

UNIVERSITY OF OKLAHOMA

GRADUATE COLLEGE

SURFACE INVESTIGATIONS OF THE MECHANISM OF SINGLE WALLED
CARBON NANOTUBE GROWTH BY CO DISPROPORTIONATION OVER A
Co Mo CATALYST.

A Dissertation

SUBMITTED TO THE GRADUATE FACULTY

In partial fulfillment of the requirements for the

degree of

Doctor of Philosophy

By

José Efraín Herrera
Norman, Oklahoma
2003

UMI Number: 3097223

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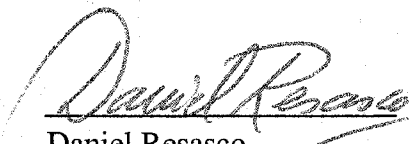
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CARBON NANOTUBE GROWTH BY CO DISPROPORTIONATION OVER A Co
Mo CATALYST.

A Dissertation APPROVED FOR THE
SCHOOL OF CHEMICAL ENGINEERING AND MATERIALS SCIENCE

BY


Daniel Resasco


Lance Lobban


Edgar O'Rear


Robert Shambaugh


Vadim Soloshonok

ACKNOWLEDGMENTS

First of all I am indebted to my advisor Dr. Daniel E. Resasco for his generous support, but most of all for his permanent encouragement and friendship. It is with gratitude that I acknowledge his invaluable guidance as well as his advice. He often steered me in the right direction when I was not certain I which path to investigate but gave me remarkable freedom as well during the final stages of this project. It is my privilege to call him my mentor.

I would like to thank everyone on the OU Heterogeneous catalysis group for their help and friendship. Particularly I would like to acknowledge Dr. Walter Alvarez for his permanent encouragement and the guidance he offered me when I started this project. I also thank Leandro Balzano and Francisco Pompeo who were directly involved in this project, the hard core engineering approach that Leandro put on the project was a permanent challenging to my scientific skills and as well as a source of motivation.

Thanks are also due to Greg Strout for his assistance with the electron microscope, to Syed Khalid at Brookhaven National Lab for his help with the X-ray absorption work and to the gentleness that Terri L. Colliver showed every time I had to handle any paperwork.

I gratefully acknowledge the Fulbright program for my two-year scholarship and the kindness of the members of the Peruvian Fulbright commission. The US-DOE, OCAST and Conoco are also acknowledged for financial support. I am also appreciative of the Richard J. Kokes Travel award that allowed me to attend the 17th. North American Catalysis Society meeting in Toronto in June 2001 and of the National Science Foundation for granting me a travel grant to go to Spain in September on 2002 to present some of the results of this work.

Thanks are also due to the faculty at the University of Oklahoma for the knowledge that they have passed along during my studies in Norman, especially to the members of my doctoral committee. I would like particularly to acknowledge the faculty in the chemistry department because they made me remember during their lectures that I am still a chemist. I also thank the CEMS faculty for teaching me to think like a chemical engineer.

I need to acknowledge also two of my professors from undergraduate school: Dr. Galina Shevtsova and Dr. Eric Cosio. I might have never embraced a PhD program without their enthusiastic encouragement.

Finally I would like to deeply thank my parents for their love, for encouraging my interest in science and for the many sacrifices they have made for my studies as well as so for the strong support and guidance that they have provided on all these years. I would like to thank also my brothers Miguel and Rafael for being a constant source of motivation through all my life. I need to thank also my other brother Oscar for his encouragement and friendship, his moral support has been most important during these years away from home. I would like to thank also Mai Salkulchaicharoen; a girlfriend is often acknowledged for her support and tolerance during a PhD program, however few people are as fortunate as I am to have a girlfriend that offers not only emotional support but intellectual support as well. For her patience and for being a sounding board for my ideas as well as giving me encouragement when I needed it I am deeply thankful. This thesis is dedicated to them all: my parents, my three brothers, my girlfriend and also to God. I would not be able to do anything without Him setting the path.

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ABSTRACT

Single-wall carbon nanotubes (SWNT) can be considered as one of the building blocks for nanoscale science and nanotechnology. Extensive research work is now focused on the large-scale manufacture of these materials at low cost since there is not yet an established method that provides large quantities of SWNT of well-determined and reproducible characteristics. A clear understanding of the formation mechanism of SWNT is therefore a key issue for the development of further advances in this topic.

This study is focused on the understanding of the processes that occur on the catalyst surface during the synthesis of SWNT nanotubes by CO disproportionation on a bimetallic Co Mo catalyst. A series of analytical techniques have been employed to fully characterize the structure and chemical state of the catalyst. The state of Co and Mo has been investigated using laser Raman spectroscopy, extended X-ray absorption fine structure spectroscopy, X-ray absorption near-edge spectroscopy, ultraviolet-visible diffuse reflectance spectroscopy, H₂ temperature-programmed reduction, X-ray photoelectron spectroscopy, and diffuse reflectance Fourier transform infrared spectroscopy of adsorbed NO, after two sequential pretreatments and after the production of SWNT under pure CO. In a similar way, the SWNT materials have been characterized using laser Raman spectroscopy, transmission electron microscopy, optical absorption spectroscopy and fluorescence. The information obtained during the catalyst characterization revealed an intrinsic dependence between the selectivity of the catalysts toward SWNT and the stabilization of Co species in a nonmetallic state, which in turn results from an interaction with Mo. The extent of this interaction is a function of the Co:Mo ratio and has different forms during the different stages of the catalyst life. From the detailed characterization conducted over the catalyst series it is concluded that after calcination, Mo is in the form of a well-dispersed Mo(VI) oxide while Co is either interacting with Mo in a

superficial Co molybdate-like structure (at low Co :Mo ratios) or as a non interacting Co_3O_4 phase (at high Co :Mo ratios). After a subsequent treatment in hydrogen, the non interacting phase is reduced to metallic Co, while the Co molybdate-like species remain as well-dispersed Co^{2+} ions. During the production of SWNT under pure CO, the Mo oxide species are converted into Mo carbide. We propose that this conversion disrupts the interaction between Co and Mo and results in the release of metallic Co in the form of extremely small clusters, which are responsible for the production of SWNT.

To examine the validity of this hypothesis that ultimately tries to elucidate the mechanism of SWNT formation from CO disproportionation, different catalyst formulations and reaction conditions have been used. These series of tests included the doping of the Co Mo catalyst with sodium, the substitution of molybdenum by tungsten in the original catalyst formulation, the variation on reaction temperature as well as the introduction of hydrogen in the gas feedstock. All these modifications were carried out in order to modify the growth conditions in which the SWNT are formed. The results are consistent with the proposed hypothesis and have opened the possibility of tailoring the properties of the SWNT obtained by means of a careful control of the synthesis conditions.

CHAPTER 1

BACKGROUND AND INTRODUCTION TO SINGLE WALLED CARBON NANOTUBES

1.1. INTRODUCTION TO SWNT

1.1.1 Introduction

Carbon Nanotubes (CNTs) can be formally described as a material lying between fullerenes and graphite, they are new members of the family of carbon allotropes that have been discovered in recent years [1]. The work in the synthesis and characterization of this new form of carbon material started in 1991 when the Japanese electron microscopist Sumio Iijima reported the discover of carbon nanotubes on an arch discharge apparatus originally designed to synthesize fullerenes [2]. A short time later, Thomas Ebbesen and Pulickel Ajayan, from Iijima's lab, showed how nanotubes could be produced in bulk quantities by varying the arc discharge conditions. This paved the way to an explosion of research into the physical and chemical properties of carbon nanotubes in laboratories all over the world.

A major event in the development of these new materials was the synthesis in 1993 of single-layer nanotubes [3]. It was found that addition of metals such as cobalt to the graphite electrodes resulted in the formation of extremely fine tubes with single-layer walls in contrast to the multiwalled carbon tubes that where formed in absence of metallic particles. Later, Smalley and coworkers showed that single-wall

carbon nanotubes (SWNT) could also be produced in high yield by laser vaporization of a graphite rod doped with Co and Ni [4]. In contrast to the material produced by arch discharge these highly uniform single tubes had a greater tendency to form aligned bundles. Initial reports seemed to indicate that the bundle samples contained a very high proportion of nanotubes with a very specific crystalline structure. Subsequent work suggested that these samples are in fact less homogeneous than originally thought. Nevertheless, the synthesis of nanotube bundles gave an important boost to nanotube research, and some of the most impressive fundamental work has been carried out on these samples.

Besides the arch discharge and laser ablation techniques, the direct decomposition of carbon-containing molecules over metal catalysts has also shown to be a useful route for SWNT synthesis. Although the arc discharge and laser ablation methods are known to produce high quality SWNT, the amount of material obtained by these techniques ranges from milligrams to grams. On the other hand, the catalytic decomposition of carbon-containing molecules over solid catalysts appears as a promising technique for scaling-up the production process and enabling applications that require larger SWNT quantities.

In the subsequent sections of this chapter a description of the structure of SWNT, as well as a deep review of the SWNT synthesis methods is presented

together with a comprehensive description of the main techniques used in the present work to characterize SWNT materials.

1.1.2 Structure and properties of SWNT

The carbon bonds in nanotubes are similar to those in graphite and it involves three-coordinated carbon atoms, in which three of the four valence electrons are located in sp^2 hybridized orbitals and the remaining one is involved in the delocalized π system. However, while the graphite lattice is made up of a flat planar honeycomb structure, the crystal structures of nanotubes involve a high degree of curvature.

Carbon nanotubes can thus be formally described as a graphene honeycomb rolled into a single-walled cylinder or into several concentric graphene cylinders. The former are termed single-walled nanotubes (SWNT) and the latter multi-walled nanotubes (MWNT). The diameter of a typical SWNT is in the order of a nanometer but its length can be up to several micrometers, or more. Each nanotube can be considered as a single molecule made up of a honeycomb network of covalently bonded carbon atoms. A schematic representation of a SWNT structure is shown in Figure 1.1. Each SWNT is fully characterized by two integers (n, m) . These integers specify the number of unit vectors $\vec{a}_1$ and $\vec{a}_2$ in the graphene structure that constitute the roll-up vector (or chiral vector) $\vec{V} = n\vec{a}_1 + m\vec{a}_2$. The graphene structure is rolled-up such that the chiral vector $\vec{V}$ forms the nanotube circumference. Therefore, the (n, m) indices determine the nanotube diameter, according to the equation:

$$d = (n^2 + m^2 + nm)^{1/2} 0.0783 \text{ nm} \quad (1)$$

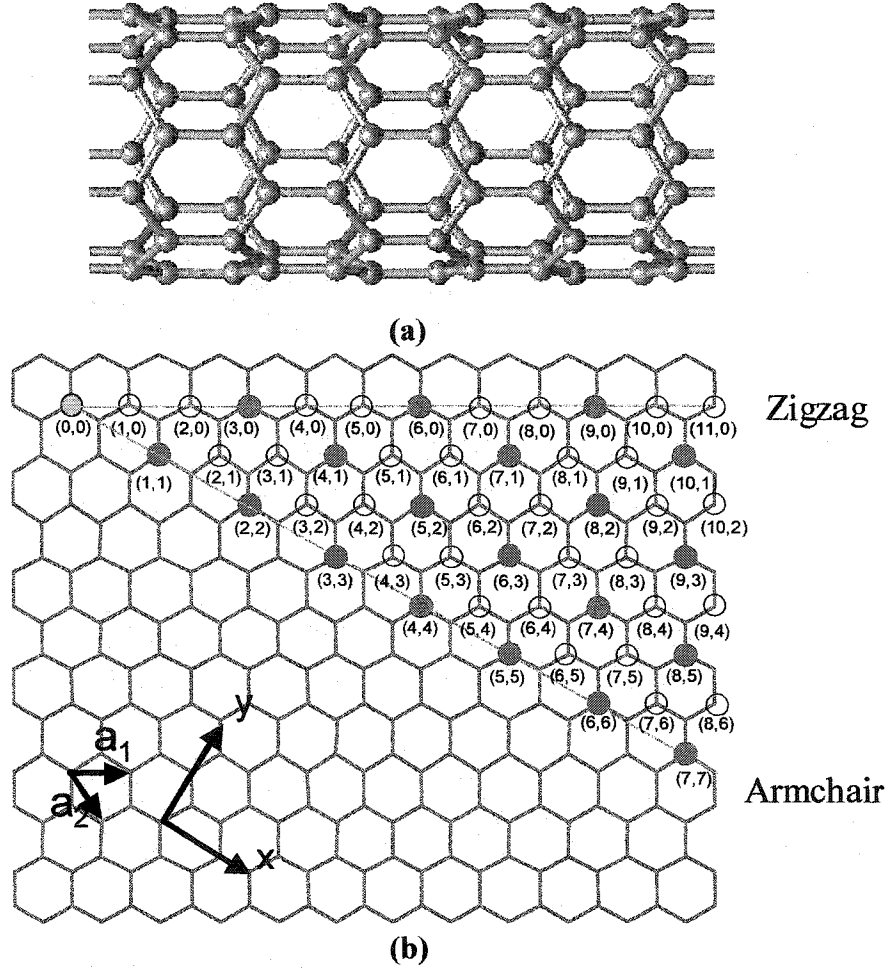


Figure 1.1. (a). Middle section of a single - walled carbon nanotube (SWNT). Copyright [V. H. Crespi.]. Distributed under the Open Content License (<http://opencontent.org/opl.shtml>). **(b).** Identification of carbon nanotubes in terms of the indices (n,m) . Consider a flat graphene sheet. Vectors n and m placed at the chosen origin $(0,0)$ determine the specific nanotube. For example, the nanotube $(7,7)$ can be obtained by drawing a line between the origin $(0,0)$ and the point indicated as $(7,7)$ and then cutting the sheet along two lines perpendicular to this line. The cut sheet can then be folded into the $(7,7)$ nanotube. Reproduced from <http://www.photon.t.u-tokyo.ac.jp/~maruyama/kataura/chirality.html> with permission from S. Maruyama.

At the same time, these indices determine the orientation of the carbon hexagons with respect to the nanotube axis. This orientation is the so-called “chirality” of the nanotube. Nanotubes with indices $(m, 0)$ are termed “zig-zag” due to the shape of the atomic configuration along the perimeter of such a nanotube. When $m=n$, the resulting nanotubes are called “arm-chair” because the position of the C atoms arrange in an “arm-chair” pattern.

A remarkable consequence of the different values the roll up vector can take is that SWNTs can be either electrically metallic or show semiconducting behavior depending on the values the (m, n) components. In fact, the most interesting properties of SWNT relate to their electronic band structure. The armchair tubes are always metallic whereas the zigzag and chiral can be either metallic or semiconducting.

Moreover, the electronic conduction process in CNTs is quantum confined because in the radial direction the electrons are confined in the singular plane of the graphene sheet. The unique electronic properties of carbon nanotubes are due to the quantum confinement of electrons normal to the nanotube axis. In the radial direction, electrons are confined within the graphene sheet. Because of this quantum confinement, electrons can only propagate along the nanotube axis, and so their wavevectors point in this direction. The resulting number of one-dimensional

conduction and valence bands effectively depends on the standing waves that are set up around the circumference of the nanotube.

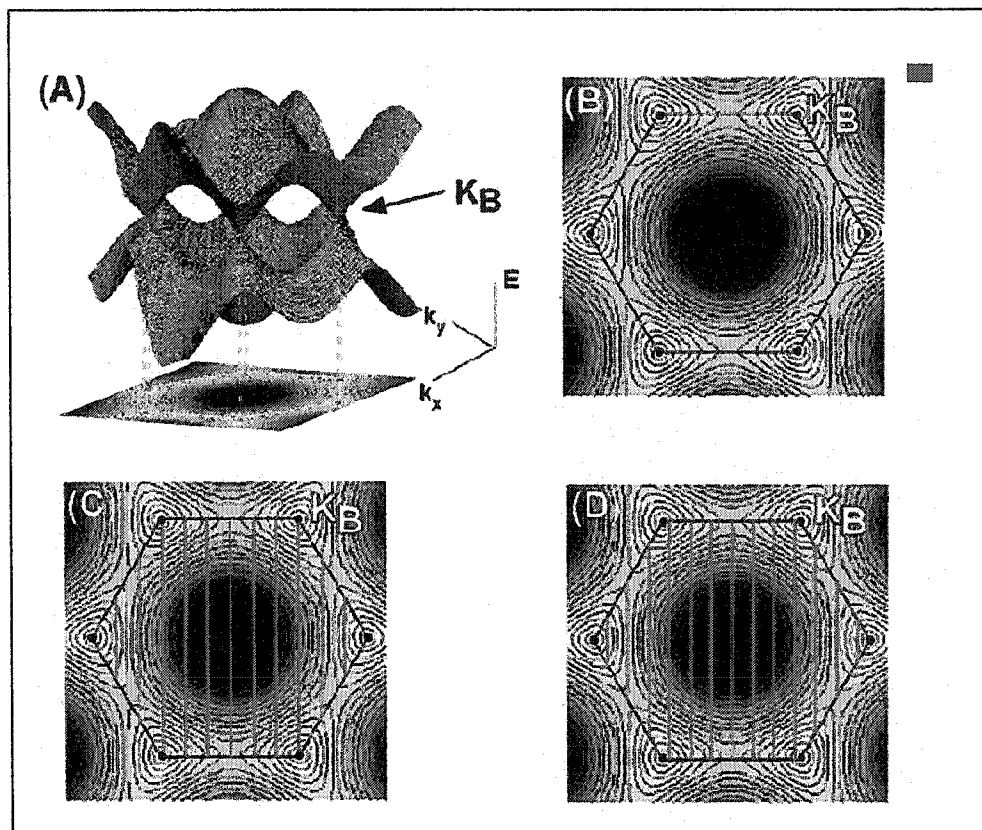


Figure 1.2. Three dimensional model of the π and π^* graphene energy bands (A) and two dimensional projection (B). (C) Allowed 1D Wavevectors for a metallic (9,0) SWNT (D) Allowed 1D Wavevectors for semiconducting (10,0) tube. (Reprinted with permission from M. Ouyang, J. L. Huang, C. L. Cheung and C. M. Lieber, *Acc. Chem. Res.* 35, 1018 (2002). Copyright (2003) American Chemical Society)

To describe the fundamental electronic properties of SWNTs a model based on the band structure of a graphene sheet is generally used. Figure 1.2 shows the band structure of a graphene sheet in the first Brillouin zone. Since there are only two

atoms per unit cell and one π electron per each atom, the lower band is completely filled. The Fermi surface then has two inequivalent Fermi points at the opposite corners of the hexagonal Brillouin zone where the conduction band and valence band meet. A total of six points where the two bands meet is obtained by translating the two inequivalent points using the reciprocal lattice vectors. Since the conduction and valence bands meet, a graphene sheet is a semiconductor with a zero energy gap. The band structure of a SWNT can then be derived from the band structure of the graphene sheet. This is accomplished by changing the periodic boundary condition used to obtain the band structure of the graphene sheet [5]. Since in a SWNT the graphene sheet does not extend to an infinite 2D structure, it is necessary to impose strict periodic boundary conditions for translation using the roll up vector that defines the nanotube. The allowed wavevectors ($\vec{k}$) values become then quantized in the direction perpendicular to the roll up vector ($\vec{k} \cdot \vec{V} = 2\pi n$), where n is an integer. Therefore the structure obtained for a SWNT consists of one-dimensional bands. Figure 1.2 shows the allowed k values for two different SWNT structures. The nanotube will have a band gap unless the lines of allowed $\vec{k}$ vectors pass thorough the two points where the conduction and valence of the original graphene structure meet. Consequently, the $(9,0)$ SWNT is metallic while the $(10,0)$ SWNT is semiconducting. In general an (n, m) SWNT has a band gap (i.e. semiconductor) unless $n - m = 3q$, where q is an integer.

1.1.3 Synthesis of SWNT

Carbon nanotubes can be produced by a variety of methods. As mentioned above, Iijima first produced nanotubes by arc discharge [2,3]. The system differed only slightly from that developed earlier by Kratschmer et al. for the production of fullerenes [6]. A similar system had been employed by Bacon more than 30 years earlier for the production of graphite whiskers [7]. In the system used by Iijima [2], the graphite electrodes were kept separated by a small gap, rather than being in contact as in the Kratschmer's method. It was observed that about half of the carbon evaporated from the anode deposited as nanotubes on the negative electrode while the rest condensed in the form of soot. One of the most important observations was that SWNT were only obtained when metal particles were present in the anode. The metals used in the earlier experiments were cobalt and nickel, packed inside bored graphite rods. Later, other metals and mixtures with lanthanides were found to catalyze the formation of SWNT as well [8]. In a typical arc discharge apparatus [9], the arc is generated between two graphite rods, which are mounted in a stainless steel vacuum chamber equipped with a vacuum line and a gas inlet. One of the graphite electrodes (cathode) is fixed and it is connected to a negative potential. The other electrode (anode) is moved from outside the chamber through a linear motion feedthrough to adjust the gap between the electrodes. A viewport is mounted on the chamber to allow for a direct observation of the arc discharge. In a standard operation, a given background pressure is stabilized within the cell by adjusting the incoming flow of an inert gas such as helium and the pumping speed. It has been

found that with a continuous flow of He better results are obtained than with a static He pressure. A stabilized voltage of about 20 V is applied while the electrodes are far apart. As the anode is moved in, a gap space is reached (1-3 mm) at which arcing occurs. Depending on the He pressure, the rod diameter and the gap between the electrodes, the electric current can vary between 40 and 250 A. During the discharge, a plasma is formed generating temperatures of the order of 3700°C. The temperature is particularly high on the anode surface and this electrode is consumed by vaporization. To keep the proper inter-electrode gap constant during operation, the position of the anode must be adjusted manually [10] or by an automated system [11]. The synthesis process lasts only a few minutes [12]. After the synthesis, several types of carbon deposits are obtained: a) a rubbery soot that condenses on the chamber walls; b) a web-like structure between the cathode and the chamber walls; c) a cylindrical deposit on the cathode face; d) a small collar around the cathode deposits, which contains the highest concentration of SWNT.

Studies have shown that a number of experimental parameters have important effects on SWNT yield and selectivity. For example, increasing the diameters of both electrodes results in yield and selectivity losses, but decreasing the anode diameter, while keeping the cathode diameter and current density constant results in an increase in yield [13]. Another critical parameter that greatly affects the SWNT yield is the pressure of the background gas, usually He. While some authors indicate that the yield increases with He pressure [13], other authors have found that beyond a certain

pressure, further increase in pressure does not result in an increase in yield [9] and it may even result in yield losses [14]. Not only the yield of SWNT, but also their diameter distribution is affected by the background gas pressure. Saito et al. [15] observed that the distribution of SWNT diameters shifted systematically to small values as the helium pressure decreased. The most frequently occurring diameters were centered at 1.4 nm for the production conducted at 1520 Torr, and it shifted to 0.95 nm for the production at 50 Torr. Among the various experimental parameters, the choice of catalytic additives is of paramount importance. In the first place, the characteristic feature that is common to all SWNT synthesis methods is the participation of a catalyst. So far, no SWNT has been synthesized without the participation of a catalyst.

Smalley et al. showed that single-wall carbon nanotubes SWNTs can also be produced in high yield by laser vaporization of a graphite rod doped with Co and Ni [16]. It has been reported that the structure of the carbon species produced in the laser ablation method strongly depends on the background argon pressure that is used [17]. When the pressure is lower than 100 Torr no SWNT are produced. They are only formed at higher pressures. Apparently, the Ar pressure plays an important role in the heat transfer phenomena and assists in the metal evaporation. Investigation of the carbon/metal target after the ablation showed that at low pressures, the metal evaporation was inhibited. The texture of the target was also found to have an effect on the quantity of SWNT produced in the laser method. For example, twice as much

SWNT were produced when carbon targets containing Ni and Co nitrates were used as when Ni-Co metals or oxides were employed. This effect was ascribed to the porous structure that results when the Ni or Co nitrates decompose inside the carbon target. At the same time, a better dispersion and smaller particle size of the metals are obtained when using nitrates than when using metals or oxides [18]. Eklund et al. have recently developed a modification of the pulsed laser vaporization technique that, according to the authors, should result in large-scale production of high-quality SWNT [19]. In this method, ultrafast ablation was achieved by using a high power free-electron laser. The modified setup includes a T-shaped quartz growth chamber placed inside a furnace to keep the chamber at 1000°C. The laser radiation enters from a sidearm that protrudes out the furnace near the center of the hot zone and strikes the carbon target, which is mounted on a rotating / translating rod. A jet of preheated argon deflects the ablation plume away from the incident laser beam, continuously sweeping the target region. The SWNT soot is then collected from a water-cooled copper coldfinger at the end of the quartz nanotube. A special feature of this method was the use of the free-electron laser (FEL) operated at a peak laser flux that is about 1000 times greater than the flux used in typical Nd:YAG based systems, but each FEL pulse is only 1/200,000 as long as the typical 10 ns Nd:YAG pulse.

The catalytic decomposition of carbon-containing compounds on appropriate metal catalysts is another method of producing SWNT. This method sometimes

referred to as CVD (chemical vapor deposition) has a good potential for the production of large quantities SWNT at low cost. It also provides the possibility of producing SWNT on a surface or inside a solid. The method is similar to those used for several decades in the synthesis of carbon filaments. The first report of SWNT obtained by catalytic decomposition appeared in 1996. This particular work used carbon monoxide as a carbon source and molybdenum supported on alumina as catalyst [20]. It has been repeatedly demonstrated [21-23] that the diameter of the carbon nanotube is determined by the size of the metal cluster responsible for its growth. It is therefore important to tailor the precursor so that the catalyst particles retain a small size during the SWNT growth. In most studies, even when the metal particles may have had nanometric dimensions before the growth started, they quickly sinter at the high temperatures needed for SWNT synthesis. Laurent et al. [24-29] and Resasco et al. [30, 31] have independently designed catalyst, which have the common characteristic of being produced only under reaction conditions. Solid oxide solutions such as $\text{Mg}_{1-x}\text{Co}_x\text{O}$ [24] or silica supported Co-molybdates have been found to be effective catalysts when they are reduced in-situ by the same carbon-containing reactant that produces the SWNT. Only under specific conditions and using the proper catalyst formulation SWNT with high selectivity can be produced. Successful examples of SWNT growth by the CVD method are the disproportionation of CO at 850°C on Co:Mo/SiO₂ (1:2 molar ratio) catalysts [30] and CH₄ decomposition at 1000°C on a $\text{Mg}_{0.9}\text{Co}_{0.1}\text{O}$ solid solution catalyst [32]. In other cases, the CVD method has resulted in low selective growth of SWNT, with simultaneous formation

of other carbon species such as graphite nanofibers and double walled or multiwalled nanotubes [33, 34].

An alternative to the CVD method of catalytic decomposition of carbon-containing molecules has been the so-called “floating catalyst” method. Sen et al. [35] prepared carbon nanotubes by decomposition of ferrocene, cobaltocene, and nickelocene under reductive conditions. In this case, the precursor provides both the carbon and the metal to catalyze the synthesis reaction. Similarly, in other methods benzene or hexane has been added to ferrocene improving the yield [36]. A variation of the floating catalyst method resulted in the commercial process known as HiPCO that produces 10 g/day of high-purity carbon single-walled nanotubes [37]. In this process, SWNT are grown at high-pressure (30–50 atm) and high-temperature (900–1100 °C) under flowing CO. The catalyst is iron in the form of small clusters that are generated in situ as continuously added iron pentacarbonyl decomposes in the reactor.

1.2. STRUCTURAL CHARACTERIZATION OF SWNT

A first step in a systematic approach towards improved SWNT synthesis study and tailoring of their electronic and mechanical properties is a feedback of information coming from reliable characterization techniques. Several methods have been applied to obtain this information. The techniques comprise local probes such as transmission electronic microscopy (TEM), electron diffraction, scanning electron

microscopy (SEM), and scanning tunneling microscopy (STM), combined with tunneling spectroscopy and bulk-sensitive probes such as Raman scattering, optical absorption spectroscopy, fluorescence and x-ray diffraction (XRD). In the subsequent section some of these methods will be introduced and the kind of information that can be obtained with them will be discussed.

1.2.1. Electron microscopy

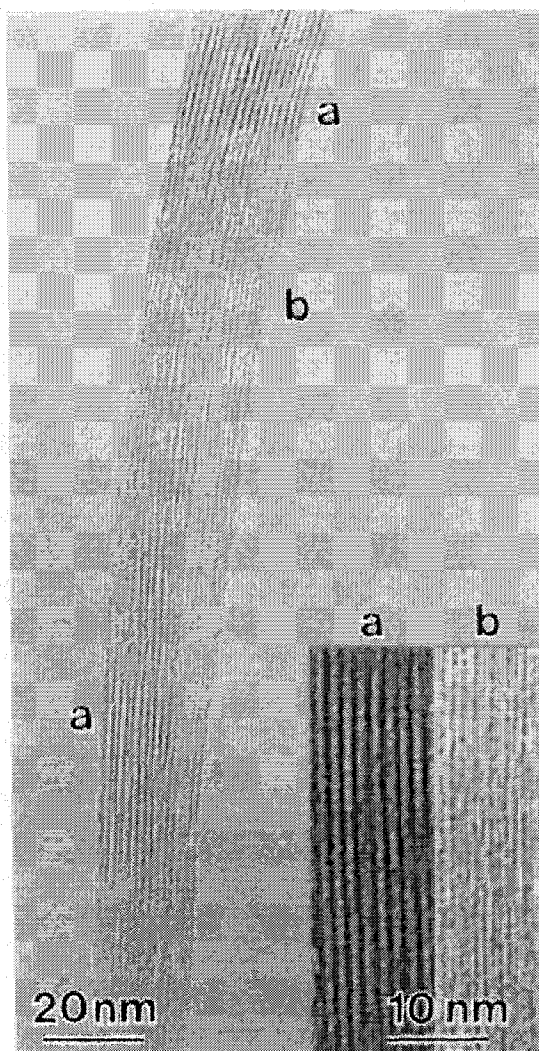
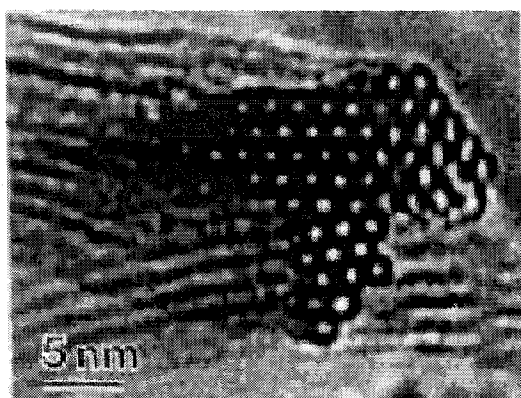
Observing structures smaller than one micrometer is not possible with light because diffraction effects limit the resolution of optical spectroscopy. So, if information at considerable higher resolution is desired, electromagnetic radiation of shorter wavelengths should be used. Electron beams offer this possibility. Their development over the past 50 years has resulted in electron microscopes that routinely achieve magnification on the order of one million times and can reveal details with resolution of up to about 0.1 nm.

When an electron beam of energy between 100 and 400keV hits a sample, many measurable signals are generated. TEM uses the transmitted electrons to form the image while SEM uses the secondary electrons emitted from the sample. Depending on the sample thickness, a fraction of the electrons passes through it without suffering significant energy loss. Since the attenuation of the electrons depends on the density and thickness of the sample the transmitted electrons form a

two dimensional projection of the sample. This is the basis for TEM imaging. Electrons can also be diffracted by particles if these are favorably oriented towards the electron beam, the crystallographic information that can be obtained from this diffracted electrons is the basis for electron diffraction. Finally the electrons in the primary beam can collide with atoms in the sample and be scattered back, backscattering is more effective for atoms of greater mass. If a region of the sample contains heavier atoms (such metal particles) than the surroundings, it can be distinguished due to higher yield of backscattered electrons. If the electron beam is rastered over the surface and the yield of secondary or backscattered electrons is plotted as function of the position of the primary electron beam it is possible to construct three dimensional images of the samples analyzed. This method is the basis for scanning electron microscopy (SEM).

1.2.1. 1. Transmission Electron Microscopy (TEM)

The existence of SWNT was first confirmed by means of high-resolution electron microscopy and electron diffraction. Due to the small physical size samples and the low atomic number of carbon, classical structural techniques such as X-ray diffraction are difficult to apply to SWNT. For this reason, TEM has been the most widespread tool for structural characterization of SWNT.



(b)

Figure 1.3. High resolution TEM images of SWNT bundles produced by arc discharge technique. Left: Cross-section like view of a polycrystalline bundle. Right: View of a twisted bundle with its axis normal to the electron beam. The inset shows a magnification of fringes related to (11) and (10) lattice planes. Reprinted from L. Henrard , A. Loiseau , C. Journet and P. Bernier, Eur. Phys. J. B 13, 661 (2000) Copyright (2003) Springer-Verlag

Figure 1.3 shows a typical TEM micrograph of a SWNT rope. One of the first observations obtained from TEM was that SWNTs have a tendency to assemble in bundles containing between 10-50 aligned nanotubes. It is generally accepted that the SWNT are held together by Van der Waals interactions. Another interesting feature is also observed in Figure 1.3. A cross sectional view, showing the individual SWNTs can be clearly distinguished. This is a common observation during TEM analysis. It occurs because the SWNT bundles are usually bent so that it becomes possible for a portion of them to get oriented parallel to the electron beam, resulting in images of the nanotube ends. TEM images show that the SWNT bundles are typically 5-20 nm in diameter and exhibit a triangular lattice with an inner nanotube diameter of around 1.7 nm [16, 38].

An important precaution to be taken into consideration when performing TEM measurements on SWNT samples is that they are highly susceptible to the 100-200keV electron beam of the TEM instrument. Beam damage makes it very difficult to carry out electron diffraction studies from isolated SWNT. Diffractions patterns can be more readily obtained from bundles of SWNT. By using low electron beam currents it has been possible to obtain good TEM measurements of lattice fringe images and electron diffraction patterns on single wall nanotubes. These studies have shown that the walls of SWNT have indeed the local structure of a graphene sheet [3].

1.2.1. 2 Scanning electron microscopy (SEM)

Scanning electron microscopy is to a certain extent a limited tool to characterize SWNT, regardless of the high magnifications that can be achieved with SEM instruments. The main problem with the application of SEM to SWNT characterization analysis is that it cannot differentiate between SWNT and MWNT. This is mostly due to the tendency of SWNT to adhere strongly to each other, forming bundles or ropes of 5-20 nm in diameter. In contrast to TEM, SEM cannot resolve the internal structure of these SWNT bundles.

Nevertheless, SEM can yield valuable information regarding the purity of a sample as well as an insight on the degree of aggregation of raw and purified SWNT materials. For instance Figure 1.4 illustrates how SEM can be used to answer substantive questions about the quality of SWNT samples [39]. Figure 1.4(a) shows a SEM micrograph of raw SWNT material produced by laser ablation. The presence of other forms of carbon besides SWNT and the occurrence of a large amount of catalysts particles is apparent. After a gas phase purification step using a gas mixture of H_2 and Cl_2 , Figure 1.4(b) shows an improvement in the degree of dispersion as well as in purity since the image predominately shows nanotube ropes. Finally the bright metal particles observed in Figure 1.4(b) (cobalt and nickel catalyst), visible after the first gas treatment can be removed by a subsequent liquid phase treatment in HCl. The final product obtained after this sequential purification process appears to be high-quality single-wall nanotube material.

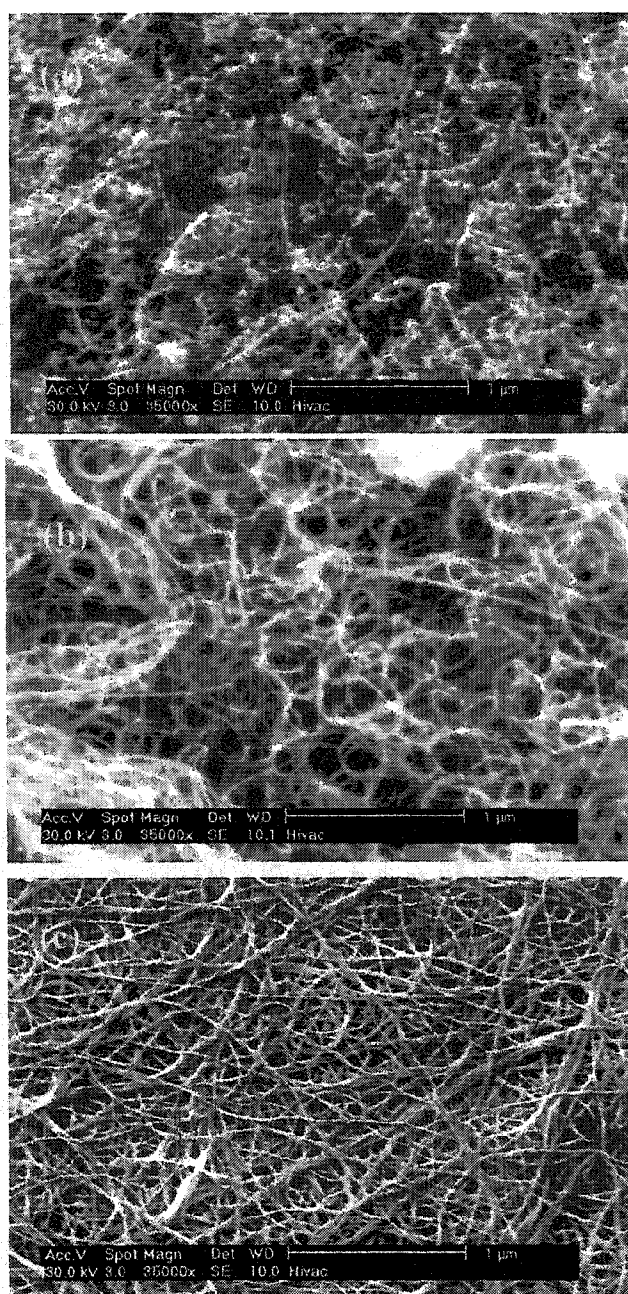


Figure 1.4. SEM micrographs of (a) Raw SWNT material obtained by laser ablation. (b) The same material in a after a gas phase purification treatment and (c) The same material in (b) after a liquid phase purification treatment in HCl. Reprinted with permission from J. L. Zimmerman, R. K. Bradley, C. B. Huffman, R. H. Hauge and J. L. Margrave *Chem. Mater.* 12, 1361 (2000) Coyright (2003) American Chemical Society.

The big disadvantage of electron microscopy in this context is that one can never be sure that the observed image is truly representative of the bulk SWNT sample. Consequently a number of bulk sensitive methods that provide information regarding the quality, diameter distribution and structural properties of a given sample have been employed. These methods comprise Raman spectroscopy, optical absorption, Temperature Programmed Oxidation and diffraction techniques.

1.2.2. Raman spectroscopy

Among the several techniques used to characterize single walled carbon nanotubes, Raman spectroscopy is perhaps the most powerful tool to get information on their vibrational and electronic structure. Raman spectroscopy is based on the inelastic scattering of visible light by matter. When electromagnetic radiation in the visible range interacts with a substance it may be absorbed by the substance, transmitted, or scattered. Light scattering may be elastic or inelastic. Elastic scattering is the most common phenomenon and occurs without loss of photon energy, i.e. without any change in the frequency of the original wave. In opposition, a very small fraction of the incoming radiation undergoes inelastic scattering, in which the scattered wave results with a different frequency than that of the incoming wave. This frequency difference is called the Raman shift, which can be positive or negative. If, upon collision with a molecule the photon loses some of its energy, the resulting radiation has a positive Raman shift (Stokes radiation). In contrast, when the

incoming photons gain energy the resulting radiation has higher frequencies (anti-Stokes radiation) and a negative Raman shift is observed.

If an adequate instrument is used to measure both the energy of the incoming and outgoing light, it will be observed that both the Stokes and anti-Stokes radiation are composed of discrete bands, which are intimately related to molecular vibrations of the substance under investigation. The information obtained by measuring the Raman shift is therefore most valuable since direct information at the molecular level of the nature of the chemical bonds and symmetry on the substance under investigation can be obtained. In the case of solids, the most elementary processes are associated with degrees of freedom of ions and electrons in crystalline and amorphous materials [40].

A limitation of Raman spectroscopy is the extremely low quantum efficiencies associated with the process (almost 1 photon is inelastically scattered for every 10^6 photons that interact with the sample). Thus, a very intense light source must be used in order to get a signal strong enough to measure adequately the Raman shift. Moreover, since a very precise measure of frequency of the incoming light is needed to calculate the Raman shift, the use of a monochromatic excitation light is preferred. A laser light source satisfies both conditions: monochromaticity and high intensity; and it is then the obvious choice for excitation light source to perform Raman spectroscopy. Different kinds of lasers are used for Raman experiments, since in

principle the position of the Raman shift ought to be independent of the laser frequency used.

The low efficiency of Raman scattering can be counterbalanced by an intensity enhancement due to the so-called resonant Raman effect. This resonant effect occurs when the photon energy of the exciting or scattered light beam matches the energy of an allowed optical electronic transition of a chromophoric group within the sample [41-42]. Excitation within the absorption band of the sample results then in the selective enhancement of just those vibrational modes on the sample that selective couple with the oscillating dipole moment induced by the excitation electric field [43]. The intensities of the resonance Raman enhanced bands can increase as much as 10^8 -fold. Thus, it becomes possible to selectively study the vibrational spectra of very dilute samples in solids by choosing excitation wavelengths in resonance with a particular analyte chromophore. However, just the intensity of Raman bands associated to this resonant process will be amplified while all other bands will fade away on the spectrum background and the band positions become dependent of the laser frequency used.

The resonant Raman effect in single-walled nanotubes is very strong due to the sharp spikes present in the one-dimensional electronic density of states (DOS). The energy difference between the spikes falls in the visible and near -infrared range [44-49]. Therefore, when the excitation laser energy is close to that of an allowed

optical transition between singularities in the one-dimensional density of states of SWNT the Raman intensity is greatly enhanced [50-52].

The energy of these allowed optical transitions depend on both the diameter and the chirality (and therefore on the metallic or semiconducting character) of the SWNT. Using the tight binding π - π overlap integral as a scaling factor, it has been possible to demonstrate that an inverse proportionality exists between the interband transitions and the nanotube diameter [53-55]. This inverse proportionality has been illustrated in a series of publications, which report the range of the allowed optical transitions for semiconducting and metallic nanotubes [50, 53, 54]. Of particular interest is the work of Kataura et al. [50] who calculated the one-dimensional energy band structure for SWNTs ranging from 0.6 up to 1.8nm in diameter. The results of the calculation of the allowed optical transitions gap energies between the mirror image spikes of the density of states are reproduced in Figure 1.5 as function of nanotube diameter.

These theoretical calculations can be used to link nanotube diameters with the energy gaps between singularities in the valence and conduction bands of the electronic density of states of SWNT. Since the energy gaps are probed through the resonant Raman effect, direct information on the nanotube diameter can be obtained from the Raman spectra. Based on this effect, Raman spectroscopy has provided a particularly valuable tool for examining not just the diameter distribution in a

nanotube sample, but also the mode frequencies of SWNT with specific diameters, as well as for evaluating the merits of theoretical modes for the 1D phonon dispersion relation, and for studying the 1D electron DOS through this electron-phonon coupling mechanism [56].

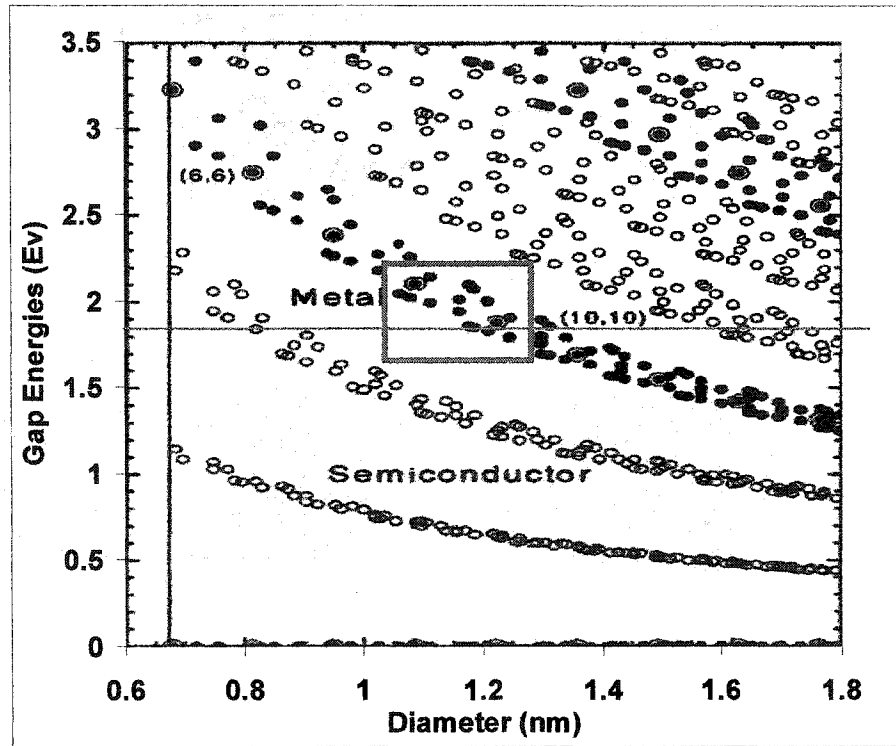


Figure 1.5. Calculated gap energies as a function of diameter for SWNT as function of diameter, obtained by Kataura et. al. A “metallic window” in which metallic tubes are in resonance is presented for SWNTs synthesized by laser ablation using a Co/Ni catalyst. Adapted from Synth. Met. 103, H. Kataura, Y. Kumazawa, Y. Maniwa, I. Umez, S. Suzuki, Y. Ohtsuka and Y. Achiba, “Optical properties of Single Wall Carbon Nanotubes” Pag. 2555, Copyright (2003) with permission from Elsevier.

To successfully analyze Raman spectra of SWNT, the vibrational modes of a SWNT need to be evaluated. A first approach considers decomposing these modes into irreducible representations of the point group in which the SWNT belongs [57]. For example, an armchair nanotube belongs to the D_{nh} symmetry group (n being an even integer), and consequently the vibrational modes can be decomposed into the following irreducible representations:

$$\Gamma^{\text{vib}} = 4A_{1g} + 2A_{1g} + 4A_{2g} + 2A_{2u} + 2B_{1g} + 4B_{1u} + 2B_{2g} + 4B_{2u} + 4E_{1g} + 8E_{1u} + 8E_{2g} + 4E_{2u} + \dots + 8E_{(n/2-1)g} + 4E_{(n/2-1)u}. \quad (2)$$

For the case of a (6,6) armchair nanotube 72 phonon branches are expected and the above equation gives a total of 48 distinct mode frequencies. Appropriate character tables can be used to determine which modes are Raman active. Thus, it can be easily demonstrated that there are 16 Raman active frequencies ($4A_{1g} + 4E_{1g}$ and $8E_{2g}$). Notice that the number of active modes depends just on the SWNT chirality but are independent of nanotube diameter.

Detailed characterization of SWNT by Raman spectroscopy started with the initial joint efforts of Dresselhaus et al. and Eklund et al.[58], who obtained the Raman spectra of SWNT bundles using several laser excitation energies. They reported a strong enhancement of the Raman intensity due to the diameter-selective resonance Raman effect. This work confirmed the theoretical predictions of the

diameter-selective Raman scattering that is particularly important for the Raman bands associated with the A_{1g} radial breathing mode (RBM) [47, 59, 60]. As a result, the presence of the RBM feature in the Raman spectrum is used today as a signature of the presence of SWNT in the sample. Variations in RBM band shape and position provide information on the nanotube diameters present in a given sample.

Following the seminal work of Dresselhaus et al., the unusual response of this line to changes in excitation energy has been discussed in many articles. *Ab initio* calculations confirmed the inverse proportionality of the A_{1g} mode frequency with the diameter, and yielded an appropriate proportionality factor [61, 62]. The RBM band appears in the Raman spectrum below 300cm^{-1} and has been proposed to be independent of chirality [63]. Bandow et al. calculated the RBM frequencies of all types of SWNT and found that all frequencies fall on a common line according to the expression [64]:

$$\bar{\gamma} = \frac{223.75}{d} \quad (3)$$

where $\bar{\gamma}$ is in units of cm^{-1} and d is the nanotube diameter in nm.

Using this expression one can obtain the diameter of the SWNTs under study just by observing the position of the RBM band. However, a slight correction should be made in this formula since intertube coupling must be considered when the nanotubes are present in a bundle. This correction was achieved by using a Lennard-

Jones potential to account for van der Waals interactions among the nanotubes in a bundle [58, 65]. A significant upshift of the RBM was found for nanotubes in bundles with respect to isolated nanotubes. The calculated data were best fitted by the following non- linear phenomenologic relation between the RBM frequency and the nanotube diameter:

$$\bar{\gamma} = \frac{238}{d^{0.93}} \quad (4)$$

where $\bar{\gamma}$ is in units of cm^{-1} and d is the nanotube diameter in nm [66].

This correlation has been widely used to study samples with different diameter distributions [47, 50, 67-69], confirming the diameter dependence of the electronic properties of SWNT. As a result, the study of the nanotube's diameter by Raman scattering has provided complementary information to the direct measurements conducted by TEM, STM and other techniques [70-76].

As mentioned above, the information obtained by Raman spectroscopy is the result of the resonant Raman effect that is particularly strong in SWNT. Therefore the nanotubes that contribute most strongly to the Raman scattering for a given excitation wavelength are those which are in resonant with the incident or scattered light. Consequently, the spectral shape and position of the Raman RBM do not directly reflect the true diameter distribution in the SWNT sample, but rather the

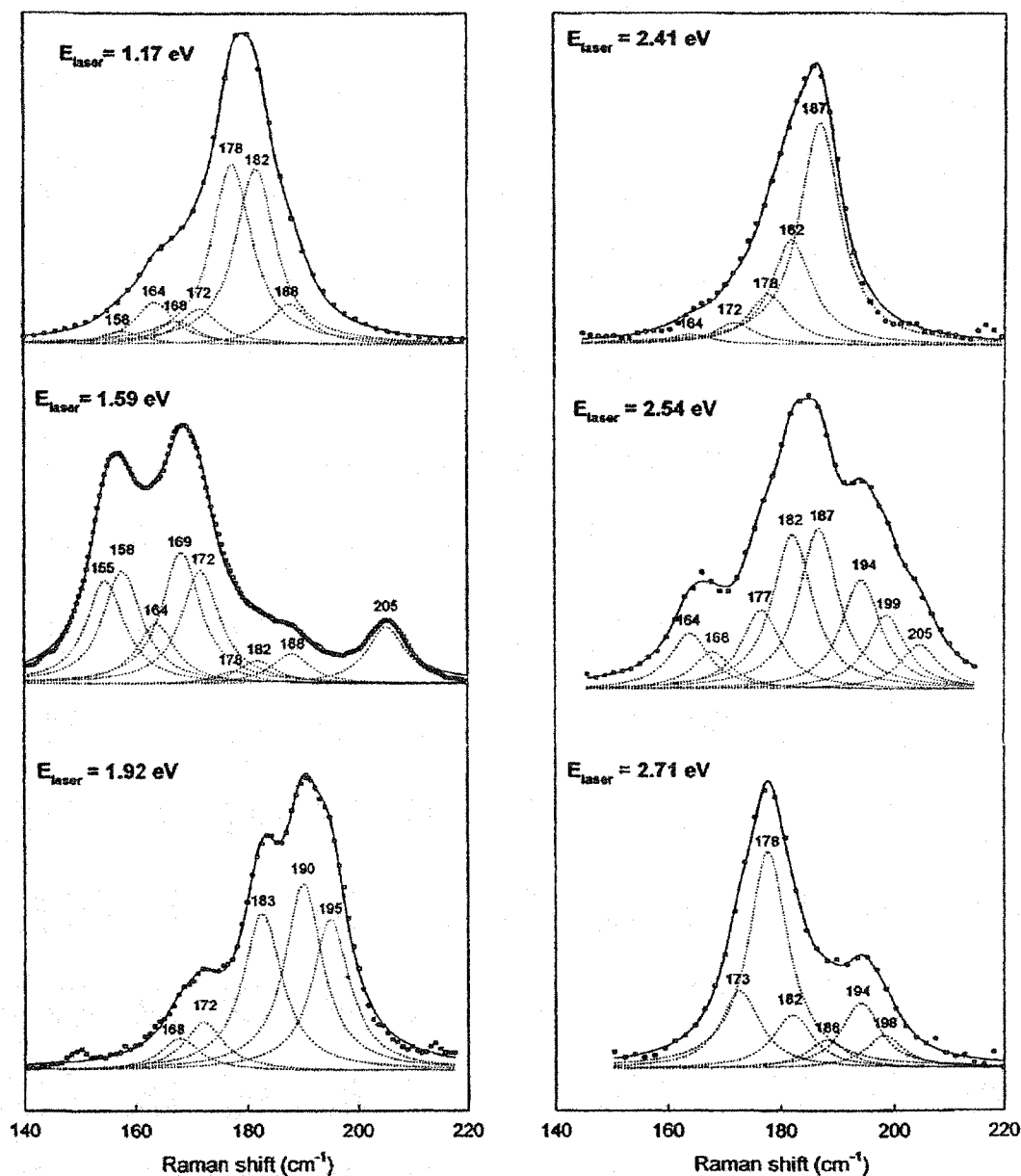


Figure 1.6. Raman spectra of the radial breathing mode (RBM) of SWNT sample collected with six different laser lines.. The dotted curves represent individual Lorentzian curves used by the authors to fit the experimental data. Reprinted with permission from M. A. Pimenta, A. Marucci, S. D. M. Brown, M. J. Matthews, A. M. Rao, P. C. Eklund, R. E. Smalley, G. Dresselhaus and M. S. Dresselhaus, *J. Mater. Res.* 13, 2396 (1998). Copyright (2003) by the Materials Research Society.

subset of nanotubes that are in resonance with the incident or scattered photon. So the relative intensities of the individual peaks that compose the RBM band are not associated only with the relative concentrations of the different nanotubes in the sample, but rather reflect their electronic properties, which in their turn modulate the Raman cross section [77, 78]. This fact has been clearly illustrated by Dresselhaus et al. in a series of publications [79-82]. Figure 1.6 illustrates the Raman band associated with the radial-breathing mode of SWNTs obtained by laser vaporization of a carbon target containing 1 to 2 atom % of Ni/Co. In this case, the Raman spectra were obtained with 6 different laser excitation energies ranging from 1.17 to 2.71 eV [79]. Notice that the band shapes are completely different from one excitation laser to another. This result is consistent with a sample containing carbon nanotubes with different diameters, which resonate at different energies. In this case, the average diameter as determined by TEM of the SWNT was 1.24 nm, but the RBM bands indicate that they range from 1.09 to 1.44nm

The differences in the average peak positions when different lasers are used complicate the analysis. Recently a better understanding of the response of the RBM has been attempted on the basis of an extended experimental and theoretical analysis [54, 83, 84]. The response of the peak position and the first and second moments of the spectra were found to oscillate with the energy of the exciting laser. This oscillation was found to be due to the microscopy quantization of the electronic levels as a consequence of the finite size of the nanotubes in direction perpendicular to the

nanotube axis and, as mentioned before, to the distribution of the states along the nanotube axis into the van Hove singularities. Furthermore, an approximation has been successfully used to evaluate the spectral moments of the RBM Raman response without explicit use of the joined density of states. This simplified model has been used to determine the mean and the width of the diameter distribution of a SWNT sample. A remarkable conclusion is that just a single laser energy could be used to evaluate the first and second moments of the spectra and, therefore, the mean and the width of the diameter distribution of the sample [84].

In principle, the radial breathing mode frequency could provide the identity (n,m) of the individual nanotubes participating in the Raman scattering since the RBM frequency is proportional to the diameter, and the value of the SWNT diameter depends on the integers (n,m) [85]. However several distinct (n,m) nanotubes can exhibit sufficiently similar diameters so that their RBM frequency differs only by 1-2 cm^{-1} . This prevents using the RBM frequencies to determine (n,m) in a sample of SWNT, since the natural linewidth of the RBM band is 6 cm^{-1} and the individual contributions to the band from nanotubes with similar diameters would be very difficult to resolve [56,64,70].

Besides the radial breathing mode band, the Raman spectra of SWNTs also comprise a disorder-induced Raman band (D band), which is a feature common to all sp^2 hybridized disordered carbon materials. This D band appears in the Raman

spectra between 1250 and 1450 cm^{-1} , and is associated with phonons close to the K point of the graphite Brillouin zone and it becomes Raman active when translational symmetry is lost [81, 82, 86]. The D band also shows a strong dependence on the excitation laser energy, although in this case the dependence is highly linear. Pimenta et al. [87] studied the D band behavior on isolated SWNT and observed that its intensity appeared to be random from one nanotube to another; although the linear dependence on the excitation laser energy was observed, this was attributed to be more a consequence of the same general trend that is observed for all sp^2 carbon materials. The authors suggested that this phenomenon is linked to phonons that are not at the center of the 1D Brillouin zone of SWNTs and concluded that they become Raman active due to the finite size of the SWNTs or to the presence of defects, which would break the translational symmetry along the nanotube axis [82, 88]. Recently, it has been proposed that the excitation energy dependence of the D band is an intrinsic property of the SWNT, and has been suggested that the metallic character of an individual nanotube can be inferred from the shape and position of its D band [89].

