainly possible that this species is only a by-product of a parallel reaction, unrelated to the formation of SWNT. It is also possible, that in fact, the formation of carbide is an undesired path, which results in the destabilization of the Co species with the subsequent encapsulation of Co by carbon. However, an interesting possibility would be that the formation of carbide is responsible for the high selectivity towards SWNT. Molybdenum could be acting as a sink of active carbon species generated by CO decomposition on cobalt species. According to this view, such active carbon would form MWNT or SWNT with Co species. When there is excess of carbon species, formation of MWNT would dominate, while when there is just the right amount, only SWNT would form. In that case, Mo would act as a moderator of the concentration of active carbon species.

Another important consequence of the characterization results reported here is the demonstration that, under reaction conditions, the mobility of the catalyst components is very high. Therefore, explanations based on pre-formed nanoscale metal particles, which in turn govern the size of the carbon nanotubes must be reconsidered. As shown here, the

Co particles continuously grow in the presence of CO, much more than under He. At the same time, Mo initially in the form of a highly dispersed oxide, becomes carbide. At the high temperatures required to grow carbon nanotubes, one cannot expect that the size of the particles will remain as that of the original preparation.

# 5.5 Conclusions

This chapter has demonstrated a number of interesting characteristics of the formation of SWNT by decomposition of CO on Co-Mo catalysts. The main conclusions of this work are the following:

a) A synergistic effect between Co and Mo has been shown. When both metals are simultaneously present, the catalyst is very selective. When they are separate they are either inactive (Mo alone) or unselective (Co alone).

b) X-ray absorption spectroscopy (EXAFS and XANES) has shown that at the beginning of the reaction, Co is in the oxidic state, but is progressively reduced to the metallic form. During this process, a metal particle growth takes place. Simultaneously, Mo is converted to the carbidic form.

c) The yield and selectivity to SWNT are a strong function of the reaction temperature and the CO concentration in the gas phase.

# 5.6 References

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