The D-band has been related not just to defects on SWNT but also to the presence of other forms of disordered carbon such as carbon nanoparticles and amorphous carbon [90]. Its relative intensity has been used as a semi-quantitative indicator of the presence of undesired forms of carbon (i.e., microcrystalline graphite, amorphous carbon, MWNT, carbon nanofibers).

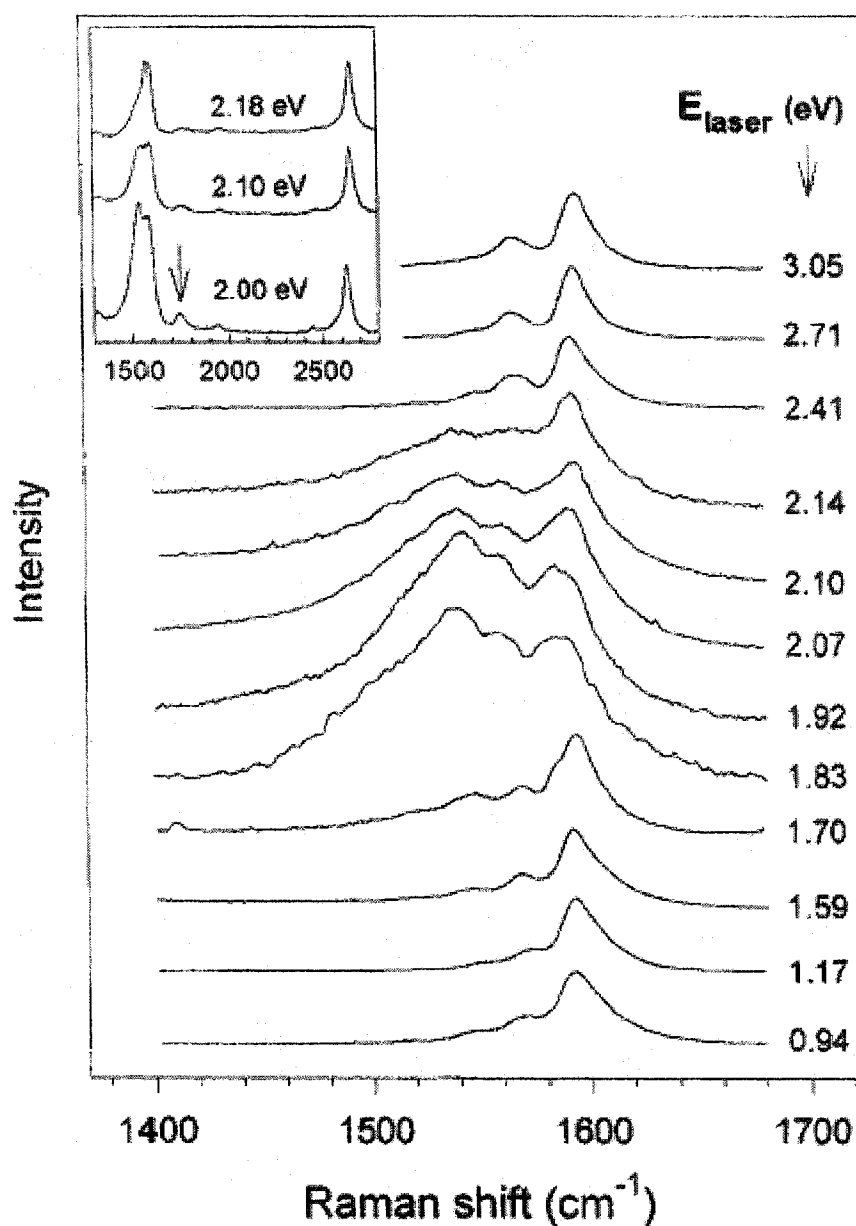


Figure 1.7. Raman spectra of the tangential modes of SWNT obtained with several laser energies. The SWNT were synthesized by laser ablation of a carbon target containing a Ni/Co catalyst. Reprinted with permission from M. A Pimenta, A. Marucci, S. A. Empedocles, M. G. Bawendi, E. B. Hanlon, A. M. Rao, P. C. Eklund, R. E. Smalley, G. Dresselhaus and M. S. Dresselhaus, Phys. Rev. B 58, R16016 (1998) Copyright (2003) by the American Physical Society.

The Raman spectra of SWNT also contain the typical G-band associated with the tangential C-C stretching modes of SWNTs, which consist of two A, two E₁ and two E₂ phonon modes for chiral nanotubes and one A_{1g} one E_{1g} and one E_{2g} mode for armchair or zigzag nanotubes, as predicted by group theory and phonon frequency calculations [57, 75, 91-94]. This tangential mode G band appears in the 1400-1700 cm⁻¹ region and involves out-of-phase intra-layer displacement in the graphene structure of the nanotubes. In contrast to the D band the G band is a measure of the presence of ordered carbon and therefore is present on all kind of sp² ordered carbonaceous materials (graphite, perfect MWNT, etc).

In SWNT samples, the most important characteristic of the G band is that the analysis of its line shape offers a method for distinguishing between metallic and semiconducting nanotubes. The G band of the semiconducting nanotubes has been extensively studied and is well accounted for using Lorentzian oscillators to describe the six Raman-active modes that have been spectroscopically identified by polarization studies of the symmetries of the various line-shape components [95, 96]. On the other hand, although Lorentzians can be used to describe the G band of metallic carbon nanotubes [97, 98], the lower frequency component of the G band spectrum that appears around 1540cm⁻¹ has to be fitted using a Breit-Wigner-Fano (BWF) line shape, due to a downshift and broadening in the tangential G band of metallic SWNTs relative to semiconducting SWNTs [99-101].

Brown et al. [102] demonstrated that only these two Raman components were needed to fit the tangential G band for metallic SWNTs. Both components were found to exhibit predominant A (A_{1g}) symmetry. The differences in their peak frequencies were attributed to a difference in the force constant of vibrations along the nanotube axis (higher force constant) versus circumferential (lower force constant) and to an additional downshifting and broadening of the lower-frequency peak due to a coupling of the discrete phonons to an electronic continuum (this continuum is characteristic of any electronic structure that shows metallic-like conduction properties) that resulted in the Breit-Wigner-Fano line shape. However, as in all resonant Raman study, the presence of this BWF in the Raman spectra will depend on the resonance conditions between the excitation energy and the DOS of the SWNT present on the sample. Accordingly, in a sample in which SWNT of different chirality are present it is possible to selectively enhance the Raman efficiency for metallic or semiconductor SWNT by carefully choosing the laser excitation energy. This method is illustrated below.

Figure 1.7 shows a wide range resonant Raman spectra of the G band for SWNT obtained Pimenta et al. [47] who investigated the line-shape variation of the band attributed to metallic nanotubes as a function of the excitation laser energy. In this study, a large enhancement in the relative intensity of the band centered at 1540 cm^{-1} was observed in the energy range 1.7 - 2.2 eV. This enhancement is shown in Figure 1.7, and it was explained in terms of the singularities in the density of states of

the metallic nanotubes together with the distribution of diameters of the sample. The nanotubes used in that particular study were obtained by laser vaporization of a carbon target containing 1 to 2% of a Ni/Co catalyst. The diameter distribution obtained from the TEM was in the 1.1-1.3 nm range and, as predicted from the plot in Figure 1.5, for those diameters the energy region of resonance for metallic nanotubes falls in the range 1.7 - 2.2 eV. This energy range is in perfect agreement with the range at which the enhancement of the BWF line shape was observed. Consequently, when using laser energies around 1.8 eV, mostly metallic SWNT are probed and a “metallic window” can be delineated in which the resonance condition for metallic nanotubes with diameter around 1.2 nm takes place. This metallic window is depicted in the Kataura plot of Figure 1.5 as well.

In spite of all the interesting information that can be obtained from Raman spectroscopy, this technique has an intrinsic limitation related to its resonant character, which permits only getting information on the nanotubes that are in resonance with the incident or scattered light. Therefore, a full characterization of all the SWNT in the sample, with different diameters and chiralities cannot be achieved. Only on those samples with a narrow diameter distribution or even better, on isolated SWNT, Raman spectroscopy can provide a full description. Recently, a series of studies on isolated SWNT grown over a silicon substrates has been reported. These studies have led to the observation of Raman spectra from an isolated nanotube, with intensities under good resonance conditions comparable to that from the silicon

substrate. Even though the ratio of carbon to silicon was approximately only one carbon atom to 10^8 silicon atoms [103-108]. All the Raman features observed in previous studies on nanotube bundles were also observed in the spectra of the single nanotubes, including the radial breathing mode, the G-band and the D-band [103,104]. However, at the single nanotube level, the characteristics of each feature were investigated in greater detail, including its dependence on diameter, chirality, laser excitation energy and closeness to resonance with electronic transitions [105]. In this case, the uniqueness of the electronic transition energies for each nanotube becomes of particular importance [106]. The high sensitivity of the Raman spectra to diameter and chirality, particularly for the characteristics of the radial breathing mode, which are also uniquely related to the same (n, m) indices, provided structural determination of (n, m) at this single nanotube level. The (n, m) assignments made to individual carbon nanotubes have been corroborated by measuring the characteristics of other features in the Raman spectra that are also sensitive to nanotube diameter and chirality. Raman spectroscopy has provided a convenient way to characterize nanotubes for their (n, m) indices, in a manner that is compatible with the measurement of other nanotube properties, such as transport, mechanical and electronic properties at the single nanotube level, and the dependence of these properties on nanotube diameter and chirality [107,108].

1.2.3. Optical Absorption

Another way to probe the electronic properties of SWNT is through their optical absorption spectra. This technique is based on the well-known phenomenon of light absorption by a chromophore group present in the sample. In the case of SWNTs when the light sent to the sample matches the energy of an allowed electronic transition between Van Hove singularities, light in the visible and near infrared range can be absorbed. The observed absorption peaks are identified with interband transitions $E_{ii}(d_t)$ between the i^{th} van Hove singularity in the valence band (occupied states) to the i^{th} singularity in the conduction band (empty states). Figure 1.8 shows typical optical absorption spectra of samples synthesized by laser ablation using different catalysts [50, 109]. For the sample obtained by laser ablation using a NiY catalyst (with an average diameter of 1.5 nm) three strong absorption bands at 0.68, 1.2 and 1.7 eV were observed, which are related to interband transitions between the first and second van Hove singularities (E_{11}^S and E_{22}^S) for semiconducting nanotubes and E_{22}^M for metallic nanotubes, as can be predicted by observing Figure 1.5. Notice that the optical absorption spectra for the SWNT obtained using a RhPd catalyst correspond to SWNT with much smaller diameters (diameters distributed from 0.68 to 1.00 nm) so the theoretical calculations depicted in Figure 1.5 predict that the optical absorption peaks should move to higher energies, as is experimentally verified [110].

As mentioned above, the same calculations that relate SWNT diameter with the energy of the optical interband transitions can be used to predict the positions of

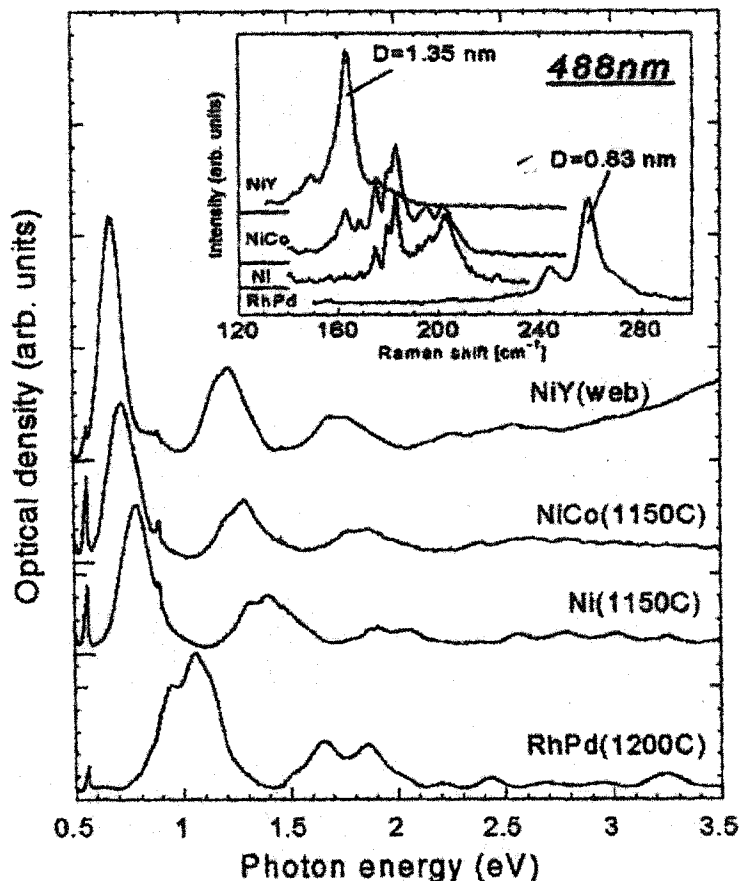


Figure 1.8. Optical absorption spectra of SWNT obtained using 4 different catalysts at different growth temperatures. Inset: Raman spectra obtained on the same set samples. Reprinted from Synth. Met. 103, H. Kataura, Y. Kumazawa, Y. Maniwa, I. Umez, S. Suzuki, Y. Ohtsuka and Y. Achiba, "Optical properties of Single Wall Carbon Nanotubes" Pag. 2555, Copyright (2003) with permission from Elsevier.

the absorption bands. The selection rules predict that the optical absorption spectra of SWNT will be dominated by transitions between peaks in the density of states of the valence and conduction bands; with momentum conservation only allowing

transitions between pairs of singularities which are symmetrically placed with respect to the Fermi level. Thus, following the van Hove singularities, the energy of the optical transitions in SWNT are also inversely proportional to the SWNT diameter. For the first two allowed optical transitions in semiconducting SWNTs, the energy of the optical transitions has been proposed to be proportional to [111]:

$$E_{11}^S = 2a_0\gamma / d \quad \text{and} \quad E_{22}^S = 4a_0\gamma / d \quad (5)$$

Where γ is the tight binding nearest neighbor π - π overlap integral, which can be calculated from the Raman spectra. For the metallic nanotubes, the energies of the optical transitions have been proposed to be $E_{11}^M = 6a_0\gamma / d$ [53]. However, these calculations showed to be inaccurate; indeed more recently it has been pointed out that the density of states of the metallic SWNT is also chirality dependent due to a trigonal warp effect [112,113]. This leads to a splitting of the singularities in metallic nanotubes, which is maximum for the zigzag variety. Therefore, a more careful accounting of the electronic transitions has to be carried out in order to obtain a more accurate model.

One of the great advantages of optical absorption is the possibility of achieving high-energy resolution, which allows the identification of fine structure within the individual absorption features [55]. This fine structure is related to individual SWNTs, or groups of SWNT with similar diameter. Moreover it has been

proposed that the analysis of such data would offer information as to whether the formation process of SWNT leads to the existence of preferred wrapping angles in the nanotube vector map [5,53,55].

In general, the results obtained by optical absorption must be compared with the information obtained by Raman spectroscopy. Since in optical absorption there is no resonance limitation as in Raman spectroscopy, in which a narrow set of SWNT is probed, the interpretation of the optical absorption information is more straightforward.

1.2.4. Fluorescence.

In direct correspondence to the concepts discussed above for optical absorption and Raman spectroscopy, the presence of the Van Hove singularities in the density of states of SWNT may result in the emission of radiation at very precise wavelengths if the SWNTs are excited to a higher electronic state through a light induced excitation mechanism. The only condition is the matching between the energy of the excitation light and one of the allowed optical transitions between singularities in the electronic structure of SWNT. The second condition for emission is that the lifetime of the excited state previous to relaxation is long enough for the process to be measurable. Hence, fluorescence can only be observed on semiconducting SWNT, in which the absence of a continuum in the density of states at the Fermi level allows a relatively long lifetime of the excited state.

Fluorescence was originally reported on SWNT samples dissolved in organic solvents and integrated in polymer matrices. In those earlier observations, the fluorescence was explained either in terms of electronic structures associated with defects in the nanotubes or in terms of the presence of functional groups that were attached to the SWNT during the functionalization processes [114-115]. However the absence of fine structure in the emission spectra did not allow linking the observed emission spectra to the intrinsic electronic structure of SWNT. A breakthrough in SWNT characterization was recently made by O'Connell et al. [116], who observed fluorescence from SWNT samples consisting of individual nanotubes suspended in aqueous solutions of sodium dodecyl sulfate. In this suspension, the samples did not undergo any chemical modification. In contrast to the earlier studies, the fluorescence spectra displayed a well-defined fine structure. Figure 1.9 compares typical emission and absorption spectra for a particular SWNT sample. There is a clear correspondence between each peak in both spectra, i. e. each absorption peak in the region of the first allowed electronic transition (E_{11}) was also present in the emission spectrum. This correspondence lead the authors to assign the emission spectra to semiconducting SWNT.

The authors also observed that the photoluminescence intensity was dramatically reduced by aggregation of the SWNT in bundles or by changes on the pH of the SDS solution. This intensity reduction can explain the absence of fine structure on SWNT fluorescence spectra reported on earlier studies.

Another remarkable consequence of this work is that by evaluating the complete excitation-emission matrix in the near infrared to the near UV ranges, structural information of individual SWNTs can be obtained. For instance, optical

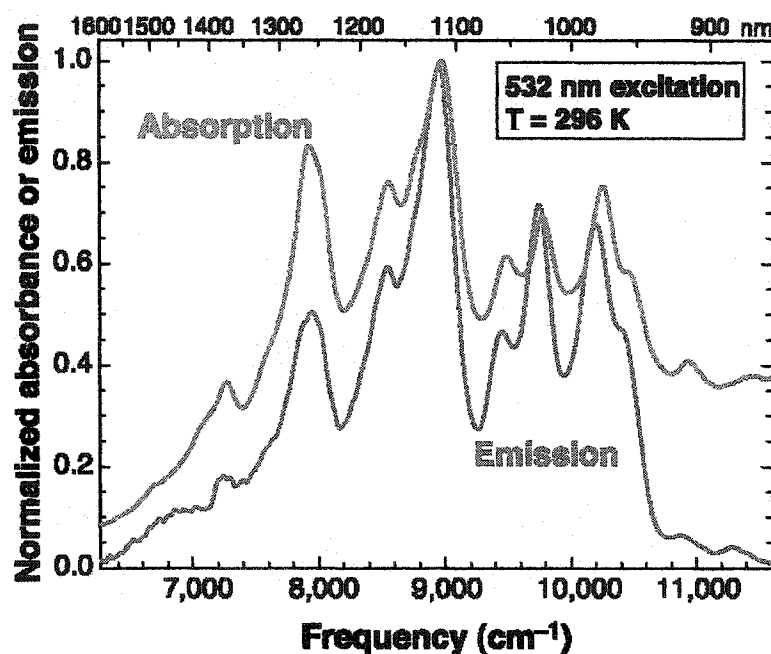


Figure 1.9. Emission spectrum (red) of individual SWNT suspended in SDS excited by 8ns, 532-nm laser pulses, overlaid with the absorption spectrum (blue) of the sample in this region of the first van Hove band gap transitions. Reprinted with permission from M. J. O'Connell, S. M. Bachilo, C. B. Huffman, V. C. Moore, M. S. Strano, E. H. Haroz, K. L. Rialon, P. J. Boul, W. H. Noon, C. Kittrell, J. Ma, R. H. Hauge, R. B. Weisman and R. E. Smalley *Science* 297, 593 (2002). Copyright 2003 American Association for the Advancement of Science

excitation of a SWNT to a second Van Hove transition (E_{22}) will be immediately followed by fast relaxation before emission in the first branch transition (E_{11}) is observed. Therefore by monitoring the intensity of the E_{11} transition while varying the excitation energy, the second branch transition E_{22} that gave rise to that particular

first branch peak E_{11} can be identified. Figure 1.10 shows that excitation spectrum for a E_{11} transition of 875nm. The excitation spectrum showed a distinct second branch (E_{22}) feature centered at 581nm. The authors were the first to point out that this information could be used to identify the specific indexes (n, m) for every SWNT present in the sample. Soon after, they reported that this goal had indeed been accomplished [117]. They were able to build the entire excitation/emission experimental matrix in the UV-NIR range and each excitation/emission pair was associated with specific E_{11} and E_{22} optical transitions for each individual SWNT. By combining these fluorescence results with the values for SWNT diameter obtained by Raman spectroscopy on the same set of samples and with the results of numerical simulations, a direct assignment of the specific (n, m) nanotube structure for each one of the fluorescence data points peaks was achieved. The measured fluorescence intensity as a function of the nanotube diameter and chiral angle was also obtained. They further assumed that the intensity distribution should closely reflect the distribution of nanotube abundance in the sample. In fact, the variation of quantum yields with diameter or chiral angle has not been clearly established yet, but, as a first approximation, this method provides a direct computation of the distribution of individual SWNT present in a sample. The particular SWNT sample studied by the authors was obtained by CO disproportionation at high pressure, using $\text{Fe}(\text{CO})_5$ as a catalyst. The diameter distribution computed for this material was centered at 0.93 nm, while the chiral angle distribution was centered at 30° . The values obtained for the diameter distribution were in good agreement with previous TEM and Raman

studies. Of special interest is the result concerning the chiral angle distribution; this outcome is in agreement with previous reports that indicated that SWNT are formed closer to the armchair rather than zigzag structure.

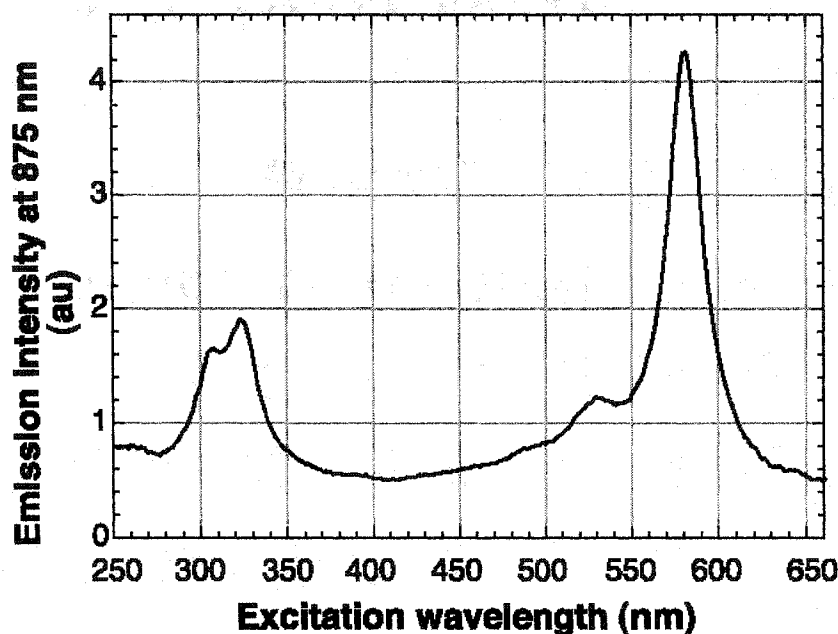


Figure 1.10. Fluorescence excitation spectrum of the 875-nm band gap emission feature in a 296 K sample of SWNT suspended in SDS in H₂O. The strong excitation feature at 581 nm is assigned as the second van Hove absorption of this nanotube species. Reprinted with permission from M. J. O'Connell, S. M. Bachilo, C. B. Huffman, V. C. Moore, M. S. Strano, E. H. Haroz, K. L. Rialon, P. J. Boul, W. H. Noon, C. Kittrell, J. Ma, R. H. Hauge, R. B. Weisman and R. E. Smalley *Science* 297, 593 (2002). Copyright 2003 American Association for the Advancement of Science

A similar work on photoluminescence in SWNT has been recently reported by another group [118]. In this particular case the SWNT material under study was obtained by pulsed laser vaporization. The authors followed the same methodology described above and obtained a diameter distribution centered at large diameters

(around 1.3 nm). Interestingly, the distribution of chiral angles was relatively similar to the one obtained by Bachilo et. al. [117] on SWNT samples produced by the HiPCO process; i. e. a chiral angle distribution with SWNT having a relatively large chiral angles.

1.2.5 Temperature Programmed Oxidation (TPO)

The detailed quantification of the different forms of carbon on a SWNT sample is a difficult task. Electron microscopy can only provide a qualitative description of the type of carbon species produced. Many times, it is hard to determine how representative of the overall production is a given micrograph. At the same time, as mentioned above the D/G band ratio in a Raman spectrum can be used as a semi-quantitative indication of the presence of undesired (disordered) carbon species. However, Raman spectroscopy does not provide a precise quantification of the relative amounts of each carbon species present in the sample. In an attempt to make this quantification more precise, Kitiyanan et al. [30] employed Temperature Programmed Oxidation (TPO), a standard technique in catalysis research used to quantify and characterize carbonaceous deposits on heterogeneous catalysts [119,120]. In a typical TPO experiment, a continuous flow of 5 % O₂/He was passed over the catalyst containing the carbon deposits while the temperature was linearly increased (11°C/min). The evolution of CO₂ produced by the oxidation of the carbon species was monitored by a mass spectrometer. Alternatively, the use of a flame

ionization detector (FID) provides a higher carbon sensitivity than the mass spectrometer. In this detection mode, the CO₂ and CO produced during the oxidation

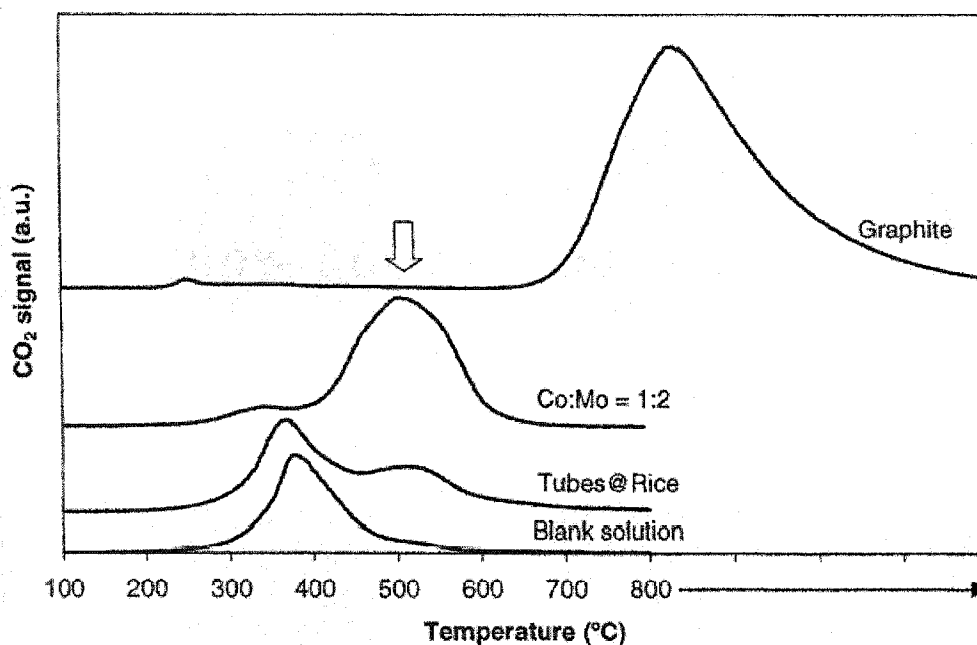


Figure 1.11. Temperature programmed oxidation (TPO) of all the carbonaceous species formed over a CoMo/SiO₂ catalyst after disproportionation of CO at 700°C, compared to similar TPO profiles of a graphite reference and commercial SWNT obtained from Tubes@Rice. Also included is the TPO of the blank solution, containing a surfactant, in which the commercial SWNT were dispersed. All the references were physically mixed with bare CoMo/SiO₂ catalyst. Reprinted from Chem. Phys. Lett. 31 B. Kitiyanan, W. E. Alvarez, J. H. Harwell and D. E. Resasco, "Controlled production of single-wall carbon nanotubes by catalytic decomposition of CO on bimetallic Co–Mo catalysts" Pag. 497, Copyright (2003), with permission from Elsevier.

was quantitatively converted to methane in a methanator [121], in which the stream coming from the TPO is mixed with a stream of H₂ over a nickel catalyst at 400°C. The methane produced in the methanator, which exactly corresponded to the CO₂ and

CO generated in the TPO, was monitored in an FID. Calibration of the evolved CO and CO₂ with pulses of pure CO₂ or oxidation of known amounts of graphite allowed the authors to get a direct measurement of the amount of carbon that gets oxidized at each temperature. TPO is 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. TGA studies [122] have shown that, in the absence of a catalyst, the ignition temperature of SWNT is 100°C higher than that of C₆₀ fullerenes and 100°C lower than that of MWNT.

Figure 1.11 illustrates the TPO profiles of the carbon species produced on a Co:Mo/SiO₂ catalyst, which exhibited high selectivity towards SWNT [30]. This sample presented a small oxidation peak centered at around 330°C, which can be ascribed to amorphous carbon, and a major peak marked in Figure 1.11 with an arrow, centered at about 510°C, which was ascribed to the oxidation of SWNT. Two reference samples were compared to this TPO and their profiles are also included in Figure 1.11. The first reference is 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 reference was a commercial sample of purified SWNT, obtained from Nanotubes@Rice (Rice University). This sample came in a liquid suspension containing a non-ionic surfactant Triton X-100. To conduct the TPO experiment, this

suspension was impregnated on the Co:Mo/SiO₂ catalyst to get 0.6 wt % SWNT on the sample. As shown in Fig. 1.11, 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 ascribed to the oxidation of SWNT. To corroborate that the first peak was indeed due to the oxidation of Triton, the authors prepared a sample using a blank solution containing only the surfactant in the same concentration. The TPO profile showed that indeed that was the case. The quantification of the amount of SWNT in the

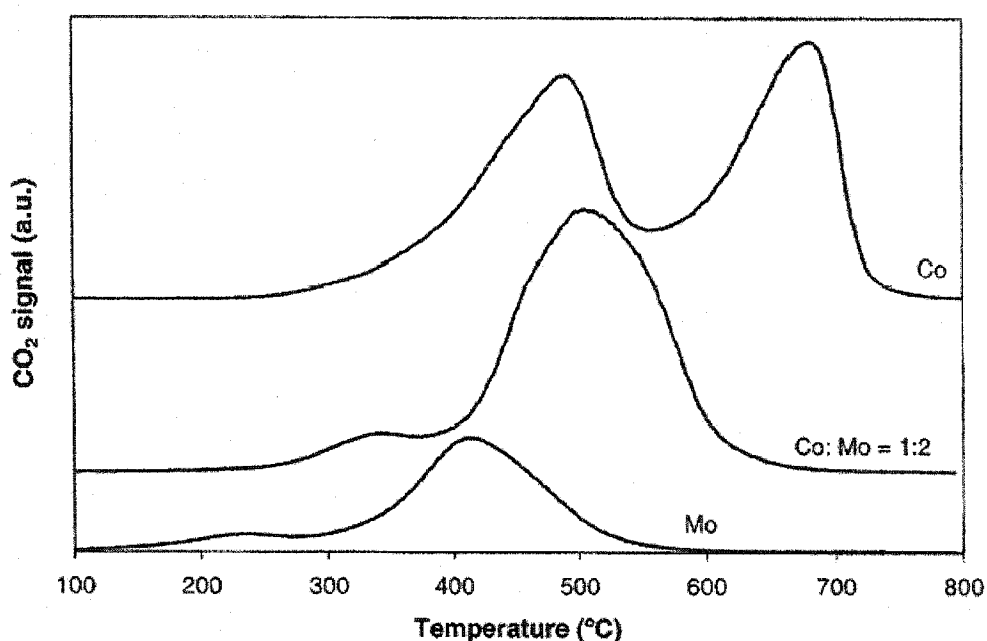


Figure 1.12. Temperature programmed oxidation (TPO) of all the carbonaceous species formed over a CoMo/SiO₂ catalyst after disproportionation of CO at 700°C, compared to monometallic Co/SiO₂ and Mo/SiO₂ catalysts, treated in identical way. Reprinted from Chem. Phys. Lett. 31 B. Kitiyanan, W. E. Alvarez, J. H. Harwell and D. E. Resasco, "Controlled production of single-wall carbon nanotubes by catalytic decomposition of CO on bimetallic Co–Mo catalysts" Pag. 497, Copyright (2003), with permission from Elsevier.

sample from the CO₂ produced gave a value of 0.64 wt %, in good agreement with the amount of SWNT loaded in the sample (0.6 wt %).

TPO has also shown to be quick test for different catalyst formulations. For example, Figure 1.12 shows a clear synergistic effect exhibited by Co and Mo [30]. In the first place, Mo alone did not produce carbon nanotubes, and only exhibited a small low-temperature peak corresponding to amorphous carbon. The authors claimed that the Mo-alone sample only produced amorphous carbon based on the absence of graphite or nanotubes in the TEM observations. On the other hand, Co alone was not selective for the production of SWNT, and generated mainly graphitic carbon and MWNT. Again, these observations were corroborated by TEM. By contrast, the combination of the two metals in appropriate ratio resulted in high selectivity for SWNT.

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CHAPTER 2

RELATIONSHIP BETWEEN THE STRUCTURE AND COMPOSITION OF Co-Mo CATALYSTS AND THEIR ABILITY TO PRODUCE SINGLE-WALLED CARBON NANOTUBES BY CO DISPROPORTIONATION^I

2.1. INTRODUCTION

As mentioned in the previous chapter, the catalytic decomposition of carbon-containing molecules over solid catalysts appears as a promising technique for scaling-up the production process of SWNT and therefore to enable applications that require larger SWNT quantities. In fact, extensive research work is now focused on the large-scale manufacture of these materials at low cost since there is not yet an established method that provides large quantities of SWNT of well-determined and reproducible characteristics. A clear understanding of the formation mechanism of SWNT is therefore a key issue for the development of further advances in this topic.

A number of researchers have investigated different catalyst formulations and operating conditions for this process [1, 2]. In 1999 Kitiyanan et al. [3] reported that the disproportionation of CO on bimetallic catalysts exhibited a high selectivity towards the production of SWNT at relatively low temperatures. Among the various

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formulations investigated, a cobalt molybdenum catalysts supported on silica gel and having low Co:Mo ratios exhibited the best performance. Nevertheless, the reason for the unusual high selectivity of this particular catalyst formulation and the intrinsic dependence of the selectivity on the Co/Mo molar ratio was not clearly understood.

Yet, the Co-Mo catalytic system has been well known in the field of catalysis due to its application in hydrotreating catalytic processes. In that case, however, silica is not the most suitable support, due to its weak interaction with the active components. Most studies on the Co-Mo catalysts have focused on alumina-supported systems since alumina interacts with Co and Mo with the appropriate strength to generate the HDS active species. For that reason, alumina-supported Co-Mo catalysts are used in industrial practice in the form of sulfides. Although the structure of the sulfided Co-Mo catalysts is known almost at the atomic level [4-7], that of the non-sulfided oxidic precursor has received less attention (8-11). Topsøe and Topsøe [12], using IR spectroscopy of adsorbed NO showed that the interaction between Mo and the alumina in the oxidic state was not greatly affected by the presence of Co. A similar conclusion was reached by Ratnasami and Knözinger, [8] who used infrared and UV/Vis DRS to infer that, in the oxidic state, a major portion of the Co is inside the alumina lattice in a tetrahedral environment of oxygen ions and is not exposed to the gas phase. Silica-supported Co-Mo, which is the system of our interest, displays a different behavior from that of the alumina-supported catalysts [12-17]. The differences have been attributed to the lower affinity of silica for the Co and Mo ions, thus facilitating the Co-Mo interaction. The exact nature of this

interaction is still unclear. While some authors have postulated that the interacting phase is different from cobalt molybdate [12, 14, 15] others have argued that a CoMoO_4 phase is indeed present [13, 16].

We also need to mention that the high selectivities to SWNT reported by Kitiyanan and coworkers were only obtained after a specific sequence of calcination at 500°C in air and reduction in H_2 at 500°C, followed by heating in He to 700°C. The present chapter deals with the characterization of the different phases and surface species present on the catalytic system used by these authors [18] after each of the above-mentioned two pretreatments and after the production of SWNT. The findings reported here are the results of information gathered during a period of almost two years in which a variety of characterization techniques including Extended X-ray Absorption Spectroscopy (EXAFS), Near Edge X-ray Absorption Spectroscopy (XANES) Ultraviolet-Visible Diffuse Reflectance Spectroscopy (UV/Vis-DRS), Laser Raman Spectroscopy (LRS), Temperature Programmed Reduction (TPR), X-ray Photoelectron Spectroscopy (XPS) and Diffuse Reflectance Infrared Fourier Transform Spectroscopy (DRIFTS) of NO adsorbed were used.

The characterization strategy presented on this and subsequent chapters is based on the abundant precedent literature on the application of these techniques to investigate the Co-Mo system used in hydrotreating. For example, UV/Vis spectroscopy has been previously used to estimate the domain size of transition metal oxides (mostly d^0 ions) by analyzing the absorption edge energy according to the

method proposed by Weber [19]. Similarly, Laser Raman Spectroscopy has proven to be an extremely useful technique to analyze the symmetries and chemical bonds of d^0 metal oxides [20]. On the other hand IR spectroscopy of adsorbed NO has been widely used to characterize the Co-Mo catalytic system because the spectra of adsorbed NO exhibit prominent absorption bands, which appear at different frequencies depending on whether the adsorption is on Mo or Co sites [10, 11, 21-26]. Therefore, this technique can be used to determine whether one of the components is blocking the other. Temperature programmed reduction, in combination with photoelectron and X-ray absorption spectroscopies can be used to determine the oxidation state of the components and to fully describe the structure of the catalyst after the different treatments. The use of a combination of techniques has been very successful in the study of sulfided Co:Mo catalysts, corroborating the CoMoS structure first proposed by Topsøe et al. [4, 6, 27-29]. In this chapter, we have used a combination of these techniques to put together a detailed picture of the structure of the selective Co-Mo catalyst, which will be used to explain the variations in selectivity towards SWNT observed when the catalyst formulations or pretreatment conditions are changed.

2.2. EXPERIMENTAL

2.2.1. Catalysts preparation and pretreatment

A series of mono and bimetallic Co-Mo catalysts supported on silica was prepared by incipient wetness impregnation. The bimetallic samples, prepared by co-

impregnation of aqueous ammonium heptamolybdate and Co nitrate solutions, had Co:Mo molar ratios of 2:1, 3:4, 1:2, and 1:3. The amount of Mo was kept constant for all catalysts at 4.6 wt. %, while the amount of Co was varied accordingly. Three monometallic catalysts were prepared with loadings of 1.4 wt % Co, 0.02 wt % Co and 4.6 wt % Mo, respectively. The SiO₂ support obtained from Aldrich had an average pore size of 6 nm, BET area 480 m²/g, pore volume 0.75 cm³/g, and particle sizes in the range 70-230 mesh. After impregnation, the solids were dried overnight at 120°C and then calcined for 3 h at 500°C in flowing dry air.

The catalysts were investigated in three different forms, the oxidic state, the reduced state, and after reaction. In the oxidic state, the catalysts were investigated directly after the calcination in air at 500 °C. Those in the reduced state were first calcined in air at 500 °C, then reduced in H₂ flow for 1 h at 500°C and finally heated in He flow to 700°C. This reduction/heating pretreatment is the one reported before for the production of SWNT, which was proven to be the most effective for this family of catalysts [3].

2.2.2. Catalyst characterization

The UV/Vis spectra of the solid samples were recorded using a Shimadzu double beam spectrometer UV-2101 with an integrating sphere for diffuse reflectance. Barium sulfate was used as reflectance standard. Several Mo and Co compounds, including MoO₃, Na₂MoO₄, (NH₄)₆Mo₇O₂₄ and CoMoO₄ were used as

references. Before each analysis, the samples were dried in air at 120°C and kept in a desiccator.

The IR spectra of adsorbed NO were obtained on a Bio-Rad FTS 40 spectrometer, equipped with a diffuse reflectance cell (Harrick Scientific Co. Praying Mantis) with an in-situ reaction chamber. Before the spectrum was acquired, the catalysts were reduced ex-situ under H₂ flow at 500°C for 1 h and then heated up in He to 700°C using a ramp temperature of 10°C/min. Then they were cooled down to room temperature in He flow and transferred to the IR cell. To eliminate any superficial oxidation caused by exposure to air during the transfer, each sample was re-reduced in situ for 1 h at 500°C in H₂ flow, purged in He flow at that temperature, and then cooled down to room temperature. Once cooled, the samples were exposed to 3% NO in He for 30 min at room temperature and purged in He for 30 min.

The X-ray absorption data were obtained at the National Synchrotron Light Source (NSLS) at Brookhaven National Laboratory, 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 ring current of 80-220 mA. The calcined, reduced and spent samples were investigated by X-ray absorption. Both reduced and spent samples, were not exposed to 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 veils until analysis. 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, Mo-Mo and Co-Mo bonds were obtained by using the FEFF and FEFFIT fitting programs from the University of Washington [30-32]. In this routine, the Debye Waller factors for each bond type (σ), the edge energy difference (ΔE_0), the coordination number N , and the difference in bond distances (ΔR) 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%. The spectra of MoO_3 , Na_2MoO_4 , $(\text{NH}_4)_6\text{Mo}_7\text{O}_{24}$, Mo_2C , CoO , Co_3O_4 , $\alpha\text{-CoMoO}_4$, as well as Co and Mo foils were also obtained at liquid nitrogen temperature and used as references.

The Raman spectra of both fresh catalysts and nanotubes were obtained in a Jovin Yvon-Horiba LabRam 800 equipped with a CCD detector and with three different laser excitation sources having wavelengths of 632 (He-Ne laser) 514 and 488 nm (Ar laser). Typical laser powers ranged from 3.0 to 5.0mW; integration times were around 15 sec for each spectrum; ten Raman spectra were averaged for each sample.

X-ray photoelectron spectroscopy data were recorded on a Physical Electronics PHI 5800 ESCA System with monochromatic AlK α X-rays (1486.6 eV) operated at 350 W and 15 kV with a background pressure of approximately 2.0×10^{-9} Torr. A 400 μm spot size and 58.7 eV pass energy were typically used for the analysis. An electron flood gun compensated sample charging during the measurements. The electron takeoff angle was 45° with respect to the sample surface. The pretreatment of the samples was performed in a packed bed micro-reactor with an on/off valve at each end of the reactor, which allowed for a quick isolation of the samples after each treatment. The reactor with the sample under He was transferred to a glove bag; the sample (in powder form) was placed on a stainless steel holder and kept in a vacuum transfer vessel (model 04-110A from Physical Electronics) to avoid any exposure to the atmosphere before the analysis. For each sample, the binding energy regions corresponding to Si (95-115 eV), Mo (220-245 eV) and Co (760-820 eV) were scanned. The binding energies were corrected by reference to the C(1s) line at 284.8 eV. A non-linear Shirley-type background was used for the area analysis of each peak. The fitting of the XPS spectra was carried out using Gaussian-Lorentzian peaks, using the MultiPak software from Physical Electronics.

The H₂-TPR experiments were conducted passing a continuous flow of 5% H₂/Ar over approximately 30 mg of the calcined catalyst at a flow rate of 10 cm³/min while linearly increasing the temperature at a heating rate of 8 °C/min. The hydrogen uptake as a function of temperature was monitored using a thermal conductivity detector, SRI model 110 TCD.

2.2.3. Production and Characterization of Carbon Nanotubes

In this contribution, the production of SWNT by CO disproportionation is compared in a series of catalysts with Co:Mo ratio of 2:1, 1:2 and 1:3. In the present work, we have selected those catalysts that display contrasting behavior in selectivity toward SWNT, as reported by Kitiyanan and coworkers [3]. For the SWNT production, 0.5 g of calcined catalyst was placed in a horizontal tubular reactor, heated in H₂ flow up to 500°C, and then in He flow up to 700°C. Subsequently, CO was introduced at a flow rate of 850 cm³/min at 84 psia and kept under these conditions for a given period of time, which ranged from 3 to 120 minutes. At the end of each run, the system was cooled down in He flow. The total amount of carbon deposits was determined by temperature programmed oxidation (TPO) following the method described in Chapter 1. Transmission electron microscopy (TEM) was used for characterizing the carbon deposits on the catalyst. The TEM images were obtained in a JEOL JEM-2000FX TEM. For this analysis, a suspension of the carbon-containing samples in isopropyl alcohol was achieved by stirring the solid sample with ultrasound for 10 min. Then, a few drops of the resulting suspension were deposited on a grid and subsequently evacuated before the TEM analysis. Finally, the quality of the nanotubes obtained over the different catalyst was investigated by Raman spectroscopy, one of the most powerful techniques available to study the structural and electronic properties of SWNT. As described in Chapter 1, the analysis of radial A_{1g} breathing mode (below 300 cm⁻¹) gives direct information about the tubes diameter [33], while the analysis of the G band in the tangential mode range i.e. 1400-1700 cm⁻¹, provides information on

the electronic properties of the nanotubes. In addition, the analysis of the so-called D-band at around 1350 cm^{-1} gives an indication of the level of disordered carbon. Therefore, we have used the intensity ratio of the D band (1350 cm^{-1}) to the G band (1590 cm^{-1}) as semi-quantitative measurement of the formation of undesirable forms of carbon [34, 35].

2.3. RESULTS

2.3.1. Characterization of the Calcined Catalysts

2.3.1.1 Diffuse Reflectance UV-Visible Spectroscopy (UV/V-DRS)

We have used UV/V-DRS to study the state of both Mo and Co in the oxidic form, after calcination in air at 500°C . In order to estimate the band energy gap of the Mo oxide compounds, it has been recommended to use the square root of the Kubelka-Munk function multiplied by the photon energy, and plot this new function versus the photon energy [19]. The position of the absorption edge can then be determined by extrapolating the linear part of the rising curve to zero [19, 36]. The values thus obtained carry information about the average domain size of the oxide nanoparticles. As in the case of a particle in a box problem, the energy band gap decreases as the domain size increases [19]. Therefore, a comparison can be made between the energy of the samples under investigation and those of references of known domain size. This comparison is made in Fig. 2.1, which shows the absorption edges of several MoO_x species together with those of two different Co:Mo/SiO₂ catalysts. As expected, the band gap energies in the reference series

decrease as the domain size increases. Those of the Co:Mo/SiO₂ catalysts lie between those of (NH₄)₆Mo₇O₂₄ and MoO₃. From this comparison, it can be inferred that the Mo species in the calcined catalysts have relatively small domain sizes. The presence of a small contribution of MoO₃ species could not be ruled out since a small tail can be observed below 3.0 eV, but most of the Mo is in a high state of dispersion.

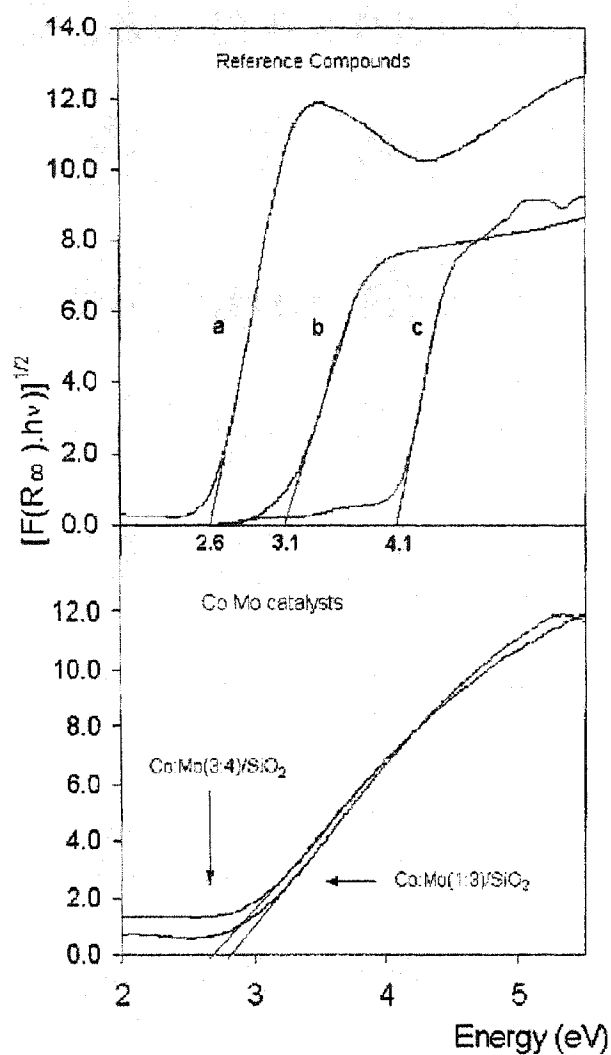


Figure. 2.1. Lower panel: UV absorption spectra for two Co : Mo/SiO₂ calcined catalysts. Upper panel: (a) MoO₃, (b) (NH₄)₆Mo₇O₂₄, (c) NaMoO₄ references.

In addition to the charge-transfer bands due to Mo, appearing in the UV region, the visible spectra of the bimetallic catalysts present bands in the 500-750 nm region, which did not appear for the Mo/SiO₂ catalyst. These bands are associated with Co species and have previously been ascribed to d-d transitions ($^4T_{2g} \rightarrow ^4A_{2g}$ and $^4T_{2g} \rightarrow ^4T_{1g}(P)$) of high spin octahedral Co complexes [13]. Figure 2.2 shows the DRS spectra in this region for three calcined catalysts, Co:Mo(3:4)/SiO₂ , Co:Mo(1:3)/SiO₂ and Co/SiO₂ . The spectrum for the Co:Mo(1:3) catalyst is very similar to that of CoMoO₄, which is typical of Co in an octahedral environment. The spectrum for the Co:Mo(1:2) was almost identical to that of the Co:Mo(1:3) catalyst, so only one of them is included in the graph. By contrast, the shape of the spectrum of the Co:Mo (3:4)/SiO₂ catalyst was markedly different and exhibited the appearance of a band at around 680 nm. This band was in turn the dominant feature in the pure Co catalyst and should be associated with Co₃O₄ species, which as shown below, are present in the pure Co catalyst in the calcined state. Therefore, it can be concluded that the catalysts with low Co:Mo ratio exhibit most of the Co interacting with Mo. However, as the Co:Mo ratio increases, free Co oxide begins to appear. In fact, the spectrum of the Co:Mo(3:4)/SiO₂ catalyst can be rationalized as a sum of contributions from two types of species, one interacting with Mo (main band at around 600 nm) and a second one in which the Co oxidic species are segregated and not interacting with Mo (main band at 680 nm). Similar conclusions have been previously drawn from Raman spectroscopy and XRD data, which indicated that a

non-interacting Co phase is formed on Co-Mo/SiO₂ catalysts at high Co:Mo ratios [16, 37].

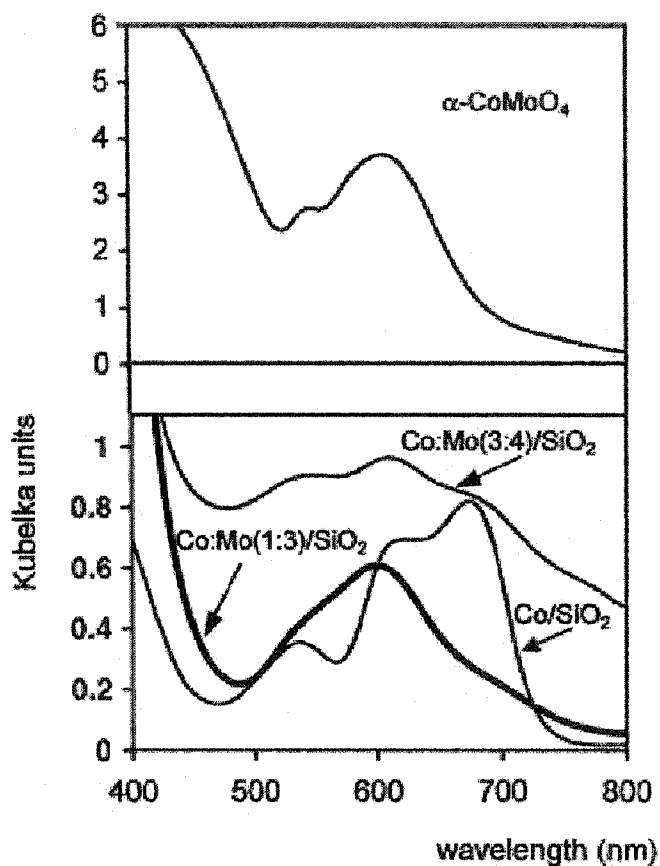


Figure 2.2. Visible spectra for two calcined bimetallic Co : Mo/SiO₂ catalysts with different Co :Mo ratios (1 : 3 and 3 : 4) and that for a monometallic Co (0.02 wt%)/SiO₂. The spectrum of a CoMoO₄ reference is included for comparison.

2.3.1.2 X-ray absorption spectroscopy (EXAFS/XANES)

Figure 2.3 shows the K-edges of Mo ($E = 20$ keV) for two different calcined catalysts with Co:Mo molar ratios of 2:1 and 1:3. Absorption spectra for the two

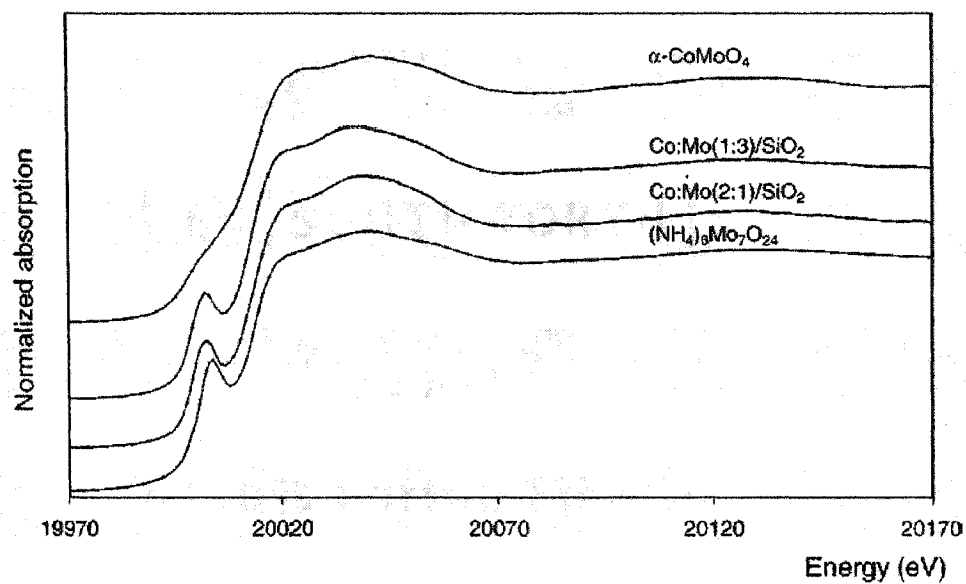


Figure 2.3. Mo-edge (20,000 eV) XANES of two CoMo calcined catalyst compared to CoMoO_4 and $(\text{NH}_4)_6\text{Mo}_7\text{O}_{24}$ references.

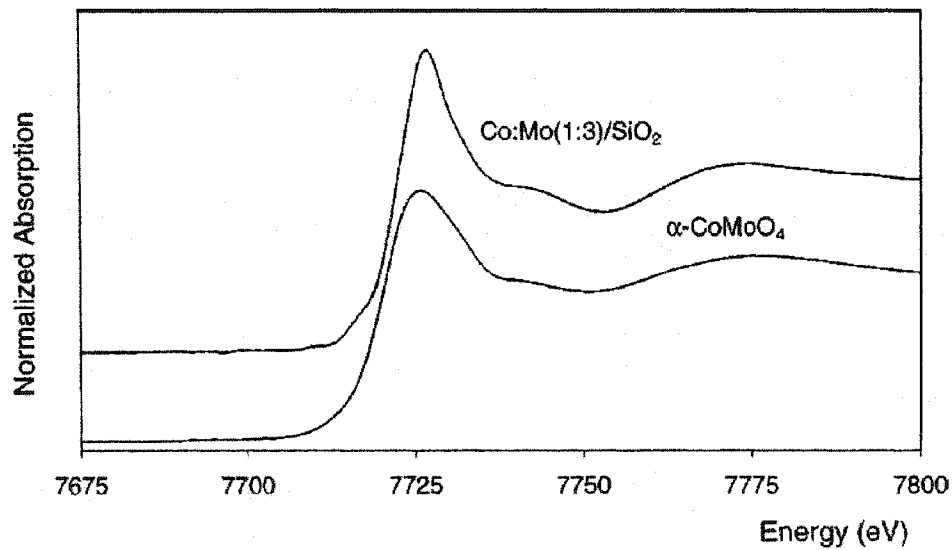


Figure 2.4. Co K-edge (7719 eV) XANES of calcined Co :Mo (1:3)/ SiO_2 catalyst compared to CoMoO_4 used as a reference.

reference compounds, CoMoO_4 and ammonium heptamolybdate, have been included for comparison. The absorption edges for both catalysts are remarkably similar. They both exhibit a pre-edge feature, which is also observed in the spectrum of ammonium heptamolybdate. This pre-edge feature is typically observed in distorted octahedral environments, such as that found in the heptamolybdate. It is due to a $1s \rightarrow 4d$ bound-state transition that in the case of a perfect octahedral geometry is formally forbidden. Accordingly, it is barely present in compounds such as MoO_3 and CoMoO_4 . However, it becomes allowed when the d-states of the metal mix with the p orbitals of the ligand, as in compounds with distorted octahedral symmetries [38, 39]. Of course, a pre-edge feature is always observed in Mo species with tetrahedral symmetry, such as in sodium molybdate. However, in such cases the feature is much more pronounced than that observed here. Therefore, it can be concluded that in the bimetallic catalysts, Mo is mostly in a structure similar to that of the heptamolybdate. Interestingly, this is the same for both, the Co:Mo(2:1) and Co:Mo(1:3) samples.

Next, it is important to investigate the same set of samples at the Co edge. Figure 2.4 compares the XANES spectra for the K-edge of Co ($E_0 = 7709\text{eV}$) in the calcined Co:Mo(1:3)/ SiO_2 catalyst and that in the CoMoO_4 reference. Except for some difference in the size of the first peak in the edge, both spectra look remarkably similar. By contrast, the Co edge for the Co:Mo (2:1) catalyst, containing excess Co, is very different from that of the CoMoO_4 reference. As shown in Fig. 2.5, the XANES of the catalyst is in fact very similar to that of Co_3O_4 , although a small shoulder appearing at around 7726 eV is more pronounced for the catalyst than for

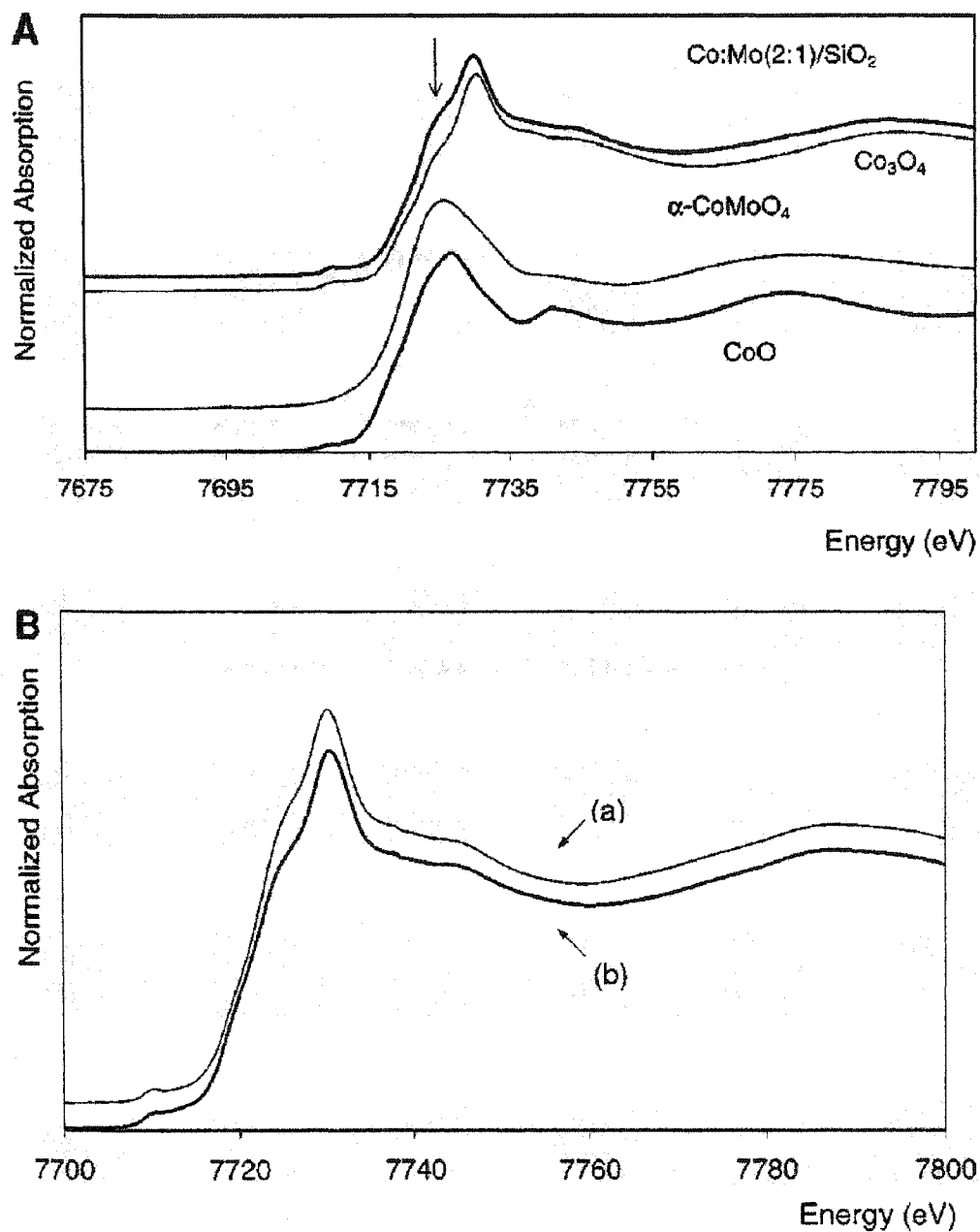


Figure 2.5. (A) Co K-edge XANES of a calcined Co:Mo (2:1)/SiO₂ catalyst compared to those of CoMoO₄, CoO, and Co₃O₄ references. (B) Co K-edge XANES of a calcined Co :Mo (2:1)/SiO₂ catalyst (curve a) and a weighted linear combination of XANES from CoMoO₄ and Co₃O₄ (curve b). The contributions resulting from the best fit were 82% Co₃O₄ and 18% CoMoO₄.

the oxide. Interestingly, this shoulder coincides with the white line of CoMoO_4 and CoO species. A first approximation of a XANES composed of two different phases can be obtained by simple addition of the XANES of the individual components. A simple fitting with a linear combination of contributions from Co_3O_4 and CoMoO_4 reproduces the XANES spectrum of the Co:Mo (2:1) catalyst (see Fig. 2.5b). This comparison indicates that in the catalyst with Co excess, most of the Co is in the form of Co_3O_4 and a small fraction as CoMoO_4 . When the fitting was attempted using CoO as a third component, the best fit did not include any contribution of this oxide. The EXAFS data was in good agreement with the conclusions reached from XANES analysis. As shown, in Fig. 2.6, the Fourier Transform for the calcined Co:Mo (2:1) catalyst is very similar to that of Co_3O_4 , indicating that this oxide is the predominant form present when Co is in excess.

The results on the sample with low Co:Mo ratio require some further consideration. It is interesting to note that while the XANES spectra for these catalysts look similar to that of CoMoO_4 from the Co side, they bear no resemblance with this compound from the Mo side. One may rationalize this contrasting behavior by proposing that while most of the Co in the catalyst is forming a CoMoO_4 phase only a fraction of Mo participates in this compound. The rest of the Mo would be in a dispersed Mo oxide. We propose that the Co is in a CoMoO_4 -like phase because, the XANES indicates that the local environment of Co in the Co:Mo(1:3) catalyst is very similar to that in CoMoO_4 , but the EXAFS data are significantly different from that of the compound. This comparison is made in Fig. 2.7, which shows

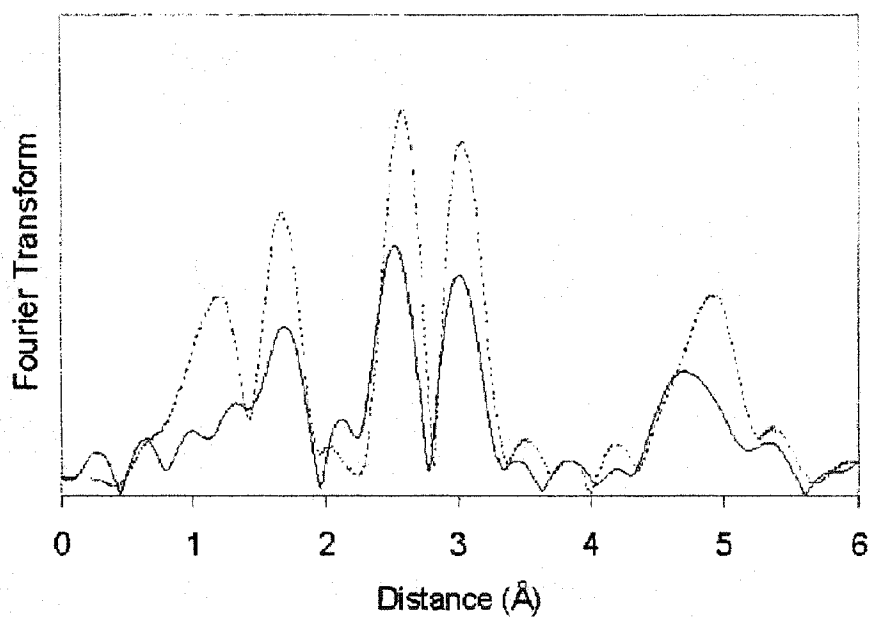


Figure 2.6. Fourier transforms of the k^3 EXAFS data of the Co K edge obtained on the calcined Co:Mo(2:1)/SiO₂ catalyst (solid line) and for Co₃O₄ reference (dotted line).

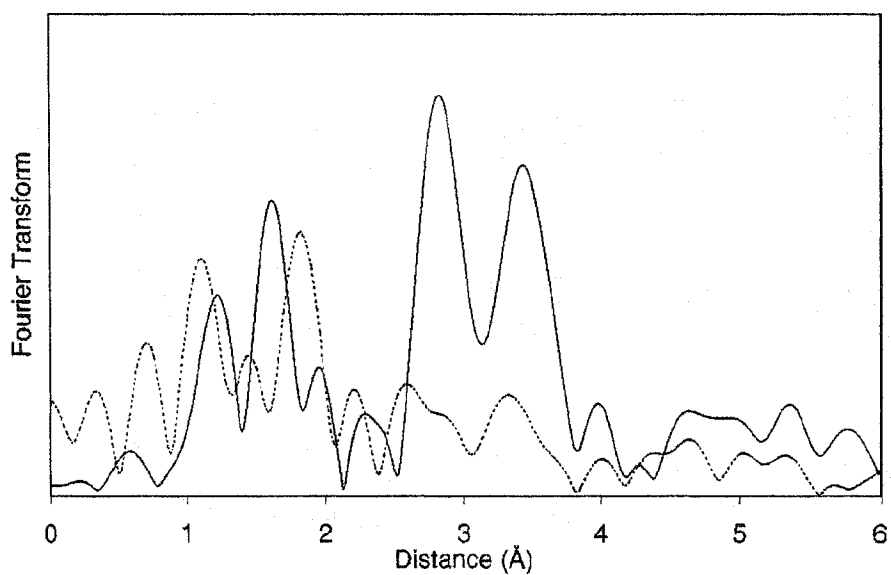


Figure 2.7. Fourier transforms of the k^3 EXAFS data of the Co K edge, obtained on the calcined Co:Mo(1:3)/SiO₂ catalyst (dotted line) and on a α -CoMoO₄ reference (solid line).

the Fourier Transforms for the K-edge of Co in the calcined Co:Mo(1:3)/SiO₂ catalyst, together with that of CoMoO₄. The low intensity observed in the catalyst for the peaks between 2.5 and 4 Å, clearly observable for the Co molybdate, would indicate that bulk CoMoO₄ is not present, but rather a highly dispersed CoMoO₄-like structure, co-existing with Mo oxide species.

2.3.1.3 Raman Spectroscopy

Figure 2.8 shows the Raman spectra obtained for the CoMo catalyst series; the Raman spectrum of an analytical sample of cobalt oxide (Co₃O₄) is also shown. The assignment for the Raman active phonon modes that are displayed in the spectrum of Co₃O₄ are as follows: the peaks at 199, 621, and 681cm⁻¹ correspond to F_{2g} phonon modes while the peaks at 477 and 525cm⁻¹ are E_g and A_{1g} phonon modes respectively [40]. As seen from Figure 2.8 this set of peaks dominates the spectra of all the bimetallic catalyst with an excess of Co. In agreement with the results obtained by DRS-UV/Vis and EXAFS and TPR it is clear that Co₃O₄ is the predominant species of Co present at high Co:Mo ratios.

Figure 2.9 compares the Raman spectrum of the highly selective bimetallic catalyst, which as mentioned before, has a low Co: Mo ratio, with that of reference samples of CoMoO₄ and MoO₃. First, it is clear that segregated Co₃O₄ species are not present on this catalyst, as evidenced by the absence of the characteristic bands described above (199, 621, and 681cm⁻¹). The peaks appearing in the 750-1000 cm⁻¹ region should be ascribed to Mo species. This is the region where the Raman bands

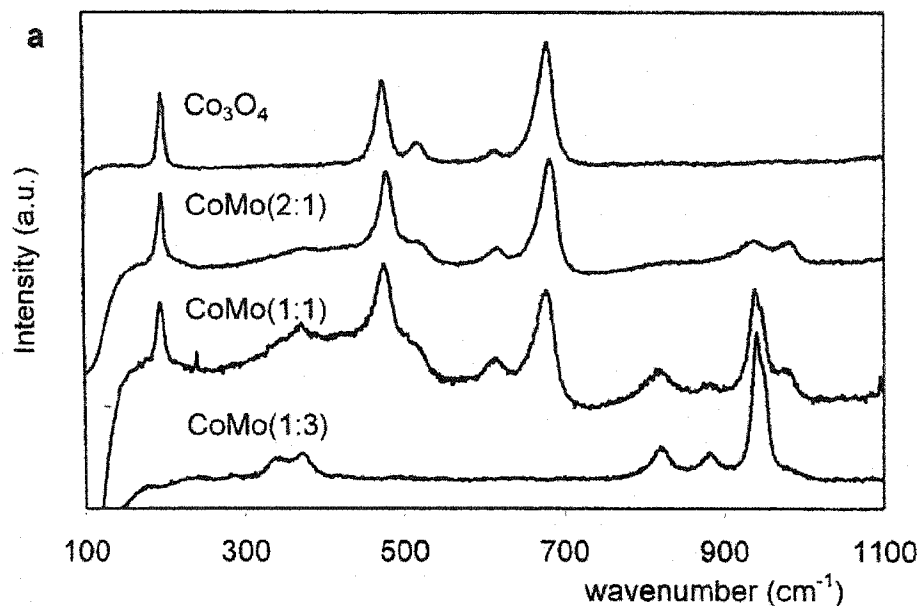


Figure 2.8. Raman spectra of various supported CoMo/SiO₂ catalysts; the spectrum of an analytical sample of cobalt oxide (Co₃O₄) is also shown. The laser excitation energy was 633 nm.

for stretching of Mo-O bonds are expected to appear [20]. Several factors such as metal loading, pH, precursor impregnation method and impurities are known to influence the exact position of the Raman bands. However, a tentative assignment can be done in light of the results obtained by UV/Vis absorption spectroscopy, preceding literature and the comparison with the reference samples. For instance, the peak centered at 943 cm⁻¹ appearing on the Raman spectrum for the selective Co-Mo (1:3)/SiO₂ catalyst has been previously ascribed to Mo₇O₂₄⁻⁶ species while the shoulder at 960cm⁻¹ has been associated to larger clusters of MoO_x species such as Mo₈O₂₆⁻⁴ [20-42] This assignment agrees with the result obtained by UV-Vis spectroscopy, which suggested the presence of well dispersed clusters of MoO_x that,

according to the calculated band energy gap, corresponded to an average domain size slightly larger than that of $\text{Mo}_7\text{O}_{24}^{-6}$.

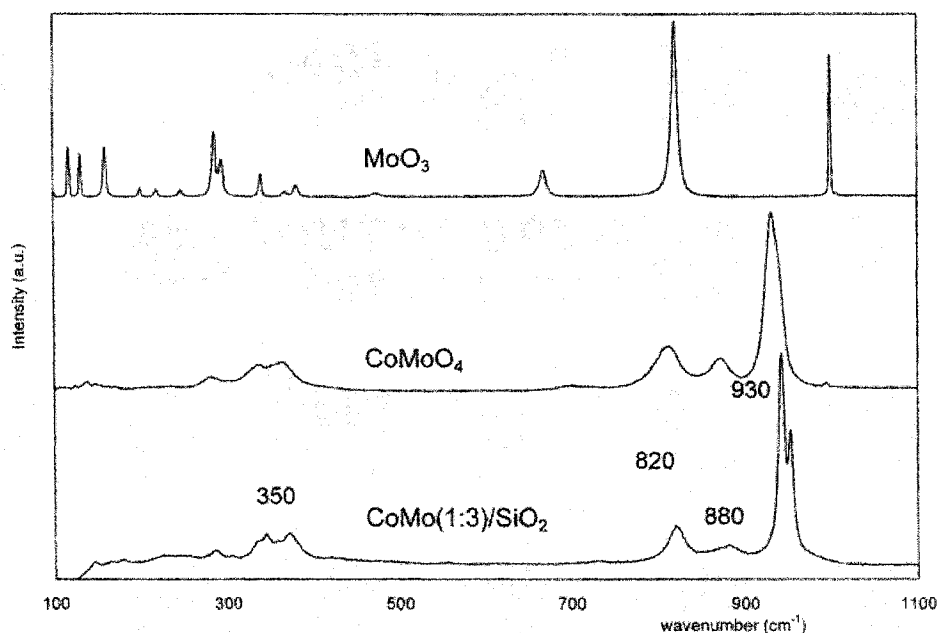


Figure 2. 9. Comparison between the Raman spectra of a selective CoMo (1:3)/SiO₂ catalyst and that of two reference samples of MoO₃ and CoMoO₄. The laser excitation energy was 633 nm.

According to previously reported results, the presence of large polymeric MoO_x species must be ruled out when there are no peaks in the 990-1000 cm⁻¹ region [43, 44]. Our results further support these conclusions. Indeed, a comparison between the Raman spectra of this catalyst and that of the MoO₃ reference indicates that such species is not present in the catalyst. The relatively high dispersion of Mo oxide might result from the interaction with cobalt; [12, 14-16] i.e. formation of a surface Co molybdate species as previously suggested. Moreover, the comparison of the

Raman spectrum of the bimetallic catalyst with that of the CoMoO_4 shown in Figure 2.9 gives strong support to the presence of this species. Therefore, the Raman band at 880 cm^{-1} , the shoulder at 930 cm^{-1} as well as the broad band at 350 cm^{-1} must all be assigned to Mo-O-Co stretching vibrations in cobalt molybdate species [45–48].

2.3.1.4 Temperature Programmed Reduction (TPR)

The reduction profiles of calcined monometallic Co/SiO_2 and Mo/SiO_2 catalysts together with that of the bimetallic Co:Mo (1:3)/SiO_2 catalyst are shown in Fig. 2.10a. The TPR profile of the Co monometallic catalyst shows two peaks at 360 and 445°C , which can be ascribed to the reduction of Co oxide species. The reduction of the monometallic Mo catalyst also exhibits two peaks, but they appear at much higher temperatures than those of Co. Therefore, from the reduction profiles it is possible to identify the presence of Co and Mo species in the absence of interactions. Accordingly, the TPR of the bimetallic Co:Mo (1:3)/SiO_2 catalyst indicates that, in this sample, the vast majority of Co oxide species are interacting with Mo. It is clear that while most of the Co in the monometallic catalyst gets reduced below 500°C , almost no reduction takes place below that temperature in the bimetallic catalyst. In a previous work it has been reported that the reduction of interacting Co-Mo supported species occurs at similar temperatures as those assigned for the reduction of free Mo species [16]. It has also been proposed that the addition of Mo oxide to Co oxide inhibits the reduction of the Co species because Mo^{6+} polarizes the Co-O bonds,

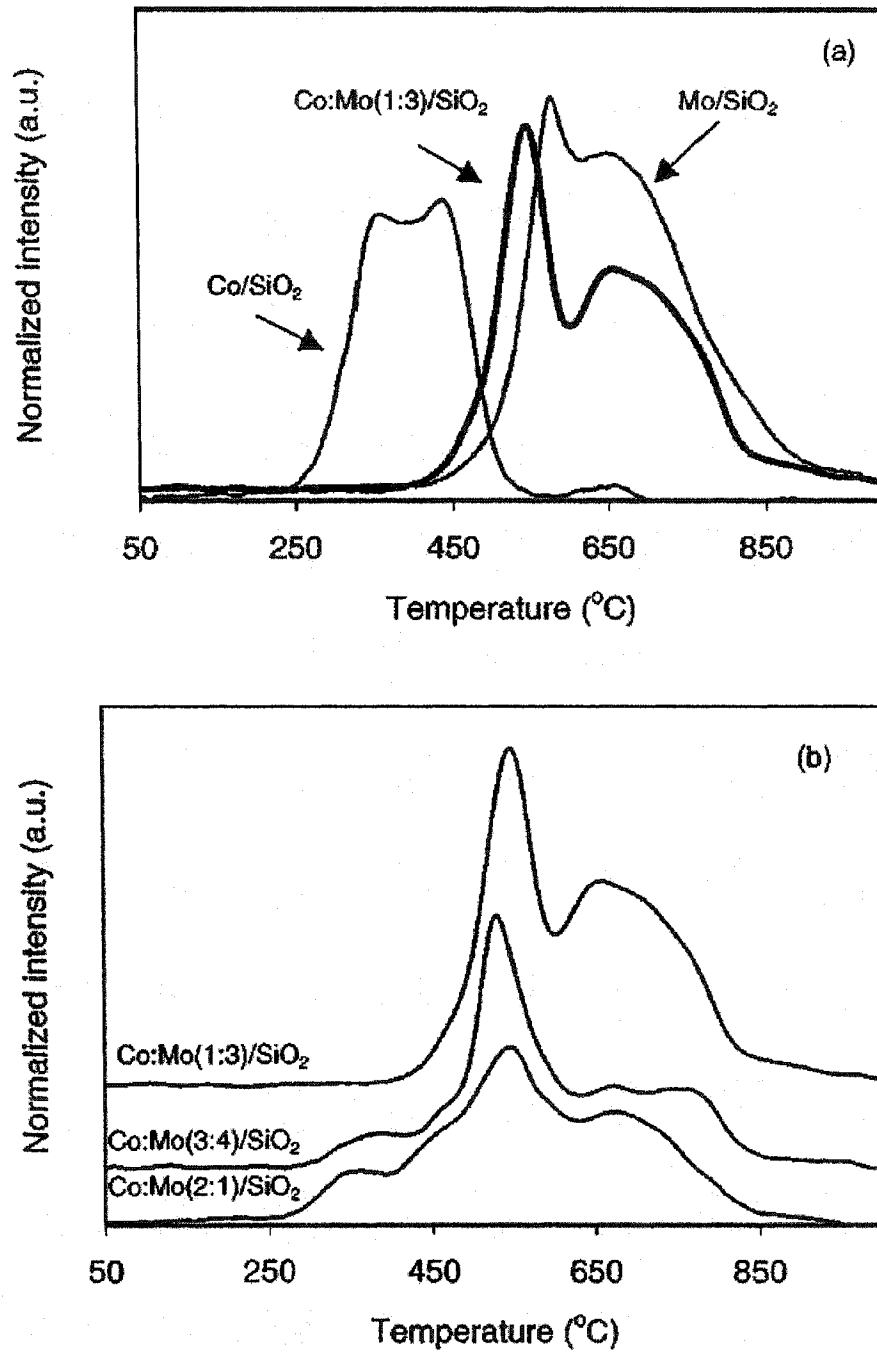


Figure 2.10. TPR profiles of several mono and bimetallic cobalt/molybdenum catalysts. The TPR was conducted with 5% H_2 /Ar at a heating rate of 8 $^{\circ}\text{C}/\text{min}$.

making them more ionic and consequently more difficult to reduce [49]. In agreement with the DRS and EXAFS/XANES data, TPR indicates that a high degree of Co-Mo interaction is only observed for the catalyst with a low Co: Mo ratio. As shown in Fig. 2.10b, as the Co:Mo ratio increases, a gradually increasing fraction of segregated Co species is apparent from the peaks at 360 and 445°C, which are associated with the reduction of non-interacting Co oxide.

2.3.2 Characterization of the Reduced Catalysts

2.3.2.1 Diffuse Reflectance Infrared Fourier Transform Spectroscopy (DRIFTS)

The vibrational spectrum of adsorbed NO was used to investigate the Co:Mo/SiO₂ catalysts after the reduction pretreatment in H₂ at 500° C. As mentioned above, both Co and Mo are able to adsorb NO at room temperature, exhibiting characteristic IR absorption bands that can be used to identify the NO adsorption on each metal. It is generally agreed that Mo^{VI} does not adsorb NO [22], but Mo^{II}, Mo^{III} and Mo^{IV} have all been suggested as potential NO adsorption sites [10, 24]. Similarly, both calcined and reduced Co catalysts are able to adsorb NO [26]. It has been reported that adsorption on reduced Co results in bands at slightly lower frequencies than on oxidized Co [25]. However, it is not always possible to determine the chemical state of Co based on NO adsorption. Therefore, although DRIFTS of adsorbed NO may not be the best technique to characterize the chemical

state of Co and Mo, it is certainly a powerful tool to quantify the degree of site blocking of one of the two components by the other.

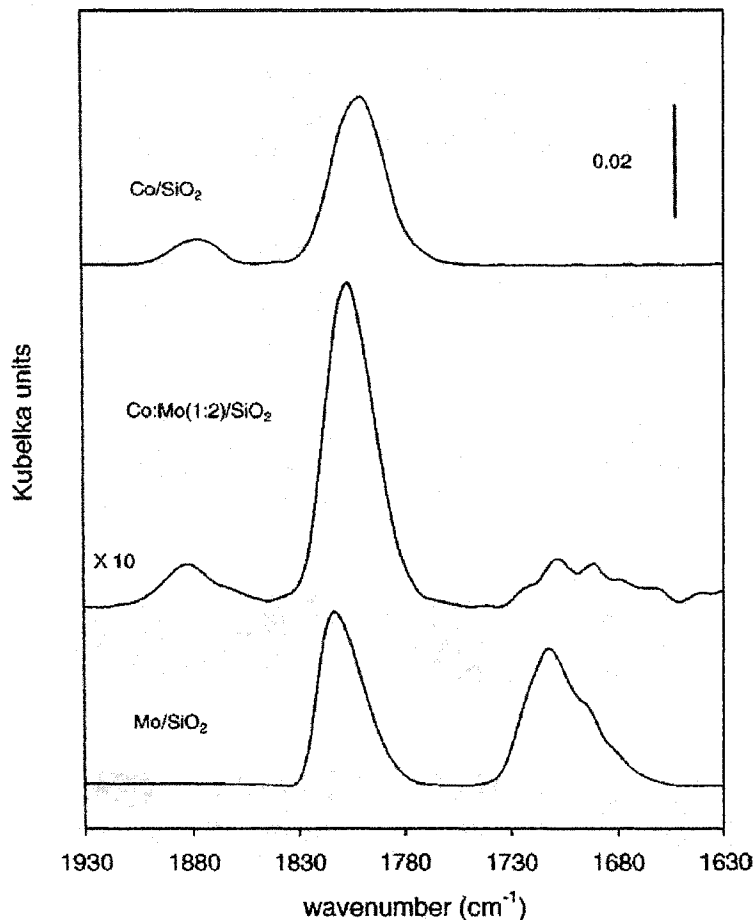


Figure 2.11. IR spectra of NO adsorbed on monometallic (Mo/SiO_2 and Co/SiO_2) and bimetallic (Co:Mo/SiO_2) catalysts. The catalysts were reduced under hydrogen at 500°C .

Figure 2.11 shows the DRIFTS spectrum of NO adsorbed on two monometallic catalysts with 4.6 wt % Mo and 1.4 wt % Co, respectively, and a bimetallic catalyst with 4.6 wt % Mo and 1.4 wt % Co ($\text{Co:Mo}=1:2$). On the monometallic Mo/SiO_2 catalyst the bands corresponding to the symmetric and anti-

symmetric stretching modes of dinitrosyl species are clearly observed. The symmetric mode exhibited a band at 1814 cm^{-1} , while the anti-symmetric mode generated a broad band centered at around 1714 cm^{-1} . Yao and Rothschild [23] have attributed the broadening of the anti-symmetric band to inhomogeneities on the surface that influence the vibrational transition moment of the asymmetric mode more than the moment of the symmetric mode. For the monometallic Co/SiO₂ catalyst, the bands of the dinitrosyl species appeared at significantly higher wavenumbers (1880 and 1803 cm^{-1}) than those on Mo. In this case, the anti-symmetric mode is the dominant band in the spectrum. Finally, the bimetallic Co:Mo(1:2)/SiO₂ catalyst showed three absorption bands that roughly correspond to those of the individual components. The dominant band appearing at 1806 cm^{-1} obviously has contribution of both, the symmetric band of NO adsorbed on Mo and the anti-symmetric band of NO adsorbed on Co. A smaller band appeared at 1883 cm^{-1} , which can be associated with the symmetric mode on Co sites and a broader band, which may include several individual bands, appeared in the region $1730\text{-}1650\text{ cm}^{-1}$ and can only be associated to adsorption on Mo. The appearance of different components associated with this asymmetric-mode band in the bimetallic catalyst contrasting to that on Mo/SiO₂ catalyst, could be explained in terms of Mo sites with different degrees of coordinative unsaturation [11], or alternatively, in terms of sites where Mo is influenced by Co to various degrees. It is also interesting to note that the overall intensity of the bands of the bimetallic Co-Mo catalysts is consistently much lower than that of the monometallic Co and Mo catalyst. This effect has been previously

observed for alumina-supported Co-Mo catalysts. In that case, a lower dispersion of the active species on the bimetallic catalysts, compared to that of the monometallic ones, was made responsible for the observed loss in intensity [22].

Figure 2.12 shows the FTIR spectra of NO adsorbed on different reduced bimetallic catalysts, in which the Mo content was kept constant while the Co content was increased. It is clear that as the Co content increases the adsorption of NO over the Mo sites is inhibited. A similar effect has been previously reported for the sulfided Co:Mo/Al₂O₃ catalyst and interpreted as a blockage of Mo sites by Co [21]. Since the low-frequency anti-symmetric NO stretching on Mo does not have contributions from species adsorbed on Co, it can be used as an indication of the density of Mo sites covered by Co. A clear decrease in the intensity of this band is observed as the Co:Mo ratio increases, becoming practically negligible when Co is in excess, e.g. for a Co:Mo ratio of 2:1. At the same time, the bands for this catalyst appear at the same wavelengths as those on the monometallic Co catalyst, i.e. 1880 and 1803 cm⁻¹. A straightforward conclusion drawn from these observations is that when Co is in excess, it almost completely covers the Mo sites, while the excess Co forms a non-interacting species.

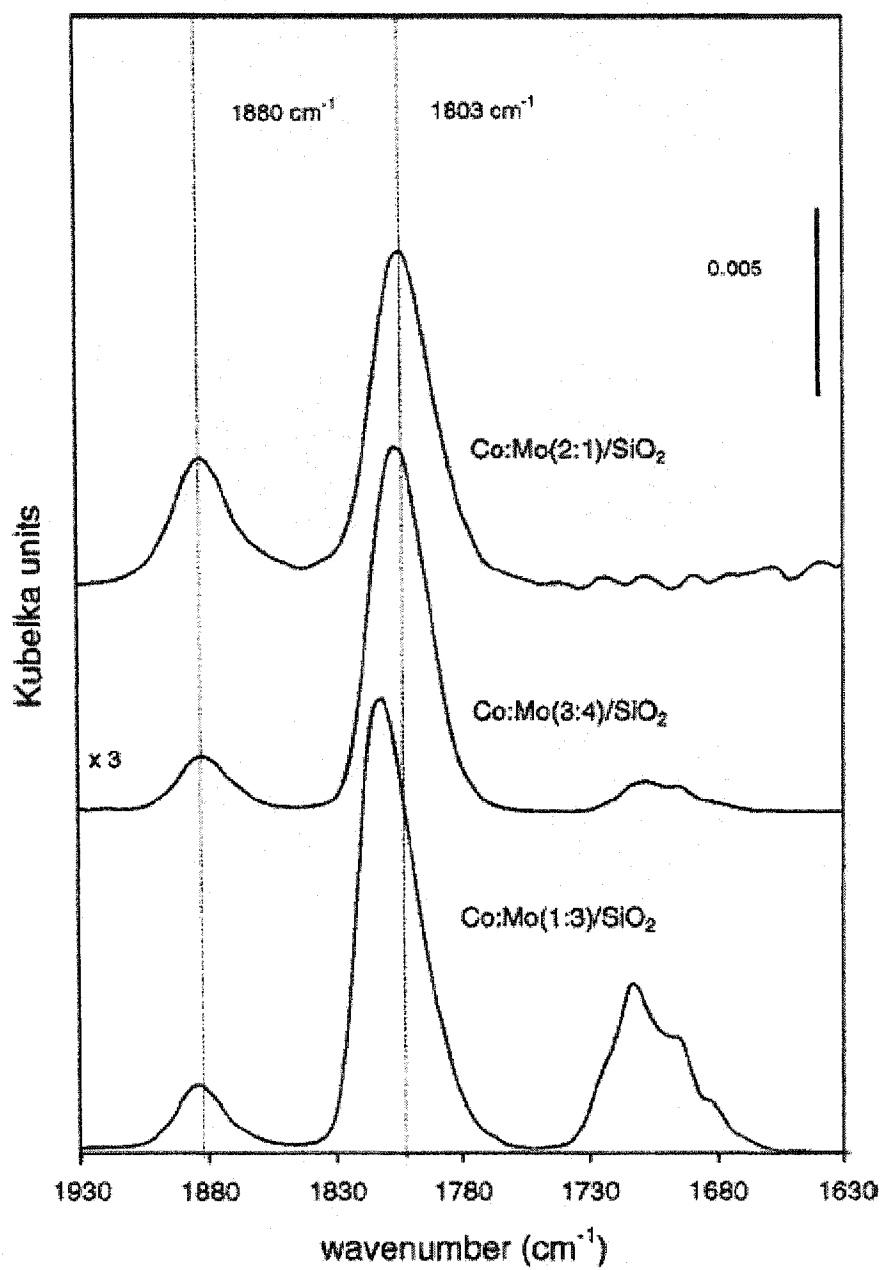


Figure 2.12. IR bands of NO adsorbed on (a) Co:Mo(2:1)/SiO_2 , (b) Co:Mo(3:4)/SiO_2 , and (c) Co:Mo(1:3)/SiO_2 . The catalysts were reduced under hydrogen at 500°C .

2.3.2.2 X-ray photoelectron spectroscopy (XPS)

XPS can be used to determine the chemical nature of the catalyst constituents and to roughly estimate their distribution on the surface. For the first purpose, the binding energy of the catalysts can be compared to those of reference compounds. In Table 2.1, the binding energies of the Co $2p_{3/2}$ and Mo $3d_{5/2}$ levels obtained for the catalysts in the reduced state are compared to those of the reference compounds. The spectra corresponding to the Co $2p_{3/2}$ levels for all the catalysts can be described in terms of two contributions, one appearing at about 778 eV and other at 781.5 eV. As shown in the table, these binding energies are in good correspondence with the binding energies that were obtained for the metallic Co (778.2 eV) and the CoMoO_4 (781.4 eV) references, respectively. Similar values for these reference materials have been previously reported in the literature [13, 26, 49, 50]. The respective surface fractions of Co in the two chemical states were obtained by fitting the spectra with Gaussian-Lorentzian curves centered at the corresponding binding energies. The fraction of Co in the metallic state after reduction at 500°C, as determined from this analysis, is shown in Fig. 2.13 as a function of the Co:Mo ratio. At low Co:Mo ratios, when the majority of the Co oxide species are interacting with Mo, most of the Co remains in the oxidic form, but as the Co:Mo ratio increases, a larger fraction of Co gets reduced. In agreement with this trend and with the TPR data shown above, previous reports have indicated that the Co-Mo interacting phase is, in fact, more difficult to reduce than Co oxide alone [16].

Table 2.1. Binding energies for reduced catalysts and reference compounds

	Binding Energies (eV)	
	Mo 3d _{5/2}	Co 2p _{3/2}
<u>Reference Samples</u>		
Co		778.2
CoO		780.5
Co ₃ O ₄		780.1
α -CoMoO ₄	232.5	781.4
MoO ₃	232.4	
MoO ₂	229.1	
(NH ₄) ₆ Mo ₇ O ₂₄ ·4H ₂ O	232.3	
<u>Reduced Catalysts</u>		
Mo/SiO ₂	229.2	
	231.0	
	233.4	
Co:Mo(1:3)/SiO ₂	228.9	778.1
	231.1	781.5
	233.9	
Co:Mo(1:2)/SiO ₂	228.3	777.9
	230.8	780.7
	233.3	
Co:Mo(3:4)/SiO ₂	228.9	778.5
	230.8	781.5
	233.1	
Co:Mo(2:1)/SiO ₂	228.7	778.4
	230.9	781.4
	233.2	

The assignment of the Mo 3d_{5/2} levels to different chemical states of Mo is not as straightforward as that of Co. As shown in Table 2.1, the spectra of the reduced catalysts can be described in terms of three contributing peaks. The one at the lowest binding energy appears in the same region as that of Mo⁴⁺ in MoO₂. The one at the

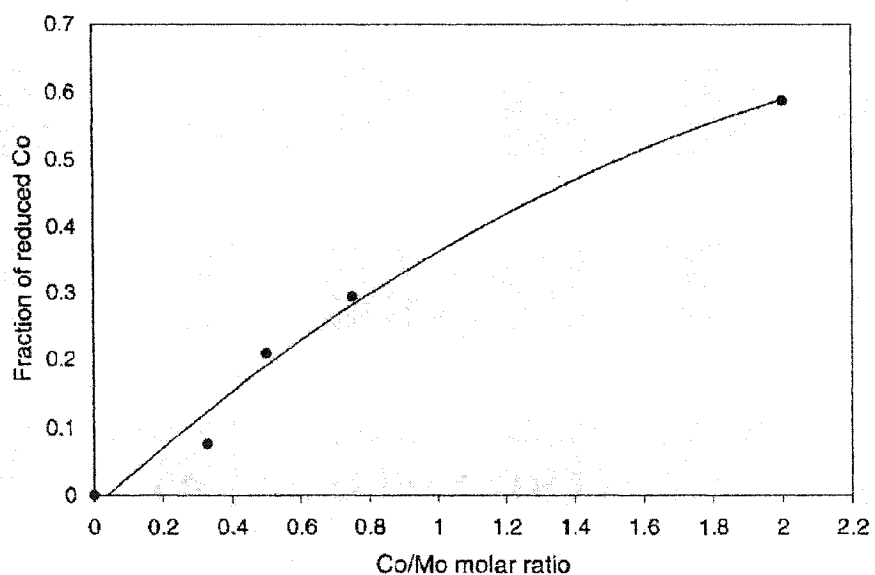


Figure 2.13. Fraction of cobalt reduced to the metallic state as a function of Co:Mo nominal ratio, as determined by XPS on samples pretreated under H_2 at $500^\circ C$ and heated in He at $700^\circ C$, without exposure to air.

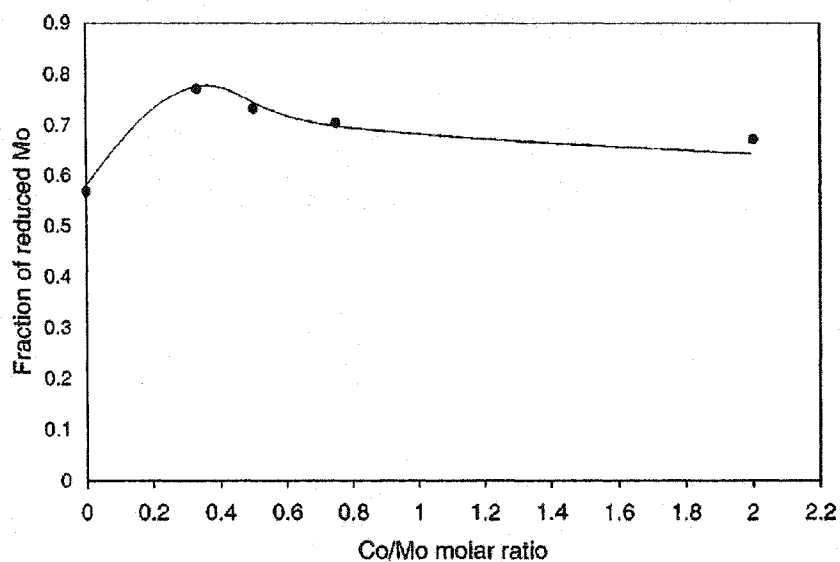


Figure 2.14. Fraction of molybdenum reduced to Mo(IV) and Mo(V) as a function of Co:Mo nominal ratio, as determined by XPS on samples pretreated under H_2 at $500^\circ C$ and heated in He at $700^\circ C$, without exposure to air.

highest binding energy (233.1 to 233.9 eV) appears at slightly higher energy than that of Mo^{6+} in MoO_3 . This peak has been previously assigned to Mo^{6+} species in an oxidic environment [49,51] although some authors have indicated that these species should have binding energies in the region 232.5-232.7 eV. [52, 53]. The remaining peak appearing at around 231 eV can be attributed to Mo in an intermediate state such as Mo^{+5} , as previously proposed [49, 54]. From the fitting of the spectra of the different catalysts with asymmetric curves centered at the indicated binding energies, the fraction of reduced Mo (i.e., $\text{Mo}^{4+} + \text{Mo}^{5+}$) have been calculated and plotted in Fig. 2.14 as a function of the Co:Mo ratio. It is observed that, except for the monometallic catalyst there is a slight decrease on the reducibility of Mo as the Co:Mo ratio increases. That is, the Co-Mo interaction is also evident from the Mo analysis, although the effect is not as pronounced as for Co.

On Table 2.2, the surface atomic fractions of Co and Mo on the catalyst after the reduction pretreatment are presented. The intensity of the Si peak remained almost constant for all samples, except for the catalyst with a Co:Mo ratio of 2:1, in which it decreased. Fig. 2.15 shows the fractions of Co/Si and Mo/Si as a function of bulk Co:Mo ratio. It is seen that, even though the Mo concentration in the catalyst was kept constant, the Mo/Si ratio clearly decreased as the amount of Co increased. In agreement with the DRIFTS data, these results show that the addition of Co results in a gradual coverage of Mo.

Table 2.2. Surface atomic concentrations for reduced catalysts as determined by XPS.

Reduced Catalysts	Atomic concentration (%)		
	Mo	Co	Si
Mo/SiO ₂	1	0	30.41
Co:Mo(1:3)/SiO ₂	0.99	0.27	31.08
Co:Mo(1:2)/SiO ₂	0.94	0.29	31.04
Co:Mo(3:4)/SiO ₂	0.58	0.43	31.42
Co:Mo(2:1)/SiO ₂	0.33	0.35	29.77

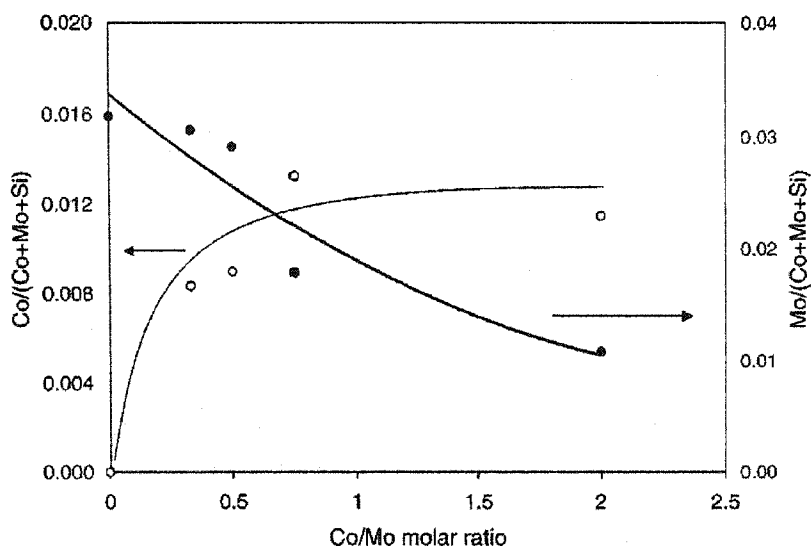


Figure 2.15. Surface atomic percentage of molybdenum (filled circles) and cobalt (open circles) as function of the nominal Co:Mo ratio, as determined by XPS on samples pretreated under H₂ at 500°C and heated in He at 700°C, without exposure to air.

2.3.2.3 X-ray absorption spectroscopy (EXAFS)

The EXAFS results for the reduced catalysts, shown in Fig. 2.16, reveal a definite trend, which ties in nicely with the XPS data. The data indicates that, keeping the amount of Mo fixed, the fraction of metallic Co increases with the Co:Mo ratio. The appearance of clearly observable peaks in the range corresponding to the 2nd and 3rd coordination spheres (0.25-0.45 nm), indicates that larger Co⁰ clusters are present on the catalyst with the higher Co content. To quantify this trend, the data for the first, second and third coordination shells of Co on the Co:Mo(2:1)/SiO₂ were isolated by applying an inverse Fourier transform over a restricted range of r (0.13-0.45 nm). The filtered data were then fitted using FEFFIT program assuming that only Co⁰ was present. As shown in Fig. 2.17, the quality of this fit was excellent. The structural parameters resulting from the fit are summarized in Table 2.3. From the above results, it can be concluded that in the reduced Co:Mo/SiO₂ with high Co:Mo ratios a large fraction of Co is in the form of metallic Co clusters.

To compare the structures of the Co phases in the catalysts with low Co:Mo ratios with those of high Co:Mo ratios, filtered EXAFS data were fitted for the Co:Mo (1:3) catalyst, as previously described. In the first attempt, the EXAFS data were fitted using a single phase, which was either metallic or oxidized Co. In both cases, the results were unsatisfactory. A more complex model was needed to obtain a good fit. In the second model used for fitting, the simultaneous presence of metallic Co clusters and oxidized Co species was considered. Satisfactory fits were only

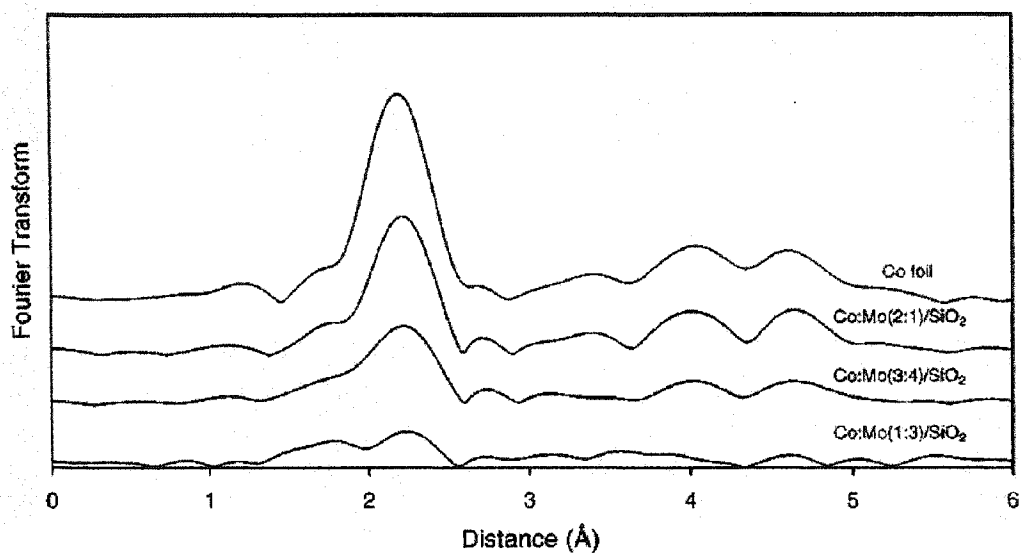


Figure 2.16. Fourier transforms of the k^3 EXAFS data of the Co K edge obtained for several Co:Mo/SiO₂ reduced catalysts with different Co/Mo ratios. The data for a Co foil is included for comparison.

Table 2.3. Structural parameters resulting from the fitting of the Co-edge EXAFS data obtained for the Co:Mo(2:1)/SiO₂ catalyst. In the table E_0 represents the energy shift, sigma the Debye-Waller factor and the r factor is a measurement of the fit quality.

Reference Phase	Fitting ($E_0 = 8.2$)				
	Bond	Coordination number	Distances	Sigma	r-factor
Co ^o	Co-Co (1 st shell)	7.8	2.492	0.0046	
	Co-Co (2 nd shell)	2.4	3.523	0.0047	0.0014
	Co-Co (3 rd shell)	9.6	4.327	0.0059	

obtained with the simultaneous presence of Co metallic clusters and a CoMoO₄ phase. Figure 2.18 illustrates the quality of the fit, while Table 2.4 summarizes the structural parameters determined from the analysis. The resulting parameters indicate that in this catalyst, cobalt is mainly forming a CoMoO₄-like phase and a small fraction is forming metallic Co.

Table 2.4. Structural parameters resulting from the fitting of the Co-edge EXAFS data obtained for the Co:Mo(1:3)/SiO₂ catalyst. Six different scattering paths were used for the Co-O (1st and 2nd shells) and Co-Mo (2nd shell) pairs.

Fitting ($E_0 = 9.88$)					
Phase	Bond	Coordination number	Distances (Å)	Sigma	r-factor
CoMoO ₄	Co-O (1 st shell)	3	2.1 ± 0.18	0.0029	0.0323
	Co-Co(1 st shell) & Co-Mo(1 st shell)	1	3.03 3.15	0.0035	
	Co-O (2 nd shell)	3	3.7 ± 0.05	0.0019	
	Co-Mo(2 nd shell)	3.2	3.9 ± 0.13	0.0027	
	Co-Co (1 st shell)	1.5	2.50	0.0035	
Co ^o	Co-Co (2 nd shell)	2.2	3.65	0.0023	
	Co-Co (3 rd shell)	1.6	4.35	0.0033	

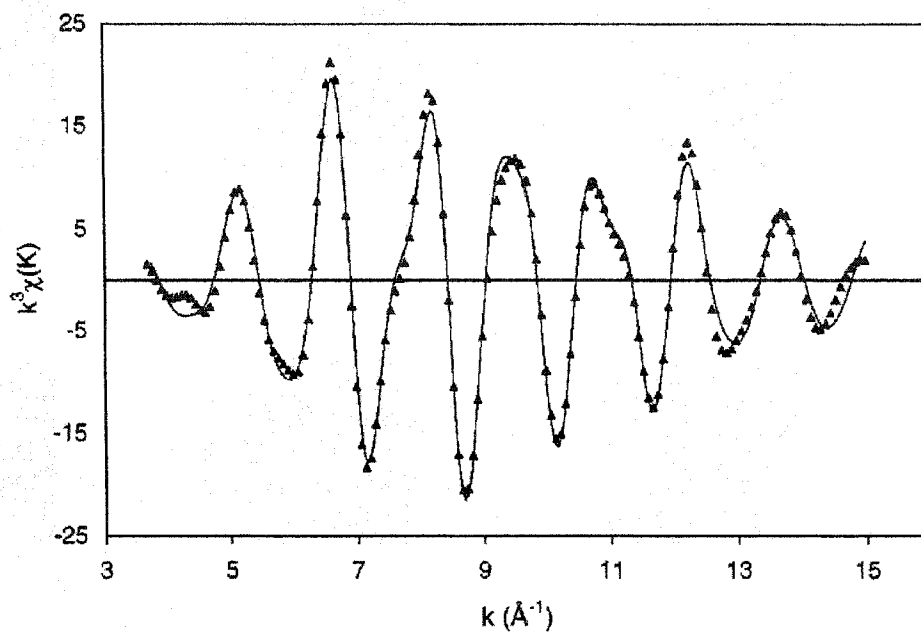


Figure 2.17. Fit in k -space for Co:Mo (2:1)/SiO₂. Experimental (triangles) and modeled EXAFS contribution around Co (full line).

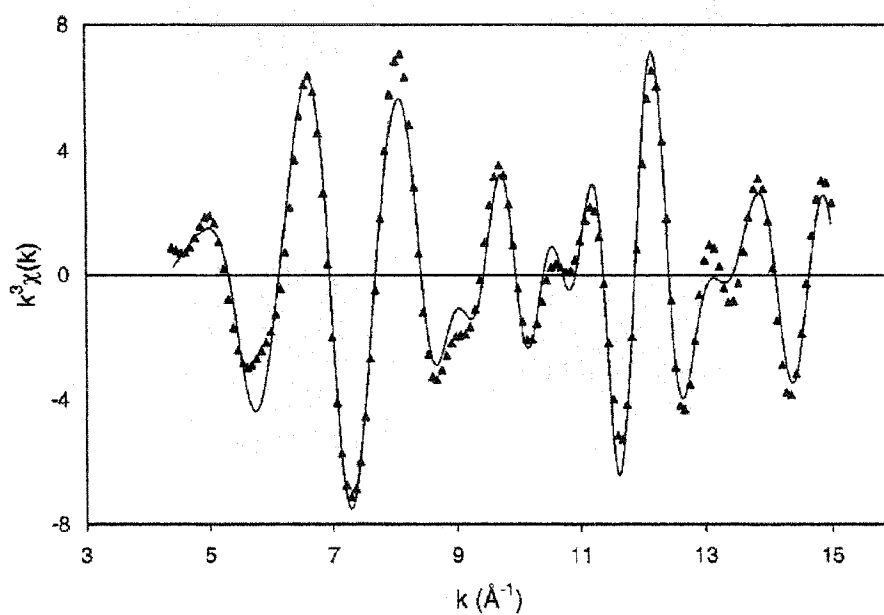


Figure 2.18. Fit in k -space for Co:Mo (1:3)/SiO₂. Experimental (triangles) and modeled EXAFS contribution around Co (full line).

2.3.3. Production of carbon nanotubes by catalytic disproportionation of CO

The ability of the different catalysts to produce SWNT by CO disproportionation was tested by passing pure CO over the catalyst at 700°C following the method described by Alvarez et al [55]. Before the reaction, the catalysts were calcined in air at 500°C, then reduced in H₂ at 500°C, and then heated in He flow up to the reaction temperature. At the end of a 2-h reaction period, the spent catalyst containing the carbon deposits was cooled down in He flow. The characterization of the carbon deposits was done by using three of the techniques introduced on Chapter 1. They are temperature programmed oxidation (TPO), transmission electron microscopy (TEM) and Raman spectroscopy. Kitiyanan et al. have previously shown that from the TPO results a quantitative measure of the carbon yield and selectivity towards SWNT can be obtained [3]. The results obtained by TPO analysis are summarized in Table 2.5 and illustrate the strong influence of the Co:Mo ratio on SWNT selectivity. The TEM observations totally support the TPO results. As shown in Fig. 2.19 and 2.20, a contrasting difference is observed on the carbon structures produced with the two different samples. While the sample with a Co:Mo ratio of 1:3 exhibited a high density of SWNT, the sample with a Co:Mo ratio of 2:1 mainly produced MWNT and graphitic carbon deposits. In the first case, one can observe the typical parallel lattice fringes characteristic of SWNT. In the second case, a spacing of 0.34 nm can be observed between the fringes, which is characteristic of the space between individual walls in multi-walled nanotubes [56].

Table 2.5. Carbon yield and selectivity for two catalysts with different Co: Mo ratio. The yield is defined as mass of total deposited carbon per mass of catalyst. The selectivity to SWNT is the mass of SWNT per total mass of carbon deposits

Catalysts	% Amorphous carbon	% SWNT	%MWNT and graphite	Total carbon yield.
Co:Mo(1:3)/SiO ₂	18.7	70.7	10.6	18.25%
Co:Mo(2:1)/SiO ₂	14.8	15.2	70.0	16.35%

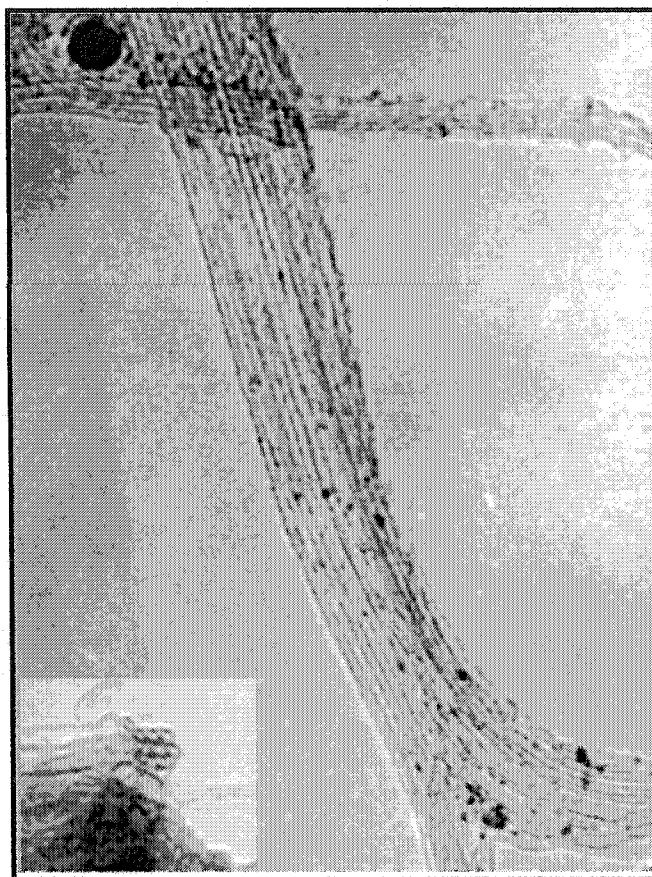


Figure 2.19. TEM images showing SWNT produced by CO disproportionation on a Co:Mo(1:3)/SiO₂ catalyst.



Figure 2.20. TEM images showing a mixture of SWNT, MWNT and graphite produced by CO disproportionation on a Co:Mo(2:1)/SiO₂ catalyst.

Likewise, Raman spectroscopy provides valuable information about the structure of carbon nanotubes. As shown in the previous chapter, the analysis of the radial A_{1g}

breathing mode (below 300 cm^{-1}) gives direct information about the tubes diameter, while the analysis of the tangential mode (TM) range i. e. $1400\text{-}1700\text{ cm}^{-1}$, provides information on the electronic properties of the tubes. In addition, the analysis of the so-called D-band at around 1350 cm^{-1} present an indication of the level of disordered carbon. The size of the D band relative to the TM band at around 1590 cm^{-1} has been used as qualitative measurement of the formation of undesirable forms of carbon [57, 58]. Figure 2.21 shows the Raman spectrum obtained for the carbon deposits formed on two different catalysts. In agreement with the TPO and TEM results, the spectrum obtained for the material obtained over the catalyst with low Co:Mo ratio shows the high selectivity towards SWNT, while the material obtained over the unselective catalyst (i. e. high Co:Mo molar ratios) shows a Raman spectrum consistent with the presence of MWNT and graphite.

It is noteworthy mentioning that when the Co:Mo(1:3)/SiO₂ catalyst that exhibited a high yield and selectivity towards SWNT was employed without the reduction step or with an exceedingly high reduction temperature, poor SWNT yields were attained. It is suggestive that the TPR indicates that the Co reduction in the Co:Mo (1:3) does not start below 500°C . One may surmise that some degree of reduction, perhaps creation of oxygen vacancies around Mo is necessary, since a totally oxidized catalyst is not efficient. On the other hand, a high degree of reduction of the catalyst, causing the appearance of metallic Co is also detrimental for

the selectivity towards SWNT. This premise will be further explored on Chapter 3 using an analogous catalytic system.

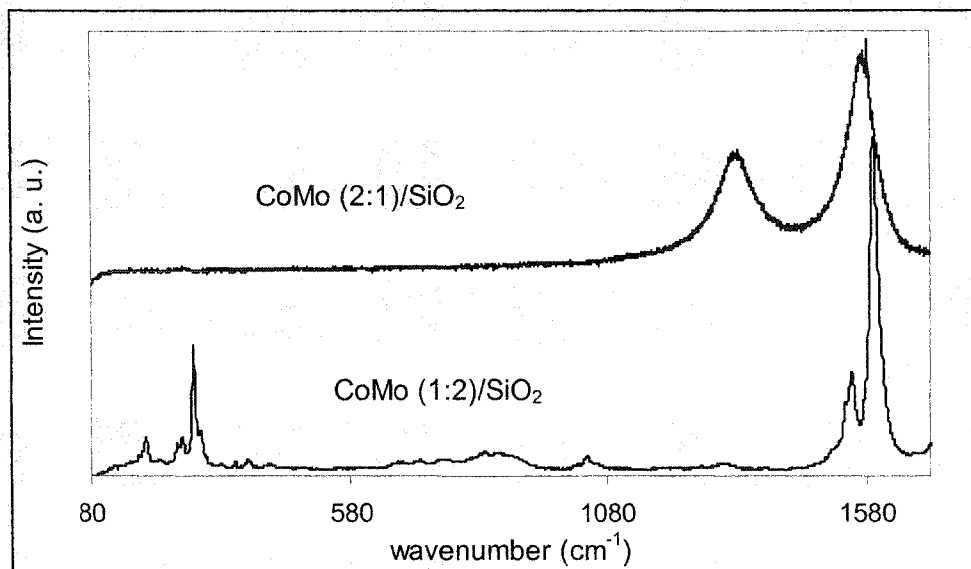


Figure 2.21. Raman spectrum of the carbon nanotubes produced by catalytic disproportionation of CO over two different CoMo/SiO₂ catalysts at 700°C. The laser excitation energy was 633nm.

2.3.4. Characterization of the Spent Catalysts

The EXAFS results for the spent catalysts are shown in Fig. 2.22. The Fourier Transform of the EXAFS data for the K edge of Co ($E_0 = 7,709$ eV) for the Co:Mo (1:2) catalyst show that after the pretreatment and before the reaction with CO, a significant fraction of Co remains oxidized. However, as the reaction proceeds, metallic Co begins to form and after 30 min., the Fourier Transform is indicative of pure Co metal. Undoubtedly during the formation of carbon nanotubes over the

selective catalyst, Co is gradually reduced to the metallic state. The detailed structural analysis of the Co EXAFS data indicated that as the reaction proceeds the Co reduction is accompanied by an increase in metal particle size. Evidence for this process is presented in Table 2.6 where an increase on the Co-Co coordination number as a function of reaction time is observed.

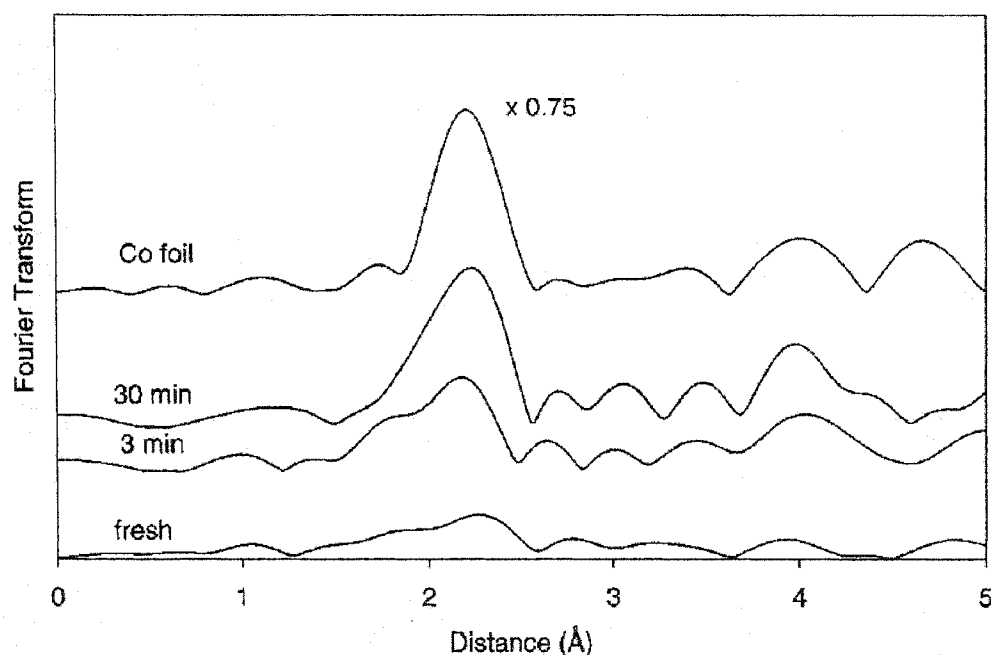


Figure 2.22. Fourier Transforms of the k^3 EXAFS data obtained for the K edge of Co for a fresh Co:Mo(1:2)/SiO₂ catalyst reduced in hydrogen (500°C), and after the growth of carbon nanotubes for reaction periods of 3 and 30 minutes. The EXAFS data of a Co foil is included for comparison.

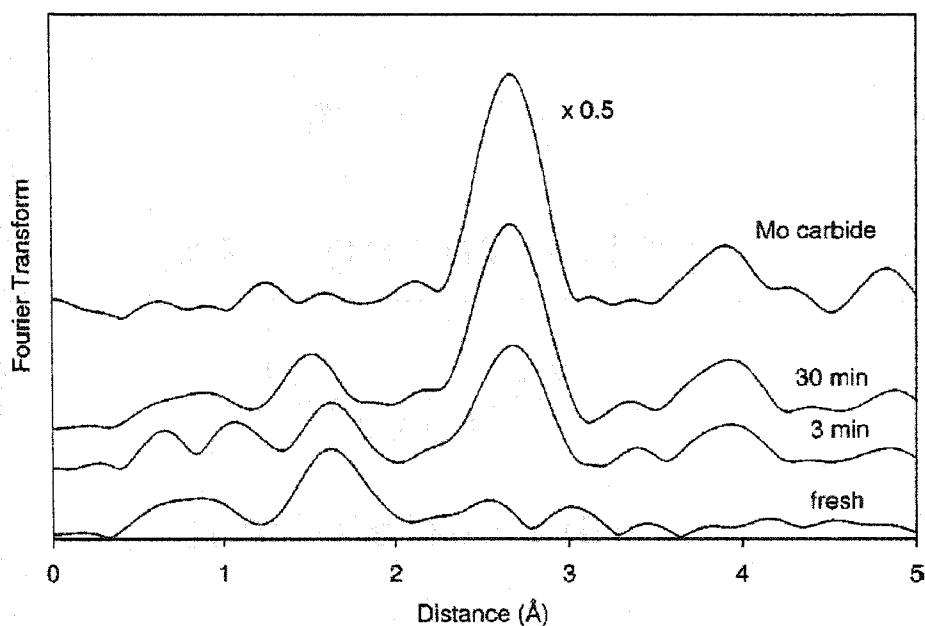


Figure 2.23. Fourier Transforms of the k^3 EXAFS data obtained for the K edge of Mo for a fresh Co:Mo(1:2)/SiO₂ catalyst reduced in hydrogen (500°C), and after the growth of carbon nanotubes for reaction periods of 3 and 30 minutes. The EXAFS data of Mo₂C is included for comparison.

In the same way, as illustrated in Fig. 2.23, after a 30-min reaction period, the Fourier Transforms of the EXAFS data of Mo ($E_0 = 20,000$ eV) reveal a drastic change, developing peaks that correspond exactly to those of the Mo₂C reference. The transformation of oxidized Mo species into Mo carbide during the reaction is indeed very clear, with a small fraction of unconverted Mo oxide remaining in the catalyst. This conversion can be clearly seen from the EXAFS analysis data of the spent catalyst summarized in Table 2.6. 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 in the spent catalyst as an oxidized species.

Table 2.6. Structural parameters for the Co:Mo(1:2)/SiO₂ catalyst after different reaction periods, as obtained from the EXAFS data analysis. N_{M-M} , N_{M-C} and N_{M-O} represent the coordination number between the metals (Mo or Co) with another metal atom, a C atom and an O atom respectively.

Sample	Sample Treatment	Edge (M)	E_0	Sigma	Coordination			Distances (Å)	r-factor
					N_{M-M}	N_{M-O}	N_{M-C}		
Co:Mo(1:2)/SiO ₂	Spent 3 min	Co	4.2	0.0068	5.8	-	-	2.47	0.043
				0.0025	-	2.2	-	2.05	
Co:Mo(1:2)/SiO ₂	Spent 30 min	Co	9.4	0.0065	9.2	-	-	2.50	0.020
				0.0003	-	1.1	-	2.07	
Mo ₂ C	Reference	Mo	6.6	0.0063	11.6	-	-	2.97	0.022
				0.0106	-	-	5.8	2.08	
Co:Mo(1:2)/SiO ₂	Spent 30 min	Mo	7.1	0.0075	6.7	-	-	2.98	0.038
				0.0075	-	0.9	-	2.09	
				0.0039	-	-	3.3	1.68	

2.4. DISCUSSION

2.4.1. Characteristics of the calcined catalysts

The UV-Vis and the X-ray absorption data indicate that, in all the calcined samples, Mo is in an octahedral environment in the 6+ oxidation state. Furthermore, from the values of the adsorption edge energy it can be concluded that the molybdenum oxide species are forming small clusters with average domain size somewhat larger than that of the heptamolybdate ion, but not larger enough to form bulk MoO_3 . Regardless of the Co:Mo ratio in the catalysts, the majority of Mo is forming these oxidic species. It is apparent that the degree of dispersion of Mo is more a result of the loading and degree of interaction with the support, rather than a consequence of the extent of interaction with Co. A contrasting picture is obtained from the characterization of Co, particularly in the catalysts with low Co:Mo ratio. In this case, both, the UV-Vis DRS and the XANES data obtained on the catalyst with a Co:Mo ratio of 1:3 demonstrated that most of the Co is in an environment similar to that in CoMoO_4 , i.e. closely interacting with Mo. However, the slight but clear differences between the spectra of the catalyst and the CoMoO_4 reference suggest that the similarity is limited to the local environment and nature of ligands. In fact, the EXAFS data demonstrate that bulk $\alpha\text{-CoMoO}_4$ is not present in the bimetallic catalysts. Bulk CoMoO_4 has only been observed by XRD in silica-supported catalysts at high metal contents [13]. All these results can be put together in a simple model for the calcined catalysts with low Co:Mo ratios. It can be proposed that Co is in the form of a CoMoO_4 -like layer on top of Mo oxide species. As a result, most of

the Co is in an interacting phase, while only a fraction of Mo is in such a phase. Therefore, the characterization of Mo does not reflect a strong interaction with Co, while the characterization of Co shows in fact a high degree of interaction with Mo.

In contrast, when the Co is in excess, more than one type of Co species is present in the catalyst. The UV-Vis-DRS data show that in addition to the interacting phase of Co, which dominates at low Co:Mo ratios, a non-interacting phase begins to form as the Co content increases. The X-ray absorption data, together with the results obtained by Raman spectroscopy (Fig. 2.6 and 2.8) undoubtedly show that this non-interacting species is Co_3O_4 , which has been previously detected by Raman spectroscopy and X-ray diffraction in Co:Mo/SiO₂ catalysts [16, 37].

2.4.2. Characteristics of the reduced catalysts

The DRIFTS data of adsorbed NO give further evidence of the interaction between Co and Mo in the reduced catalysts with low Co: Mo ratios. When the position of the symmetric-stretching band of dinitrosyl adsorbed on Co is compared for the monometallic Co and bimetallic Co-Mo catalysts, a shift of about 8 cm^{-1} to higher wavenumbers is observed on the bimetallic catalyst (Fig. 2.11). Furthermore, the binding energy obtained by XPS for the fraction of Co that remains unreduced after the reduction treatment in the bimetallic catalyst (around 781.4 eV) corresponds to that of Co interacting with Mo oxide, rather than of a non-interacting Co oxide species (780.1-780.5 eV).

However, as the amount of Co in the reduced catalyst increases, the shift in the IR main band to higher wavenumbers becomes gradually smaller, until the position of the band coincides with that of the monometallic Co/SiO₂ catalyst, i.e. 1803 cm⁻¹. At the same time, the intensity of the band ascribed to the Mo sites gradually decreases until it practically disappears for the catalyst with a Co:Mo ratio of 2:1. This trend is consistent with the XPS data, which indicate that the Mo sites are progressively covered by Co as the Co: Mo ratio increases. Delmon et al. have proposed that cobalt molybdate is present in the silica-supported catalyst, and that the non-interacting Co or Mo species (depending on which metal is in excess) agglomerate over CoMoO₄ forming a geode-like structure [13]. Our results clearly show that when Mo is in excess, this is not the case. The DRIFTS data show that the Co sites are strongly influenced by the presence of Mo but they are not covered by it. On the other hand, a geode-like structure could be postulated for the catalysts in which Co is in excess. That is, Co oxide could partially cover the Co molybdate species.

From the combined analysis of the XPS, TPR, and EXAFS data, one can infer that the reducibility of the Co species is strongly influenced by the presence of Mo in the catalyst. The amount of reducible Co clearly increases with the Co: Mo ratio. This trend can be explained in terms of the formation of an interacting Co molybdate-like species in the oxidized catalyst, which should be more difficult to reduce than non-interacting Co oxide [16]. At the same time, as shown in Fig. 2.14, the reducibility of the Mo species is also affected by the presence of Co, indicating that

although the techniques that probe bulk Mo do not show an interaction with Co (XANES, UV/V DRS), an interaction indeed exists at the catalyst surface and it is more pronounced at low Co: Mo ratios.

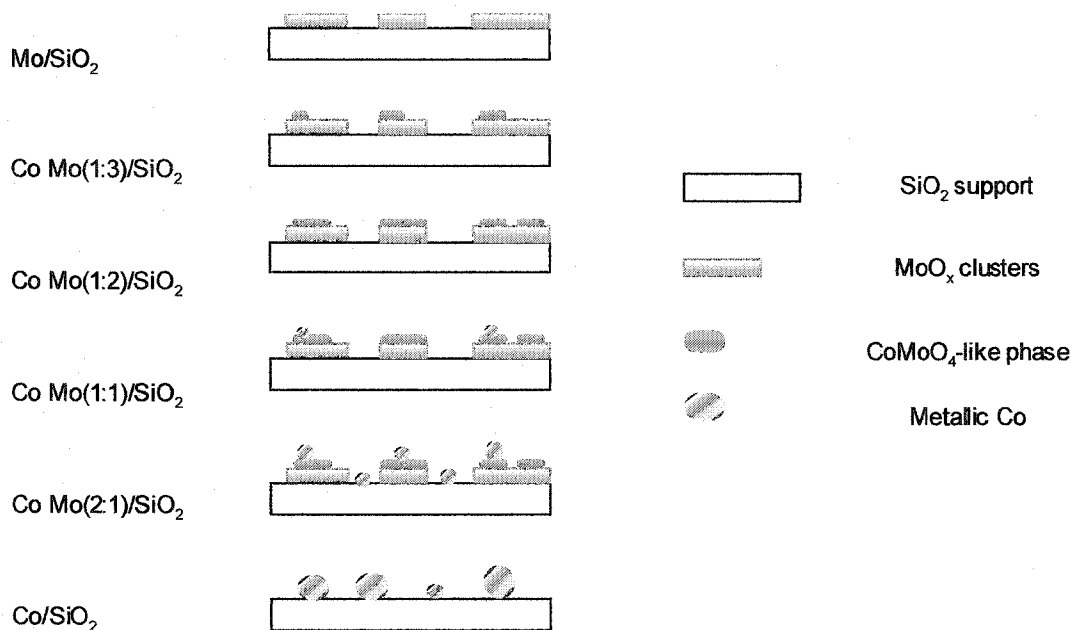


Figure 2.24. Schematic description of the structure of the reduced catalysts as derived from the characterization methods.

Combining all the information obtained from FTIR, LRS, XPS, UV/V DRS, H₂-TPR and XAS, a coherent representation of the catalyst structure, as it stands right before the beginning of the SWNT reaction, can be put together. This picture is schematically represented in Fig. 2.24. Three main phases have been identified in the reduced catalyst just before reaction: molybdenum oxide clusters, cobalt interacting

with molybdenum oxide in a cobalt molybdate-like structure, partially covering the Mo oxide clusters, and segregated metallic cobalt particles. The fraction of each of these species depends on the Co:Mo ratio.

2.4.3 Relationship between catalyst morphology and selectivity towards SWNT

In previous works, it has been reported that although MWNT and other carbonaceous forms can be produced from CO disproportionation on monometallic Co catalysts, these catalysts are not selective for the production of SWNT [3, 55]. On the other hand, monometallic Mo catalysts are inactive at the reaction temperatures employed in this study (around 700-800°C). However, it has been shown that when Co and Mo co-exist in the catalysts, especially when Mo is in excess, SWNTs are formed with high selectivity [3]. The results obtained by EXAFS on the spent Co:Mo(1:2)/SiO₂ catalyst, clearly show that Co suffers a severe transformation under reaction conditions. Before reaction, but after pretreatment in H₂ at 500°C and then in He at 700°C, a considerable fraction of Co is still in the oxide state closely interacting with Mo on the surface, as shown by FTIR, XPS and XAS. After 3 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. Simultaneously Mo that was initially in the oxidized state is converted to the carbidic form, as clearly demonstrated by EXAFS.

Alvarez and coworkers previously proposed that the role of Co is the activation of CO [55]. However, when it is in the form of large metal aggregates, it has the tendency to generate mostly MWNT, carbon filaments and graphite [59]. When Mo is present in the catalyst and there is no Co in excess, a well-dispersed Co^{+2} species in the form of a Co molybdate-like phase is stabilized. From the detailed characterization studies described in this chapter, it can be confirmed that the formation of this interacting Co molybdate-like species plays a determinant role in the catalyst selectivity toward the formation of SWNT.

The effect of having Co^{II} stabilized on this cobalt-molybdate like environment is dramatic. First of all, it avoids the reduction and formation of large metallic aggregates. The importance of preventing the reduction of Co is evident when the selective catalyst is compared with a non-selective one (Co:Mo ratio of 2:1). In the non-selective catalyst, most of the Co in the oxidic state after calcination is in the form of Co_3O_4 and, as in the monometallic Co/ SiO_2 catalyst, this oxide is converted into large metallic Co clusters upon reduction, which produced the unwanted forms of carbon during reaction at 700-800°C. By contrast, on the selective catalyst, a concerted mechanism should take place during the reaction. As the CO disproportionation starts, Mo oxide is converted into Mo carbide. This transformation breaks up the Co molybdate-like structure, allowing for the reduction of Co by CO. However, the Co ions are now highly dispersed and in the presence of high concentration of CO in the gas phase. This environment seems to be favorable for the production of SWNT instead of the sintering that would normally occur during

a high temperature reduction process. This proposed mechanism is illustrated in Figure 2.25. We may envision the release of extremely small metal Co clusters into the gaseous CO environment in a way that resembles the vapor-phase production of SWNT by the CO disproportionation coupled with decomposition of Fe pentacarbonyl that has been developed by Nikolaev et al. [2]. In that case, like in the one described in this chapter, the production of large metal clusters causes losses in SWNT yield and selectivity.

On the very small Co clusters the production of MWNT, carbon filaments, and graphite does not occur. Such production normally occurs on larger Co clusters, following the well-known mechanism for carbon filament growth [60]. That is, the metal clusters begin to decompose CO producing Co carbide particles, which then tend to precipitate graphite at their end in the form of cylindrical filaments. When the Co clusters are so small that they are only composed by a few atoms, or even by isolated Co atoms, a different mechanism must be considered [61]. For instance, a so-called “scooter” mechanism has been proposed, this mechanism takes into consideration the known fact that, without a catalyst present, the carbon precursors would tend to grow into C₆₀-Buckminsterfullerenes. However, in the presence of a catalyst, the structure does not close into a hemisphere but it is kept open. It has been proposed that metal atoms would diffuse (scoot) along the open edge and prevent the closure of the carbon rings while catalyzing the incorporation of carbon to the

growing tube [62]. A model similar to the previous one, but that does not regard the catalyst as isolated atoms, but rather as a metal cluster has been proposed.

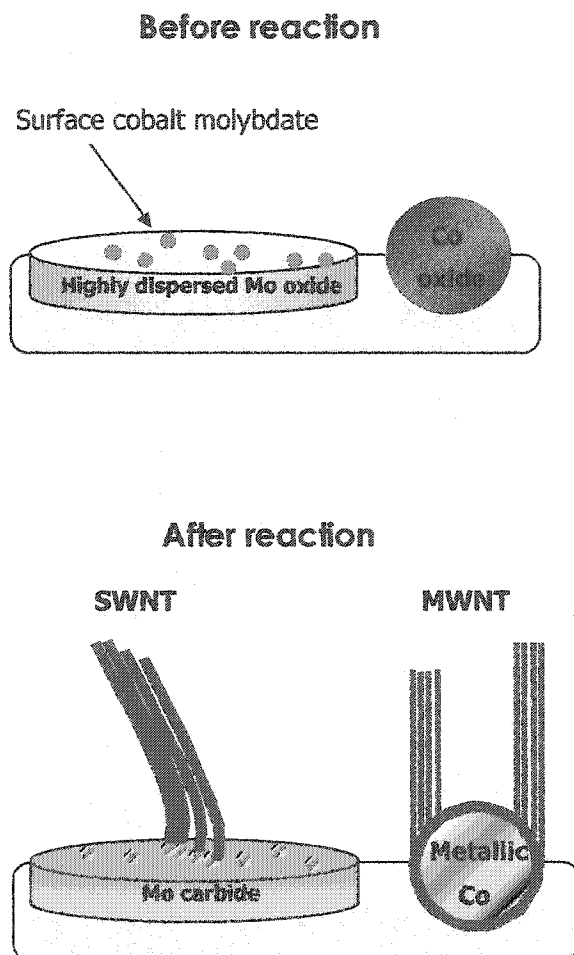


Figure 2.25. Schematic representation of the state of the catalyst components before and during the production of SWNT. The Co species stabilized by Mo resist reduction and sintering before the reaction. Under CO, Mo becomes carbide while Co becomes metallic and generates the SWNT. The excess Co, not stabilized by Mo, produces MWNT and fibers.

In this model, the addition of carbon to the tube occurs at the end of the tube over a metal cluster that is suspended by the growing tube. In this mode, the metal cluster is of the same size or slightly smaller than the diameter of the tube. The metal cluster allows for the stabilization of reactive bonds dangling at the tube tip and prevents the tube closure by moving up with the growing tip [63, 64]. But when the catalyst particle becomes larger the strain energy of the overcoating becomes smaller, and as a result, the formation of a graphitic overcoat is favored (65).

When all these observations are put together, a consistent picture of the detailed catalyst structure is obtained and a hypothesis on the reasons for which this particular catalytic formulation system shows high selectivity can be outlined. The following chapters describe work in which this hypothesis is tested. In Chapter 3 and Chapter 4 we present the results obtained when the catalyst formulation is varied and in Chapter 5 and 6 we present the results obtained when the growth conditions (i.e. feed and temperature) are changed.

2.5. CONCLUSIONS

We can summarize the main findings reported in this chapter in the following conclusions:

- a) The selectivity of the Co-Mo catalysts towards SWNT production by CO disproportionation strongly depends on the stabilization of Co^{2+} species, which result from an interaction with Mo.

- b) The extent of the Co-Mo interaction is inversely proportional to the Co:Mo ratio and has different forms during the different stages of the catalyst life.
- c) In the oxidic state after calcination, Mo is forming small clusters of in the form of well dispersed Mo (6+) species and Co is either interacting with Mo in a superficial Co molybdate-like structure (at low Co:Mo ratios) or as a non-interacting Co₃O₄ phase (at high Co:Mo ratios).
- d) During the subsequent reduction treatment, the non-interacting phase is reduced to metallic Co, while the Co molybdate-like species remain as well-dispersed Co²⁺ ions.
- e) Under reaction conditions, the Mo oxide species are converted into Mo carbide, thus breaking the interaction and releasing the metallic Co in a state of high dispersion, which is responsible for the production of SWNT. By contrast, the large Co clusters are responsible for the non-selective forms of carbon (MWNT, filaments, graphite, etc.)

ACKNOWLEDGEMENTS

The work presented in this chapter is the result of a two-years collaborative effort of the Heterogeneous Catalysis Group at the University of Oklahoma. I would like to thank specially Dr. Walter Alvarez for his help with catalyst characterization (specially XPS and DRIFTS) and his extremely helpful discussions, Dr. B. Kitiyanan and Leandro Balzano for his help on catalyst preparation, reaction testing and TEM

analysis, Dr. Armando Borgna for his work on the analysis of the X-ray Absorption data, Greg Strout (OU S. R. Noble Electron Microscopy Laboratory) for his assistance during TEM analysis and Syed Khalid (NSLS, Brookhaven National Lab.) for technical support during X-ray absorption experiments. I am also very thankful to the North American Catalysis Society for granting me with a Kokes award to travel to Canada in 2001 to present the results of the work described in this chapter. I would like also to thank the Oklahoma Center for the Advancement of Science and technology (OCAST) and Conoco Inc. for financial support. Finally I would like to thank the Fulbright-CAREC program for my scholarship; the work described here was performed during the period covered by it.

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CHAPTER 3

ROLE OF THE Co-W INTERACTION IN THE SELECTIVE GROWTH OF SWNT AND ITS ANALOGY WITH THE Co-Mo SYSTEM^{II}

3.1. INTRODUCTION

In the previous chapter a battery of characterization techniques was used to study the Co-Mo catalytic system in order to explain its high selectivity toward SWNT synthesis. Based on the characterization results a hypothesis that links an intimate Co-Mo interaction to the catalyst performance has been drafted. Equally important, it was proposed that the form of this Co-Mo interaction has the form of a surface cobalt molybdate –like structure that under reaction conditions would control the growth of the metallic cobalt nanoparticles, allowing this metallic particles to selectively catalyze the growth of SWNT.

As mentioned before, the Co-Mo system is a catalyst commonly employed in petroleum refining for hydrotreating processes; however, most studies on these catalysts have focused on alumina- supported systems since alumina interacts with the metals with the appropriate strength to generate the species with the optimum hydrotreating activity. Intense research by several groups has revealed the structure of

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the sulfide Co-Mo catalysts at the atomic level [1-6]. Other characteristics of these catalysts have also been investigated. For instance, tungsten has been investigated as a catalyst component due to its strong chemical similarity with Mo. Indeed, it has been found that the addition of W to the Co-Mo bimetallic catalyst significantly increases the hydrotreating activity [7]. However, a Co-promoted W catalyst without Mo is generally regarded as an unsuccessful combination for hydrotreating [8, 9]. Reports of supported Co-W catalysts are scarce and the reason for the lack of synergy between Co and W in the sulfide state is still unclear [10-14].

In this chapter we focus on the Co-W catalytic system for SWNT synthesis and have designed a characterization strategy on the basis of the precedent literature and the work described on the previous chapter. With all the information gathered by the catalyst characterization results we have been able to put together a detailed picture of the structure of this catalyst, and built up an analogy with the Co-Mo system, which we will use to explain the variations in selectivity towards SWNT observed when the catalyst formulations, pretreatment and/or reaction conditions are changed in both catalytic systems.

3.2. EXPERIMENTAL

3.2.1. Catalysts preparation and pretreatment

A series of mono and bimetallic Co-W catalysts supported on silica was prepared by incipient wetness impregnation. The bimetallic samples, prepared by co-

impregnation of aqueous ammonium metatungstate and Co nitrate solutions, had Co:W molar ratios of 2:1, 1:1, 2:3, 3:4, 1:2, and 1:3. In this series, the amount of Co was kept constant for all catalysts at 1.3 wt. %, while the amount of W was varied accordingly. Three monometallic catalysts were prepared with loadings of Co 0.02 wt %, Co wt. 1.3% and 4.6 wt % W respectively. The SiO₂ support obtained from Aldrich had an average pore size of 6 nm, BET area 480 m²/g, pore volume 0.75 cm³/g, and particle sizes in the range 70-230 mesh. Five grams of SiO₂ support were impregnated using a liquid-to-solid ratio of 0.6 cm³/g. After impregnation, the solids were dried overnight at 120°C and then calcined in a 1 inch diameter horizontal fixed bed reactor for 3 h at 500°C in dry-air flow of 50 scc/min.

3.2.2. Catalyst characterization

The UV/Vis spectra of the calcined catalysts were recorded using a Shimadzu double beam spectrometer UV- 2101 with an integrating sphere for diffuse reflectance. Barium sulfate was used as reflectance standard. Several W and Co compounds, including WO₃, Na₂WO₄·2H₂O, (NH₄)₁₀W₁₂O₄₁, CoWO₄ and CoMoO₄ were used as references. Before each analysis, the samples were dried in air at 120°C.

The X-ray absorption data were obtained at the National Synchrotron Light Source at Brookhaven National Laboratory, 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 ring current of 80-220 mA. 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. The spectra of Co_3O_4 and CoWO_4 were also obtained at liquid nitrogen temperature and used as references.

The temperature programmed reduction (TPR) experiments were conducted passing a continuous flow of 5% H_2/Ar over approximately 30 mg of the calcined catalyst at a flow rate of $10 \text{ cm}^3/\text{min}$, while linearly increasing the temperature at a heating rate of $8^\circ\text{C}/\text{min}$. The hydrogen uptake as a function of temperature was monitored using a thermal conductivity detector, SRI model 110 TCD. The TCD was calibrated for hydrogen consumption using TPR profiles of known amounts of CuO and relating the peak area to hydrogen uptake.

The Raman spectra of both fresh catalysts and nanotubes were obtained in a Jovin Yvon-Horiba LabRam 800 equipped with a CCD detector and with three different laser excitation sources having wavelengths of 632 (He-Ne laser) 514 and 488 nm (Ar laser). Typical laser powers ranged from 3.0 to 5.0 mW; integration times were around 15 sec for each spectrum; ten Raman spectra were averaged for each sample.

3.2.3. Production and Characterization of Carbon Nanotubes

To study the effect of reaction parameters in the Co-W system, the production of SWNT by CO disproportionation was conducted on a catalyst with a Co:W molar ratio of 1:3 under different conditions. The choice of this particular composition was based on the results obtained in the previous chapter in which we demonstrated that the silica-supported Co-Mo system displays a very high selectivity in the production of single wall nanotubes by CO disproportionation only when low Co:Mo molar ratios were used. By contrast, when high Co:Mo ratios were used, undesired forms of carbon, such as graphite and irregular nanofibers were obtained. For the SWNT production on the Co-W/SiO₂ catalysts, 0.5 g of a calcined sample was placed in a horizontal tubular packed-bed reactor; the reactor was 12 inches long and had a diameter of 0.5 inches. After loading the catalyst, the reactor was heated in 50 scc/min H₂ flow to different temperatures in the range 500-1000°C at 10°C/min; once the desired reduction temperature was reached the system was heated up under 50 scc/min flow of He at the same rate to 850°C. Subsequently, CO was introduced at a flow rate of 850 cm³/min at 84 psia for 2 hours. At the end of each run, the system was cooled down under He flow. The total amount of deposited carbon was determined by temperature-programmed oxidation (TPO) following the method described on Chapter 1.

3.3. RESULTS

3.3.1. Characterization of the Calcined Catalysts

3.3.1.1 Diffuse Reflectance UV-Visible Spectroscopy (UV/V-DRS)

We have followed the method described in Chapter 1 to use UV/V-DRS to study the state of both W and Co in the oxidic form, after calcination in air at 500°C. As in the case of molybdenum, we use the square root of the Kubelka-Munk function multiplied by the photon energy to estimate the band energy gap of W(VI) oxidic species [15]. The values thus obtained carry information about the average domain size of the oxide nanoparticles [16]. Therefore, a comparison is made between the energy of the samples under investigation and those of references of known domain size. This comparison is made in Fig. 3.1, which shows the absorption edges of several WO_x species together with those of two different Co:W/SiO₂ catalysts. As expected, the band gap energies in the reference series decrease as the domain size increases. Those for the two Co:W/SiO₂ catalysts investigated lie between the values corresponding to $(\text{NH}_4)_{10}\text{W}_{12}\text{O}_{41} \cdot 5\text{H}_2\text{O}$ and WO_3 . From this comparison it can be inferred that the W species in the calcined catalysts have relatively small domain sizes and that little difference is observed in the state of W as the Co:W ratio changes. The presence of a small contribution of WO_3 species is clear on the CoW(3:4)/SiO₂ sample since a small tail can be observed below 3.0 eV, nevertheless most of the W is certainly in a high state of dispersion.

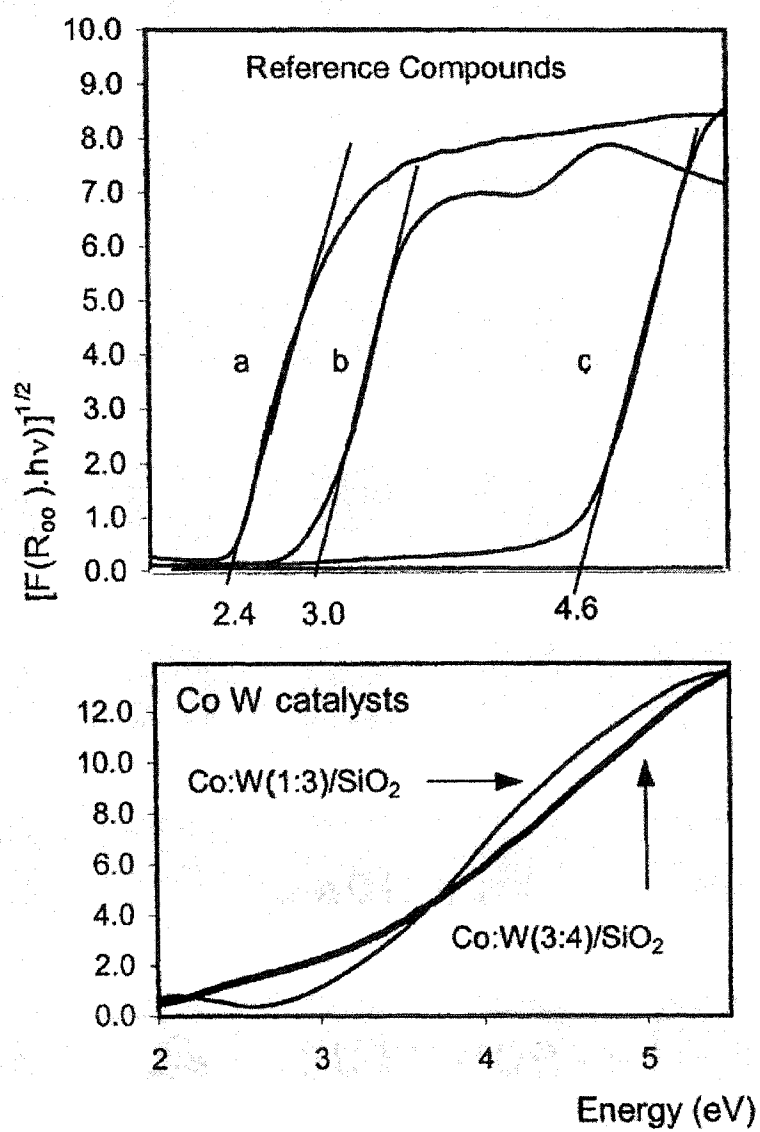


Figure 3.1. Lower panel: UV absorption spectra for two Co:W/SiO₂ calcined catalysts. Upper panel: (a):WO₃, (b): (NH₄)₁₀W₁₂O₄₁, (c): Na₂WO₄ references.

In addition to the charge-transfer bands due to W, appearing in the UV region, the visible spectra of the bimetallic catalysts also present bands in the 500-750 nm region, which are associated with Co species and are ascribed to d-d transitions (${}^4T_{2g}$, ${}^4A_{2g}$ and ${}^4T_{2g} \rightarrow {}^4T_{1g}(P)$) of high spin octahedral Co complexes [17,18]. Figure 3.2 shows the DRS spectra in this region for three calcined catalysts, Co:W(3:4)/SiO₂, Co:W(1:3)/SiO₂ and Co/SiO₂. The spectrum for the Co:W(1:3) catalyst is very similar to that of CoWO₄, in which Co is in an octahedral environment [19-21]. For comparison, Figure 3.2a includes the spectrum of a CoMo(1:3)/SiO₂ catalyst, which as shown in the previous chapter, is highly selective for the production of SWNT and has all the Co in an octahedral environment also. The small difference in the position of the maximum in the spectrum of the Co-W catalysts compared to that of the Co-Mo catalyst observed in Figure 3.2a is attributed to a difference in the strength of the ligand field. Nevertheless, the identical shape of the spectra of both samples indicates that both catalysts have the same ligand symmetry around Co. By contrast, the shape of the spectrum of the Co:W(3:4)/SiO₂ catalyst shown in Fig. 3.2b, is markedly different and exhibited the appearance of a band at around 680 nm. This band was in turn the dominant feature in the pure Co catalyst and can be associated with Co₃O₄ species, which as shown below, are present in the pure Co catalyst in the calcined state. Therefore, it can be concluded that, similar to the Co-Mo catalytic system, a catalysts with low Co:W ratio exhibits most of the Co in interaction with W but, as the Co:W ratio increases free Co oxide starts appearing.

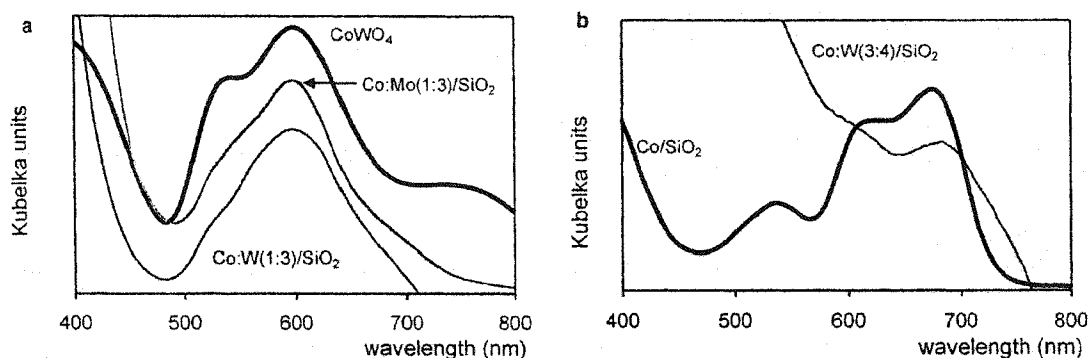


Figure 3.2. Visible spectra for two calcined bimetallic Co:W/SiO₂ catalysts with different Co:W ratios (1:3 and 3:4) and that for a monometallic Co/SiO₂. The spectra of a bimetallic CoMo(1:3)/SiO₂ catalyst and CoWO₄ (adapted from reference 13) are included for comparison.

3.3.1.2 X-ray absorption spectroscopy (EXAFS/XANES)

Figure 3.3 compares the Co K-edge ($E_0 = 7709$ eV) XANES spectra for two bimetallic Co:W(1:3)/SiO₂ and Co:Mo(1:3)/SiO₂ catalysts in the calcined form together with those of two reference compounds, CoWO₄ and CoMoO₄. Except for some small differences in the intensity of the first peak in the edge, the four spectra look remarkably similar. In agreement with the conclusions reached from the UV/Vis results, the X-ray absorption data indicate that in a catalyst with low Co:W molar ratio, Co is interacting strongly with W in a local environment similar to that in CoWO₄. By contrast, the Co edges from the Co:W (2:1) and CoMo(2:1) catalysts, which contain excess Co, are very different from that of the cobalt tungstate

(molybdate) reference. As shown in Fig. 3.4, the XANES of these catalysts are in fact very similar to that of Co_3O_4 .

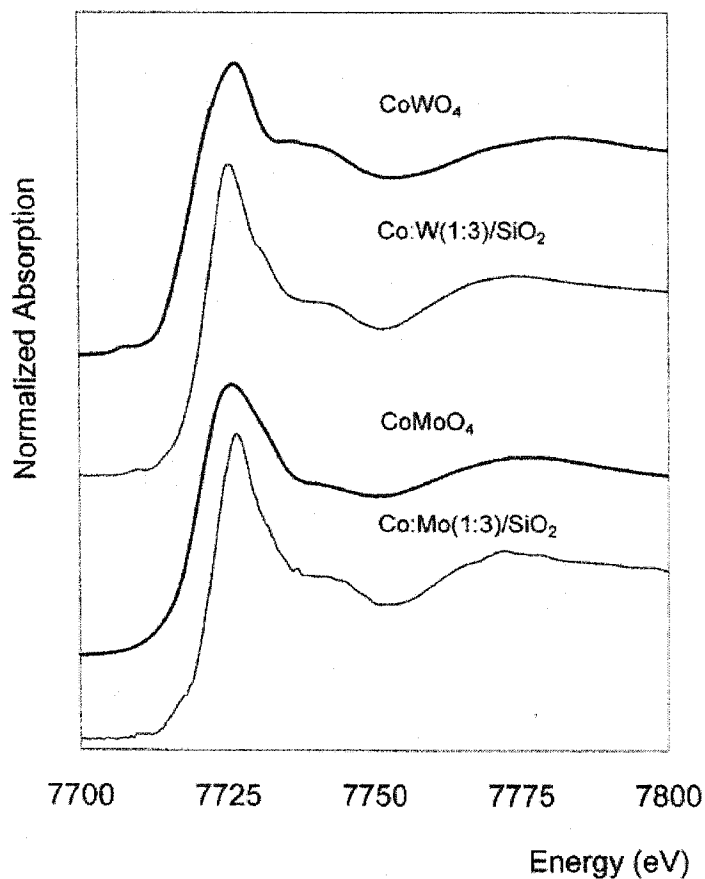


Figure 3.3. Co K edge (7,709 eV) XANES of calcined CoW(1:3)/SiO_2 and Co:Mo(1:3)/SiO_2 catalysts compared to CoWO_4 and CoMoO_4 used as a references.

We need to emphasize that this overall behavior is similar to the observed before on the Co-Mo system (also shown in Figures 3.3 and 3.4); hence the formation of a cobalt tungstate at low Co:W ratios and a segregated cobalt oxide phase at high Co:W ratios clearly suggest an inherent analogy between the Co-W and Co-Mo systems.

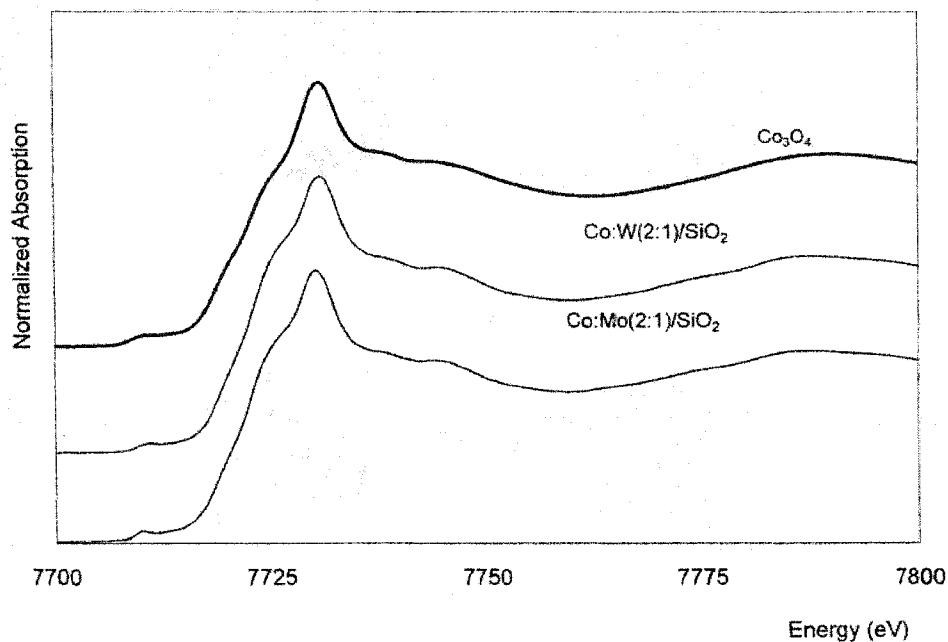


Figure 3.4. Co K edge XANES of a calcined CoW(2:1)/SiO_2 and Co:Mo(2:1)/SiO_2 catalysts compared to Co_3O_4 reference.

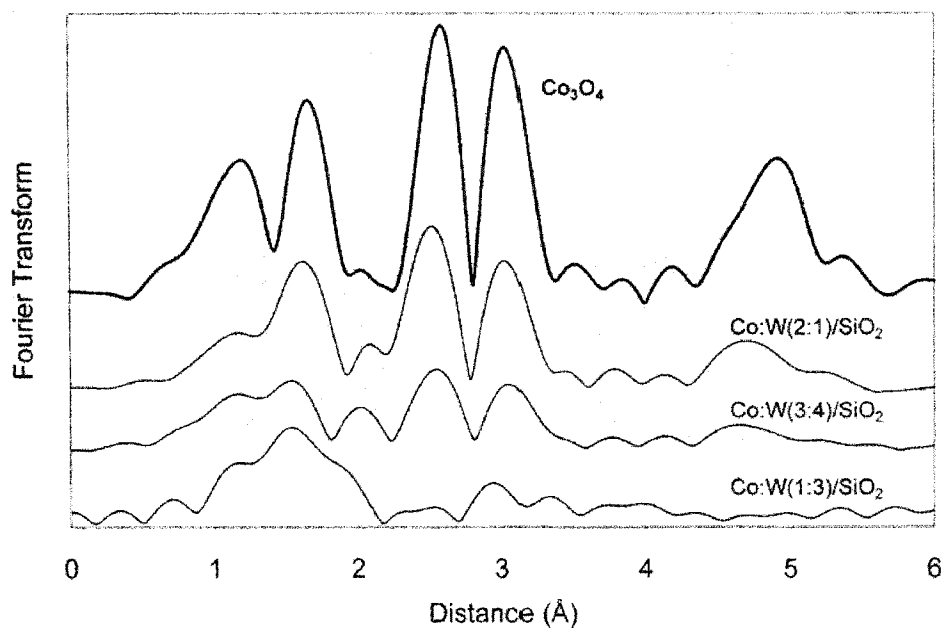


Figure 3.5. Fourier transforms of the k^3 EXAFS data of the Co K edge obtained on the calcined CoW(1:3)/SiO_2 , CoW(3:4)/SiO_2 and CoW(2:1)/SiO_2 catalysts and for Co_3O_4 reference.

The EXAFS data was in good agreement with the conclusions reached from the XANES analysis. As shown, in Fig. 3.5, the Fourier Transform for the calcined catalyst becomes very similar to that of Co_3O_4 as the Co:W ratio increases, indicating that this oxide is the predominant form present at high Co:W ratios. On the other hand, the results on the sample with low Co:W ratio require some further consideration. While most of the Co in this catalyst is forming a CoWO_4 -like phase, only a fraction of W participates in this compound. The rest of the W is in a dispersed tungsten oxide form, as demonstrated by the results obtained by UV/Vis

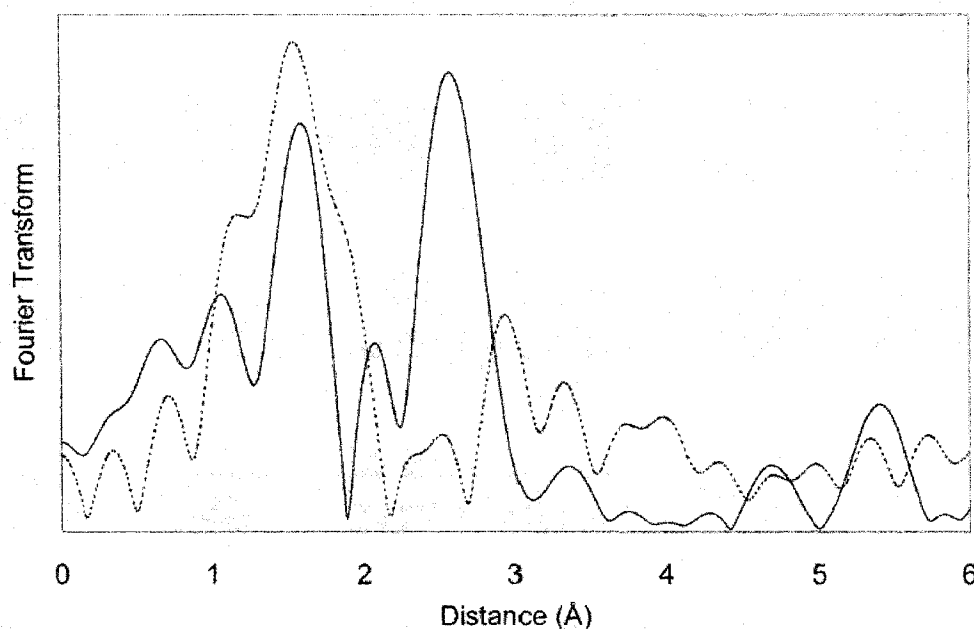


Figure 3.6. Fourier transforms of the k^3 EXAFS data of the Co K edge, obtained on the calcined Co:W(1:3)/ SiO_2 catalyst (dotted line) and on a CoWO_4 reference (solid line).

spectroscopy. We propose that, similar to the Co-Mo system, the Co is in a CoWO_4 -like phase on the basis of the XANES data, which suggest that the local environment of Co in the Co:W(1:3) catalyst is very similar to that in CoWO_4 . At the same time, the EXAFS data are significantly different from that of the bulk CoWO_4 compound. This comparison is made in Fig. 3.6, which shows the Fourier Transforms for the K-edge of Co in the calcined Co:W(1:3)/ SiO_2 catalyst, together with that of bulk CoWO_4 . The low intensity observed in the catalyst for the peak between 2.0 and 3.0 Å, clearly observable for the cobalt tungstate, shows that bulk CoWO_4 is not present, but rather a highly dispersed CoWO_4 -like structure, co-existing with well dispersed W oxide species.

3.3.1.3 Temperature Programmed Reduction (TPR)

The reduction profiles of calcined monometallic Co/ SiO_2 , Mo/ SiO_2 and bimetallic Co:Mo (1:3)/ SiO_2 catalysts obtained on the previous chapter and together with that of the W/ SiO_2 and Co:W (1:3)/ SiO_2 catalysts are shown in Fig. 3.7. The TPR profile of the Co monometallic catalyst shows two peaks at 360 and 445°C, which can be ascribed to the reduction of Co oxide species. The reduction of the monometallic W and Mo catalysts also exhibit two peaks [22, 23] but they appear at much higher temperatures than those of Co; moreover it is evident that the reduction of the W/ SiO_2 catalyst starts at higher temperatures than that of the Mo/ SiO_2 catalyst. Similar as in the case of the Co-Mo system, it is possible to identify the presence of Co and W species in the absence of interactions from the reduction profiles.

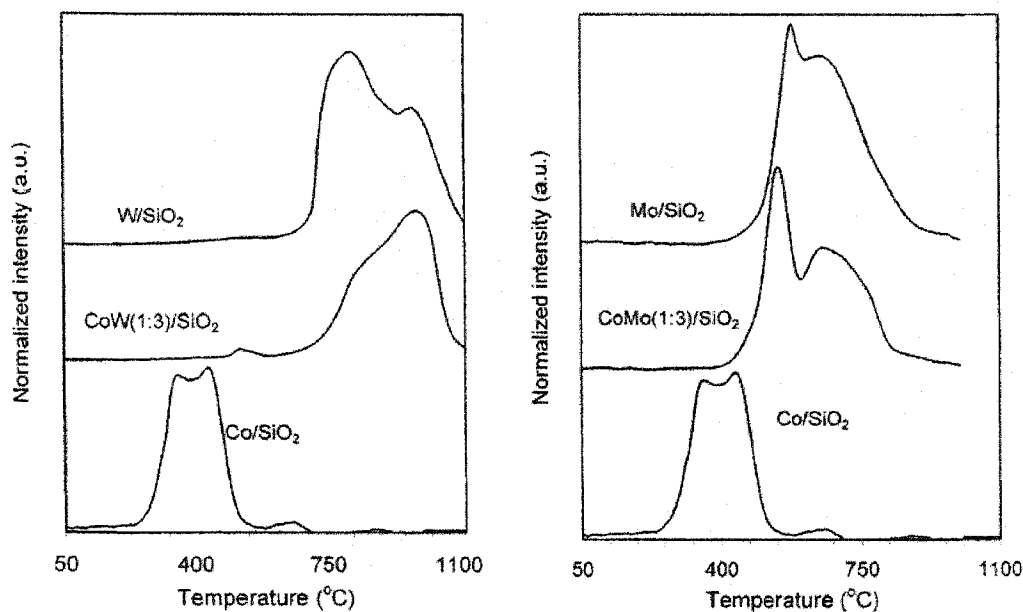


Figure 3.7. TPR profiles of several mono and bimetallic cobalt/tungsten and cobalt/molybdenum catalysts. The TPR was conducted with 5% H₂/Ar at a heating rate of 8°C/min.

Accordingly, the TPR of the bimetallic Co:Mo (1:3)/SiO₂ and Co:W (1:3)/SiO₂ catalysts indicates that, in these samples, the vast majority of Co oxide species are interacting either with Mo or W. It is clear that while most of the Co in the monometallic catalyst gets reduced below 500°C, almost no reduction takes place below this temperature in the bimetallic catalysts. It has been proposed that the addition of Mo oxide to Co oxide inhibits the reduction of the Co species because Mo⁶⁺ polarizes the Co-O bonds, making them more ionic and consequently more difficult to reduce [24], we can extend this idea to the bimetallic CoW system. In agreement with the DRS and EXAFS/XANES data, TPR indicates that a high degree of Co-W interaction is observed for the catalyst with a low Co: W ratio.

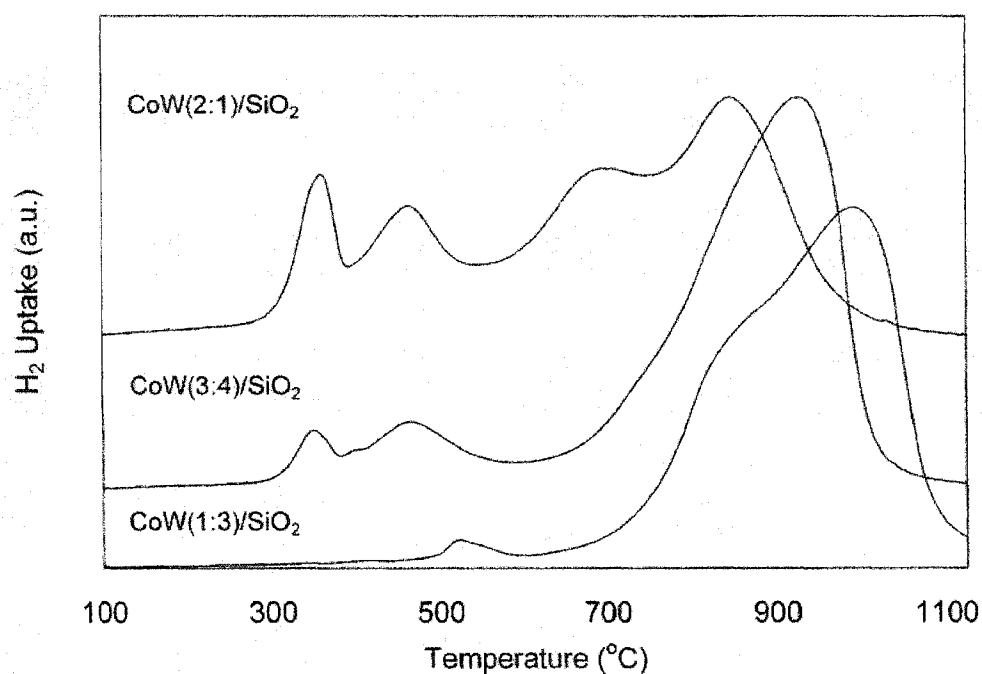
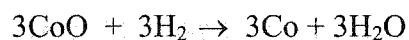
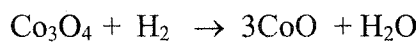


Figure 3.8. TPR profiles of three bimetallic cobalt/tungsten catalysts. The TPR was conducted with 5% H_2 /Ar at a heating rate of $8^\circ\text{C}/\text{min}$.

As shown in Fig. 3.8, a gradually increasing fraction of segregated Co species as a function of the Co:W ratio is apparent from the peaks growing at 350 and 450°C . It has previously been reported that the reduction of Co_3O_4 to Co passes through an intermediate phase (CoO) before the metallic state is reached, following a two-step reduction route that proceeds as [25]:



Therefore, in the overall process, a mol of H_2 is first consumed to produce CoO , and 3 moles of H_2 are consumed to produce the metal. The anticipated ratio of the area of the first peak at $350^\circ C$ with the broader peak at $450^\circ C$ should be then close to 0.33, which is in perfect agreement with values obtained for the ratio between the areas of both peaks (0.33 ± 0.02). The peak at $350^\circ C$ was, therefore, assigned to the reduction of Co_3O_4 to CoO while the peak at $450^\circ C$ peak corresponded to reduction of CoO to Co . The peaks appearing at temperatures above $600^\circ C$ should be attributed to reduction of species for which there exists a range of degrees of interaction between the tungsten oxide and Co .

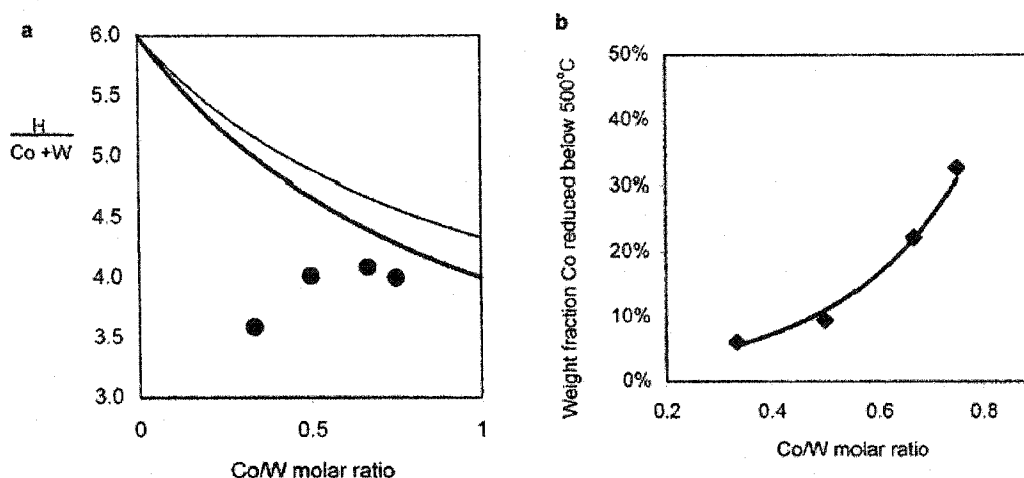


Figure 3.9. Fraction of cobalt reduced to the metallic state after treatment with H_2 at temperatures below $500^\circ C$ as a function of Co:W nominal ratio; as determined by calculating the hydrogen uptake from the TPR profiles.

Another interesting trend can be observed in the amount of hydrogen consumed during the TPR process as calculated by integrating the area under the TPR peaks. The total consumption of hydrogen during the TPR process is expressed as $H/[Co+W]$; where H is the molar uptake of atomic hydrogen and $Co+W$ is the total molar content of metal in the sample. The total hydrogen consumptions of the catalysts can be compared to the theoretical consumption that would result in two limiting cases (see Fig. 3.9a). In the first limiting case, Co and W interact forming $CoWO_4$ and in the second case they are segregated as Co_3O_4 and WO_3 , respectively. In the first assumption, all the cobalt would be as $CoWO_4$ while the residual W would be as WO_3 . Accordingly, the maximum hydrogen consumption $H/[Co+W]$ for a Co/W ratio of 0 (i.e. only W present as WO_3) would be 6. For a Co/W ratio of 1, the value would be 4 since all the cobalt and tungsten would be as $CoWO_4$. At an intermediate Co/W ratio, such as 0.5, both $CoWO_4$ and WO_3 would be present and the hydrogen consumption value would be 4.67. On the other hand, for the other limiting case in which Co and W do not interact and are only forming Co_3O_4 and WO_3 , respectively, the hydrogen consumption values for total reduction would range from 6 to 4.88 as the Co/W ratio increases from 0 to 1. A comparison of these limiting cases with the experimental data in Figure 3.9a indicates that the reduction of Co and W species is not complete since the hydrogen consumption in all catalysts is much lower than the theoretical values for any of the two limiting cases. What is clear is that the reducibility of the catalysts increases with the Co/W ratio. One expects that as the Co/W ratio increases the fraction of cobalt in the form of non-interacting Co_3O_4 will

also increase. However, if only Co_3O_4 gets reduced, the total hydrogen consumption would only be 2.67. Therefore, a partial reduction of the tungsten species also occurs during the TPR. To quantify the fraction of non-interacting Co we use the area under the first two hydrogen consumption peaks. Figure 3.9a shows the results of these calculations. Since the cobalt loading was the same in all the catalysts, the observed trend makes obvious that the amount of cobalt interacting with W increases with the W loading; that is, decreasing Co/W ratio.

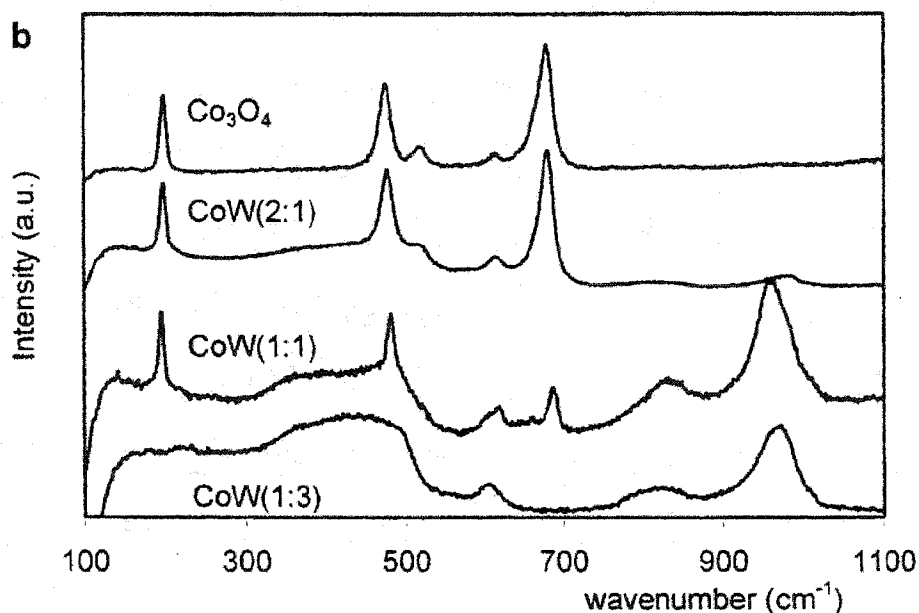


Figure 3.10. Raman spectra of various supported CoW/SiO_2 catalysts; the spectrum of an analytical sample of cobalt oxide (Co_3O_4) is also shown. The laser excitation energy was 633 nm.

3.3.1.4 Raman spectroscopy:

Figure 3.10 shows the Raman spectra of the CoW catalyst series; the Raman spectrum of an analytical sample of cobalt oxide (Co_3O_4) is also shown. The assignment for the Raman active phonon modes that are displayed in the spectrum of Co_3O_4 are as follows: the peaks at 199, 621, and 681cm^{-1} correspond to F_{2g} phonon modes while the peaks at 477 and 525cm^{-1} are E_g and A_{1g} phonon modes respectively [26] As seen from Figure 3.10 this set of peaks dominates the spectra of all the bimetallic catalyst with an excess of Co. In agreement with the results obtained by XAS and TPR it is clear that Co_3O_4 is the predominant species of Co present at high Co:W ratios.

3.3.2 Production of single-walled carbon nanotubes by catalytic disproportionation of CO

As reported in previous chapter, the silica-supported Co-Mo system displays a very high selectivity in the production of single wall nanotubes by CO disproportionation. Interestingly, the high yields and selectivities to SWNT were only obtained after a specific sequence of calcination at 500°C in air and reduction in H_2 at 500°C . It is noteworthy mentioning that when the Co:Mo(1:3)/ SiO_2 catalyst that exhibited a high yield and selectivity towards SWNT was employed without the reduction step or with an exceedingly high reduction temperature, poor SWNT yields were attained. We have previously found that with the CoMo catalyst a pre-reduction step in hydrogen was critical to obtain an active and selective catalyst. In this chapter

we have investigated a CoW (1:3)/SiO₂ catalyst for SWNT production after different pre-reduction treatments. The reaction temperature for the CO disproportionation after a pre-reduction step was fixed at 850°C. A more extensive comparison including different reaction temperatures will be reported on Chapter 5. At the end of a 2-h reaction period, the spent catalyst containing the carbon deposits was cooled down in He flow. The characterization of the carbon deposits was done by way temperature programmed oxidation (TPO), transmission electron microscopy (TEM) and Raman spectroscopy.

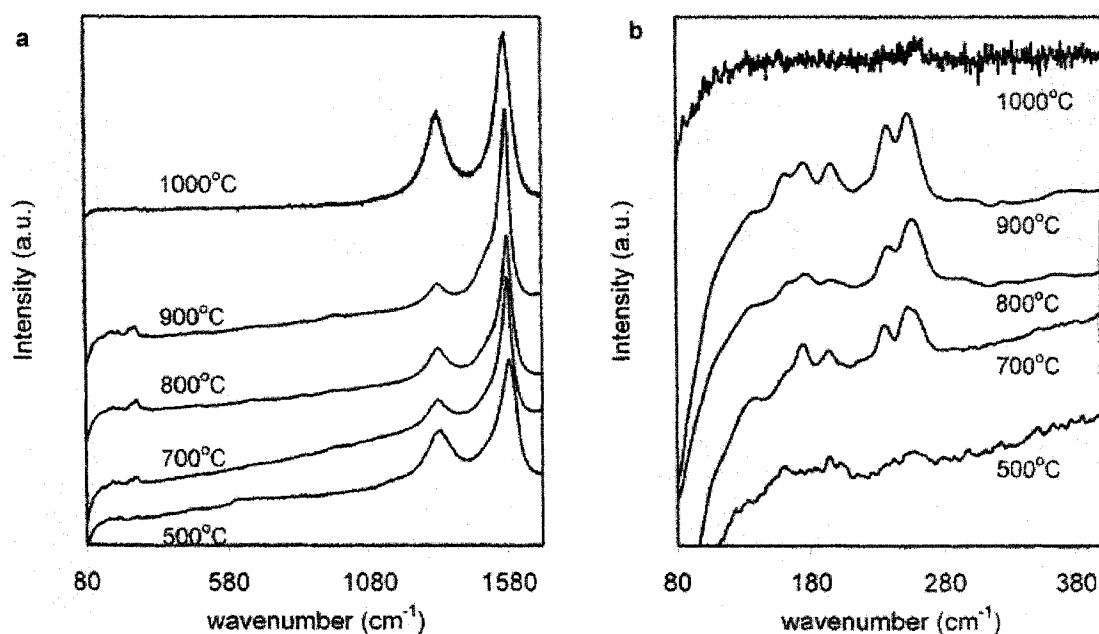


Figure 3.11. (a) Raman spectra of the carbon deposits obtained by disproportionation of CO at 850°C over a CoW(1:3)/SiO₂ catalyst after different pretreatment temperatures in hydrogen. (b) Detail of the breathing mode band. The laser excitation energy was 514 nm.

In Chapter 1 we showed that from the TPO analysis one can obtain a quantitative measure of the carbon yield and selectivity towards SWNT. The TPO results obtained in this study are summarized in Table 3.1 and illustrate the strong influence of the reaction temperature and catalyst pretreatment on SWNT yield and selectivity. In addition to TPO, Raman spectroscopy provides valuable information about the structure of carbon nanotubes. As mentioned before, the analysis of radial A_{1g} breathing mode (below 300 cm^{-1}) gives direct information about the tubes diameter [27-29], while the analysis of the G band in the tangential mode range i.e. $1400\text{-}1700\text{ cm}^{-1}$, provides information on the electronic properties of the nanotubes [30- 32]. In addition, the analysis of the so-called D-band at around 1350 cm^{-1} gives an indication of the level of disordered carbon. The size of the D band relative to the G band at around 1590 cm^{-1} has been used as qualitative measurement of the formation of undesirable forms of carbon [33, 34]. Figure 3.11 shows the Raman spectra obtained on the carbon deposits formed on the CoW(1:3)/SiO₂ catalyst for different reduction pretreatments. A pronounced variation is observed in the carbon structures produced with the same catalyst after different reduction temperatures. Table 3.1 shows the parameter (1-D/G) , is a quality indicator for the carbon products obtained using these different reduction treatments. In this parameter D and G are the integrated areas of the D (disorder) and G bands respectively. A (1-D/G) parameter approaching unity is representative of a high quality product. As can be observed in Figure 3.11 and Table 3.1, the sample pretreated in H₂ at 900°C exhibited a high (1-D/G) quality parameter, while the samples pretreated at lower temperatures show

Table 3.1. Carbon yield and selectivity (expressed as the D/G band area ratio obtained from the Raman spectra) for carbon deposits obtained by CO disproportionation under different pretreatments and reactions conditions over a CoW(1:3)/SiO₂ catalysts. The yield is defined as mass of total deposited carbon per mass of catalyst. The selectivity to SWNT is the mass of SWNT per total mass of carbon deposits.

Catalyst	Reduction Temperature (°C)	Reaction Temperature (°C)	Yield (%C)	1- D/G quality parameter
CoW(1:3)/SiO ₂	500	850	9	0.20
CoW(1:3)/SiO ₂	600	850	10	0.54
CoW(1:3)/SiO ₂	700	850	6.5	0.68
CoW(1:3)/SiO ₂	800	850	8	0.70
CoW(1:3)/SiO ₂	900	850	9	0.86
CoW(1:3)/SiO ₂	1000	850	6	0.33
CoMo(1:3)/SiO₂	500	850	12	0.95

much lower values, which indicates the presence of undesirable forms of carbon. As we approach 900°C, which seems to be the optimal pretreatment temperature, the (1-D/G) parameter increases; however, when we pre-reduced the catalyst at 1000°C the selectivity decreased once again. We can attribute this last observation to a high degree of reduction of the catalyst, causing the appearance of large metallic Co particles, which as established in Chapter 2, has shown to be disadvantageous for SWNT selectivity. The results previously reported on Chapter 2 for a highly selective CoMo catalyst are also included.

3.4. DISCUSSION

In Chapter 2 we reported the characterization results obtained on the Co:Mo system during the production of SWNT. The most important results of that chapter were that the extent of the Co-Mo interaction was a function of the Co:Mo ratio in the catalyst and that this interaction had different forms during the different stages of the catalyst life. For example, we found that in the calcined state, Mo was in the form of a well dispersed Mo(VI) oxide while the state of Co strongly depended on the Co:Mo ratio. At low Co:Mo ratios, it interacted with Mo forming a superficial Co molybdate-like structure. At high Co:Mo ratios, it forms a non-interacting Co_3O_4 phase. During the subsequent reduction treatment in hydrogen, the non-interacting Co phase reduced to metallic Co, while the Co molybdate-like species remained as well-dispersed Co^{2+} ions.

We proved that the effect of having Co stabilized in the Co-molybdate environment was crucial. First of all, this stabilization prevented the sintering of Co into large metallic aggregates, which generates undesired forms of carbon, as it occurs in the non-selective catalysts. By contrast, we proposed that when metal atoms begin to agglomerate on the selective catalyst in the presence of gaseous CO, there was a nucleation period over which there was no growth of nanotubes. This nucleation involved the disruption of Co atoms from its interaction with Mo oxide when the latter became carbidic.

In the characterization of the CoW catalyst series presented on this chapter, we have found a strong similarity and some interesting differences with the CoMo system previously described. The UV-Vis and the X-ray absorption data indicate that similar to the case of Mo, in the calcined catalyst, W is in an octahedral environment and in the VI oxidation state. Furthermore, from the values of the adsorption edge energy it can be concluded that the tungsten oxide species are forming small clusters with average domain size to some extent larger than those of the metatungstate ion, but not large enough to form bulk WO_3 . The majority of W seems to be forming these oxidic species, regardless of the Co:W ratio in the catalysts; although for catalysts with higher W loadings (i.e. $\text{CoW}(3:4)/\text{SiO}_2$) contribution of larger WO_x species becomes apparent (see Figure 3.1). Therefore, it appears that the W dispersion is more a result of the metal loading and the degree of interaction with the support rather than a consequence of the extent of interaction with Co. A contrasting picture is obtained from the Co side, particularly in the catalysts with low Co:W ratio. In this case, both, the UV-Vis and XANES data of the catalyst with a Co:W ratio of 1:3 demonstrated that most of the Co is in an environment similar to that in CoWO_4 i.e. closely interacting with W. However, the slight but clear differences between the spectra of the catalyst and the CoWO_4 reference suggest that the similarity is limited to the local environment and nature of ligands. In fact, the EXAFS data show that bulk CoWO_4 is not present in the bimetallic catalysts.

The results for the calcined catalysts with low Co:W ratios can be put together in a simple model. Similar to our description of the Co-Mo system on Chapter 2, we propose that in the Co-W catalysts dispersed Co species get stabilized over the tungsten oxide in the form of a CoWO_4 -like layer. This layer is thin enough, so although most of the Co is in this Co-W interacting phase, only a small fraction of W forms part of such a phase, while the rest remains as tungsten oxide. Therefore, the characterization of W does not reflect a strong interaction with Co, while the characterization of Co shows in fact a high degree of interaction with W. In this context, we need to stress that it is necessary to have an excess of W in order to guarantee the formation of this cobalt tungstate phase. Otherwise, more than one type of Co species will be present and the catalyst becomes unselective. For example, the UV-Vis-DRS data clearly show that in addition to the interacting phase of Co, which dominates at low Co:W ratios, a non-interacting phase begins to form as the W content decreases. The X-ray absorption data (Fig. 3.5) together with the results obtained from the TPR and Raman experiments undoubtedly show that this non-interacting species is Co_3O_4 .

Alvarez and coworkers proposed that the role of Co is the activation of CO, while the role of Mo is the stabilization of Co(II) ions [35]. On Chapter 2 we showed that when Co is not interacting with Mo, in the reduced state it sinters and forms large metal aggregates. These large metallic Co aggregates have the tendency to generate defective MWNT, carbon filaments and graphite nano-fibers. However, when Mo is

present in the catalyst and there is no excess of free Co, a well-dispersed Co^{+2} species in the form of a Co molybdate-like phase is stabilized. From the detailed studies conducted over the CoW system reported in this contribution, we can propose that the formation of a similar interacting Co tungstate-like species plays a determinant role in the catalytic activity towards the formation of SWNT.

Equally important, on the previous chapter we reported we found that in the case of the Co-Mo system a pre-reduction step at 500°C in hydrogen before starting the nanotube growth was essential to maximize the SWNT selectivity. We proposed then that a certain degree of reduction associated with the creation of oxygen vacancies around Mo was necessary since a catalyst fully oxidized before the reaction is not efficient. By contrast, a high degree of reduction before the reaction is detrimental for the selectivity towards SWNT. It is suggestive that the TPR profile (Fig. 2.10) obtained for the CoMo(1:3) sample indicated that reduction of the Co-Mo pair does not start until about 500°C , while the corresponding result for the CoW system shows that for this case the reduction begins at 750°C . In agreement with the previous behavior observed for the Co-Mo catalyst, a poor performance of the CoW catalysts is observed when it is pretreated at a temperature lower than the onset of reducibility, in this case about 750°C . The data in Table 3.1 and the Raman spectra in Fig. 3.11 show that very low selectivities are achieved with low reduction temperatures. The optimum pre-reduction treatment is around 900°C .

3.5. CONCLUSIONS

We can summarize the main findings of the present work in the following conclusions:

- a) As in the case of the Co-Mo system, the selectivity of the Co-W catalysts towards SWNT production by CO disproportionation strongly depends on the stabilization of Co^{2+} species, which result from an interaction with W. The extent of this interaction is inversely proportional to the Co:W molar ratio. At high Co:W ratios, there exists a fraction of Co not stabilized by W and that fraction is responsible for a decrease in selectivity.
- b) In the oxidic state after calcination, W is forming small clusters in the form of well dispersed W (VI) species and Co is either interacting with W in a superficial Co tungstate-like structure (at low Co:W ratios) or as a non-interacting Co_3O_4 phase (at high Co:W ratios).
- c) During the subsequent reduction treatment, the non-interacting phase is reduced to metallic Co, while the Co tungstate-like species remain as well-dispersed Co^{2+} ions.
- d) The role of the oxygen vacancies is critical for the good performance of the selective Co-W catalyst. The highest selectivity is reached when the catalyst is

pre-reduced at 900°C, higher reduction temperatures create large metallic Co particles, which are responsible for selectivity losses.

ACKNOWLEDGEMENTS

The work presented in this chapter is the result of a collaborative effort of the Heterogeneous Catalysis Group at the University of Oklahoma. I would like to particularly thank my advisor Dr. Daniel Resasco for giving me the autonomy to further explore different catalytic formulations. Dr. Walter Alvarez and the OU College of Engineering for their commitment on getting a new Raman system, which tremendously simplified the work described in this chapter. I also thank Syed Khalid (NSLS, Brookhaven National Lab.) and the EXAFS team of the winter of 2002 for their help during X-ray absorption experiments. I would like also to thank the Department of Energy, Office of Basic Energy Sciences (grant No. DE-FG03-02ER15345) and the Oklahoma Center for the Advancement of Science and Technology (OCAST) for financial support.

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CHAPTER 4

LOSS OF SINGLE-WALLED CARBON NANOTUBES SELECTIVITY BY DISRUPTION OF THE Co-Mo INTERACTION IN THE CATALYST

4.1. INTRODUCTION

In the previous chapter an analogy between the Co-Mo and the Co-W catalytic systems has been established. The results obtained not just allowed us to put together an analogy but also to reveal the importance of the role of oxygen vacancies generated during catalyst activation in H_2 to get a successful catalytic process. Equally important, from the results described in that chapter it was proposed that similar to the case of the Co-Mo system, a Co-W interaction in the form of a surface cobalt tungstate-like structure particles is critical for a good catalyst performance.

Since in our proposed model the interaction of Co and Mo (in the form of cobalt molybdate) is critical for a good catalyst performance, the introduction of a third element that will compete with cobalt for the formation of the molybdate is expected to be detrimental for the catalytic selectivity. This chapter focuses on the testing of this hypothesis.

Interestingly, the doping of the Co-Mo system from the perspective of hydrotreating processes has been widely studied. However, most these studies have

focused on alumina-supported systems, since alumina interacts with the metals with the appropriate strength to generate the species with the optimum hydrotreating activity [1-4]. In this context the influence of alkali dopants on the structure and activity of the Co-Mo catalytic system has been investigated [5-8]. However, there is still some controversy about this issue in the literature, although it seems clear that the presence of these alkali dopants predominantly affects the dispersion of molybdenum species [8-12].

In the present chapter we turn our attention to study the effect of the presence of sodium in the Co-Mo catalytic system for the SWNT production. As mentioned above, in our proposed model, the interaction of Co and Mo is critical for a good catalyst performance. Therefore, the introduction of an element such as sodium that will compete with Co for the interaction with molybdenum is expected to be detrimental for a good catalytic performance. We have followed a characterization strategy on the basis of the work described on Chapter 2 and 3 to investigate this multicomponent system. Based on the results of this characterization, we will attempt to put together a consistent schematic picture of the doped catalyst, and built up an analogy with the undoped Co-Mo system, which will be used to explain the variations in selectivity towards SWNT observed when the catalyst is doped with sodium.

4.2. EXPERIMENTAL

4.2.1. Catalysts preparation and pretreatment

A series of Na-doped and undoped silica-supported Co-Mo catalysts was prepared. For the Na-doped catalysts different amounts of sodium were added to the SiO₂ support by incipient wetness impregnation using aqueous solutions of NaNO₃ of appropriate concentrations. The SiO₂ support obtained from Aldrich had an average pore size of 6 nm, BET area 480 m²/g, pore volume 0.75 cm³/g, and particle sizes in the range 70-230 mesh. After evaporation of water at room temperature, the solid was dried at 110°C overnight and then calcined at 500°C for three hours. Subsequently, the Na-doped and undoped supports were loaded with molybdenum (4.6 wt. %) and cobalt (1.4 wt. %) by incipient wetness co-impregnation of a solution of cobalt nitrate and ammonium heptamolybdate to achieve a Co: Mo molar ratio of 1:3. After impregnation, the solids were dried overnight at 120°C and then calcined for 3 h at 500°C in dry-air flow. Two monometallic Na-doped catalysts were also prepared, containing 1.3% wt. Co and 4.6 wt. % Mo.

4.2.2. Catalyst characterization

The Raman spectra of calcined catalysts were obtained in a Jovin Yvon-Horiba LabRam 800 equipped with an air-cooled CCD detector equipped with a He-Ne laser (632.8nm). Typical laser powers ranged from 1.0 to 2.0mW; integration times were around 15 sec for each spectrum; ten Raman spectra were averaged for each sample.

The UV/Vis spectra of the calcined catalysts were recorded using a Shimadzu double beam spectrometer UV- 2101 with an integrating sphere for diffuse reflectance. Barium sulfate was used as reflectance standard. Several Mo and Co compounds, including MoO_3 , Na_2MoO_4 , $(\text{NH}_4)_6\text{Mo}_7\text{O}_{24}$ and CoMoO_4 were used as references. Before analysis, the samples were dried in air at 120°C .

Temperature programmed reduction (TPR) experiments were conducted passing a continuous flow of 5% H_2/Ar over approximately 30 mg of the calcined catalyst at a flow rate of $10\text{ cm}^3/\text{min}$, while linearly increasing the temperature at a constant heating rate of $8^\circ\text{C}/\text{min}$. The hydrogen uptake as a function of temperature was monitored using a thermal conductivity detector, SRI model 110 TCD.

X-ray photoelectron spectroscopy data were recorded on a Physical Electronics PHI 5800 ESCA System with monochromatic Al $\text{K}\alpha$ X-rays (1486.6 eV) operated at 350 W and 15 kV with a background pressure of approximately 2.0×10^{-9} Torr. A $400\text{ }\mu\text{m}$ spot size and 58.7 eV pass energy were typically used for the analysis. An electron flood gun compensated sample charging during the measurements. The electron takeoff angle was 45° with respect to the sample surface. For each sample, the binding energy regions corresponding to Si (95-115 eV), Mo (220-245 eV) and Co (760-820 eV) were scanned. The binding energies were corrected by reference to the C(1s) line at 284.8 eV. A non-linear Shirley-type background was used for the area analysis of each peak. The fitting of the XPS

spectra was carried out with Gaussian-Lorentzian peaks, using the MultiPak software from Physical Electronics.

4.2.3. Production and Characterization of Carbon Nanotubes

For the SWNT production, 0.5 g of calcined catalyst was placed in a horizontal tubular reactor, heated in H₂ flow up to 500°C, and then in He flow up to 850°C. Subsequently, CO was introduced at a flow rate of 850 cm³/min at 80 psia and kept under these conditions for two hours. At the end of each run, the system was cooled down in He flow. The total amount of carbon deposits was determined by temperature programmed oxidation (TPO) following the method described in Chapter 1.

The quality of the nanotubes obtained over the different catalyst was investigated by Raman spectroscopy, following the methods reported in Chapter 1. From the analysis of radial A_{1g} breathing mode (below 300 cm⁻¹) direct information about the tubes diameter was obtained [13], while the analysis of the G band in the tangential mode range i.e. 1400-1700 cm⁻¹, provided information on the electronic properties of the nanotubes. In addition, the analysis of the so-called D-band at around 1350 cm⁻¹ gave an indication of the level of disordered carbon. Therefore, we have used the intensity ratio of the D band (1350 cm⁻¹) to the G band (1590 cm⁻¹) as semi-quantitative measurement of the formation of undesirable forms of carbon [14, 15].

4.3. RESULTS

4.3.1. Characterization of the Calcined Catalysts

4.3.1.1 Raman Spectroscopy

Raman spectroscopy has shown to be an extremely powerful tool to characterize supported heterogeneous catalysts containing d^0 transition metal oxide species [9]. In fact, substantial information about the dispersion of molybdenum oxide species over the high surface-area support has been obtained from detailed analysis of Raman spectra [11, 16-20]. Those studies provide the basis for interpreting the results of the present catalyst characterization. Figure 4.1 shows the Raman spectra of an undoped CoMo (1:3)/SiO₂ and of two Na-doped CoMo (1:3)/SiO₂ catalyst; the Raman spectra of reference samples of cobalt oxide (Co₃O₄), cobalt molybdate (CoMoO₄) and sodium molybdate (Na₂MoO₄) are also shown in the figure.

Figure 4.1a compares the Raman spectrum of the undoped and Na-doped catalysts with that of a CoMoO₄ reference sample. The peaks appearing in the 750-1000 cm⁻¹ region should be ascribed to Mo species. This is the region where the bands for stretching of Mo-O bonds are typically observed [9]. Several factors such as metal loading, pH, precursor impregnation method, and impurities are known to influence the exact position of the Raman bands. However, a preliminary assignment can be done based on the preceding literature and the comparison with the reference samples. For instance, in the case of the undoped catalyst the peak centered at 943

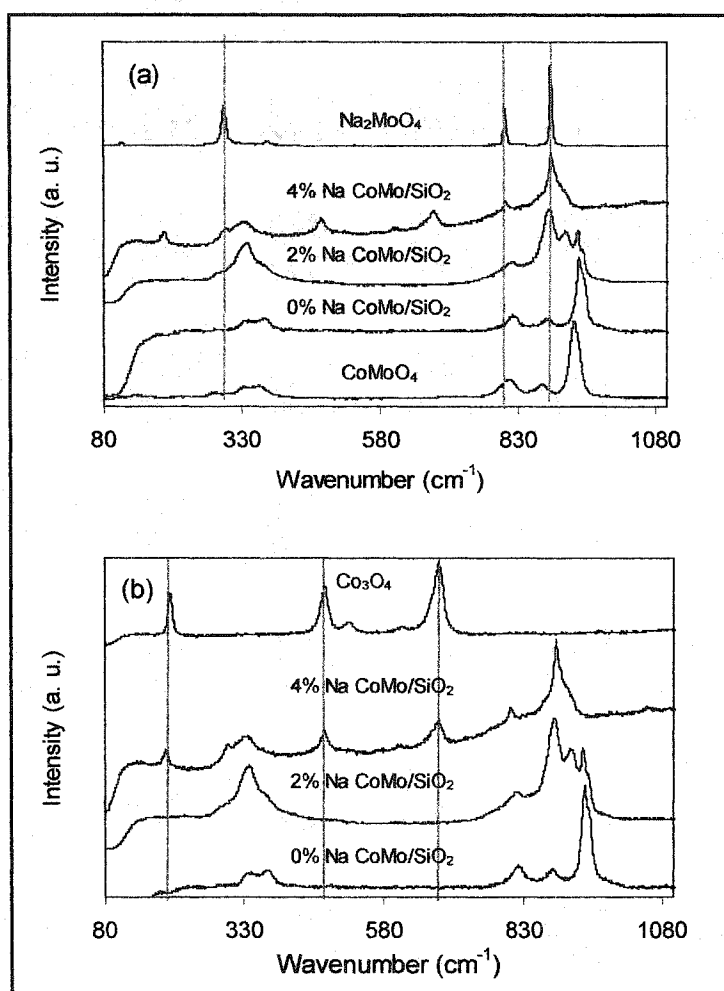


Figure 4.1. Raman spectra of an undoped and two Na-doped CoMo(1:3)/SiO₂ catalysts compared to (a) the spectra of two analytical sample of cobalt molybdate (CoMoO_4) and sodium molybdate (Na_2MoO_4) and compared to (b) the spectrum obtained for a reference sample of cobalt oxide Co_3O_4 . The laser excitation energy was 633 nm.

cm^{-1} has been previously ascribed to $\text{Mo}_7\text{O}_{24}^{-6}$ species while the shoulder at 960cm^{-1} has been associated with larger clusters of MoO_x species, such as $\text{Mo}_8\text{O}_{26}^{-4}$ [9, 19, 20]. This assignment is in good agreement with the previous UV-Vis spectroscopy results, which suggested the presence of well-dispersed clusters of MoO_x . According

to the calculated band energy gap, the average domain size of these species was estimated to be slightly larger than that of $\text{Mo}_7\text{O}_{24}^{6-}$. At the same time, the presence of large polymeric MoO_x species must be ruled out when there are no peaks in the 990-1000 cm^{-1} region [12, 21]. A conclusion that we also indicated based on the previous UV-Vis data. Moreover, the comparison of the Raman spectrum of the undoped bimetallic catalyst with that of the CoMoO_4 gives strong support to the presence of this type of species. Therefore, the Raman band at 880 cm^{-1} , the shoulder at 930 cm^{-1} as well as the broad band at 350 cm^{-1} must all be assigned to Mo-O-Co stretching vibrations in cobalt molybdate-like species [19, 22-25].

A noticeable change in the Raman bands is observed when sodium is present in the catalyst. First of all, when inspecting the spectrum of the Na-doped CoMo (1:3)/SiO_2 catalysts, a new band at 889 cm^{-1} becomes prominent. This band has been previously assigned to Mo=O stretching of isolated monooxo (MoO_4^{2-}) species [26]. Also, the band at 825 cm^{-1} (asymmetric Mo-O-Mo stretching) shows a dramatic shift to lower wavenumbers (805 cm^{-1}), which is consistent with a decrease in the amount of Mo-O-Mo moieties on the catalysts, and can be attributed to the increase of isolated mono-oxo species in the sample. It is also important to mention that the bands assigned to Co-O-Mo species present on the undoped catalyst (350, 880 and 930 cm^{-1}) become very weak until they almost totally vanish for the catalyst with the highest Na loading.

Figure 4.1b shows a comparison of the Raman spectra of the Na-doped catalysts with the spectrum of the cobalt oxide reference. The assignments for the Raman active phonon modes that are displayed in the spectrum of Co_3O_4 are as follows. The peaks at 199, 621, and 681 cm^{-1} correspond to F_{2g} phonon modes, while the peaks at 477 and 525 cm^{-1} are E_g and A_{1g} phonon modes, respectively [27]. As seen in Figure 4.1b, this set of peaks is undoubtedly present in the spectrum of the 4% Na-doped catalyst, while it is entirely absent in the case of the undoped catalyst. From this evidence, it is clear that segregated Co_3O_4 species are not present on the undoped catalyst while the addition of Na seems to favor the formation a new segregated cobalt oxide phase.

4.3.1.2 Diffuse Reflectance UV-Visible Spectroscopy (UV/Vis-DRS)

We have used UV/Vis-DRS to study the state of both Mo and Co in the fresh catalyst. As described in previous chapters, in order to estimate the band energy gap of d^0 oxides, it has been recommended to use the square root of the Kubelka-Munk function multiplied by the photon energy, and to plot this new function versus the photon energy [28]. The position of the absorption edge can then be determined by extrapolating the linear part of the rising curve to zero. The values thus obtained carry information about the average domain size of the oxide nanoparticles. It has been shown that the energy band gap decreases as the domain size increases [28, 29]. Therefore, a comparison can be made between the energy of the samples under investigation and those of references of known domain size. This comparison is

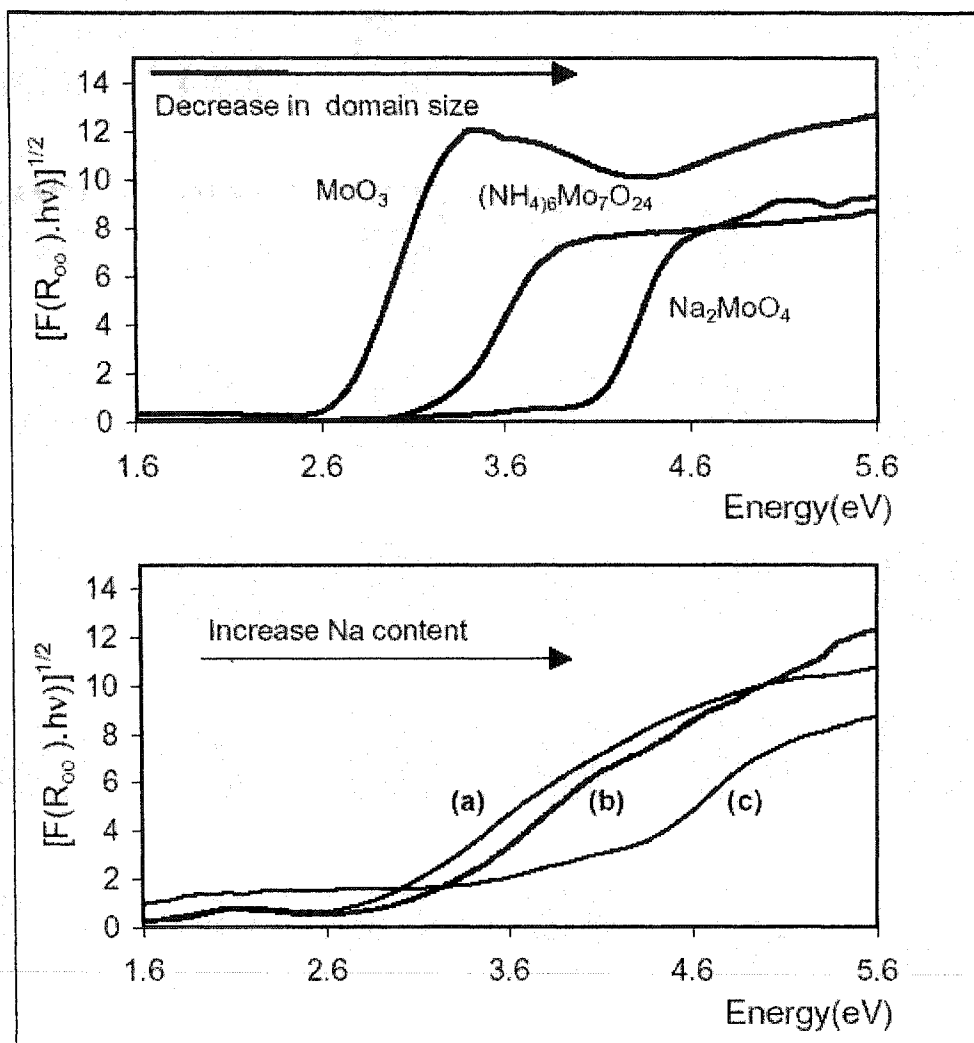


Figure 4.2. Lower panel: UV absorption spectra for (a): An undoped CoMo(1:3)/SiO₂ catalysts (b): 2.0 wt % Na-doped CoMo(1:3)/SiO₂ catalyst and (c) a 4.0 wt % Na-doped CoMo(1:3)/SiO₂ catalyst. Upper panel: UV absorption spectra for three molybdenum oxide species of known domain size.

made in Figure 4.2, which shows the absorption edges of several MoO_x species together with those of two different Na-doped and an undoped Co:Mo(1:3)/SiO₂ catalysts. As expected, the band gap energies in the reference series (top panel)

decrease as the domain size increases. An analogous behavior is observed for the case of the Co:Mo(1:3)/SiO₂ catalysts (bottom panel). An increase in the gap energy values is observed when the amount of Na in the catalysts increases. While for the undoped catalyst the energy gap lies between the values corresponding to (NH₄)₆Mo₇O₂₄ and MoO₃, for the doped catalysts the energy gap shifts to higher values, indicating a decrease in the average size of the molybdenum domains. Indeed, for the catalyst with the higher loading of Na this value shifts up to 4.2 eV, which is very close to the value obtained for MoO₄²⁻ tetrahedral species. In agreement with the results obtained by Raman spectroscopy it is clear that the dispersion of oxidic molybdenum species is deeply influenced by the presence of sodium.

In addition to the charge-transfer bands due to Mo, appearing in the UV region, the visible spectra of these catalysts exhibit bands in the 500-750 nm region, which are associated with Co species and are ascribed to d-d transitions (⁴T_{2g} → ⁴A_{2g} and ⁴T_{2g} → ⁴T_{1g} (P)) of high spin octahedral Co complexes [30, 31]. Figure 4.3 shows the DRS spectra in this region for two Na-doped and an undoped Co:Mo(1:3)/SiO₂ catalysts. The spectrum for the undoped catalyst is very similar to that of CoMoO₄, in which Co is in an octahedral environment. The identical shape of the spectra of both samples indicates that the same type of ligand and symmetry around Co are common for the undoped catalyst and the cobalt molybdate. By contrast, the shape of the spectrum of the heavily doped catalyst is markedly different

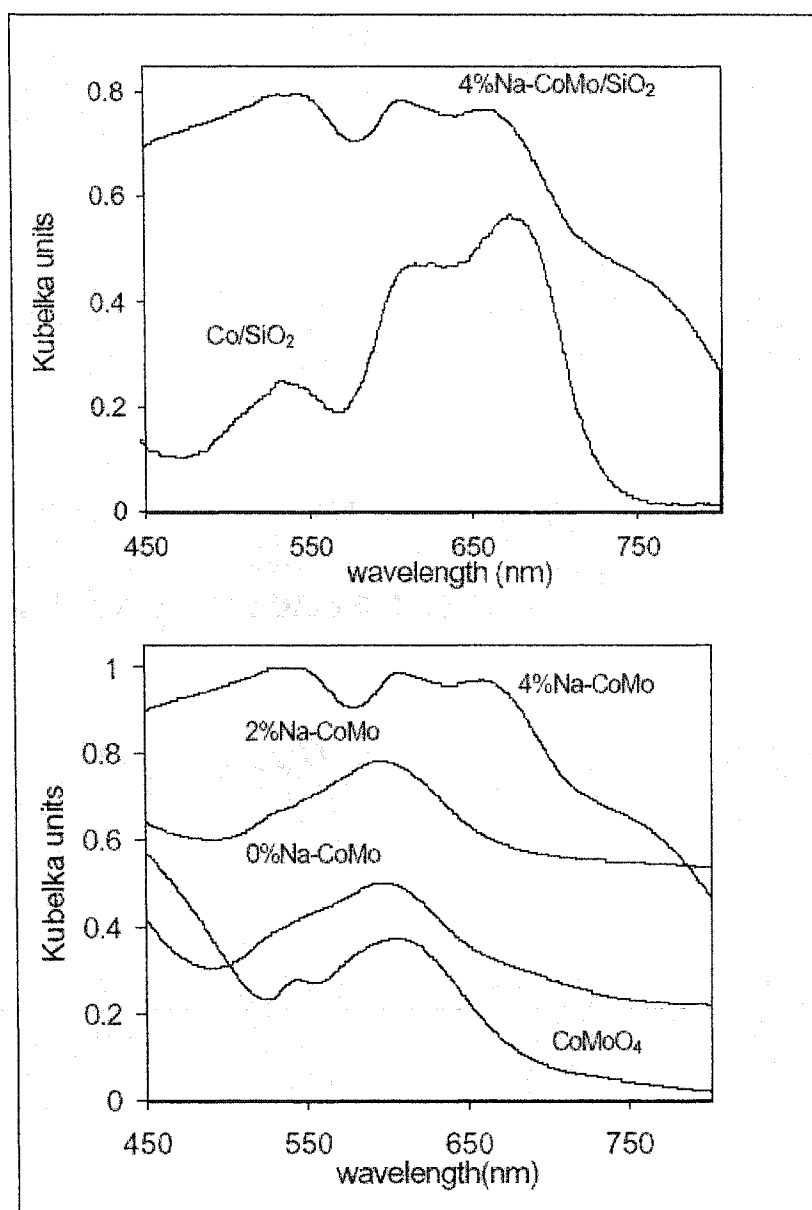


Figure 4.3. Visible spectra obtained for an undoped and two Na-doped $\text{CoMo}(1:3)/\text{SiO}_2$ catalysts compared to the spectra of a reference sample of cobalt molybdate (CoMoO_4). The spectra obtained for a Co/SiO_2 catalyst is also included for comparison.

and exhibits two new bands at around at 525 and 670 nm. These bands are in turn the characteristic features of the pure Co catalyst (Fig. 4.3 upper panel) and can be associated with Co_3O_4 species, which as previously shown in Chapter 2, are present in the fresh monometallic Co catalyst. Therefore, it can be concluded that the addition of Na to the catalyst breaks up the interaction between Mo and Co in such a way that free Co oxide starts appearing. This conclusion is in perfect agreement with the Raman spectroscopy results.

4.3.1.3 Temperature Programmed Reduction (TPR)

The reduction profiles of the undoped and two Na-doped Co:Mo (1:3)/ SiO_2 catalysts in the pre-calcined state, together with those of the pre-calcined Co/ SiO_2 and Na-doped Mo/ SiO_2 catalysts are shown in Fig. 4.4a. The TPR profile of the pre-calcined Co catalyst shows two peaks at 360 and 445°C, which can be ascribed to the reduction of Co oxide species. On the other hand, the reduction profile of the Na-doped Mo catalysts exhibits three different peaks that appear at much higher temperatures than those of Co. As discussed in Chapter 2, it is then possible to use the reduction profiles to identify the presence of Co and Mo species in the absence of mutual interactions. Accordingly, the TPR of the undoped Co:Mo (1:3)/ SiO_2 catalyst indicates that, in this sample, the vast majority of Co oxide species are interacting with Mo. While most of the Co in the monometallic catalyst gets reduced below 500°C, almost no reduction takes place below this temperature in the undoped bimetallic catalysts. It has been proposed that the addition of Mo oxide to Co oxide

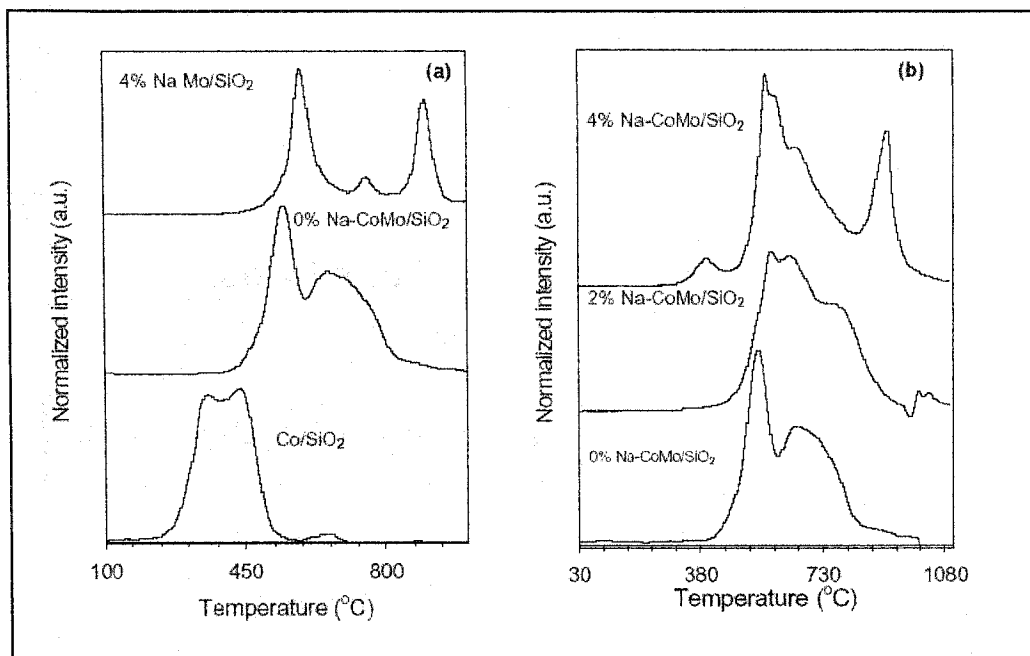


Figure 4.4. (a) TPR profiles of a Co/SiO₂ and Na-doped Mo/SiO₂ catalysts compared to the undoped Co:Mo (1:3)/SiO₂ bimetallic catalyst. (b) TPR profiles obtained for an undoped and two Na-doped CoMo(1:3)/SiO₂ catalysts. In all cases the reduction was conducted under 5% H₂/Ar, using a heating linear ramp of 8°C/min.

inhibits the reduction of the Co species because Mo⁶⁺ polarizes the Co-O bonds, making them more ionic and consequently more difficult to reduce [32]. That is, in agreement with the Raman and UV/Vis DRS data, TPR indicates that a high degree of Co-Mo interaction is observed for the undoped Co:Mo (1:3)/SiO₂ catalyst.

A contrasting behavior is observed in Figure 4.4b. In this case, the TPR profiles of the Na-doped Co:Mo (1:3)/SiO₂ catalyst are compared to the undoped

catalyst. As shown in Fig. 4.4b, a gradually increasing fraction of segregated Co species as a function of the sodium content is apparent from the peak growing at 400°C which is associated with the reduction of non-interacting Co oxide [33]. The observed trend agrees with the results obtained by UV/Vis DRS and Raman spectroscopy on the Na-doped catalysts. It is obvious that the fraction of cobalt interacting with Mo decreases with increasing Na content.

4.3.1.4 X-ray photoelectron spectroscopy (XPS)

XPS studies were performed on the air calcined Na-doped and undoped catalysts to get an insight into the chemical state of the catalyst constituents. Figure 4.5 shows the Co 2p spectra of the undoped and doped Co:Mo (1:3)/SiO₂ catalysts compared to the spectra obtained for the monometallic Co/SiO₂, CoMoO₄ and Co₃O₄. As summarized in Table 4.1, the binding energies for the bimetallic catalysts seem to decrease as the Na content increases, which is the trend that one would expect if CoMoO₄ species in the catalyst are converted into Co₃O₄ species [32, 34]. However, the values are too close to be conclusive. A more convincing evidence for this conversion is obtained by analyzing the shake up satellite peaks appearing at 5-6 eV higher binding energies than the main peak in the Co 2p spectrum. The relative intensity of these satellite peaks has often been used for the identification of the cobalt species [35-37] since the intensities of the shake up peaks satellites associated with the Co 2p_{3/2} of both oxides are quite different. As shown in Fig. 4.5, this satellite peak is very small in the spectrum of Co₃O₄ but very strong in the spectrum

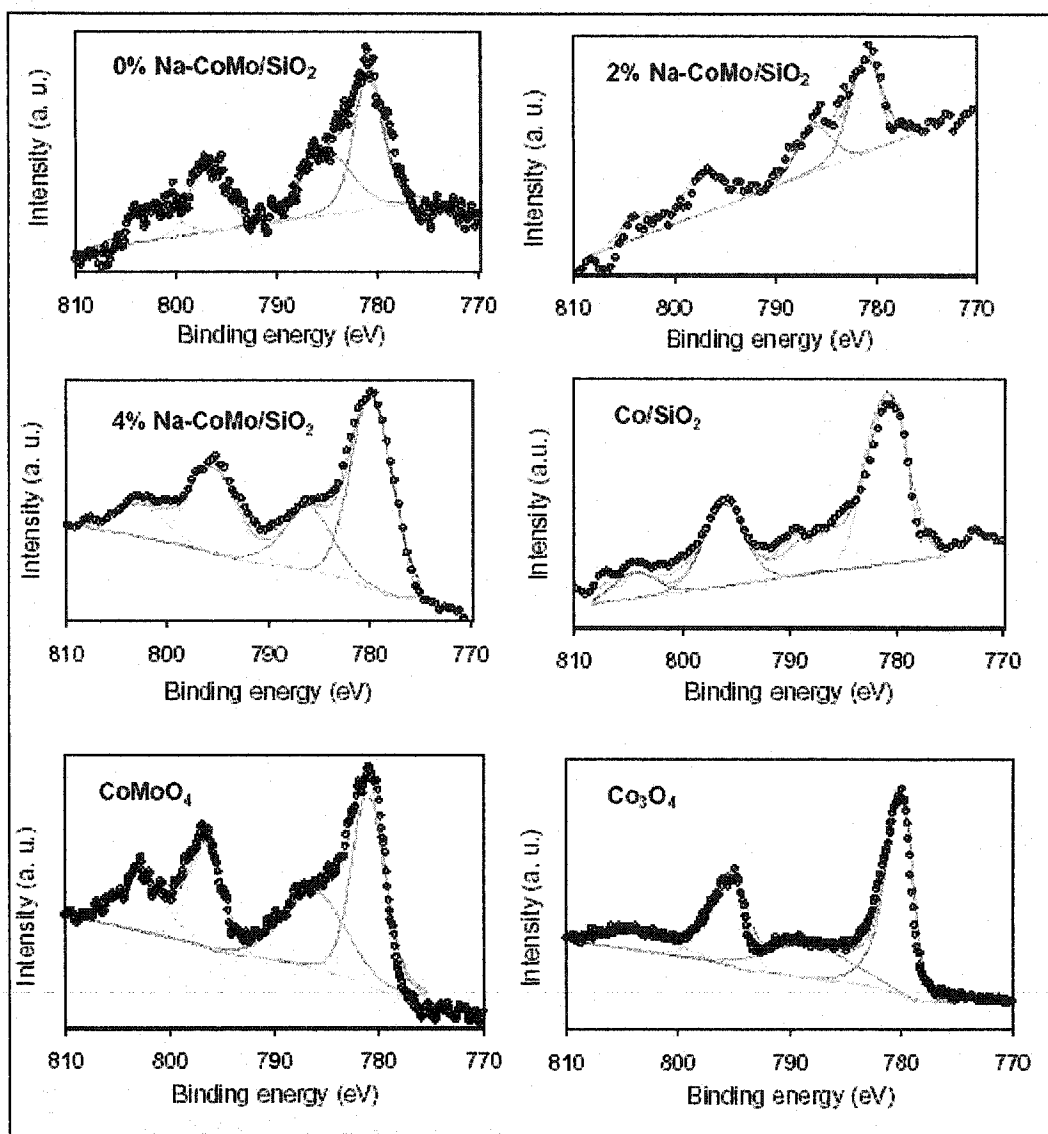


Figure 4.5. XPS Co 2p spectra an undoped and two Na-doped CoMo(1:3)/SiO₂ catalysts. The spectra obtained for a monometallic Co/SiO₂ catalyst is also included for comparison. The spectra obtained for two reference samples of cobalt oxide Co₃O₄ and CoMoO₄ are also presented.

of cobalt molybdate, as previously observed [37, 38]. Therefore, it is easy from the features of the Co 2p spectra to determine whether the Co species are present as cobalt molybdate or as cobalt oxide (Co₃O₄) on the catalyst. A clear trend is observed in Table 4.1 for the relative intensities. The intensity ratio for the undoped catalyst is high (0.6) and close to that of stoichiometric CoMoO₄, but gradually approaches the value of cobalt oxide (0.3) as the Na content increases.

Table 4.1. Co 2p binding energies for undoped and Na-doped catalysts. The position of the Co 2p_{1/2} satellite peak and its relative intensity is also indicated. The values obtained for two analytical samples of cobalt oxide Co₃O₄ and CoMoO₄ are also presented.

Catalyst	Co 2p _{3/2} peak position (eV)	Co 3p _{3/2} satellite peak position (eV)	Intensity ratio (Co 2p _{3/2} / satellite)
0% Na- CoMo (1:3)/SiO ₂	780.9	785.5	0.60
2% Na- CoMo (1:3)/SiO ₂	780.6	786.5	0.58
4% Na- CoMo (1:3)/SiO ₂	779.5	786.5	0.33
Co/SiO ₂	780.5	787.3	0.34
Co ₃ O ₄ (reference)	779.6	788.2	0.30
CoMoO ₄ (reference)	780.7	785.9	0.79

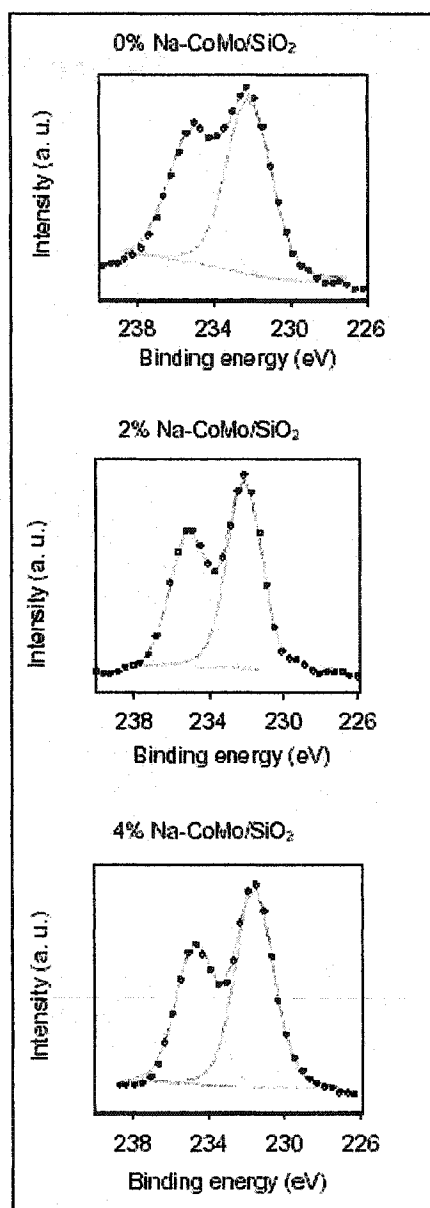


Figure 4.6. XPS Mo 3d spectra an undoped and two Na-doped CoMo(1:3)/SiO₂ catalysts. The spectra were fitted using Gaussian-Lorentzian functions to resolve the individual 3d_{5/2} and 3d_{3/2} contributions.

Figure 4.6 shows the Mo 3d spectra of the doped and undoped Co:Mo (1:3)/SiO₂ catalysts. The values of the binding energies of the two spin orbit components ($3d_{5/2} = 232.0$ eV; $3d_{3/2} = 234.7$ eV) are characteristic of Mo (VI) species [39-41]. However an interesting difference can be observed on the linewidth of the spectra. The linewidth of the Mo 3d peaks obtained for the sample without sodium is wider than those for the Na-doped sample. This effect has been previously reported in the literature and has been attributed to the presence of monomeric MoO₄⁻² species [37]. Even though this observation cannot be conclusive by itself, it perfectly agrees with the results obtained by Raman and UV/Vis spectroscopy, which indicate that the dispersion of oxidic molybdenum species is deeply influenced by the presence of sodium.

4.3.2. Production and characterization of single-walled carbon nanotubes by catalytic disproportionation of CO.

As we have shown in Chapter 2, the silica-supported Co-Mo system displays a very high selectivity in the production of single wall nanotubes by CO disproportionation. Interestingly, the high yields and selectivities to SWNT were only obtained after a specific sequence of calcination at 500°C in air and reduction in H₂ at 500°C. On this chapter we compare the activity of undoped and Na-doped CoMo (1:3)/SiO₂ catalysts for SWNT production. The reaction temperature employed for the CO disproportionation after a pre-reduction step was kept at 850°C. At the end of a two-hour reaction period, the spent catalyst containing the carbon

deposits was cooled down in He flow. The characterization of the carbon deposits was done by way of temperature programmed oxidation (TPO), transmission electron microscopy (TEM), and Raman spectroscopy with varying excitation energy, following the methods described in Chapter 1.

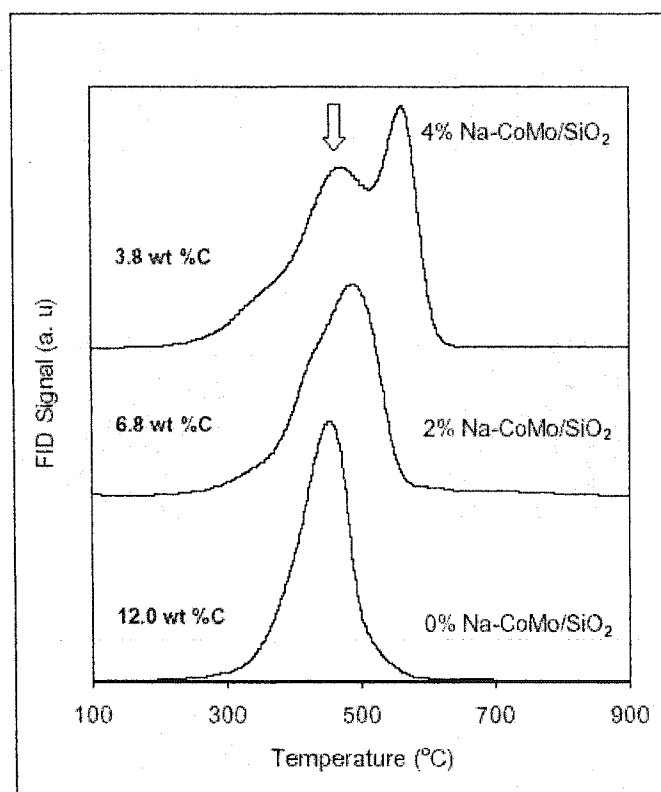


Figure 4.7. Temperature programmed oxidation profiles of all the carbonaceous species present in an undoped and two Na-doped CoMo(1:3)/SiO₂ catalysts after CO disproportionation at 850°C for 2h. The arrow indicates the center of the peak corresponding to the oxidation of SWNT. The total yield of carbon is also indicated.

As shown on Chapter 1, from the TPO analysis one can obtain a quantitative measurement of the carbon yield and selectivity towards SWNT. The TPO results obtained in this study are summarized in Figure 4.7 and illustrate the strong influence of the sodium doping on SWNT yield and selectivity. For instance, the TPO profile of the product obtained over the undoped CoMo (1:3)/SiO₂ catalyst displays a single TPO peak centered at 570°C. We showed in Chapter that under the TPO conditions and while still immersed in this particular catalyst, the SWNT get oxidized in a relatively narrow temperature range, which lies below the temperature in which MWNT, graphite, and carbon fibers are oxidized, but above the temperature at which amorphous and chemically impure carbon species are oxidized. A contrasting behavior is observed in the TPO profile of the material obtained over the 4% Na-doped catalysts (see Fig. 4.7). Instead of the single TPO peak observed in the previous case, three oxidation peaks are obtained on this sample. Although it is not possible to make a direct assignment of the different carbon species that originate each of the different peaks in the TPO profile based solely on the TPO data (Appendix 1), this result clearly indicates a decrease in the selectivity to SWNT originated by the presence of sodium in the catalyst.

Raman spectroscopy is another useful technique to evaluate the structure of carbon nanotubes. As mentioned above, from the position of the radial breathing mode band, direct information about the tubes diameter can be obtained [13] while the relative intensity of the D band relative to the G band is widely used as qualitative

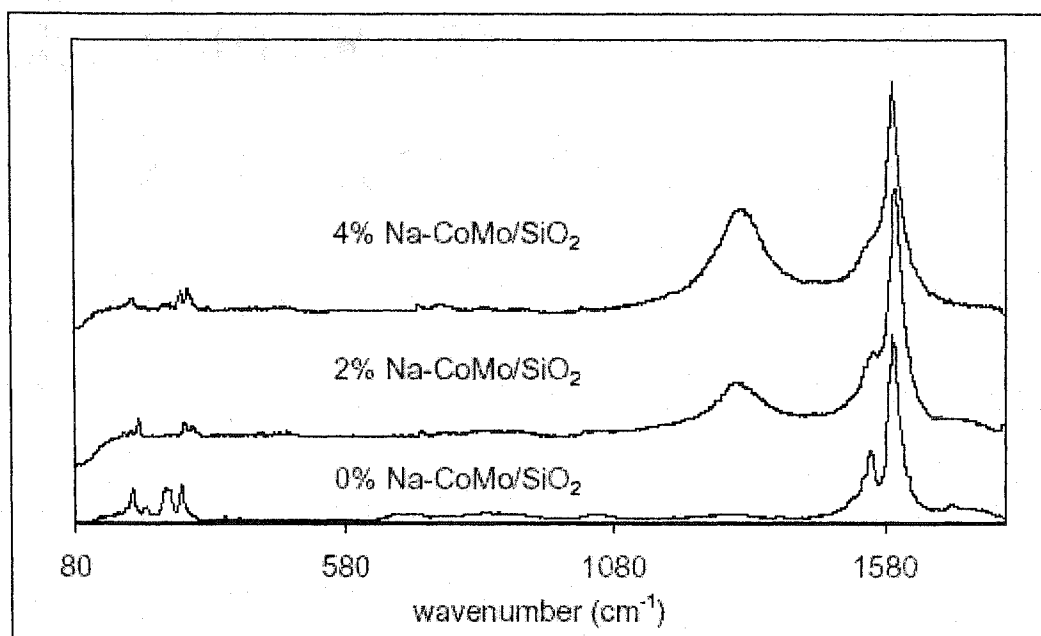


Figure 4.8. (a) Raman spectra of the carbon deposits obtained by disproportionation of CO at 850°C over an undoped and two Na-doped CoMo(1:3)/SiO₂ catalysts after a pretreatment at 500°C in hydrogen. The laser excitation energy was 633 nm.

measurement of the formation of undesirable forms of carbon [14,15]. Figure 4.8 shows typical Raman spectra obtained on the carbon deposits formed on the undoped and doped CoMo(1:3)/SiO₂ catalysts. Depending on the amount of sodium present on the catalysts a pronounced variation is observed in the relative intensity of the D band. As a matter of fact Figure 4.8 shows that the SWNT material obtained over the undoped catalyst are of high quality, while the samples obtained in both doped catalysts show much lower quality, which undoubtedly indicates the presence of undesirable forms of carbon in the Na-doped catalysts. In agreement with the results

obtained by TPO analysis, it is evident that the presence of Na has a negative impact on the selectivity of the CoMo(1:3)/SiO₂ catalysts.

4.4. DISCUSSION

On Chapter 2 we have discussed the characterization results obtained on the undoped Co:Mo system used for SWNT production. The most important conclusions on that chapter were that the extent of the Co-Mo interaction strongly depended on the Co:Mo molar ratio in the catalyst and that this interaction had diverse forms during the various stages of the catalyst life. We were able to establish that the state of Co strongly depended on the Co:Mo ratio. At low Co:Mo ratios, it interacted with Mo forming a superficial Co molybdate-like structure. At high Co:Mo ratios, it forms a non-interacting Co₃O₄ phase. During the subsequent reduction treatment in hydrogen, the non-interacting Co phase reduced to metallic Co, while the Co molybdate-like species remained as well-dispersed Co²⁺ ions.

We established that the effect of having Co stabilized in the Co-molybdate environment was critical for a good performance during the nanotube growth. First of all, this stabilization avoided the sintering of Co into large metallic aggregates, which generate undesired forms of carbon, as it occurs when the non-interacting cobalt oxide phase gets reduced before nanotube growth. By contrast, in the selective catalyst, Co clusters are only formed after the Mo oxide has become Mo carbide, thus breaking the Co-Mo interaction. Under the reaction conditions (high temperature and

CO pressure), CO dissociates on the nascent Co clusters and carbon atoms begin to nucleate over Co and generate the nanotube cap that is the precursor of the single-walled nanotube.

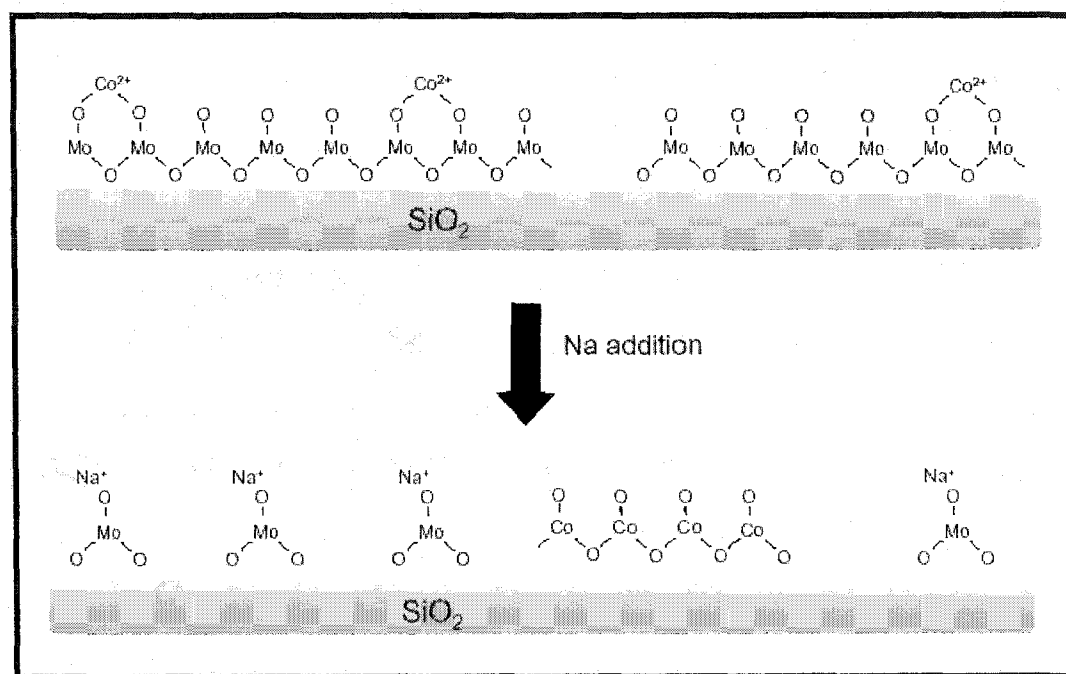


Figure 4.9. Schematic description of the structure of the CoMo(1:3)/SiO₂ catalyst with and without sodium as derived from the characterization methods.

The characterization results for the Na-doped CoMo catalyst series reported in this work can be put together in an analogous picture. For instance the Raman, UV-Vis/DRS and XPS data clearly indicate that the dispersion of molybdenum has been strongly affected by the presence of sodium in the catalyst. Furthermore, the development of new bands in the Raman spectra as well as the values of the gap

energies (Fig. 4.2) clearly indicate that molybdenum is interacting with the Na dopant forming sodium molybdate moieties in the catalyst. In fact, it has been argued that alkali ion impurities such Na^+ or K^+ have higher affinity for molybdenum species than the silica support does [19, 42], although still some disagreement remains on this particular topic [9]. Another plausible explanation could be that the presence of alkaline ions results in an increase of the surface pH values at the point of zero charge (PZC). Thus when Na is present, large molybdenum oxide polyanions become less favorable to monomeric species [43]. In either case, it is clear that the presence of sodium deeply changes the dispersion of molybdenum species.

When these sodium molybdate monomeric species are formed, the interaction of molybdenum and cobalt is hindered. In fact the Raman, UV/Vis DRS, TPR and XPS results clearly show that a segregated phase of cobalt oxide (Co_3O_4) is formed. In this context, it is important to note that a sodium excess is needed to break the Co-Mo interaction in the cobalt molybdate phase. For example, the UV-Vis-DRS data clearly show that a relative large amount of sodium (i.e., 4 wt. %) has to be added to the catalyst before a non-interacting Co oxide bulk phase begins to form. The Raman spectra (Fig. 4.1b) together with the results obtained from X-ray photoelectron spectroscopy (Fig. 4.5) undoubtedly show that this non-interacting phase is Co_3O_4 . These results are schematically represented in Figure 4.9.

On Chapter 2 it was discussed how the role of Co is the activation of CO, while the role of Mo is the stabilization of Co(II) ions. When Co is not interacting with Mo, in the reduced state it sinters and forms large metal aggregates. These large metallic Co aggregates have the tendency to generate defective MWNT, carbon filaments and graphite nano-fibers. As mentioned above, when Mo is present in the catalyst and there is no excess of free Co, a well-dispersed Co^{+2} species in the form of a Co molybdate-like phase is stabilized. From the detailed studies conducted over the Na- doped Co-Mo system reported on this chapter, we can propose that the disruption by sodium of the cobalt-molybdenum interaction is responsible for the loss of selectivity towards the formation of SWNT in the catalyst. The driving force for this disruption is either the tendency of Na to form sodium molybdate or the change of the surface pH values. The disruption of the Co-Mo interaction causes the segregation of cobalt into a new Co_3O_4 phase. As a consequence, the Na-doped catalyst shows a low selectivity because the ability of a Co-Mo catalyst to form SWNT depends on the formation of the surface cobalt molybdate species.

4.5. CONCLUSIONS

We can summarize the main findings of the present chapter in the following conclusions:

- a) The presence of sodium deeply affects the dispersion of molybdenum. In the undoped catalyst, molybdenum forms small aggregates with domain size close

to that of heptamolybdate species while in the case the doped catalyst monomeric sodium molybdate species are formed.

- b) When sodium molybdate species are formed, the interaction between molybdenum and cobalt is disrupted and a new phase of segregated Co_3O_4 is formed.
- c) During the reduction pretreatment, the non-interacting Co_3O_4 phase is reduced to metallic Co, which easily sinters at the nanotube growth conditions. Large Co particles generate defective MWNT, carbon filaments and graphite nano-fibers under reaction conditions, originating a loss in selectivity of the Co Mo catalyst.

ACKNOWLEDGEMENTS

This research was conducted with financial support from the Department of Energy, Office of Basic Energy Sciences (grant No. DE-FG03-02ER15345) and the Oklahoma Center for the Advancement of Science and Technology (OCAST). I would like to thank my advisor Dr. Daniel Resasco for giving me the autonomy to further explore the Co Mo catalytic system. I also thank Dr. Zhongrui Li for his diligence on getting the XPS data.

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CHAPTER 5

EFFECT OF THE GROWTH TEMPERATURE ON THE PROPERTIES OF SINGLE WALLED CARBON NANOTUBES PRODUCED BY CO DISPROPORTIONATION OVER A Co-Mo CATALYST^{III}

5.1. INTRODUCTION

In the previous chapters were centered on the chemical structure of the Co Mo catalysts and how this structure influences the catalyst activity. We established an analogy between the Co-Mo and the Co-W catalytic systems (Chapter 3) and demonstrated how breaking the Co Mo interaction by means of Na lessens the catalyst selectivity (Chapter 4). The present and the following chapters will explore the influence of the reaction conditions on the catalytic activity. This chapter is focused in particular on the how the reaction temperature affects the quality of the SWNTs produced by CO disproportionation over in-situ generated metallic cobalt nanoparticles.

For any catalytic process in which metallic particles are involved, an increase on the metallic particle size should be expected when the reaction temperature is

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increased. This occurs because at higher temperatures the metallic clusters acquire higher mobility and, since the atoms are always more stable at the surface of a large particle than at the surface of a small particle, they will migrate from the small particles to the large at faster rates when the temperature is increased [1-6]. In this context, the increase on the rate of agglomeration of metallic cobalt nanoparticles should have dramatic consequences on the properties of the SWNT obtained, provided that the hypothesis drawn in Chapter 2 is correct.

In fact, the tailoring of the properties of SWNT materials is an attractive prospect given that the diameter and chirality of a SWNT determine its electronic structure, as discussed in Chapter 1. However, scientists have not yet been able to produce significant amounts of homogeneous SWNT material with specific physical properties [7, 8]. The catalytic decomposition of carbon-containing molecules on low-surface area samples, such as catalytically patterned surface or over isolated metal nanoparticles have been proposed as an approach to diameter control [9]. However, these methods are not amenable to the development of continuous processes nor suitable for large-scale operations. The use of small metal particles dispersed on a high-surface- area support opens the possibility of producing large amounts of SWNT, using continuous processes that are similar to conventional catalytic processes, such as ethylene polymerization. Some reports have indicated that synthesis of nanotube samples with varying diameter distributions is possible with the catalytic method by using different types of metal catalysts [10] or by changing the

working temperature. For instance, Peigney et al. [8] using a Fe-alumina catalyst for the synthesis of SWNT by CH₄ decomposition, found different diameter distributions as the reaction temperature varied. However, low selectivities to SWNT were achieved in that study; together with SWNT, the product showed a substantial amount of double and triple walled carbon nanotubes. In another recent study [11] no trend in the diameter of the SWNT produced at different temperatures was found from CH₄ decomposition over a Fe-Mo alumina supported catalyst. However, in this case, the selectivity to SWNT was also low and any trend may have been masked by the presence of other carbon formations.

Clearly, without an effective tailoring of the catalyst formulation, the variation in temperature by itself cannot ensure control of both, SWNT selectivity and specific diameter. In the following pages we will analyze the effect of temperature on our own catalytic system and will explain the temperature effects on SWNT quality in terms of the morphology changes that occur on the catalyst as the reaction proceeds.

5.2. EXPERIMENTAL

Silica-supported Co-Mo and Co-W bimetallic catalysts were prepared using cobalt nitrate, ammonium heptamolybdate and ammonium metatungstate salts as precursors following the methods described in Chapter 2 and 3. The total metallic loading in the catalyst ranged from 2 wt. % to 6 wt. % and the Co:Mo molar ratios ranged from 1:3 to 2:1, the Co:W ratio was fixed at 1/3. Prior to the production of SWNT by CO disproportionation, the Co Mo catalysts were heated in H₂ flow to

500°C while the Co W catalyst was pretreated at 900°C in H₂. After this initial activation step the catalysts were heated in He flow to the reaction temperature (700-950°C). The CO disproportionation reaction used for the production of SWNT was conducted in the temperature range 700-950°C in flow of pure CO at a total pressure between 1 and 5 atm. The SWNT grown by this method remained mixed with the spent catalyst, which is composed of the silica support and the metallic species. Following reaction, a sequence of treatments was carried out in order to remove most of these impurities. The first step in this sequence was a low-temperature oxidation for the elimination of the amorphous carbon, which was accomplished by calcination in air at 300°C for 2 h. The second step was the elimination of the silica support. In this step, 1 g. of the material was suspended in a NaOH 0.2 M solution while stirring for 24 h at 65°C. After filtering through a Teflon-PTFE 0.2 mm membrane, the remaining solid was washed with deionized water until the pH was neutral and then the solid was dried overnight at room temperature inside a desiccator. The third step was the elimination of the metals (Co and Mo). This was accomplished by an acid attack in reflux of 2 M nitric acid, until the evolution of NO₂ vapors subsided. Again, the solid part was filtered and washed as before. The total removal of silica and metals after both steps was about 95-99%, as determined by atomic absorption analysis.

The TEM images were obtained in a JEOL JEM-2000FX TEM. For this analysis, a suspension in isopropanol was achieved by stirring the solid sample with

ultrasound for 10 min. A few drops of the resulting suspension were deposited on a TEM grid and subsequently dried and evacuated before the analysis. In the present contribution, the yield is defined as the total mass of carbon per mass of catalyst, as determined by the temperature-programmed oxidation (TPO) method described in Chapter 1. Raman spectra were obtained with two different instruments, on a Nicolet Almega Dispersive Raman spectrometer with a 532 nm laser at Nicolet Instruments Corp. and in a Jovin Yvon-Horiba Lab Ram equipped with a CCD detector and with three different laser excitation sources having wavelengths of 632 (He-Ne laser) 514 nm and 488 nm (Ar laser).

To perform the fluorescence analysis, the purified SWNT were added to an aqueous solution containing the surfactant sodium dodecylbenzene sulfonate (NaDDBS) at twice its critical micelle concentration, and ultrasonically agitated for 1 h using a Fisher Scientific Model 550 homogenizer (550 W output). This created a stable suspension of individual and bundled nanotubes. This suspension was centrifuged for 1 h at 72,600 g to separate residual metallic catalyst particles and suspended tube bundles from the lower density surfactant-suspended individual nanotubes. Only a small fraction of the product deposited at the bottom of the centrifuge tube. Finally, the supernatant liquid, enriched in individual SWNT in surfactant suspension, was withdrawn and adjusted to a pH between 8 and 9 for spectral analysis. The intensity of light emission as a function of excitation and emission wavelengths was measured using a J-Y Spex Fluorolog 3-211

spectrofluorometer with a liquid-N₂ cooled InGaAs detector. Excitation and emission spectral slit widths were 6 nm, and scan steps were 2 to 3 nm on both axes.

5.3. RESULTS

5.3.1. TEM, TPO and preliminary analysis by Raman spectroscopy

To characterize the SWNT, we have used a combination of transmission electron microscopy (TEM), Raman spectroscopy, temperature programmed oxidation (TPO) and fluorescence data. Figure 5.1 shows a typical micrograph obtained by transmission electron microscopy (TEM) on a sample obtained at 850°C on a Co-Mo (1:3)/SiO₂ catalyst. It is interesting to note the small metal clusters that appear intermingled with the nanotubes and have about the same diameter as the nanotubes. A small number of larger metal particles are also observed, but they do not seem to be associated with the nanotubes.

As discussed in Chapter 1, Raman spectroscopy is a powerful technique for characterizing the structure of carbon nanotubes. The tangential mode G band appearing in the 1400-1700 cm⁻¹ region is related to the Raman-allowed phonon mode E_{2g} and involves out-of-phase intra-layer displacement in the graphene structure of the nanotubes. It provides information about the electronic properties of the tubes and is a measure of the presence of ordered carbon. The so-called D-band at around 1350 cm⁻¹ is related to defects or the presence of nanoparticles and amorphous carbon [12]. Although pure SWNT also have some contribution in this region [13], the D-band provides an indication of the level of disordered carbon. Hence, the size of the

D-band relative to the G band can be used as a qualitative measurement for the formation of undesired forms of carbon. Finally, information about the distribution of tube diameters can be obtained from the analysis of the radial A_{1g} breathing mode frequency range (RBM), as shown below [14]. Although Raman spectroscopy is very

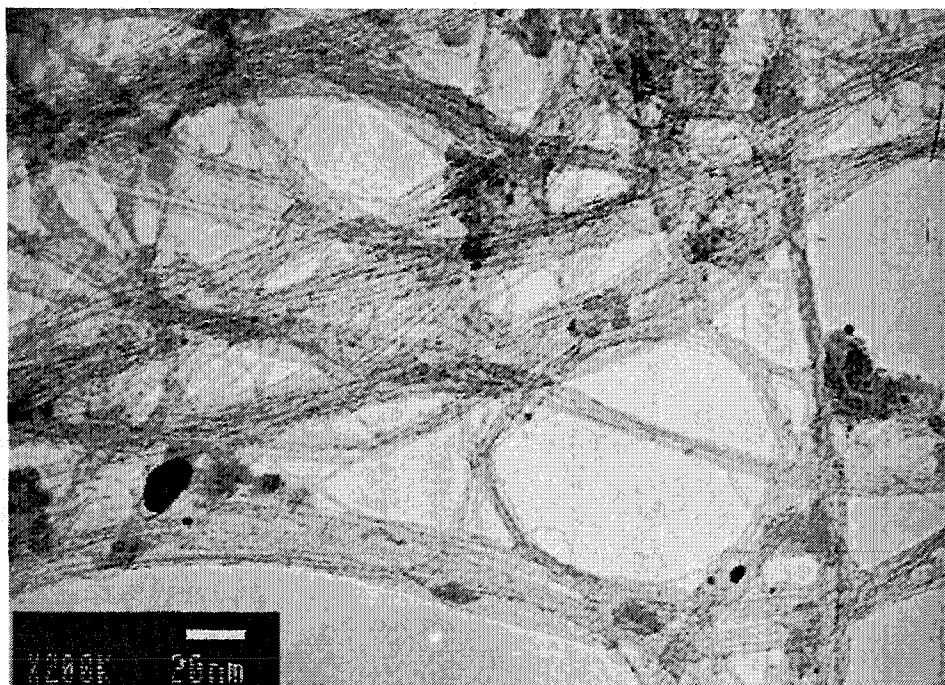


Figure 5.1. Typical TEM micrograph of SWNT produced by CO disproportionation at 850oC on a Co:Mo catalyst during 2h. The carbon yield on this sample is approximately 15 wt % C.

useful for a comparative analysis of the relative amounts of disordered and ordered carbon species, in our case, it cannot provide a quantitative measurement of the amount of SWNT produced over the whole catalyst sample. On the other hand, TPO can provide a quantitative measure of the carbon yield and selectivity. For instance, as we have previously shown in Chapter 1, under the TPO conditions and while still

immersed in the Co-Mo catalyst, the SWNTs get oxidized in a relatively narrow temperature range, which lies below the temperature in which MWNT, graphite, and carbon fibers are oxidized, but above the temperature at which amorphous and chemically impure carbon species are oxidized. Figure 5.2 illustrates how Raman spectroscopy and TPO can be used to characterize the SWNT produced catalytically. As previously shown, the TPO peak with a maximum at about 520°C is due to SWNT, while that at 620°C is due to multiwalled nanotubes, nanofibers, and graphitic carbon. A clear difference is observed when the product from a selective catalyst (e.g. Co/Mo = 1:1) is compared to that of a non-selective catalyst (e.g. Co/Mo = 2:1). In the TPO of the product obtained on the non-selective catalyst, the high-temperature peak is dominant, revealing the low selectivity of the 2:1 catalyst. These results are very well paralleled by the Raman spectra shown on the same figure. It is clear that the D band contribution becomes much stronger in the spectrum of the product obtained using the non-selective (Co/Mo = 2:1) catalyst than for the selective catalyst (Co/Mo = 1:1). In perfect agreement with these results, the TEM observations indicated the presence of large quantities of MWNT and fibers on the non-selective catalyst.

A similar characterization routine can be used to investigate the variation of selectivity as a function of reaction time. The rate of growth of an individual SWNT is very fast. Iijima et al. studying the growth of SWNT by laser ablation observed the formation of vortexes propagating forward during 200 ms and then flowing

downward to the target [15, 16]. They determined that the time available for the SWNT growth in the vortices is from a few milliseconds to about 1 sec. Similarly,

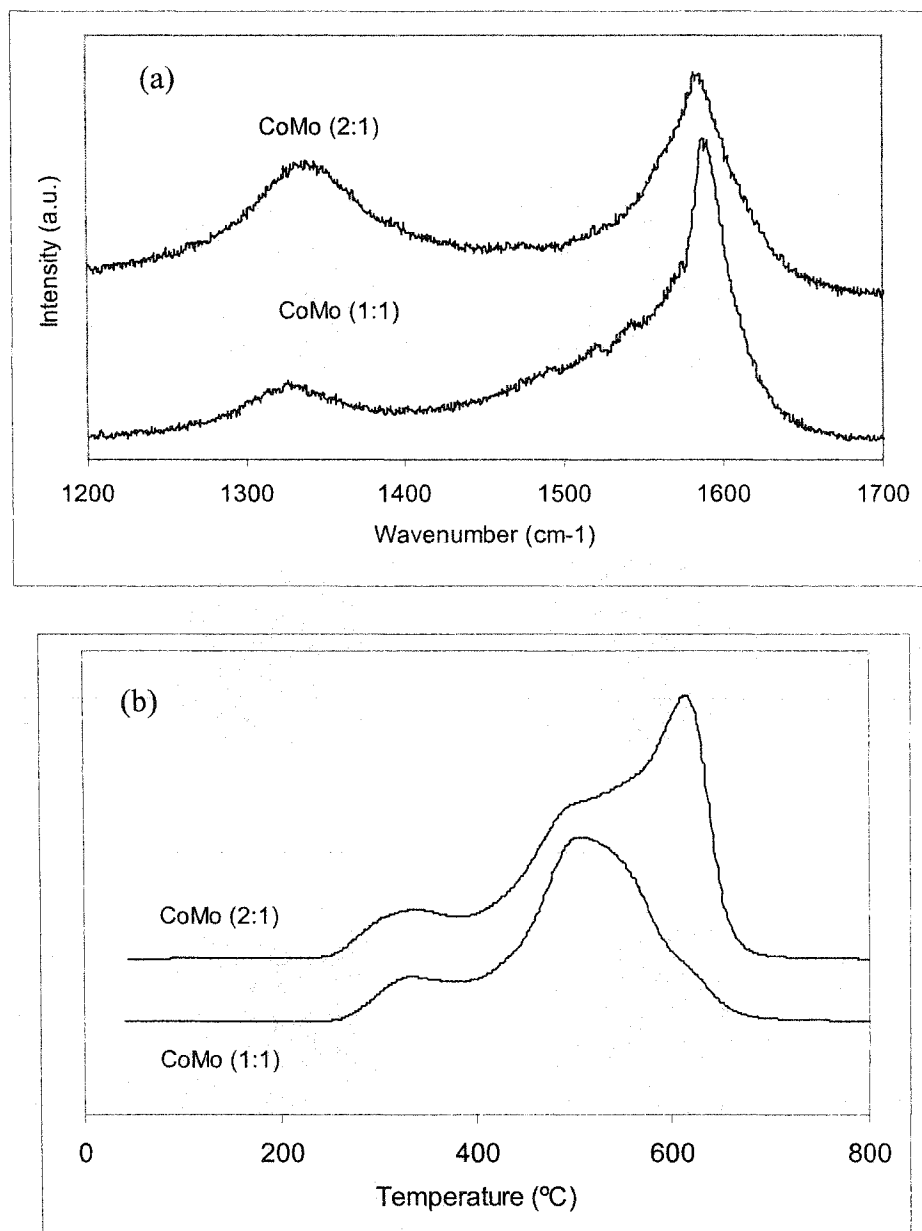


Figure 5.2. (a) Raman spectra of SWNTs grown by CO disproportionation at 700°C over two different catalysts with varying Co:Mo ratios. The total metallic loading in both catalysts

was 6 wt %. The laser excitation wavelength was 514 nm (b) Temperature Programmed oxidation profiles conducted on the same samples as those of part (a).

Gorbunov et al. from results obtained at varying Ar flow rates, have determined that the growth time is less than a second [17]. By contrast, on the formation of tubes by the catalytic method on a solid catalyst, the carbon deposition is relatively slow and the yield of SWNT keeps increasing for hours [18-20]. It is then apparent that the intrinsic growth rate of each individual SWNT is very rapid and when the growth begins on a given site on the solid surface, it should proceed at a rate comparable to that on the vapor phase. The observed slow rate of formation on solid surfaces must then be ascribed to a slow rate of nucleation. That is, in order for the nanotube growth to occur, the metal particle and the incipient carbon deposits must acquire a proper configuration, but after nucleation, the growth should be very rapid. It is then interesting to monitor the selectivity of the carbon product as a function of reaction time, because, as the time on stream increases, the metal particles on the catalysts may suffer sintering or other morphological modifications, which may cause losses in their ability to selectively produce SWNT.

This trend is illustrated in Figure 5.3, which shows the Raman spectra of the SWNT obtained as a function of time on stream on the most selective catalyst. As the reaction progresses, there is an increase in the intensity of all the bands because of the increasing carbon deposition. However, it is interesting to point out that the relative intensity of the D band, with respect to the G band clearly increases with reaction time. Figure 5.4 shows the relative intensity of the D band, together with the carbon

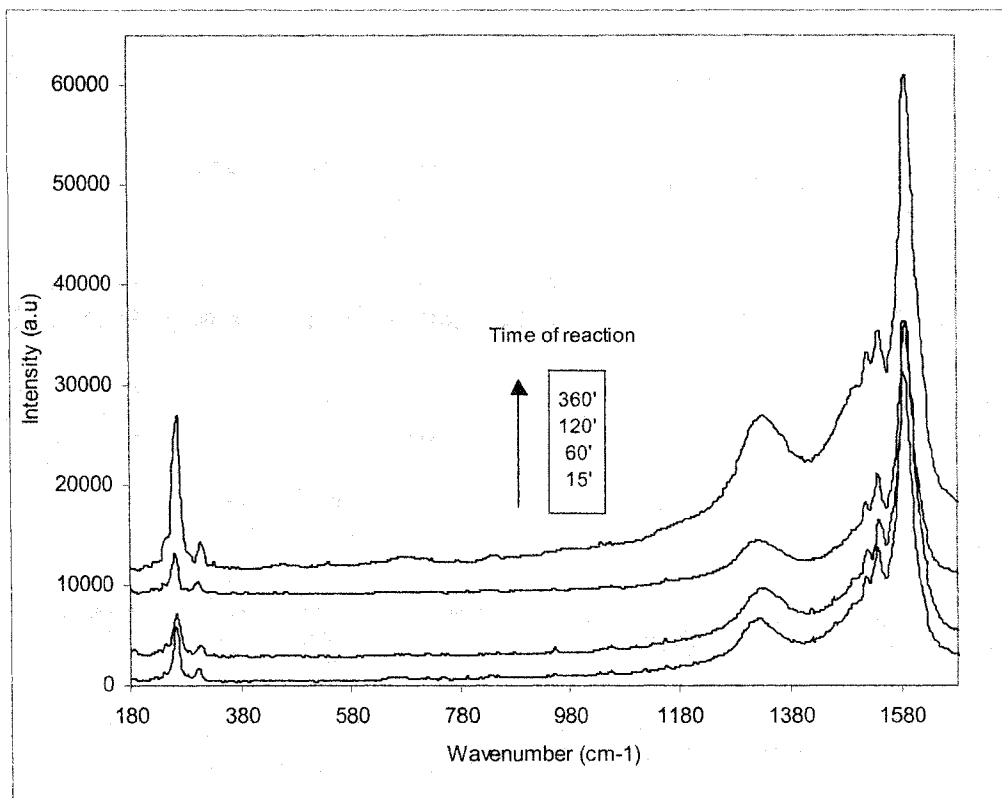


Figure 5.3. Raman spectra of SWNTs grown at increasing reaction times. The product was obtained at 750°C in a catalyst with Co:Mo ratio of 1:3 and a total metal loading of 2 wt %. The excitation wavelength was 514 nm.

yield measured by TPO as a function of time on stream. During the first two hours, the carbon yield increased rapidly with reaction time, while the SWNT selectivity remained relatively high. However, at longer times, not only the carbon deposition became slower, but also the selectivity to SWNT was greatly reduced. The TEM

observations were in perfect agreement with these conclusions, showing a higher density of MWNT and graphite after long times on stream than after the first couple of hours.

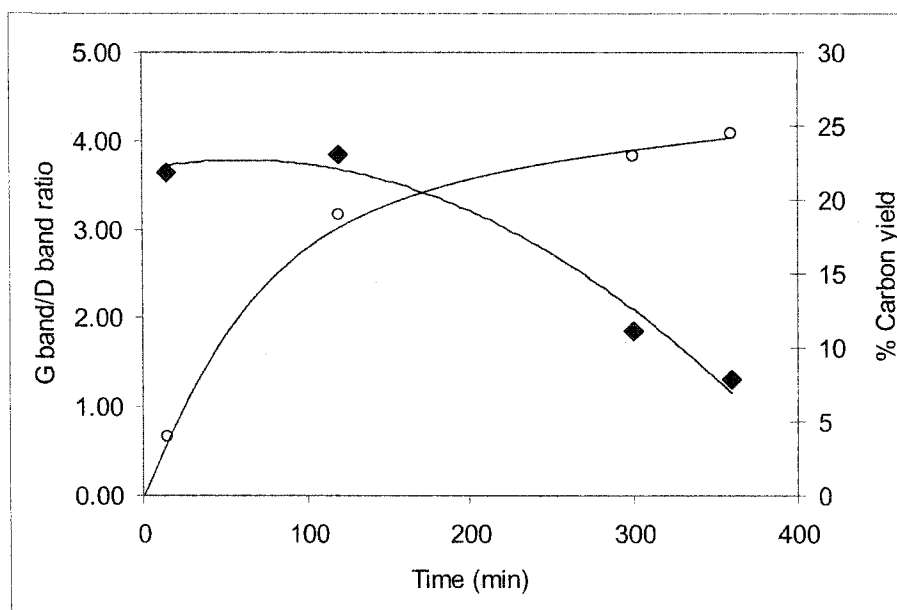


Figure 5.4. Filled squares: ratio of intensities G band over D band as obtained from the spectra in Figure 5.3. Open circles: total yield of carbon, as obtained by TPO.

To study the effect of the reaction temperature on the structure of the SWNT obtained by the catalytic method, we conducted the decomposition of CO at temperatures ranging from 750 to 950°C. Kitiyanan et al. have previously showed that when the temperature is lower than 700°C, the selectivity to SWNT is greatly reduced [21]. Soon after, Alvarez and coworkers shown that although the amount of carbon deposited on a Co:Mo catalyst with molar ratio 1:2 was larger at 600°C than at higher temperatures (e.g., 700 - 800°C), the selectivity greatly decreased at low

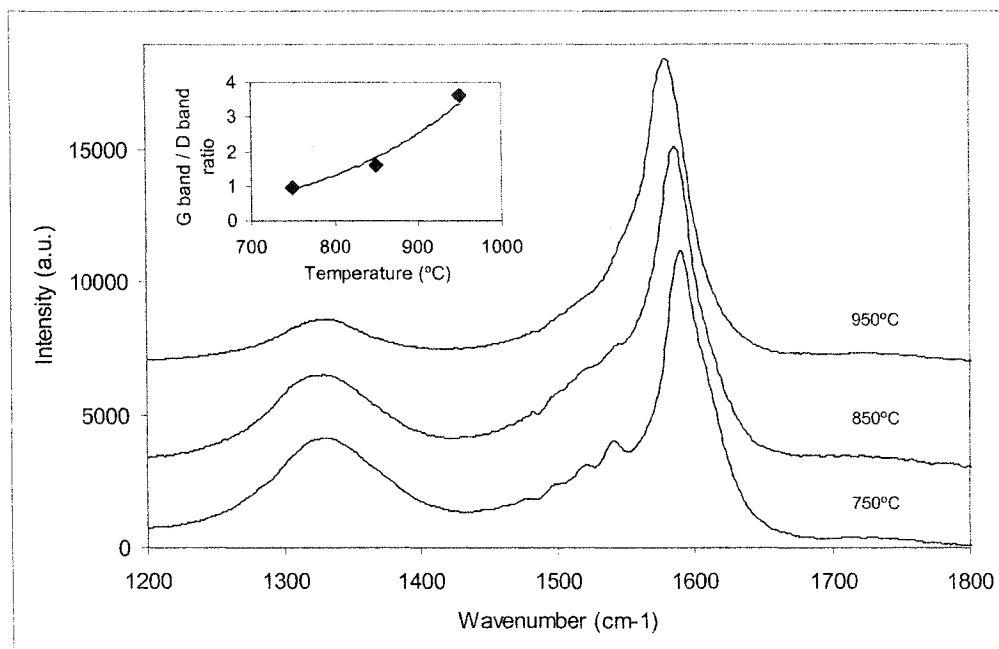


Figure 5.5. High frequency Raman spectra of SWNT grown for 2 hours at different temperatures on a catalyst with Co:Mo ratio 1:3 and a total metallic loading of 2 wt %. The excitation wavelength was 532 nm. Inset: G to D band intensity ratio as a function of reaction temperature.

temperatures due to the formation of larger fractions of MWNT and carbon fibers [22]. Here, more subtle changes observed when the reaction temperature is increased are reported. A preliminary analysis by Raman spectroscopy (laser excitation wavelength 532 nm) obtained for runs at different temperatures is shown in Figure 5.5 and 5.6 for the high and low frequency ranges, respectively. In the first place, and in agreement with the results previously obtained by Alvarez and coworkers, the increase in the G-to-D band intensity ratio with temperature indicates a selectivity

improvement as the reaction temperature increases. However, the most interesting result is illustrated in Figure 5.6 for the radial breathing mode region. The product

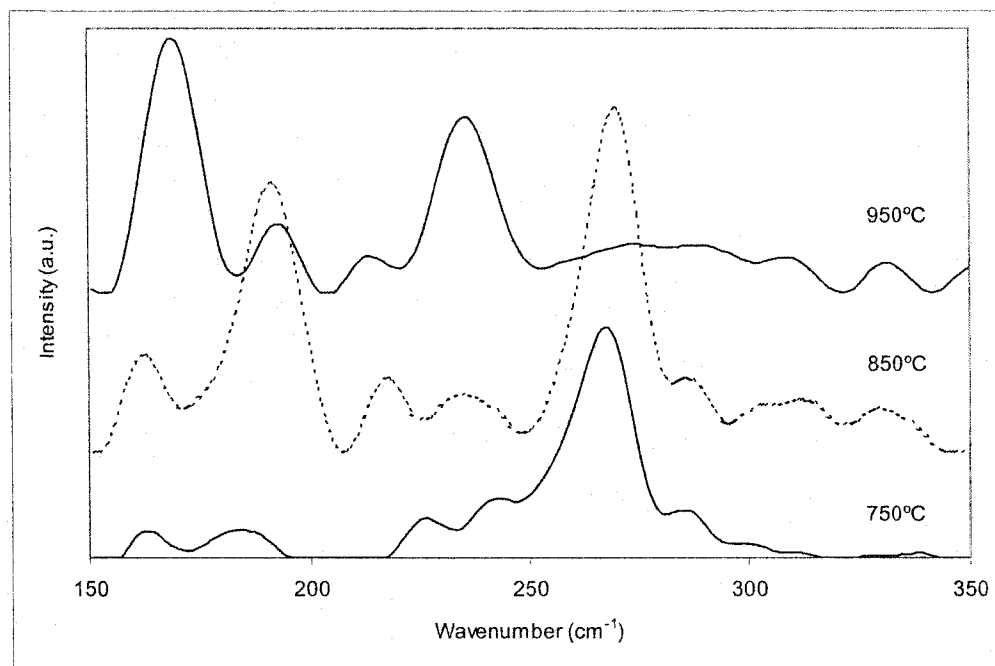


Figure 5.6. Low frequency Raman spectra of SWNT grown for 2 hours at different temperatures on a catalyst with Co:Mo ratio 1:3 and a total metallic loading of 2 wt %. The excitation wavelength was 532 nm.

obtained 750°C exhibited a dominant peak centered at around 268 cm^{-1} , which as discussed in Chapter 1 would correspond to a tube diameter of approximately 0.9 ± 0.05 [23]. Much weaker side bands are also present in the spectrum; they would correspond to a small amount of tubes with diameters about 0.6 and about 1.2 nm. By contrast, when the temperature was increased to 850°C a new peak came out at lower wavenumbers (191 cm^{-1}) and when the temperature was increased to 950°C the main peaks appeared at 236 and 170 cm^{-1} . The positions of these bands indicate that the

SWNT produced at 850°C have diameters of 0.9 and 1.25 nm, whereas those obtained at 950°C, have diameters around 1.00 and 1.40 nm.

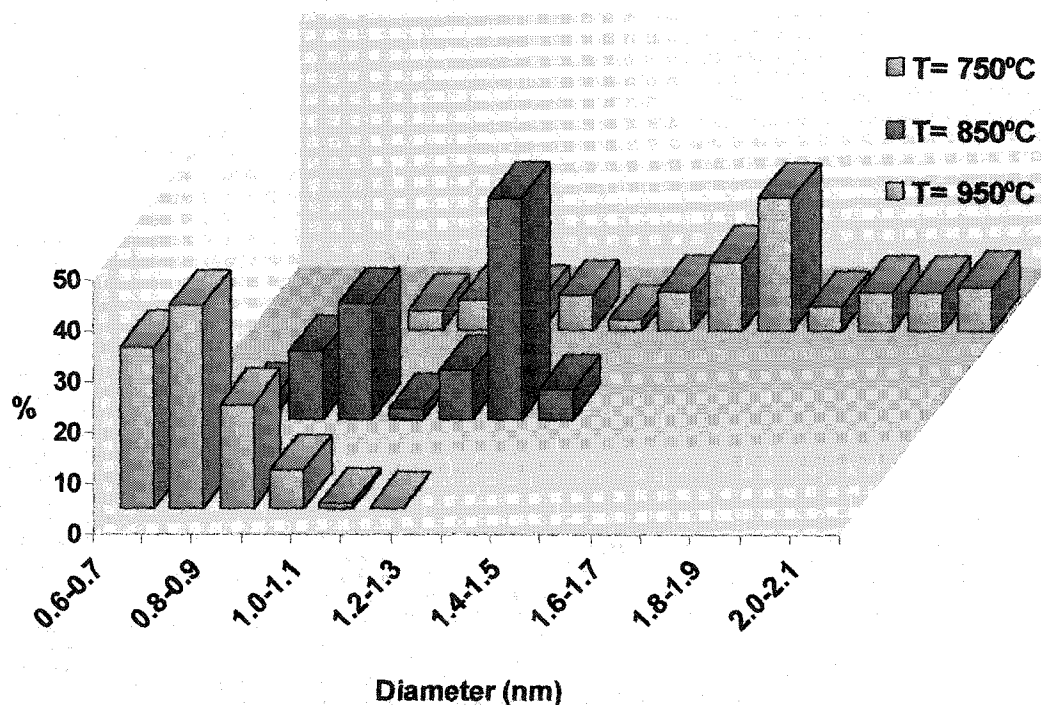


Figure 5.7. Diameter distribution of SWNT produced by CO disproportionation at 750°C on a Co:Mo catalyst with 1:3 molar ratio, as obtained from TEM micrographs.

To corroborate these results, we conducted a detailed analysis of several TEM micrographs acquired on the same samples as those used in the Raman study. The diameters of 100-150 tubes were measured for each sample and the results of those measurements were summarized in the histograms shown in Figure 5.7. The observed distribution matches the preliminary Raman results. The results leave no doubt that, as the reaction temperature increases, the diameter of the tubes increases. As mentioned above, a possible explanation for this increase could be that the

sintering of the Co clusters accelerates with temperature. As a result, at higher temperatures there is a higher density of larger metal clusters on the catalyst surface. These larger clusters are in turn responsible for the formation of tubes of larger diameter. Similar increases in tube diameter have been observed when the ambient temperature increases in other vapor phase techniques [15, 24,25].

5.3.2. Detailed Raman analysis

Although in the last section the trend observed in the preliminary Raman spectra harmonize those observed by TEM, the information resulting from that preliminary Raman analysis using only one laser energy does not represent the whole range of nanotube diameters. Since the Raman intensity is strongly affected by resonance phenomena, the radial breathing mode peaks obtained at each laser energy do not reflect the entire diameter distribution of the sample, but rather the sub-set of nanotubes that are in resonance with the laser photons. Moreover, as described in Chapter 1, due to resonance phenomena, Raman spectroscopy can be used to probe both, structural and electronic features of the nanotubes [26]. In particular, the analysis of the tangential band offers a method for distinguishing between metallic and semiconducting single-walled carbon nanotubes, since peak broadening and extra bands centered at around 1540 cm^{-1} are clearly seen when metallic nanotubes are present in a sample [27]. Therefore, in order to get a more detailed picture of the quality of SWNT produced at different temperatures, it is necessary to expand the number of laser lines employed in this type of analysis.

Figure 5.8 shows one of such analysis; in this case the breathing modes bands in the Raman spectra were obtained with three different laser excitation energies on SWNT samples obtained at different temperatures over a Co Mo catalyst. The spectra for a given sample are quite different, depending on the laser excitation energy used, but the same trend is observed at all energies. That is, the bands clearly shift to lower wavenumbers as the reaction temperature increased. Since the frequency of the radial breathing mode is inversely proportional to the nanotube diameter, this shift indicates an increase in diameter as temperature increases, in excellent agreement with the results obtained by TEM. To validate this result we conducted the same type of analysis on samples obtained by CO disproportionation over a CoW catalysts, following the synthesis method described in Chapter 3. Figure 5.9 shows these results, which depict the Raman spectra obtained for SWNT grown at different reaction temperatures, after pretreatment at the optimal reduction temperature of 900°C (Chapter 3). In this case the spectra were taken using two different laser excitation energies in order to get a more accurate description of the SWNT diameter distribution in these samples. The same trend can be observed at both laser energies, that is, the bands shift to lower frequencies as the reaction temperature increases. This shift indicates that, as we reported for the CoMo system, the average nanotube diameter increases when higher reaction temperatures are used.

As described in Chapter 1, linking nanotube diameters with the energy gaps between singularities in the valence and conduction bands of the electronic density of

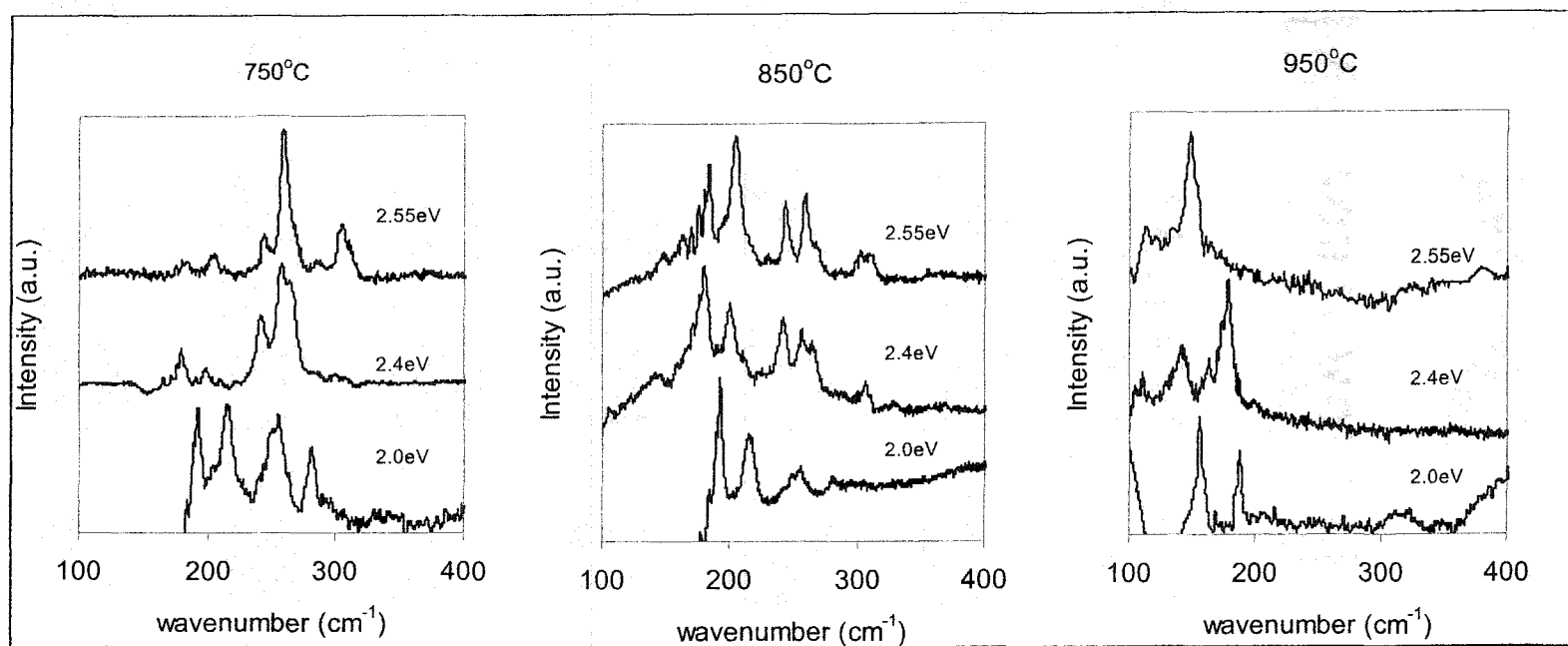


Figure 5.8. Radial breathing mode resonant Raman spectra of SWNT grown for 2 hours at three different temperatures on a Co:Mo catalyst. The excitation wavelengths were 488 nm (2.55 eV), 514 nm (2.4 eV) and 633 nm (2.0 eV).

states of SWNT is possible by calculating the one-dimensional energy band structure of SWNT. These calculations have been conducted by Kataura and coworkers [28] and their results are reproduced in Figure 5.10 and are compared to the experimental data obtained for the SWNT obtained over the Co Mo catalyst. In this figure, the calculated results for each individual nanotube were used as a background, with the solid and open circles represent nanotubes with metallic and semiconducting character, respectively. Superimposed over this background, the Raman data obtained in the present chapter are indicated with solid diamonds. Points are marked for the particular energy of the laser employed (i.e., 2.0, 2.4, or 2.55 eV) and for each observed nanotube diameter, as inferred from the frequency of the radial breathing mode bands.

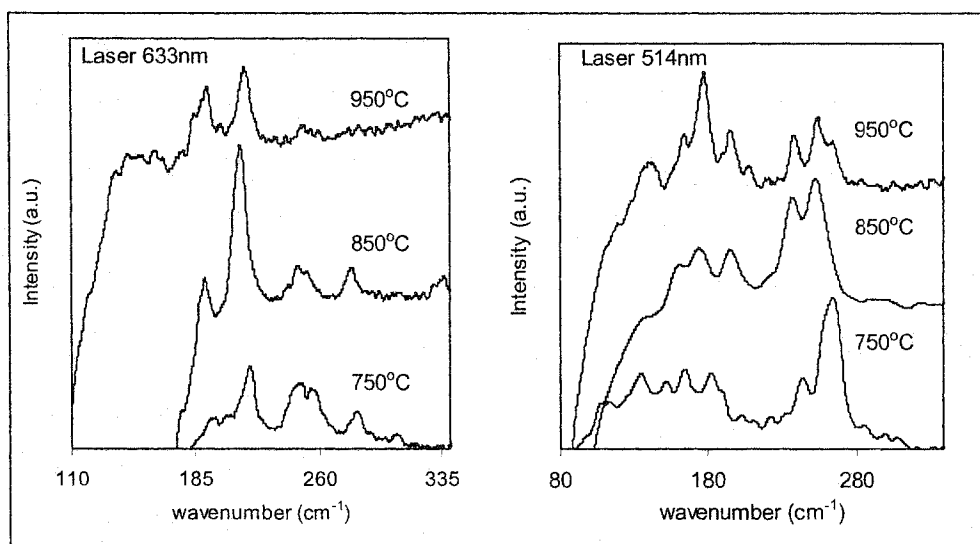


Figure 5.9. Raman spectra of the SWNT growth by disproportionation of CO at 750°C, 850°C and 950°C over a CoW(1:3)/SiO₂ catalyst after a pretreatment at 900°C in hydrogen

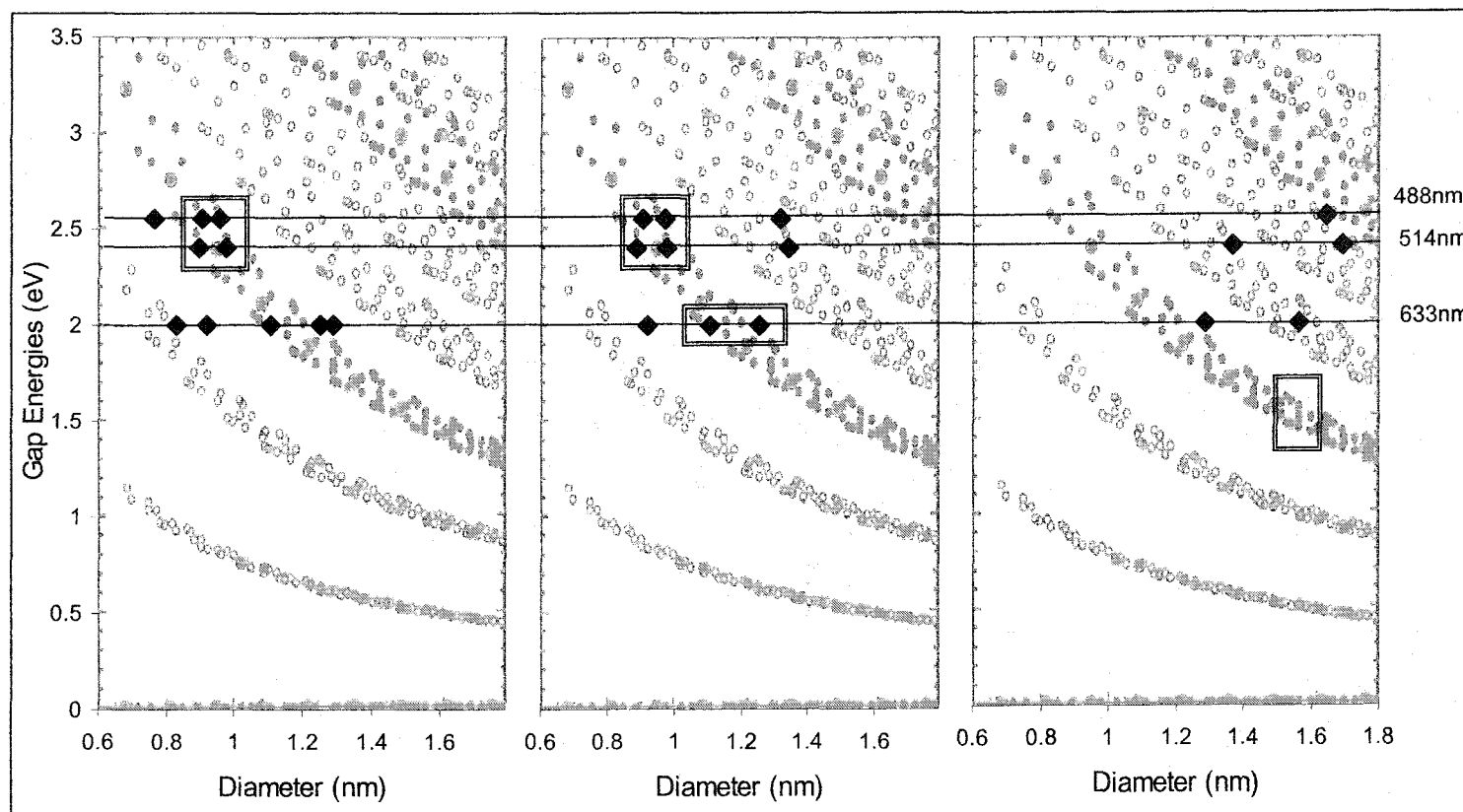


Figure 5.10. Calculated gap energies as a function of diameter for SWNT with chiral indexes with larger diameter than (5,5) as function of diameter, calculated by Kataura et. al. (reproduced from ref. 28). The solid circles indicate the metallic SWNT and open circles the semiconducting ones. The filled diamonds indicate the diameter of the SWNTs probed in each of the samples obtained at three different temperatures.

As mentioned above, the TEM observations for the SWNT sample obtained at 750°C indicated an average nanotube diameter of 0.9nm. Consequently, a “metallic window” can be delineated around this average diameter, for which the resonance condition for metallic nanotubes would take place in the energy region 2.4-2.7 eV. Therefore, it is expected that, for this diameter range, the two lasers with higher energy (2.4 and 2.55 eV), which fall within this window would only probe metallic nanotubes. By inspecting Fig. 5.10, one can see that, in agreement with this expectation, the RBM bands detected with the two lasers of higher energy correspond to metallic SWNT only. By contrast, with the lower energy laser (2.0 eV) we probe both semiconducting and metallic nanotubes. In fact, since the TEM observations indicated that the majority of the nanotubes in this sample had diameters around 0.9 nm, the bands observed at frequencies corresponding to larger diameters and with metallic character should represent only a small fraction of the sample.

In good correspondence with these data, the high frequency Raman spectra of Fig. 5.11a corresponding to the sample synthesized at 750°C displays a clear difference between the features seen at each laser energy. With the laser excitations of 2.55 eV and 2.4 eV, a broad and asymmetric Raman peak was observed to the left of the G band, which clearly demonstrates the presence of metallic nanotubes in resonance with the laser excitation energy. However, for the 2.0 eV laser, the left shoulder was much smaller. Pimenta et al. [26] have also investigated the variation of

the band attributed to metallic nanotubes and described by the Breit-Wigner-Fano line shape

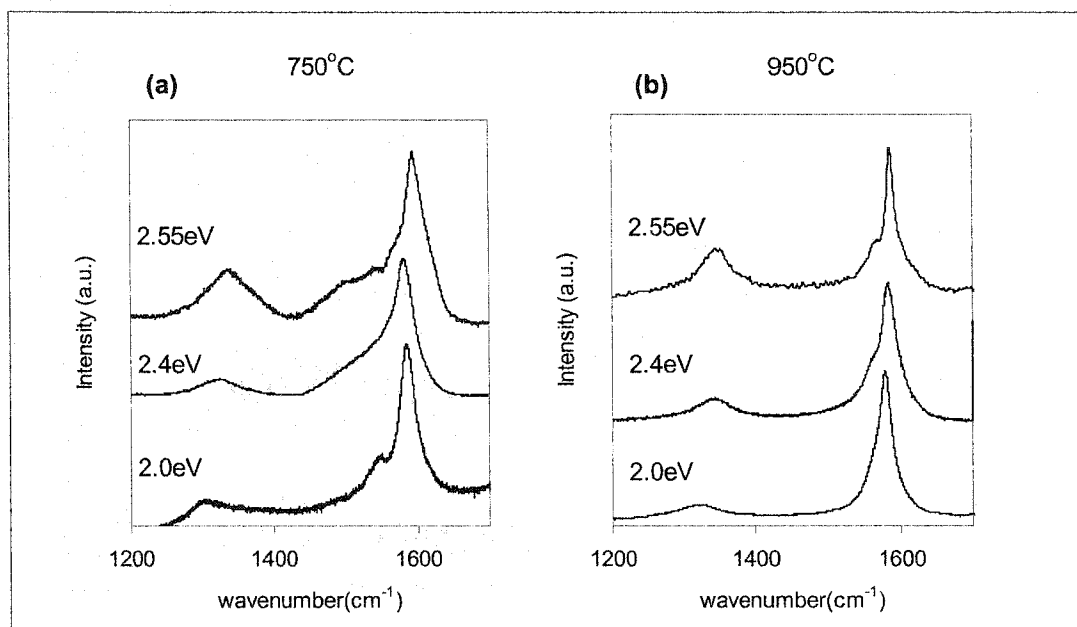


Figure 5.11. Resonant Raman spectra in the tangential mode (G mode) obtained using three different laser excitation energies, for SWNT samples produced by CO disproportionation at 750°C (left) and 950°C (right).

centered at 1540 cm^{-1} as a function of the laser energy. However, in that particular study the large enhancement in the $1540\text{ cm}^{-1} / 1593\text{ cm}^{-1}$ intensity ratio was observed at lower laser energies than those at which we observe the enhancement. The position of the “metallic window” was shifted, because the nanotubes they used had diameters in the 1.1-1.3 nm range. As can be predicted from the plot in Figure 5.10 for those diameters the energy region of resonance for metallic nanotubes falls in the range 1.7 - 2.2 eV; which agrees very well with the range at which they observed

enhancement of the 1540 cm^{-1} / 1593 cm^{-1} intensity ratio. A similar conclusion was reached by Kataura et al. [28]. for SWNT obtained by arc-discharge using a RhPd catalyst. In this particular case, most of the SWNT produced had diameters distributed from 0.7 to 1.0 nm and consequently when using laser energies around 1.8 eV mostly metallic SWNT were probed.

We can expand the same analysis to interpret the data obtained on the samples synthesized at higher temperatures. For instance, Fig. 5.11b shows the high frequency Raman spectra obtained using three different laser energies on the nanotubes produced at 950°C . In this case, the contribution of the 1540 cm^{-1} band to the overall spectra is less significant for all three different excitation energies than on the sample synthesized at 750°C . As seen in Fig. 5.10, the “metallic window” for a sample with average diameter of 1.5 nm should occur at laser energies below 1.6 eV. Then, all of the observed bands at laser energies above 2.0eV correspond to semiconducting nanotubes. In good agreement with this analysis, the Raman spectra did not show the characteristic resonance that is described by the Breit-Wigner-Fano line.

Another interesting trend is illustrated in Fig. 5.12; in this case, we plot the ratio of the area under the 1540 cm^{-1} feature to that of the 1593 cm^{-1} main G band of the Raman spectra obtained with two different excitation energies, for nanotubes grown at three different temperatures. The results obtained at 2.0 eV and 2.4 eV

show a remarkable contrast. First, it can be seen that the ratio for the SWNTs probed with the 2.4 eV laser greatly decreased as the reaction temperature increased. This can be interpreted in terms of the gap energy plots as a function of nanotube diameter shown in Fig 5.10. As the reaction temperature increased, nanotubes of larger diameters were formed and, at this particular laser energy, the fraction of semiconducting nanotubes probed by Raman increased. In consequence, of all the SWNT formed at 750°C, only the metallic ones were probed at 2.4 eV, while of all those formed at 950°C, only the semiconducting nanotubes were probed.

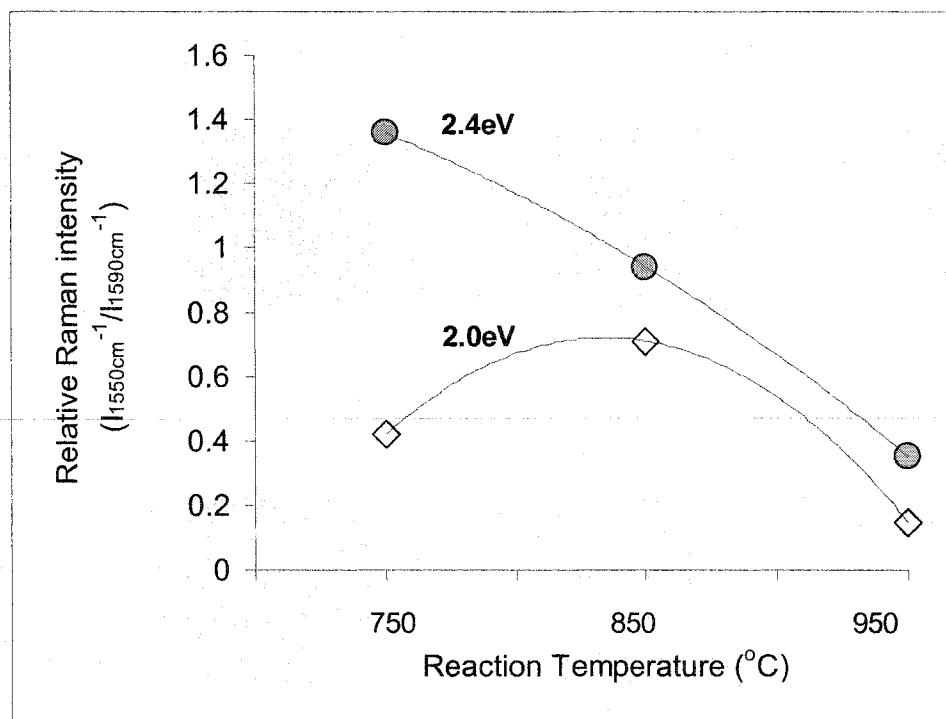


Figure 5.12. Relative Raman intensity of the metallic (1540cm^{-1}) and the semiconductor (1590cm^{-1}) contribution to the SWNT Raman spectra in the tangential mode (G band) obtained using laser excitation energies of 2.4 eV and 2.0 eV for SWNT samples produced by CO disproportionation at 750°C, 850°C and 950°C.

The results obtained with the 2.0 eV excitation energy clearly confirm the previous trend. In this case, the maximum contribution of modes characteristic to metallic nanotubes occurred for the SWNT grown at 850°C. The appearance of this maximum is explained by inspecting Fig. 5.10 again. With the 2.0 eV laser, we probed a mixture of metallic and semiconducting SWNTs on the samples synthesized at 750°C and 950°C, but majority of metallic SWNTs on the one synthesized at 850°C. Therefore, the contribution of the feature centered at 1540 cm^{-1} is more pronounced on the latter sample.

5.3.3. Fluorescence analysis

Figure 5.13 shows the fluorescence spectra obtained with an excitation light of 671 nm (1.85 eV) on SWNT samples obtained at two different temperatures. As described on Chapter 1, the optical excitation of a semiconducting nanotube to its second van Hove transition (E_{22}) will be followed by rapid electronic relaxation before emission in the first-branch van Hove transition (E_{11}) [29, 30]. Therefore, by monitoring the intensity of the different emission peaks generated during the first-branch transition process at different wavelengths (energy) using a fixed excitation wavelength within the second van Hove branch, one can easily identify the first branch transition energies of the nanotubes [31]. Figure 5.13 clearly shows that for the sample synthesized at 750°C three main peaks are present: 964nm ($E_{11} = 1.29\text{eV}$), 1037nm ($E_{11} = 1.19\text{ eV}$) 1132nm ($E_{11} = 1.09\text{ eV}$), while for the sample obtained at

850°C five different bands are apparent: 956 nm (1.30 eV), 1026 nm ($E_{11} = 1.21\text{eV}$), 1122 nm ($E_{11} = 1.11\text{ eV}$), 1180 ($E_{11} = 1.12\text{eV}$) and 1255 nm ($E_{11} = 0.99\text{eV}$).

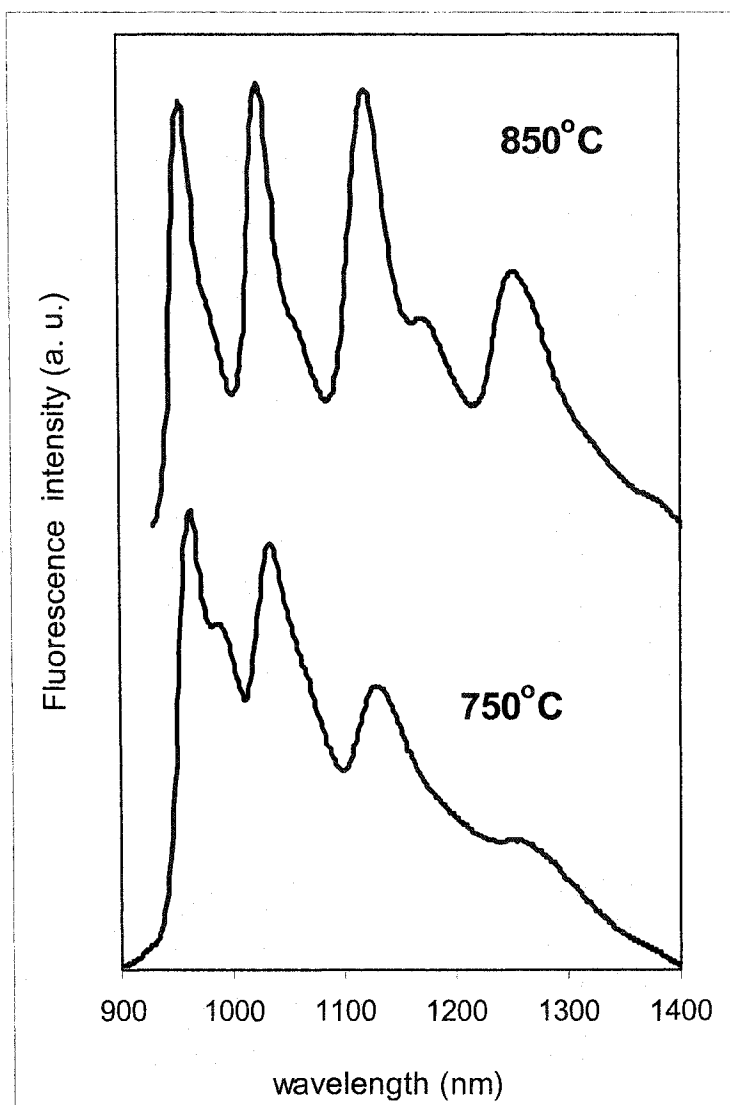


Figure 5.13. Emission spectrum of SWNTs obtained by CO disproportionation at two different reaction temperatures. The excitation energy was 1.85 eV.

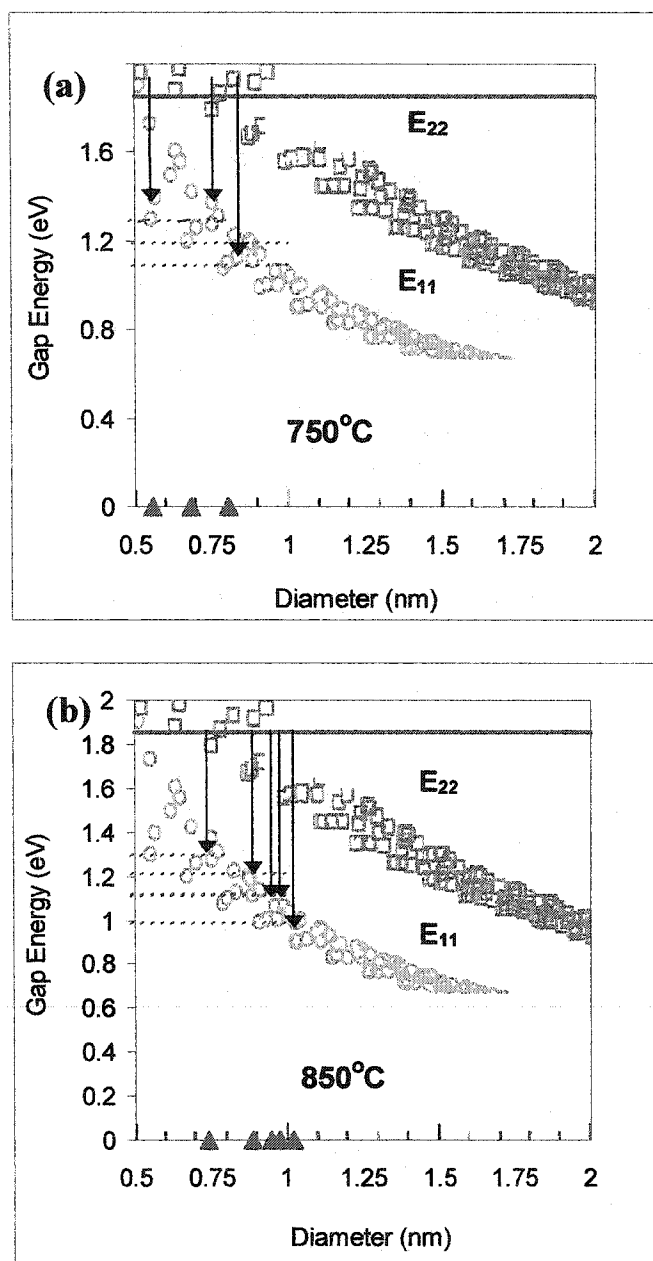


Figure 5.14. Light induced emission processes described as a function of the optical transitions for SWNTs obtained at two different temperatures by CO disproportionation; the solid triangles indicate the diameters of the SWNTs observed, as deduced from the fluorescence experiments.

These results can be easily interpreted based on the Kataura plot depicted in Figure 5.10; as the energy used to generate the second Van Hove transitions is known (1.85 eV). This kind of analysis is presented in Figure 5.14 for the two samples synthesized at 750°C and 850°C. Here using experimental values of the energy of the first and second Van Hove transitions as a function of nanotube diameter reported by Weissman and Bachilo [32], the spectroscopic processes that take place during the fluorescence experiments can be located for each sample. From the comparison between Fig 5.14a (750°C) and Fig.5.14b (850°C), it is clear that the sample obtained at higher temperatures has a larger distribution of diameters; a trend that flawlessly matches the results obtained by Raman and TEM analysis.

5.4. DISCUSSION

In Chapter 2, 3 and 4 we have verified how a synergism between Co and Mo is critical for the performance of the Co:Mo catalytic system. As mentioned above, a supported metal particle is highly susceptible to aggregation by sintering, particularly when it is subjected to the high temperatures needed for the synthesis of SWNT. A rule of thumb to determine the onset of rapid sintering is the so-called Tamman temperature (one-half the melting point temperature in K) [1]. Accordingly, when metallic Co particles are employed in SWNT synthesis, they would rapidly sinter on any support at temperatures above 610°C. This temperature is much lower than that needed for the synthesis of SWNT by CO disproportionation. Therefore, one cannot have reduced metal particles on a support before starting the synthesis process

because by the time the nanotube growth starts the metal particles will be too large to catalyze the growth of SWNT. Even when the metal particles may have had nanometric dimensions before the growth started, they quickly sinter at the high temperatures needed for SWNT synthesis [33, 34].

As demonstrated in Chapter 2 large metal clusters are known to catalyze the growth of defective multi-walled nanotubes and nanofibers. The growth of these forms of carbon follows a well-known mechanism, which has been documented extensively in the past [35]. That is, the C deposited on the surface of the metal particles begin to dissolve into the particle, which then precipitates graphite in the form of cylindrical filaments. Consequently, when precautions to avoid metal sintering are not taken during the CVD process particles of a broad distribution of sizes are produced and the selectivity towards SWNT is drastically reduced. Therefore, although SWNT are produced in many CVD processes, only a few are able to produce SWNT with high selectivity (i.e. low production of undesired forms of carbon).

By contrast, the Co-Mo interaction described in Chapter 2 inhibits the Co sintering that typically occurs at the high temperatures required for the formation of carbon nanotubes and only SWNT are produced. In that case, the metal clusters are so small that they are only composed of a few atoms and a different mechanism must be considered [36]. One could expect that under the bombardment of carbon-

containing species from the gas phase, a very unstable metal-carbon cluster will rapidly change its configuration and carbon concentration. At a given point and after the carbon concentration has exceeded the solubility limit in this small cluster a favorable configuration may nucleate and generate the starting point for nanotube growth. We propose to call this configuration embryo. When this embryo is formed, the subsequent incorporation of carbon and SWNT formation proceeds at a fast rate, perhaps only controlled by mass transfer to the growing site, but keeping the nanotube diameter fixed and specified by the size of the embryo that originated the growth. For this reason, we observe that the deposition of carbon on a solid catalyst continues for hours (Figure 5.4), although the growth of a single tube only takes milliseconds [15, 16]. Moreover, as diameter of the tube is determined by the size of this embryo, a direct control of nanotube diameter is achieved by controlling of the size of the metal cluster varying the reaction temperature (Figure 5.10). This sequence is better illustrated in Fig. 5.15.

5.5. CONCLUSIONS

By means of detailed analysis by TEM, fluorescence and Raman spectroscopy we have been able to demonstrate that the diameter of SWNTs obtained by CO disproportionation over Co-Mo catalysts can be varied by changing the operating temperature. As the temperature is increased, the average SWNT diameter increases. The consequence of this result on our proposed hypothesis has been analyzed. The use of Raman spectroscopy with several excitation lasers has proven to be a useful

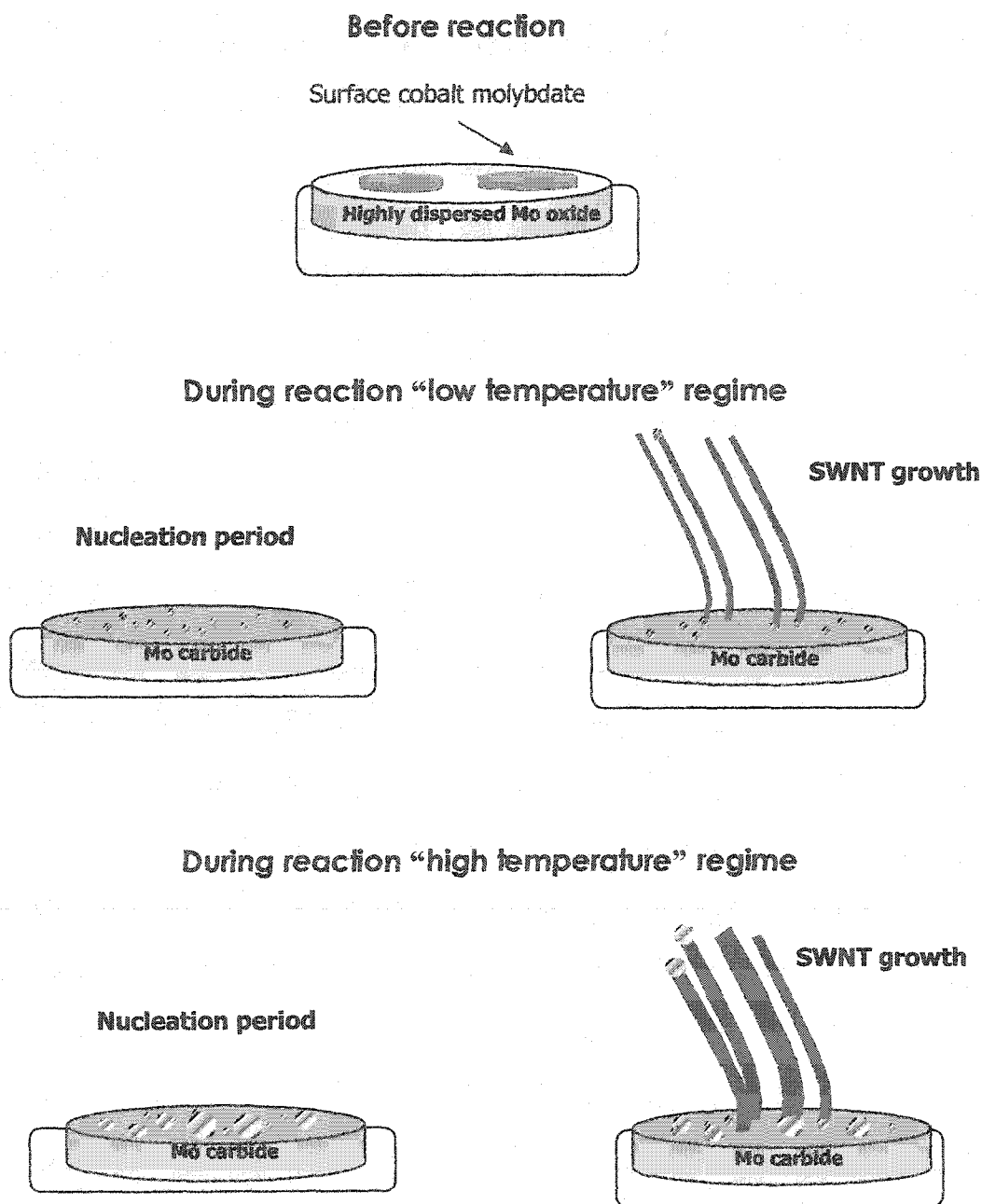


Figure 5.15. Schematic representation of the state of the catalyst components before and during the production of SWNT at two different temperatures. Once CO is introduced the Co-Mo interaction is broken and metallic Co nanoparticles start to sinter, at the same time CO decomposes over these Co particles and begin to nucleate to form embryos, which finally lead to the formation of SWNTs

tool to obtain both a complete description of the SWNT diameter distribution and information on the metallic or semiconducting nature of the nanotubes. A good agreement has been obtained between previously published theoretical calculations and the combination of excitation energy and SWNT diameter as inferred from the position of the breathing mode bands. At the same time, the analysis of the tangential G band including a low-frequency feature, which can be fitted with a Breit-Wigner-Fano line, has been used to distinguish between metallic and semiconducting nanotubes.

ACKNOWLEDGMENTS

The work presented in this chapter is the result of a truly collaborative effort of the Heterogeneous Catalysis Group at the University of Oklahoma. First, I would sincerely like to thank Leandro Balzano, the work described here would have not been possible without the carefulness he took to set up properly reaction conditions to run the SWNT synthesis reaction. I also thank Dr. Walter Alvarez and Francisco Pompeo for their meticulousness in obtaining the TEM histograms. I would also like to thank the OU College of Engineering for its commitment to provide a Raman spectrometer, Dr. Bruce Weissman's group work at Rice University and Nicolet Instruments for facilitating the fluorescence and some of the Raman data respectively. I am also very thankful to the National Science Foundation and the OU Graduate College for granting me a travel award to go to Spain in 2002 to present the results of the work described in this chapter. I would like to thank the Oklahoma Center for the

Advancement of Science and Technology (OCAST) and the College of Engineering at OU for financial support. Finally I would like to thank the Fulbright program for my scholarship; part of the work described here was performed during the period covered by it.

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CHAPTER 6

INFLUENCE OF H₂ ADDITION DURING THE GROWTH OF SINGLE WALLED CARBON NANOTUBES PRODUCED BY CO DISPROPORTIONATION OVER A Co-Mo CATALYST

6.1. INTRODUCTION

In Chapter 2 we showed how a synergism between Co and Mo is critical for the performance of a silica supported Co-Mo catalyst used for production of SWNT by CO disproportionation. Moreover, through a detailed characterization process that involved a variety of characterization techniques such as Raman spectroscopy, EXAFS, XANES, UV/Vis-DRS, XPS, TPR and DRIFTS of adsorbed NO, we were able to explain the reasons for the high selectivity of this catalyst.

As described in Chapter 5, a supported metal particle is highly susceptible to aggregation by sintering when it is in the metallic state (zero valent) and is subjected to the high temperatures needed for the synthesis of SWNT. The rule of thumb to determine the onset of rapid sintering (Tamman temperature [1]) was also introduced on Chapter 5. Accordingly, metals usually employed in SWNT synthesis, such as Ni and Co, would rapidly sinter on any support at temperatures above 590°C and 610°C, respectively. These temperatures are much lower than those needed for the synthesis of SWNT. As a result, one cannot have reduced metal particles on a support before

starting the SWNT growth because by the time the reaction starts the metal particles will not be small enough to catalyze the growth of SWNT [2], and large metal clusters known to catalyze the growth of defective multi-walled nanotubes and nanofibers will be formed instead [3-6].

We have described in the earlier chapters how we can avoid particle sintering by designing a catalyst that is produced only under reaction conditions. The surface cobalt molybdate structure proposed in Chapter 2 is an effective catalyst when it is reduced in-situ by the same carbon-containing reactant that produces the SWNT. Only under these specific conditions SWNT with high selectivity can be produced.

The selectivity of this particular catalyst towards SWNT production strongly depends on the stabilization of Co^{2+} species by Mo oxide species. We found that the extent of the Co-Mo interaction is a function of the Co:Mo ratio in the catalyst and has different forms during the different stages of the catalyst life. We demonstrated that in the calcined state, Mo is in the form of a well dispersed Mo(6+) oxide, while the state of Co strongly depends on the Co:Mo ratio. At low Co:Mo ratios, it interacts with Mo in a superficial Co molybdate-like structure. At high Co:Mo ratios, it forms a non-interacting Co_3O_4 phase. During the subsequent reduction treatment in hydrogen, the non-interacting Co phase is reduced to metallic Co, while the Co molybdate-like species remain as well-dispersed Co^{2+} ions. This Co-Mo interaction inhibits the Co sintering that typically occurs at the high temperatures required for the

formation of carbon nanotubes. When large Co particles are present less desirable forms of carbon (mostly graphitic nanofibers) are produced. By contrast, when the Co clusters are very small only SWNT are produced.

In the previous chapter, we proposed that when metal atoms begin to agglomerate in the presence of gaseous CO, there is a nucleation period over which there is no growth of nanotubes. This nucleation involves the disruption of Co atoms from its interaction with Mo oxide when the latter becomes carbidic. This disruption would be then followed by surface migration leading to agglomeration into mobile clusters that continue to grow under the bombardment of CO molecules. Subsequently these molecules decompose and begin to rearrange (nucleate) until a given configuration and carbon surface concentration is reached, which favor the formation of the nanotube. We proposed to call this configuration *embryo*. When this embryo is formed, the subsequent incorporation of carbon and SWNT formation would proceed at a fast rate, perhaps only controlled by mass transfer. As a result, we concluded that the growth of each nanotube is limited by nucleation, and after nucleation is completed, mass transfer controls it. The diameter of the nanotube therefore should be determined by the size of the embryo. As a consequence, we suggested that the control of nanotube diameter is in principle possible by control of the size of the metal cluster.

We have tested the validity of this hypothesis in the previous chapters. On Chapter 3 we tested a bimetallic Co-W catalyst that is chemically similar to the Co-Mo system and successfully elaborated an analogy between both catalytic systems. On Chapter 4 we broke up the Co-Mo interaction by introducing sodium that competes with Co for the formation of a Na-molybdate. In correspondence to our proposed hypothesis, we observed how the addition of Na had a negative effect on nanotube selectivity.

Similarly, in Chapter 5 we tested our model by varying the growth temperature. By means of a detailed analysis we were able to demonstrate that the diameter of SWNTs obtained by CO disproportionation over a Co-Mo catalyst can indeed be varied by changing the operating temperature. This result was linked to the sintering rate of the Co metal clusters that originate the nanotubes, which is faster at higher temperatures.

On this last chapter we will test the validity of our proposed hypothesis once again. We will attempt to control the metallic cluster growth by incorporating different amounts of hydrogen to the reaction feedstock. It is known that the presence of hydrogen in the gas phase greatly reduces the *fugacity* of carbonaceous species on the surface. Therefore, it is expected that this reduction in surface fugacity would delay the nanotube growth by delaying the nucleation process. If that were the case, in the competition between metal cluster agglomeration and nanotube growth, the

former would be favored. If our hypothesis is correct, depending on the hydrogen concentration we ought to observe an increase in nanotube diameter or even a loss in nanotube selectivity compared to nanofibers when the particle diameter becomes too large to form embryos able to grow SWNT.

6.2. EXPERIMENTAL

6.2.1. SWNT synthesis and purification

The details of the synthesis of SWNT from CO disproportionation over a highly selective CoMo catalyst have been described in Chapter 2. In brief, the SWNT samples were obtained using a supported bimetallic Co-Mo catalyst with a total metallic loading of 2 wt. % and a Co:Mo molar ratio of 1:3. Prior to the production of SWNT by CO disproportionation, the CoMo catalyst was heated in H₂ flow to 500°C, and then in He flow to the reaction temperature (750°C), the incorporation of hydrogen to the feed was achieved by premixing pure CO with controlled amounts of H₂ by means of mass flow controllers. After nanotube growth the reactor was cooled to room temperature in He flow.

Following reaction, a sequence of treatments was carried out in order to remove the catalyst. The first step in this sequence was a low-temperature oxidation for the elimination of the amorphous carbon, which was accomplished by calcination in air at 300°C for 2 h. The second step was the elimination of the silica support. In this step, 1 g. of the material was suspended in a NaOH 0.2 M solution while stirring

for 24 h at 65°C. After filtering through a Teflon-PTFE 0.2 mm membrane, the remaining solid was washed with deionized water until the pH was neutral and then the solid was dried overnight at room temperature inside a desiccator. The third step was the elimination of the metals (Co and Mo). This was accomplished by an acid attack in reflux of 2 M nitric acid, until the evolution of NO₂ vapors subsided. Again, the solid part was filtered and washed as before. The total removal of silica and metals after both steps was about 95-99%, as determined by atomic absorption analysis.

6.2.2. SWNT characterization

To characterize the SWNT, we have used a combination of transmission electron microscopy (TEM), Raman spectroscopy, and optical absorption spectroscopy. The TEM images were obtained in a JEOL JEM-2000FX TEM. For this analysis, a suspension in isopropanol was achieved by stirring the solid sample with ultrasound for 10 min. A few drops of the resulting suspension were deposited on a TEM grid and subsequently dried and evacuated before the analysis. Raman spectra were obtained in a Jovin Yvon-Horiba Lab Ram equipped with a CCD detector and with three different laser excitation sources having wavelengths of 632 (He-Ne laser) 514 and 488 eV (Ar laser).

To perform the optical absorption analysis, the purified SWNT were added to an aqueous solution containing the surfactant sodium dodecylbenzene sulfonate

(NaDDBS) at twice its critical micelle concentration, and ultrasonically agitated for 1 h using a Fisher Scientific Model 550 homogenizer (550 W output). This created a stable suspension of individual and bundled nanotubes. This suspension was centrifuged for 1 h at 4000 rpm to separate residual metallic catalyst particles and suspended tube bundles from the lower density surfactant-suspended individual nanotubes. Finally, the supernatant liquid was withdrawn for spectral analysis. The absorption of light as a function of wavelength was measured using a Bruker Equinox 55 FTIR/FTNIR/FTVis; 60 scans at 30cm^{-1} resolution were averaged on each spectrum in order to achieve a high signal to noise ratio.

6.3. RESULTS AND DISCUSSION

6.3.1. Raman Spectroscopy

The quality of the nanotubes obtained at different reaction conditions was investigated by Raman spectroscopy, following the method described in Chapter 1. As mentioned before, from the analysis of radial A_{1g} breathing mode direct information about the tubes diameter was obtained [7], while the analysis of the G band in the tangential mode range i.e. $1400\text{-}1700\text{ cm}^{-1}$, provided information on the electronic properties of the nanotubes. In addition, the analysis of the so-called D-band at around 1350 cm^{-1} gave an indication of the level of disordered carbon. Therefore, we have used the intensity ratio of the D band (1350 cm^{-1}) to the G band (1590 cm^{-1}) as semi-quantitative measurement of the formation of undesirable forms of carbon [8, 9] as in the case described in Chapter 5.

Figure 6.1 shows the Raman spectra of the product obtained by CO disproportionation in the presence of three different concentrations of hydrogen in the feed. A clear difference is observed when the product obtained in the absence of H_2 is compared to that obtained when using 10% H_2 in the feed. It is clear that the D band contribution becomes much stronger in the spectra of the products obtained using a higher H_2 concentration. This trend is better illustrated in Fig. 6.2, which shows the gradual increase of the D band in terms of the expression $(1 - D/G)$ as a function of the H_2 concentration. From this analysis it becomes clear that the selectivity to SWNT has been greatly reduced by the presence of hydrogen in the feed. We can suggest that this loss in nanotube selectivity is originated by a large increase in the particle diameter in such a way that it becomes too large to spawn embryos able to form SWNT and MWNT and graphitic fibers are generated instead.

From Figure 6.1 a more subtle change on the RBM region can be also observed, when the amount of H_2 to the feed increases from 0 to 6%. The product obtained without any hydrogen present in the feed exhibits a dominant peak centered at around 278 cm^{-1} , which would correspond to a nanotube diameter of approximately 0.85 nm. When 6% of hydrogen is present in the feed a new peak becomes dominant at lower wavenumbers (188 cm^{-1}), clearly indicating the appearance of nanotubes of larger diameter. Again, as described in Chapter 1 due to the resonant character of the Raman spectra of SWNT the diameter values obtained by the analysis of the breathing mode band from the Raman spectra acquired using only one laser energy

may not represent the whole range of nanotube diameters other than the sub-set of nanotubes that are in resonance with the laser energy. Therefore, in order to get information that is more representative of the diameter distribution of the SWNTs in the sample it is necessary to probe the SWNT with several excitation energies.

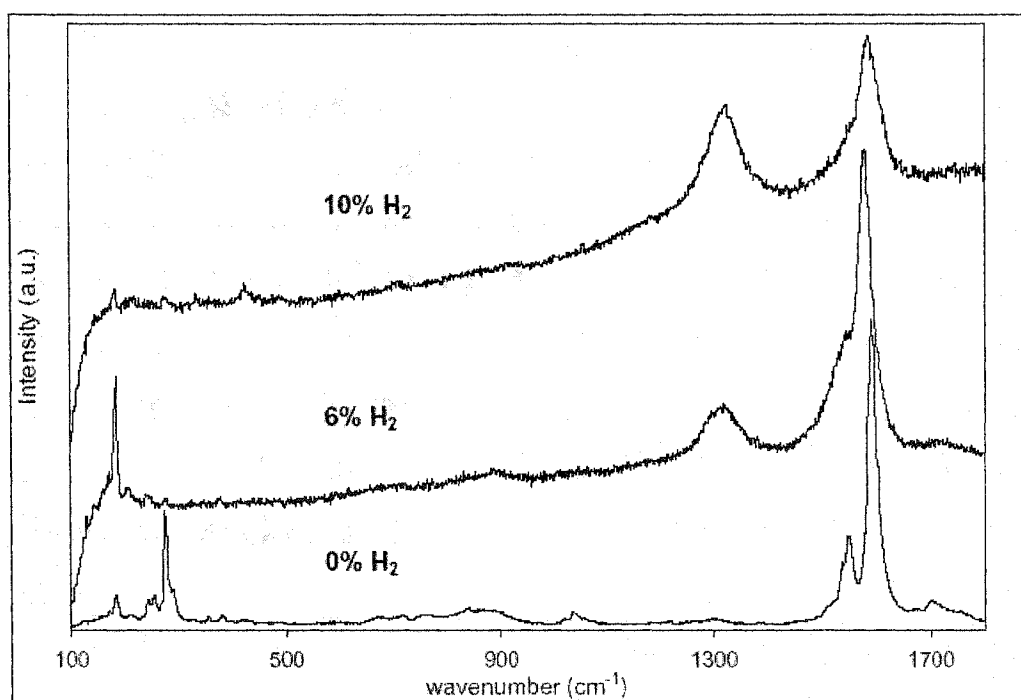


Figure 6.1. Raman spectra of the SWNT growth at 750°C over a CoMo(1:3)/SiO₂ catalyst by CO disproportionation adding three different amounts of H₂ to the reaction feedstock. The laser excitation line was 633nm.

Figure 6.3 shows one of such analysis; in this case the breathing modes bands in the Raman spectra were obtained with three different laser excitation energies on SWNT samples obtained by CO disproportionation in the presence of different

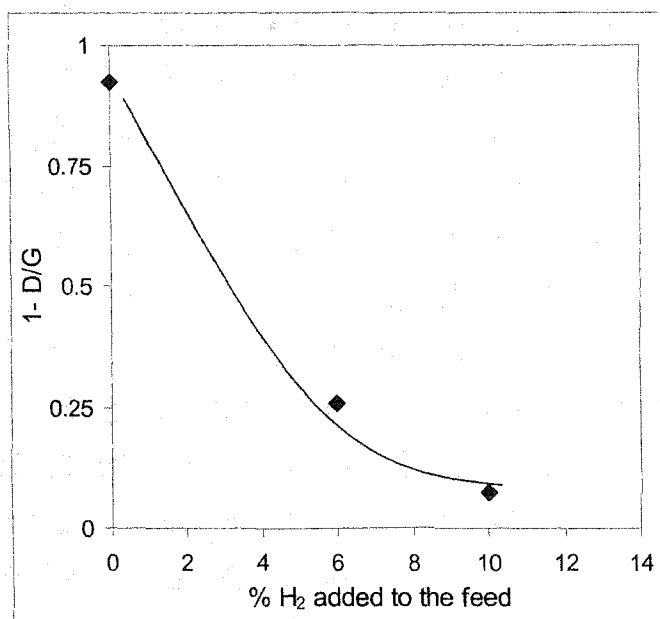


Figure 6.2. Contributions of the D band to the Raman spectra of the carbon deposits growth at 750°C over a CoMo(1:3)/SiO₂ catalyst by CO disproportionation adding three different amounts of H₂ to the reaction feedstock. The contributions of the D band to the Raman spectra are expressed using a quality parameter: $1 - D/G$; where D and G are the integrated areas of the D and G Raman bands respectively. The laser excitation line was 633 nm

hydrogen concentrations. The 3 spectra for the same given sample are quite different, depending on the laser excitation energy used, but the same trend is observed at all energies. That is, the bands clearly shift to lower wavenumbers as the hydrogen concentration in the feed increases. Since the frequency of the radial breathing mode is inversely proportional to the nanonotube diameter, this shift indicates an increase in diameter as the amount of H₂ present in the feed increases.

As described in Chapter 1 and 4, it is possible to link nanotube diameters with the energy gaps between singularities in the valence and conduction bands of the

electronic density of states of SWNT by calculating the one-dimensional energy band structure of SWNT. The earliest of these kind of calculations was performed by Kataura et al. [10] in 1999. Those results are reproduced in Figure 6.4 and are compared to the experimental data obtained for the SWNT synthesized by CO disproportionation in the presence of different hydrogen concentrations. In this figure, the calculated results for each individual nanotube were used as a background, with the solid and open circles representing nanotubes with metallic and semiconducting character, respectively. Superimposed over this background, the Raman data obtained in the present chapter are indicated with solid triangles. Points are marked for the particular energy of the laser employed (i.e., 2.0, 2.4, or 2.55 eV) and for each observed nanotube diameter, as inferred from the frequency of the radial breathing mode bands.

Following the same method described in Chapter 4 it is possible to delineate a “metallic window” for which the resonance condition for metallic nanotubes would take place in the energy region 2.4-2.7 eV for the SWNT obtained without H₂ present in the feed. Therefore, it is expected that for this particular sample, the two lasers with higher energy (2.4 and 2.55 eV), which fall within this window would only probe metallic nanotubes. By inspecting Fig. 6.5a one can see that, in agreement with this expectation, the shape of the G band detected with the 514 nm laser correspond to metallic SWNT only for the product obtained without H₂. In contrast, as the amount of H₂ present in the feed increases the shift to larger nanotube diameter is connected

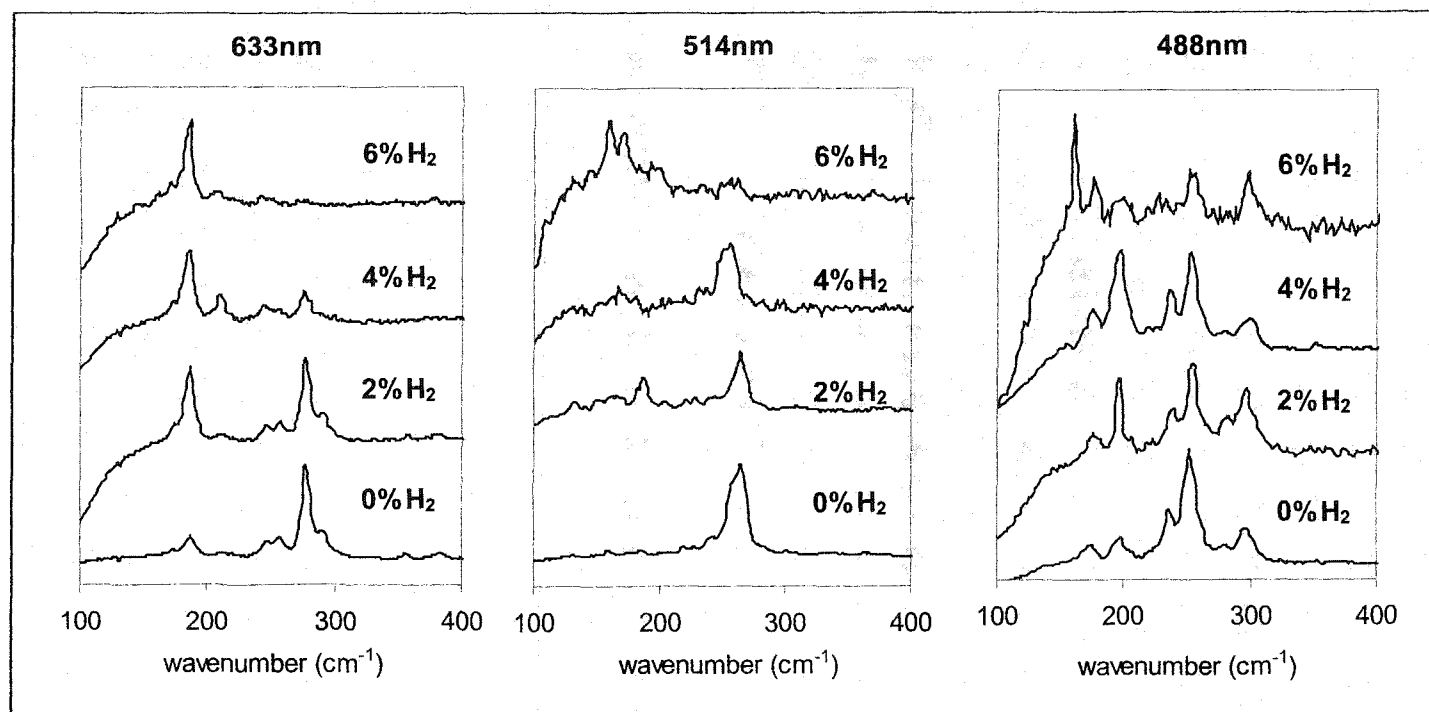


Figure 6.3. Radial breathing mode resonant Raman spectra of SWNT grown for 2 hours at 750°C over a CoMo(1:3)/SiO₂ catalyst by CO disproportionation adding three different amounts of H₂ to the reaction feedstock. The excitation wavelengths were 488 nm (2.55 eV), 514 nm (2.4 eV) and 633 nm (2.0 eV).

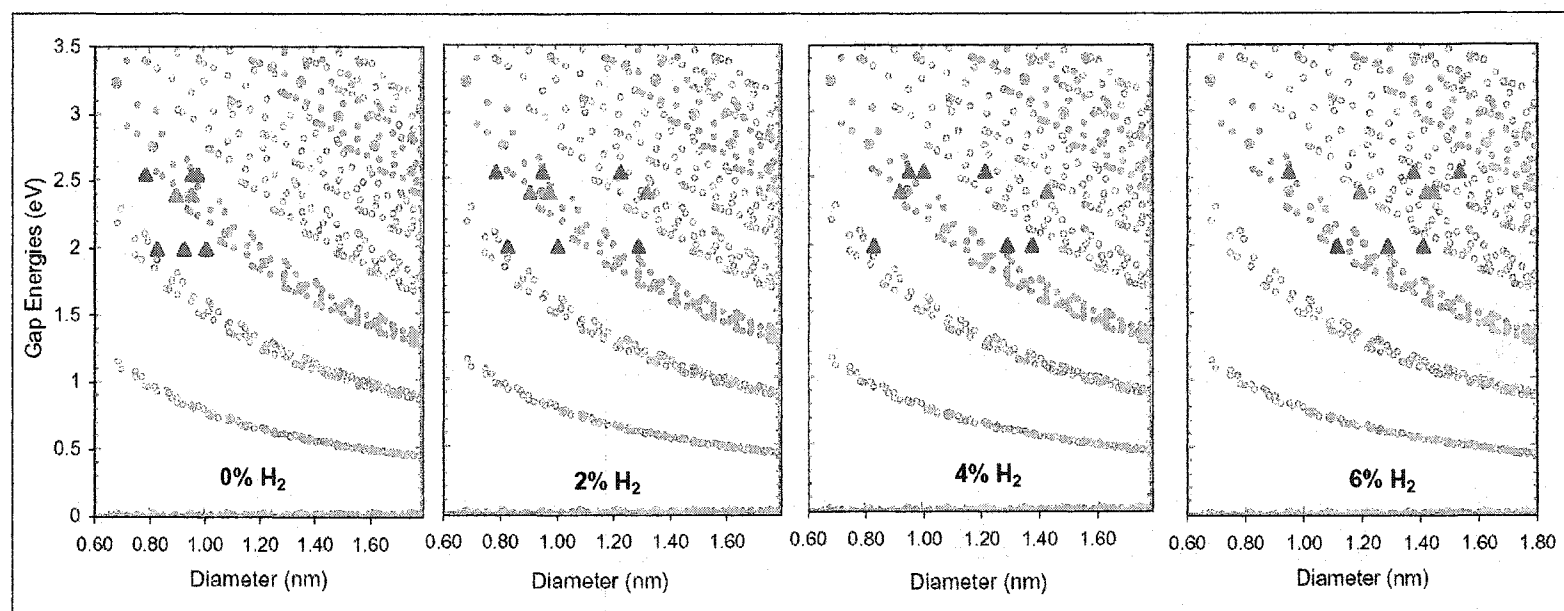


Figure 6.4. Calculated gap energies as a function of diameter for SWNT, calculated by Kataura et. al. (reproduced from ref. 10). The solid circles indicate the metallic SWNT and open circles the semiconducting ones. The filled diamonds indicate the diameter of the SWNTs as determined from the radial breathing mode bands of the Raman spectra of the samples obtained by adding four different amounts of H_2 to the reaction feedstock with three different laser energies.

a decrease on the metallic character of the SWNT probed with this particular laser which in turn originates a decrease in the contribution of the Breit-Wigner-Fano feature centered at 1540 cm^{-1} as can be observed in Figure 6.5.

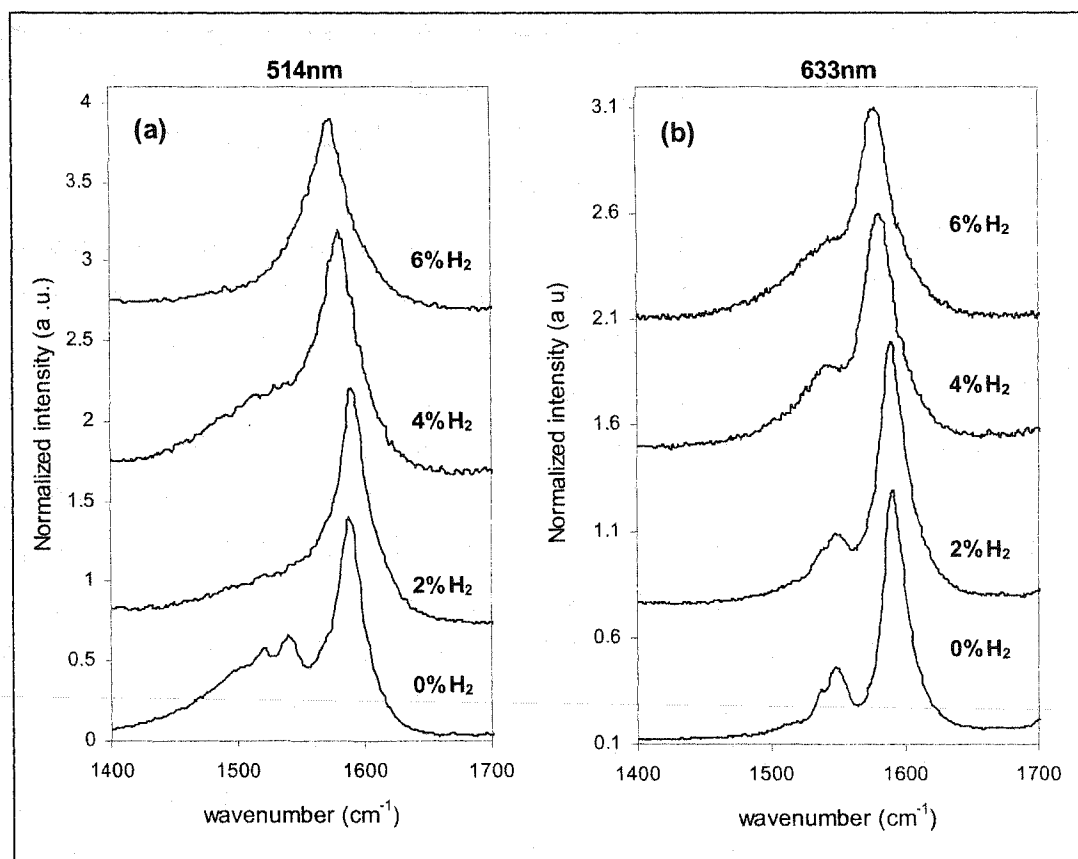


Figure 6.5. Resonant Raman spectra in the tangential mode (G mode) obtained using two different laser excitation energies, for SWNT samples produced by CO disproportionation adding three different amounts of H₂ to the reaction feedstock.

Another interesting trend is illustrated in Fig. 6.5b; in this case we perform the same kind of analysis but using the Raman spectra obtained with the 633 nm laser

The results obtained with this laser show a remarkable contrast to the results described in Figure 6.5a. While in the case of the 514 nm laser a decrease on the metallic character of the probed SWNTs was apparent when the amount of H_2 present on the feed increased, for the 633nm laser an increase on the metallic character is observed. This can be interpreted in terms of the gap energy plots as a function of nanotube diameter shown in Fig 6.4. As the amount of H_2 in the reaction feed increased, nanotubes of larger diameters were formed and, at this particular laser energy (633nm), the fraction of semiconducting nanotubes probed decreased.

6.3.2 Optical absorption

In the last section, a clear trend to larger diameters was observed in the Raman spectra as the amount of hydrogen increased in the feed. However, as discussed in Chapter 1, the information resulting from the Raman analysis might not represent the whole range of nanotube diameters and can be masked by resonance phenomena. Therefore, in order to get more representative information of the SWNT diameter distribution, optical absorption spectroscopy was performed on each of the samples.

In Chapter 1 we illustrated how light in the visible and near infrared range can be absorbed by SWNT when its energy matches an allowed electronic transition between Van Hove singularities. The observed absorption peaks are thus related to interband transitions E_{ii} between the i^{th} van Hove singularity in the valence band (occupied states) to the i^{th} singularity in the conduction band (empty states)[11-16].

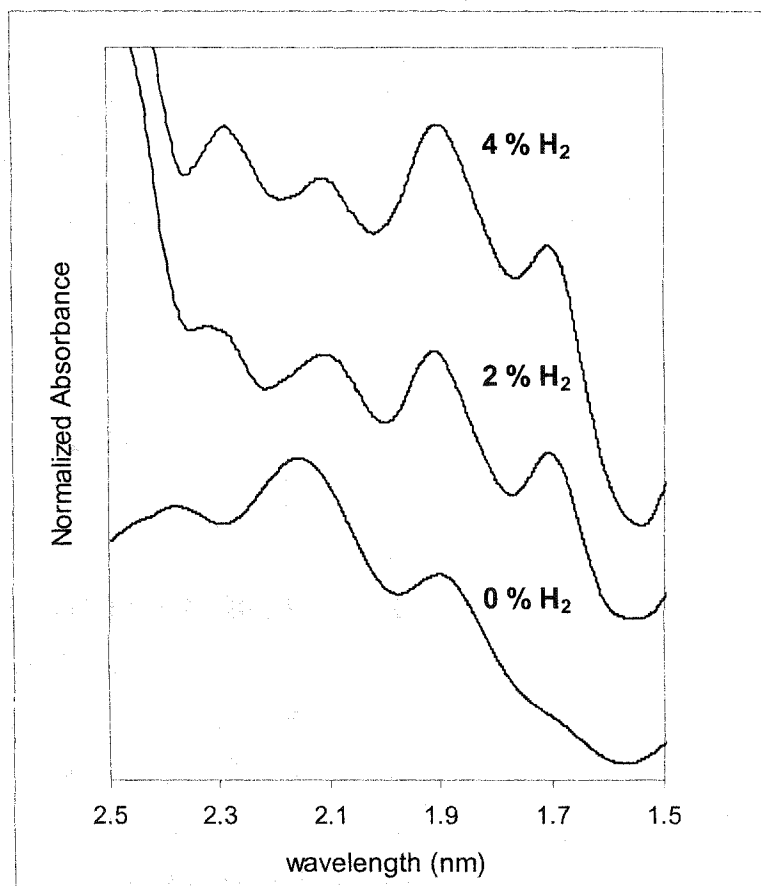


Figure 6.6. Optical absorption spectra showing the second Van Hove transitions for three different SWNT samples produced by CO disproportionation adding three different amounts of H₂ to the reaction feedstock.

Figure 6.6 shows typical optical absorption spectra in the visible range (500 to 800 nm) obtained for three different samples synthesized from CO disproportionation with different amounts of H₂ present in the feed. For the sample obtained without hydrogen in the feed a prominent absorption band at 2.14 eV and two smaller bands at 2.37 and 1.89 eV are observed. These bands are related to interband transitions

between the second van Hove singularity (E_{22}^S) for semiconducting nanotubes and E_{22}^M for metallic nanotubes, as can be predicted by observing Figure 6.4. By contrast for the samples obtained with 2% and 4% hydrogen present on the feed a band at 1.90eV becomes prominent and a new band at 1.70eV appeared. The theoretical calculations depicted in Figure 6.4 indicate that this kind of red shift in the optical absorption to higher energies displayed for the samples obtained with H_2 present should be related to an increase on the average diameter of the SWNT.

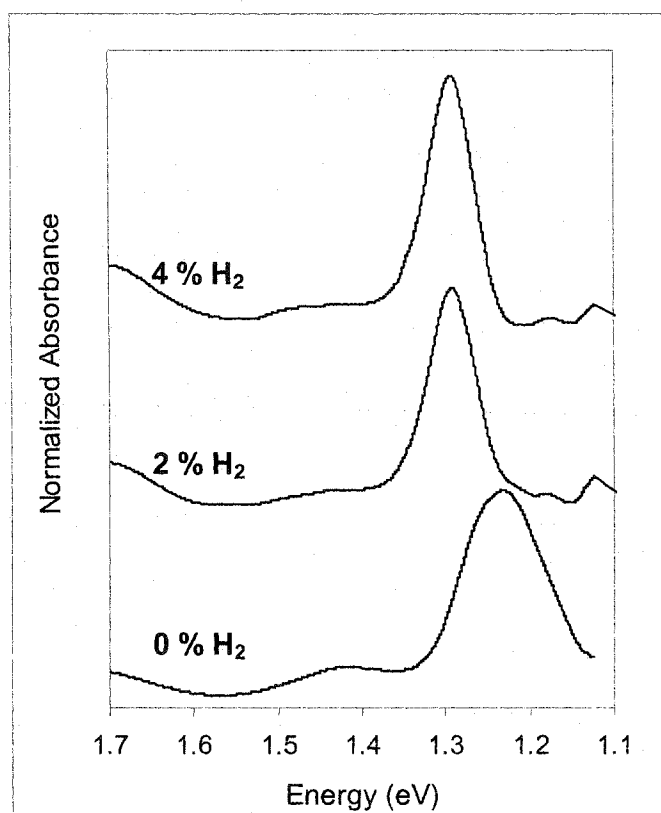


Figure 6.7. Optical absorption spectra in the near infrared region for three different SWNT samples produced by CO disproportionation adding three different amounts of H_2 to the reaction feedstock.

In Chapter 1 we illustrated how Bachilo and coworkers [17] described a method for relating the SWNT diameter and chirality with the position of the experimental values of the first and second Van Hove transitions obtained by fluorescence experiments. Recently the same authors have reported an extension of their method that comprises results obtained by optical absorption spectroscopy [18-20]. Table 6.1 shows the results obtained when the method proposed by these authors is used to rationalize the peak positions observed in Figure 6.6. The table shows the position of the absorption bands in eV and also in nanometers as well as potential values of SWNT diameters and chiralities that are related to these particular transitions.

To perform a direct assignment of the diameters and chiralities of the semiconducting SWNT present in the sample, the values for the first van Hove transitions that generate the peaks in the low energy region of the absorption spectra must be analyzed. Figure 6.7 shows the low energy absorption spectra for the same sample series presented in Figure 6.6. In this region an analysis as the one described in Table 6.1 is not as straightforward because the regions for the first and second van Hove transitions overlap. However a tentative assignment can be done in light of the results obtained by Raman spectroscopy, the high-energy region of the optical absorption spectra, and recent fluorescence results obtained [21]. For example, the prominent band centered at 1.23eV in the optical absorption spectrum of the sample obtained by CO disproportionation without H₂ present in the reaction mixture is

Table 6.1. Potential structure assignment for semiconducting SWNTs based on the position of the second van Hove optical transitions (as predicted by reference 18) for the samples obtained by disproportionation of CO at 750°C over a CoMo(1:3)/SiO₂ catalyst with three different amounts of H₂ added to the reaction feedstock. The relative intensities of the observed bands are marked as m (medium intensity) and h (high intensity).

0 % H₂					
<i>Energy (eV)</i>	<i>wavelength (nm)</i>	<i>Peak Intensity</i>	<i>Diameter (nm)</i>	<i>Chirality (α) (deg)</i>	<i>Chiral indexes (n, m)</i>
2.374	526	m	0.556	21.7	5,3
2.457	508	m	0.706	17.0	7,3
2.307	541	m	0.79	0	10,0
2.105	593	h	0.84	19.1	8,4
2.146	582	h	0.69	23.41	6,4
1.863	662	m	0.78	15.3	8,3
1.878	664	m	0.64	0	8,0
1.845	677	m	0.976	20.63	9,5
2 % H₂					
<i>Energy (eV)</i>	<i>wavelength (nm)</i>	<i>Peak Intensity</i>	<i>Diameter (nm)</i>	<i>Chirality (α) (deg)</i>	<i>Nanotube index (n, m)</i>
2.307	541	m	0.79	0	10,0
2.251	555	m	0.806	9.8	9,2
2.374	526	m	0.556	21.7	5,3
2.101	594	m	0.84	19.1	8,4
2.146	582	m	0.69	23.4	6,4
1.88	664	m	0.64	0	8,0
1.878	669	m	0.64	0	8,0
1.845	676	m	0.976	20.63	9,5
1.70	735	h	0.89	8.95	10,2
1.68	743	h	1.032	27.8	8,7
4 % H₂					
<i>Energy (eV)</i>	<i>wavelength (nm)</i>	<i>Peak Intensity</i>	<i>Diameter (nm)</i>	<i>Chirality (α) (deg)</i>	<i>Nanotube index (n, m)</i>
2.307	541	m	0.79	0	10,0
2.251	555	m	0.806	9.8	9,2
2.374	526	m	0.556	21.7	5,3
2.101	594	m	0.84	19.1	8,4
2.146	582	m	0.69	23.4	6,4
1.88	664	m	0.64	0	8,0
1.878	669	m	0.64	0	8,0
1.845	676	m	0.976	20.63	9,5
1.70	735	h	0.89	8.95	10,2
1.68	743	h	1.032	27.8	8,7

possibly originated by the first van Hove transition of the SWNT with small diameters (0.7-0.8nm), which are the same tubes observed by Raman spectroscopy (see Figure 6.4). In contrast the band centered at 1.28eV that appears on the samples obtained when H₂ is present in the action feedstock might be assigned to second van Hove transitions of nanotubes with large diameters (around 1.2 nm), as can be inferred from the Kataura plot in Fig. 6.4.

Once the results presented in Figures 6.6 and 6.7 are combined in such a way that the values for the first (observed and predicted) and second (observed) Van Hove transitions are compared, it is possible to perform a direct assignment of the semiconducting SWNT structures present in the sample. Figure 6.8 presents this kind of analysis for samples obtained by CO disproportionation with two different amounts of H₂ present in the feed. The assignment of the chiral indexes for the SWNT structures are based on empirical formulas reported by Bachilo and Weisman [18], which relate the position of the first and second Van Hove transition to the SWNT chiral indexes. The corresponding map of possible nanotube structures for the same two samples is presented also in Figure 6.8 in the form of a graphene sheet segment, with (n,m) values labeling semiconducting SWNT structures. This map clearly reveals a change on the diameter of the SWNT obtained as the amount of H₂ in the feed varies. Although in this analysis only the semiconducting SWNT are considered, the same trend obtained during the Raman analysis is observed, that is,

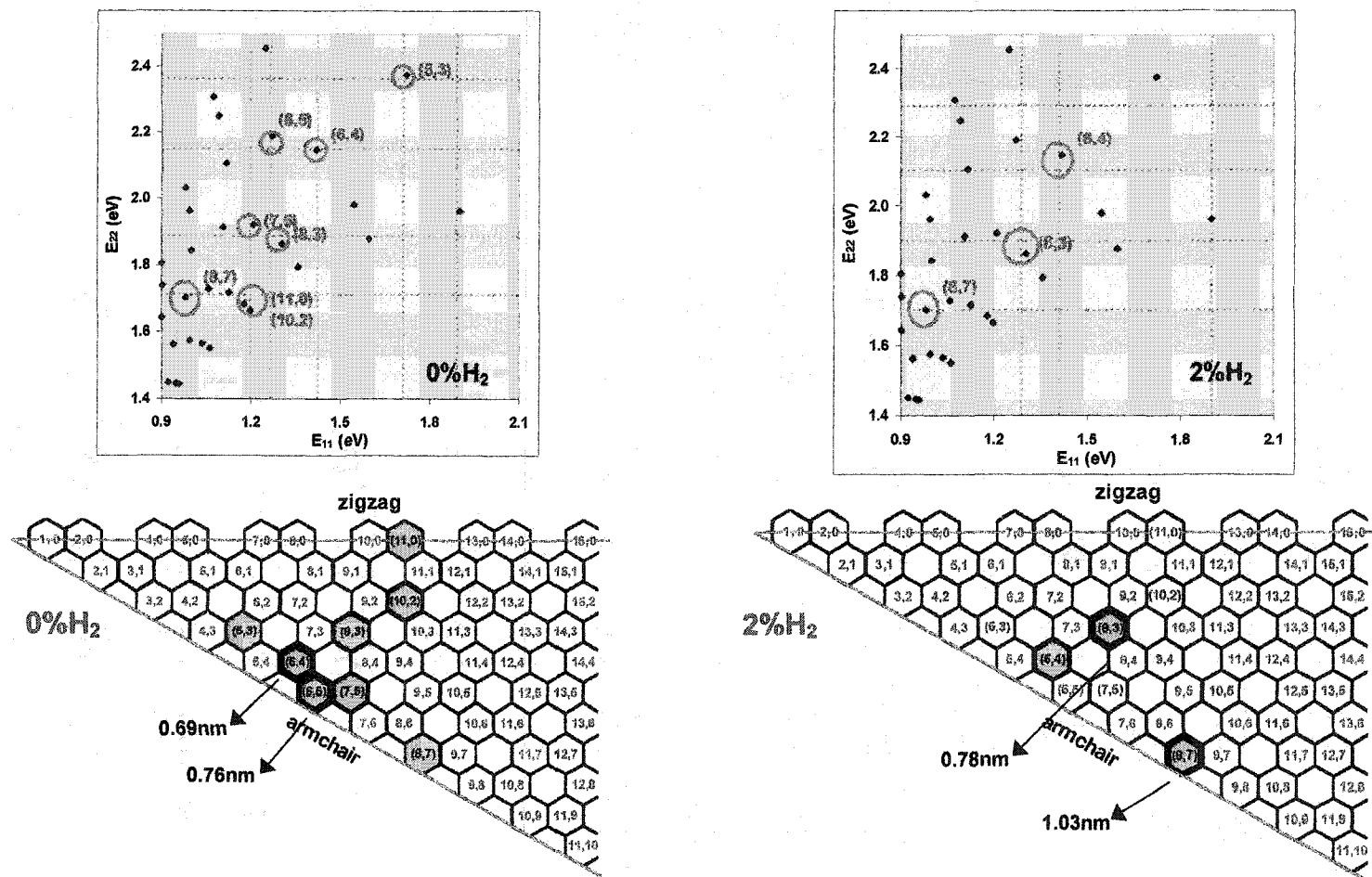


Figure 6.8. Upper panels: Observed first and second van Hove transitions and structure assignment for semiconducting SWNT (as predicted by reference 18) obtained with two different amounts of H_2 . Lower panels (n,m) resolved map of semiconducting SWNT for the same set of samples in the form of a graphene sheet segment. The thickness of each hexagonal cell in the graphene sheet is proportional to the observed intensity for that structure. The tube diameter is also indicated for the main SWNT structures present on each sample.

the nanotube diameters shift to larger values the amount of hydrogen increases in the reaction feedstock.

6.3.3 TEM analysis

Electron microscopy was performed on the samples to corroborate the results obtained from Raman and optical absorption spectroscopy. A typical TEM image of the sample obtained by CO disproportionation without hydrogen in the feed is shown in Figure 6.8a, which provides structure details of the SWNT sample. It shows the exclusively presence of bundled SWNTs. In perfect agreement with the results obtained by Raman spectroscopy and optical absorption the diameter of the tubes measured from the TEM micrograms is around 0.9 nm as shown in Figure 6.9. Together with the SWNT bundles many metallic particles (1 nm average diameter) are also observed.

A typical TEM image of the sample obtained with 10% hydrogen in the feed is shown in Figure 6.9b. SWNT were also observed in this sample, however the proportion of SWNT bundles versus that of MWNT was observed to be very small for the sample obtained with 6% H₂, and almost negligible for the sample obtained with 10% of H₂ in the feed. The observations of the catalyst particle sizes obtained by TEM also revealed that the samples synthesized with more than 5% of H₂ in the feed generate very large metallic particles. In particular in Figure 6.9b it is easy to observe big metallic particles with diameter larger than 10 nm, partially superimposed with

the silica support. As proposed by our hypothesis these particles are too large to have been active for the catalytic growth of a nanotubes and as a consequence they have been encapsulated by graphene sheets. We need to emphasize also that, in agreement

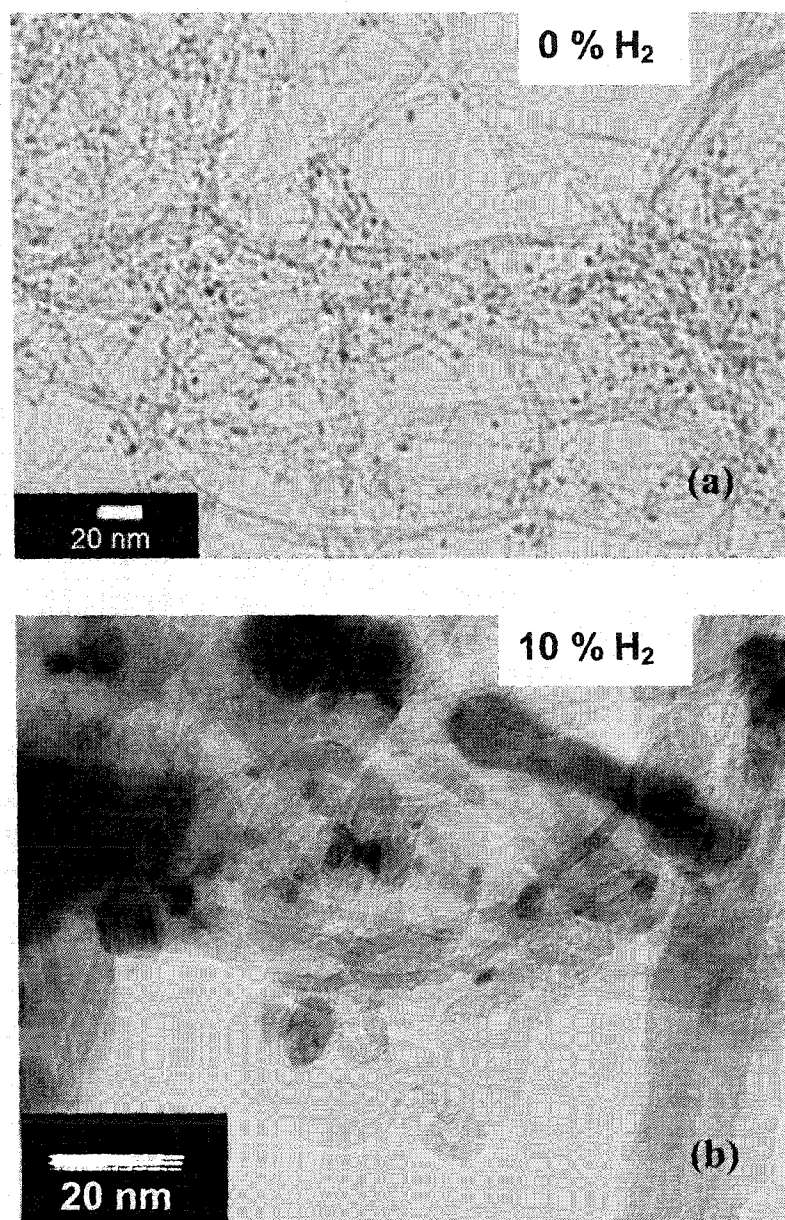


Figure 6.9. Typical TEM micrographs of SWNT produced by CO disproportionation at 750°C on a Co:Mo catalyst using two different amounts of H₂ in the reaction feedstock.

with the results obtained by Raman and optical absorption spectroscopy, bundles of small SWNTs (0.9 nm) as those showed in Figure 6.9a were not observed on this particular sample.

As pointed out in Chapter 5, the distributions in tube diameter should reflect a mechanism in which the diameter is established by the catalytic particle. [22-25]. In this context , if the average diameter distribution of the metallic particles

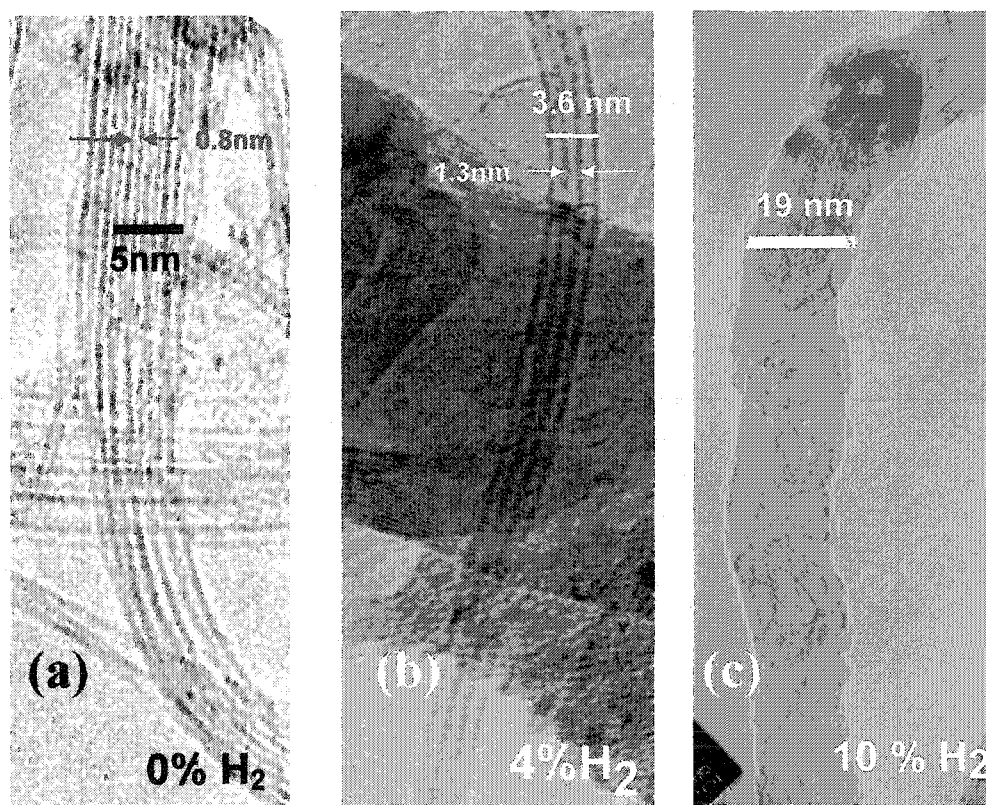


Figure 6.10. Detailed TEM micrographs of the different carbon species produced by CO disproportionation at 750°C on a Co:Mo catalyst using three different amounts of H₂ in the reaction feedstock.

shown in Figure 6.9a is compared to the one obtained from the micrographs shown in Figure 6.9b the results obtained is in excellent agreement with our hypothesis; that is catalyst particles with a diameter below 1 nm are observed together with SWNT, while larger metallic particles, like the ones observed in Figure 6.8b are encapsulated.

Figure 6.10 shows more detail on the structure of the carbon species obtained with different concentrations of H_2 in the feed. As shown in Chapter 4 and Figure 6.10a the sample obtained by CO disproportionation at $750^\circ C$ without H_2 present yields mostly SWNT with an average diameter of 0.9 nm. By contrast with a small amount of hydrogen is present in the sample, SWNT of larger diameters are formed. In the particular case of 4% H_2 present in the feed nanotubes of diameters up to 1.5 nm should be formed as observed by Raman spectroscopy. The detailed TEM micrograph for this sample shown in Figure 6.10b fully supports this result; if a careful measurement of the diameter of the SWNTs present in the thin bundled shown in Fig. 6.10b is performed an average value of 1.3 nm would be obtained. Another interesting observation can be seized from the TEM micrographs of the sample obtained using a larger amount of H_2 in the feed; graphitic nanofibers (Figure 6.10c) and very crystalline MWNT with lattice spacing 3.4 Å (not shown) were observed.

6.4. CONCLUSION

The presence of hydrogen in the reaction feedstock greatly reduces the *fugacity* of carbonaceous species on the metallic particles that generate the embryos

that start off SWNT growth. This reduction in surface fugacity delays the nanotube growth by slowing down the nucleation process described in Chapter 4. When this occurs during the competition between metal cluster agglomeration and nanotube growth, the former is favored. As a result, depending on the hydrogen concentration we observed an increase in nanotube diameter at low H₂ concentrations and a loss in nanotube selectivity compared to MWNT and nanofibers when the particle diameter becomes too large to form embryos able to grow SWNT. These results are in agreement with the model proposed in Chapter 5.

ACKNOWLEDGEMENTS

This research was conducted with financial support from the Department of Energy, Office of Basic Energy Sciences (grant No. DE-FG03-02ER15345) and the Oklahoma Center for the Advancement of Science and Technology (OCAST). I would like to thank Dr. Guoda Lian for his diligence on getting the TEM micrographs.

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PUBLICATIONS, PATENTS AND PRESENTATIONS

RESULTING FROM THIS THESIS

Publications

1. *"Influence of the hydrogen incorporation during SWNT growth by CO disproportionation"*
In preparation
2. *"Loss of single-walled carbon nanotubes selectivity by disruption of the Co-Mo interaction in the catalyst"*
Jose E. Herrera and Daniel E. Resasco*
Journal of Catalysis, in press
3. *"Narrow (n,m) distribution of single walled carbon nanotubes growth using a solid supported catalysts"*
Sergei M. Bachilo, L. Balzano, Jose E. Herrera, Francisco Pompeo, Daniel Resasco and R. Bruce Weisman
Journal of the American Chemical Society, 2003ASAP
4. *"Decomposition of carbon-containing compounds on solid catalysts for SWNT production"*
Daniel E. Resasco, Jose E. Herrera and L. Balzano
J. Nanosci. Nanotech. In press
5. *"In-Situ TPO/Raman to Characterize Single-Walled Carbon Nanotubes"*
J. E. Herrera and D. E. Resasco
Chem. Phys. Lett. 376 302-309, 2003
6. **Book Chapter:** *"Structural Characterization of Single-Walled Carbon Nanotubes"*
Daniel E. Resasco and Jose E. Herrera.
Encyclopedia of Nanoscience and Nanotechnology, (2003) American Scientific Publishers (H. S. Nalwa Ed.), Vol. 10, pp 1-23
7. **Patent Application:** Daniel E. Resasco, Walter E. Alvarez, Jose E. Herrera and Leandro Balzano. *Method and catalyst for producing single walled carbon nanotubes.* U.S. Pat. Appl. Publ. (2003), 35 pp. CODEN: USXXCO US 2003091496 A1 20030515 CAN 138:371051 AN 2003:376121
8. *"Role of Co-W Interaction in the Selective Growth of Single-Walled Carbon Nanotubes from CO Disproportionation"*

J. E. Herrera and D. E. Resasco
J. Phys. Chem. B. 107 (2003) 3738-3746

9. *"Raman Characterization of SWNT of Various Diameters Obtained by Catalytic Disproportionation of CO"*
J. E. Herrera, L. Balzano, F. Pompeo, and D.E. Resasco
J. Nanosci. Nanotech. 3 (2003) 133-138
10. *"Characterization of single-walled nanotubes (SWNT) produced by CO disproportionation on Co-Mo catalyst"*
W. E. Alvarez, F. Pompeo, J. E. Herrera, L. Balzano, D. E. Resasco
Chemistry of Materials, 14 (2002) 1853-1858
11. *"A Scalable Process for Production of Single-Walled Carbon Nanotubes (SWNT) by Catalytic Disproportionation of CO on a Solid Catalyst"*
D. E. Resasco, W. E. Alvarez, F. Pompeo, L. Balzano, J. E. Herrera, B. Kitiyanan, and A. Borgna
Journal of Nanoparticle Research, 4 (2002) 131-136
12. *"Relationship Between the Structure/Composition of Co-Mo Catalysts and their ability to Produce Single-Walled Carbon Nanotubes by CO Disproportionation"*
J. E. Herrera, L. Balzano, A. Borgna, W. E. Alvarez, D. E. Resasco
Journal of Catalysis 204, 129-145 (2001).

Presentations

1. *"Comparison between the activities of CoMo and CoW silica supported catalyst for SWNT production by CO disproportionation"*
J. E. Herrera, D. E. Resasco
18th North American Catalysis Society Meeting Cancun, Mexico, June 1-6, 2003
2. *"Temperature Programmed Techniques to Help Identify Different Fractions of Carbon in SWNT Samples" (Invited talk)*
J. E. Herrera,, F. Pompeo, L. Balzano, D. E. Resasco
Purity and Dispersion Measurement Issues Workshop on Single-Wall Carbon Nanotubes, NIST, Gaithersburg, MD
May 27-29th, 2003
3. *"Comparison of SWNT prepared by Catalytic Decomposition of Methane and Disproportionation of CO over Different Catalysts"*

- S. Xuto, T. Boonphyoong, P. Chungchamroenkit, J. E. Herrera, S. Chavadej, B. Kitiyanan, D. E. Resasco
2002 AIChE Annual Meeting (American Institute of Chemical Engineers)
Indianapolis, Indiana; November 3 - 8, 2002
4. "Control of Diameter and Diameter-related Reactivity of Carbon Nanotubes"
D. E. Resasco, J. E. Herrera, L. Balzano, F. Pompeo
2002 AIChE Annual Meeting (American Institute of Chemical Engineers)
Indianapolis, Indiana; November 3 - 8, 2002
 5. "Use of Raman spectroscopy to characterize the catalytic production of single wall carbon nanotubes"
J. E. Herrera, D. E. Resasco, L. Balzano, F. Pompeo
FACSS 2002 29th meeting of the Federation of Analytical Chemistry and Spectroscopy Societies
Providence, Rhode Island October 13-17 2002
 6. "Controlled synthesis of single walled carbon nanotubes by catalytic disproportionation of CO on a solid catalyst"
J. E. Herrera, L. Balzano, F. Pompeo, D. E. Resasco
Trends in Nanotechnology 2002 (TNT 2002) Santiago de Compostela (Spain)
September 9-13, 2002
 7. "Control of diameter and diameter-related reactivity of SWNT produced by catalytic decomposition"
D. E. Resasco, J. E. Herrera, W. E. Alvarez, L. Balzano, F. Pompeo
NT-02 International Conference on the Science and Application of Nanotubes
Boston July 6-11, 2002
 8. "Controlled Synthesis of Single-Walled Carbon Nanotubes (SWNT) by Catalytic Disproportionation of CO on a Solid Catalyst"
D. E. Resasco, J. E. Herrera, L. Balzano, F. Pompeo
5th. International Conference on Integrated Nano/Micro/Bio Technology for Space, Medical and Commercial Applications Galveston, Texas June 24-28, 2002 (Invited talk)
 9. "Characterization of single-walled carbon nanotubes (SWNT) produced by CO disproportionation on Co-Mo catalysts"
W. E. Alvarez, F. Pompeo, J. E. Herrera, L. Balzano, D. E. Resasco
223rd ACS National Meeting (Orlando, April 7-11, 2002)
 10. "Synergism of Co and Mo in the Catalytic Production of Single-wall Carbon Nanotubes by Decomposition of CO"

D. E. Resasco, W. E. Alvarez, L. Balzano, J. E. Herrera, F. Pompeo, B. Kitiyanan

2001 AIChE Annual Meeting (American Institute of Chemical Engineers)
Reno, Nevada; November 4 - June 9, 2001

11. "Highly Selective Catalyst for Synthesis of SWNT by CO disproportionation"
J. E. Herrera, L. Balzano, W. E. Alvarez, D. E. Resasco
NT-01 International Workshop on the Science and Application of Nanotubes,
Potsdam-Germany July 22-25, 2001
12. "Cost-effective Controlled Production of Single-Walled Nanotubes"
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13. "Qualitative and Quantitative Assessment of the SWNT Produced by the
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F. Pompeo, L. Balzano, H. Barraza, J. E. Herrera, E. O'Rear, S. Dahl, W. E.
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NT-01 International Workshop on the Science and Application of Nanotubes,
Potsdam-Germany July 22-25, 2001
14. "Design of effective catalysts for the production of single-wall carbon
nanotubes"
J. E. Herrera, L. Balzano, A. Borgna, W. E. Alvarez, and D. E. Resasco
17th Meeting of the North American Catalysis Society, Toronto, Ontario,
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15. "Single-Wall Carbon Nanotubes Production By Co Disproportionation With
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APPENDIX A

IN-SITU TPO/RAMAN TECHNIQUE TO CHARACTERIZE SINGLE-WALLED CARBON NANOTUBES ^{IV}

A.1. INTRODUCTION

As described in Chapter 1, the methods for producing SWNT range from electric arc discharge and laser ablation of carbon targets containing metals to direct decomposition of carbon-containing molecules over metal catalysts [1-5]. Several researchers has shown how among these different alternatives the catalytic decomposition of carbon-containing molecules has the potential to be scaled-up at a relatively low cost, enabling applications that require large SWNT quantities [6].

Nevertheless, besides SWNT the raw material obtained by any of the methods mentioned above contains varying degrees of carbon impurities such amorphous carbon, graphite fibers as well as residual metals from the catalyst used in the production [7-11]. Hence, a crucial step on the production of SWNT is a reliable characterization of the type and amounts of impurities present on a given sample. Electron microscopy (TEM/SEM) and thermal gravimetric analysis (TGA) have been used to obtain mostly qualitative assessments of the various carbon species present on

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a given sample and a quantitative measurement of the overall concentration of residual metals, respectively [12-14].

In 1999, Kitiyanan et al. proposed the temperature programmed oxidation (TPO) method as a useful tool for quantifying the amount of SWNT present on a sample [15] since when embedded in the catalyst, SWNT burn in narrow temperature range, below the temperature in which MWNT, graphite, and carbon fibers are oxidized, but above the temperature at which amorphous carbon species are oxidized [16]. At the same time, as described in Chapter 1, Raman spectroscopy is an exceptionally powerful technique for characterizing the structure of SWNT. The Raman-allowed phonon mode E_{2g} has extensively been used as a measure of the presence of ordered carbon, while the so-called D-band is related to defects or the presence of nanoparticles and amorphous carbon [17]. Hence, the size of the D-band relative to the G band can be used as a qualitative measurement for the formation of undesired forms of carbon. Nevertheless an accurate quantitative account of the different types of carbonaceous materials present on the sample cannot be obtained by Raman spectroscopy.

This appendix presents the results of a novel combination of these two techniques developed as a corollary of the work described in Chapter 4 for SWNT characterization: in-situ Raman spectroscopy - Temperature Programmed Oxidation. This particular combination of techniques has allowed us to identify different

carbonaceous species present in raw and purified SWNT samples, as well as to investigate the effect of residual metal catalysts in the SWNT reactivity.

A.2. EXPERIMENTAL

A.2.1. Materials and treatments.

Several nanotube samples were analyzed. One of them was a raw sample as obtained from CNi produced by the HiPCO process, which as it is well known its major impurity is residual Fe catalyst [10]. This sample was also investigated after a purification step in nitric acid used to remove the residual iron species present. A couple of samples prepared by catalytic disproportionation of CO over solid catalysts were also investigated. One of them was obtained over an unselective Co-W catalyst and the other over a highly selective Co-Mo catalyst. The synthesis of SWNT with high selectivity was described in Chapter 2, while the synthesis of SWNT with varying selectivities using a Co W catalyst was described in Chapter 3.

A.2.2. Temperature programmed oxidation analysis.

To conduct the TPO analysis, a continuous flow ($50 \text{ cm}^3/\text{min}$) of 2 % O_2 in He was passed over the sample while the temperature was linearly increased at a rate of $12^\circ\text{C}/\text{min}$. To enhance the sensitivity of the technique, the CO_2 and CO produced during the oxidation are quantitatively converted to methane in a methanator [18], where the stream coming from the TPO is passed with a $50 \text{ cm}^3/\text{min}$ stream of H_2 over a 15% Ni/ $\gamma\text{-Al}_2\text{O}_3$ catalyst at 400°C . The evolution of the methane produced in

the methanator quantitatively corresponds to the CO₂ and CO generated in the TPO is monitored in a flame ionization detector, SRI model 110 FID. Quantification of the evolved CO and CO₂, calibrated with 100 µL pulses of pure CO₂ and oxidation of known amounts of graphite gives a direct measurement of the amount of carbon that gets oxidized at each temperature.

A.2.3. In-situ Raman spectroscopy.

The Raman spectra were obtained in a Jovin Yvon-Horiba Lab Raman equipped with a CCD detector and with three different laser excitation sources, having wavelengths of 633 (He-Ne laser) 514 and 488 nm (Ar laser). This system is equipped with an in-situ reaction chamber that can be heated up to more than 1000°C under flowing gases. Before each spectrum was acquired, the sample was placed in the in-situ cell and then exposed to a continuous flow of a mixture of 2 % O₂ in He while the temperature was linearly increased at a rate of 12 °C/min, reproducing the exact conditions of the TPO. The heating was stopped at a given temperature and, to obtain the Raman spectrum, the sample was cooled down to room temperature under the same flow. To make meaningful comparisons, it is essential to acquire the spectra on the same spot of the sample every time this heating-cooling sequence is followed.

A.3. Results and Discussion

Figure A.1 illustrates the TPO profiles of the carbon species present on the raw and purified HipCO materials. It was found that the amount of carbon present on

both samples was 83% and 99% respectively as obtained from the quantification of the amount of CO and CO₂ evolved during the TPO process. This undoubtedly shows

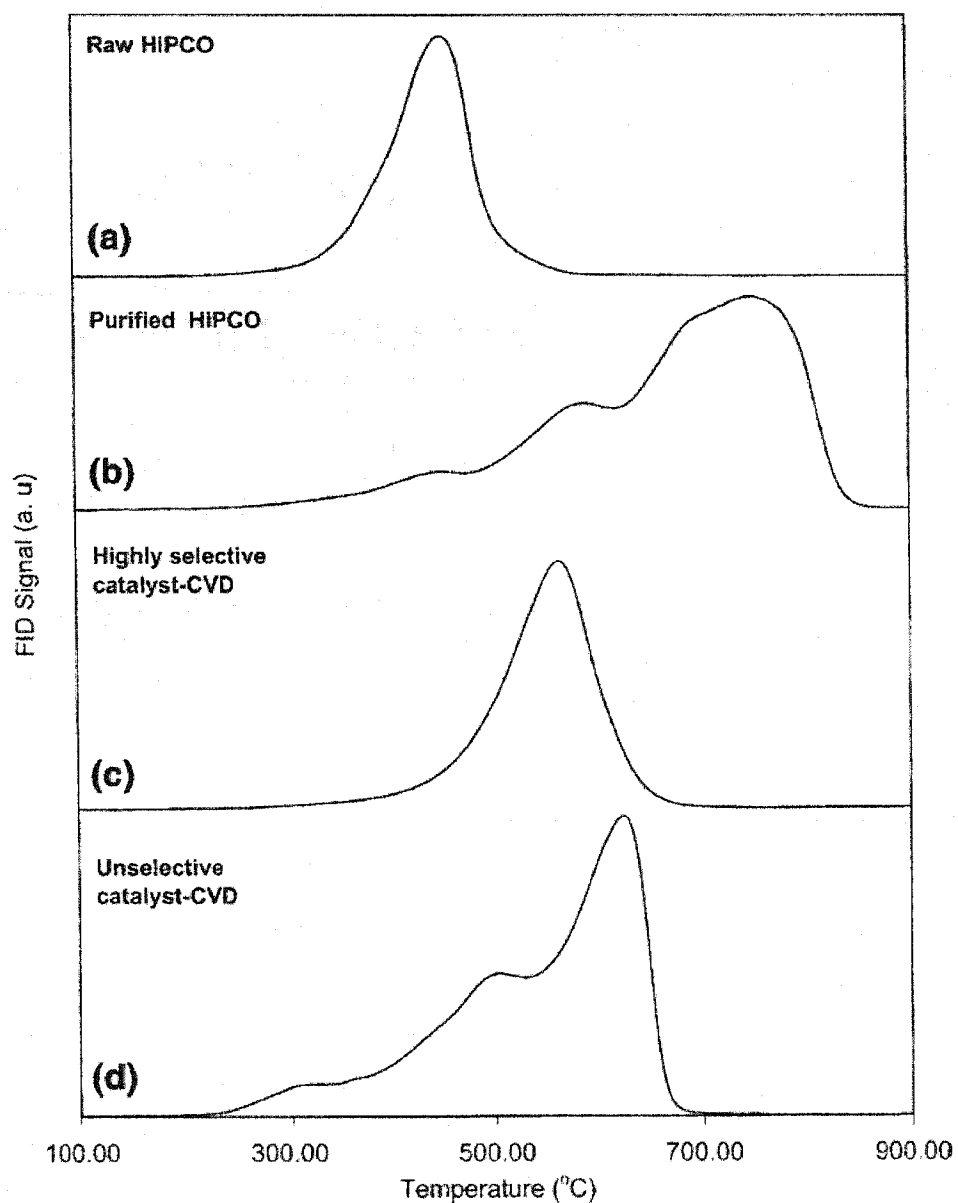


Figure A.1. Temperature programmed oxidation (TPO) profiles of the carbonaceous species present in (a) Raw HiPCO material, (b) Purified HiPCO material, (c) the product obtained by by CVD over a highly selective Co-Mo catalyst and (d) the product obtained by CVD over an unselective Co-W catalyst. The profiles were obtained using a mixture of 5% of O₂ in He at a heating rate of 12°C/min.

that most of the Fe present in the sample was removed by the purification process. However, a first comparison between both profiles would indicate that after purification there are three different carbonaceous species present on the purified material, each one showing a different behavior towards O₂ oxidation. Two of these new carbonaceous species (peak position 600 and 765°C in the TPO profile shown in Fig.A.1b) have been originated during the purification process. On the other hand, the first peak in the profile of the purified material (peak at 460°C in Fig. A.1a) is at the same position as the only peak observed for the raw SWNT.

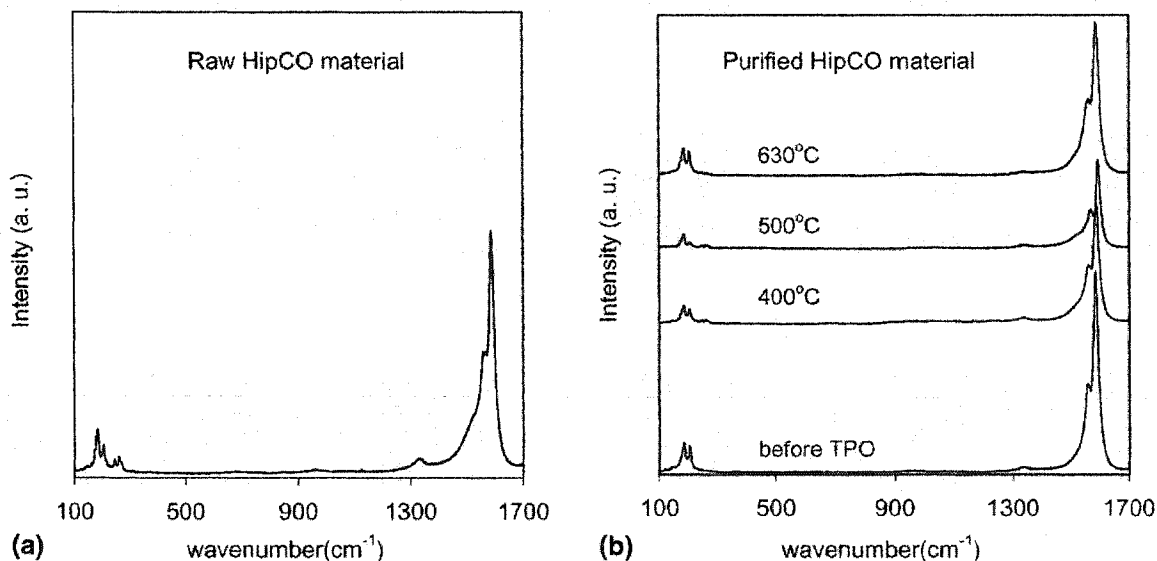


Figure A.2. Resonant Raman spectra obtained for (a) Raw HipCO material at room temperature and (b) Purified HipCO material before and after subsequent in-situ oxidation steps at 400°C, 500°C and 630°C. The laser excitation wavelength was 514 nm.

To determine the kind of carbonaceous species present on the purified sample that are responsible for each one of the peaks appearing in the TPO profile, Raman

spectroscopy was carried out on the raw and purified materials. For the purified material, Raman spectra were also acquired after each in-situ oxidation step, that corresponds to the valleys in the TPO profiles, i.e. the spectra were acquired at room temperature and then after a oxidation steps at 400°C, 500 °C and 630°C under the same conditions used to get the TPO profiles, to determine the changes in the Raman spectra after elimination of the corresponding species.

Figures A.2 and A.3 summarize the results of this study. Relatively small variations are observed between the Raman spectra of the raw and purified samples, or even among the spectra of the purified sample after each consecutive oxidation step, indicating that SWNT are undoubtedly the main carbon species present on both purified and raw samples. However, clear trends are still possible to observe. First, a decrease in the intensity of the D band is observed when comparing the raw HipCO material with the purified sample, indicating that the purification procedure not just removes the residual Fe form the sample but also decreases the amount of amorphous carbon that might have been originated during the synthesis process. Second, as the oxidation temperature of the purified sample was increased, the relative contribution of the D band clearly decreased. This trend is better illustrated in Fig. A.3a, which shows the gradual decrease of the D band in terms of the previously used expression $(1 - D/G)$, quality parameter of the SWNT sample, since it qualitatively measures the amount of SWNT compared to other disordered carbon species. As discussed in Chapter 1, amorphous and chemically impure carbon species are oxidized at

temperatures below 400°C, consequently subsequent oxidation steps remove increasing amounts of amorphous carbon material from the samples which results in the decrease of the relative intensity of the D band in the Raman spectra.

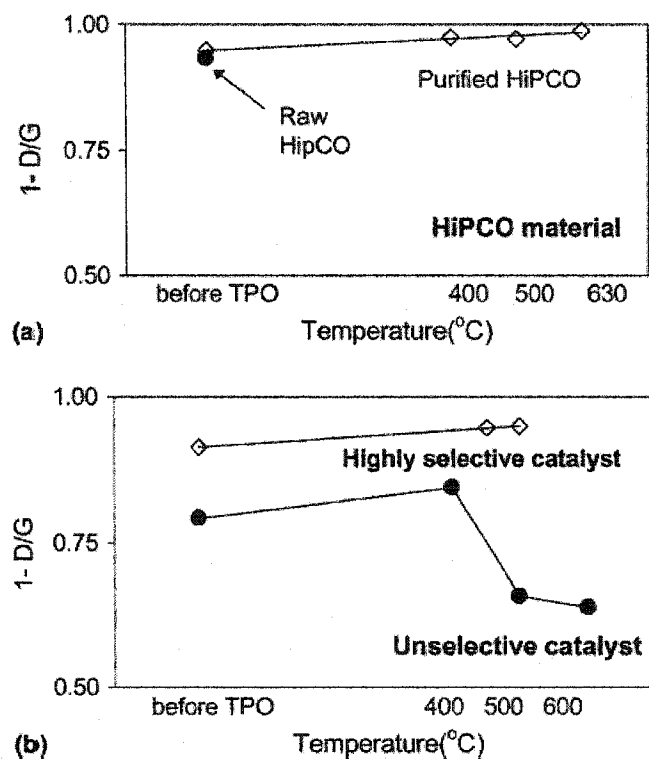


Figure A.3. Contributions of the D band to the Raman spectra for: (a) the HipCO purified materials before and after subsequent in-situ oxidation steps at 400°C, 500°C and 630°C (the data for the raw HipCO sample is also shown for reference) and (b) two different carbon deposits obtained by CVD over a highly selective Co-Mo and over an unselective Co-W catalyst before and after subsequent in-situ oxidation treatments at the indicated temperatures. The contribution of the D band to the Raman spectra is expressed using a quality parameter: $1 - D/G$; where D and G are the integrated areas of the D and G Raman bands respectively.

Although during these oxidation treatments disordered carbon was preferentially eliminated, based on the results obtained by Raman spectroscopy it is clear that the three peaks observed in the purified HiPCO sample do not correspond to different carbon species. As we have mentioned before in Chapter 1, TPO is a catalytic process in which residual metal can have a significant impact. On the unpurified raw material, the amount of Fe is so high that all the different forms of carbon in the sample are essentially oxidized simultaneously at 460°C. By contrast, on the purified sample, the amount of iron present is considerably lower (just about 1%). Therefore, the catalytic influence of iron during the TPO process is smaller. Consequently, we attribute the difference between the TPO profiles of the raw and purified materials to the different amounts of iron present on these two materials. Accordingly, it is possible that both, the peak at 460°C present in the TPO profile of the purified material and the single peak shown in the TPO of the raw SWNT sample are originated by SWNT contaminated with iron species. On the other hand, the peaks appearing at 500°C and 630°C in the purified sample are originated from SWNT associated to small or negligible amounts of metal.

A similar analysis was performed on two different raw SWNT materials synthesized by CO disproportionation on solid catalysts. One of them was obtained over a selective Co-Mo bimetallic catalyst, in which as demonstrated in Chapter 2 SWNT is the dominant product. The other sample was obtained over an unselective Co-W metallic catalyst (see Chapter 3), in which SWNT, MWNT, graphite and

amorphous carbon are all present. Figures A.1c and A1.d show the TPO profiles of each of these two materials, respectively. It can be seen that the sample obtained over the selective catalyst, which contains mostly SWNT, displays a single TPO peak centered at 570°C. However, an interesting difference is observed in this case compared to the TPO profile obtained for the raw HipCO material shown in Fig. 1a. That is, although both profiles shown a single main peak, the peak position for the SWNT obtained from the Co-Mo catalyst is at more than 100°C higher than that for the HipCO material. This difference is primarily due to the different amount of residual metal catalyst left in each sample. While the raw material obtained by the HipCO process contains up to 30% in weight [8,19], the sample obtained over the Co-Mo catalyst contains less than 2% of Co and Mo metal impurities. Consequently, the material obtained by the HipCO process has a larger amount of metallic species able to catalyze the oxidation reaction during the TPO process, lowering the temperature needed to oxidize the SWNT. In addition to the difference in the amount of residual metal in the two samples, another important difference is the presence of the silica support on the raw material prepared from the Co-Mo/SiO₂ catalyst. The silica support is essentially a thermal insulator that may separate the SWNT bundles and consequently prevent the propagation of the oxidation.

To further characterize the material obtained over the selective Co-Mo catalyst, we used the in situ TPO/Raman technique. In this case, the in-situ oxidation steps were performed at 450°C and 500°C under the same conditions used to get the

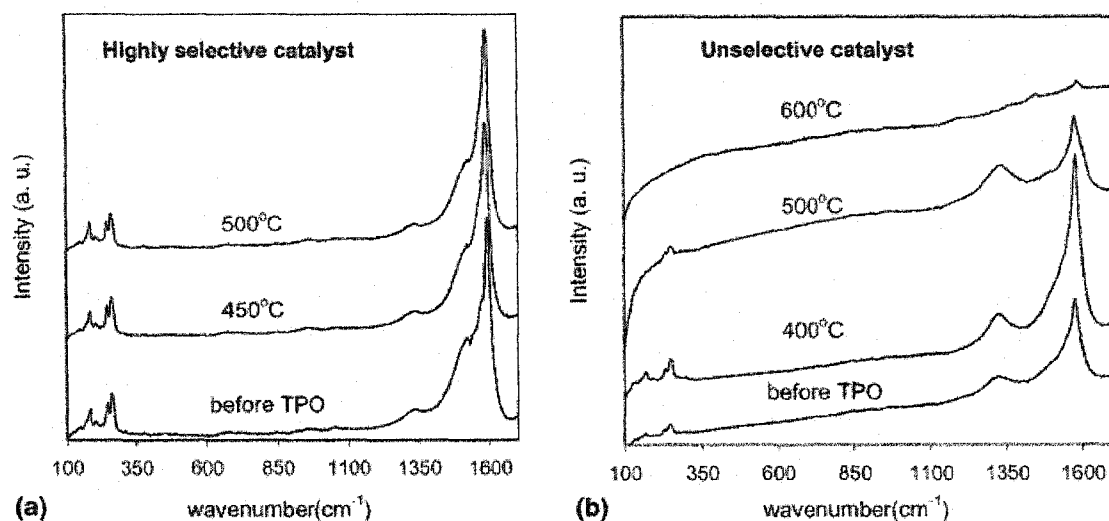


Figure A.4. (a) Resonant Raman spectra for (a) the carbon deposits obtained over a highly selective Co-Mo catalyst. The spectra were acquired before and after subsequent in-situ oxidation steps at 450°C and 500°C and for (b) the carbon deposits obtained over an unselective Co-W catalyst. The spectra were acquired before and after subsequent in-situ oxidation steps at 400, 500 and 600°C. The laser excitation wavelength was 514 nm.

TPO profiles. Figure A.4a shows the results that undoubtedly corroborate that the sample is mostly composed by SWNT. As in the case of the HiPCO material, there were some variations in the Raman spectra after the different TPO stages. A decrease in the contribution of the D band was observed after the higher oxidation temperatures. As with the HipCO purified material, we integrated the areas of the G and D bands and calculated its relative area. Figure A.3b shows the results of the “quality parameter” ($1 - D/G$), which is high even for the raw material, but clearly increases after the oxidation treatments. As mentioned above, below 450°C amorphous and chemically impure carbon species are burned; therefore the first oxidation step eliminates the amorphous carbon material from the samples. This

oxidation results in the decrease of the relative intensity of the D band in the Raman spectra. However, as shown in Figures A.3b and A.4a, a subsequent oxidation step (500°C) does not change the contribution of the D band to the spectra, since at this temperature all amorphous carbon has been removed.

A contrasting behavior is observed in the TPO profile of the material obtained over the unselective catalyst (see Fig. A.1d). Instead of the single peak observed in the previous case, three oxidation peaks are obtained on this sample. To identify the nature of the species responsible for these peaks, in-situ Raman spectroscopy was carried out on this sample. As before, the spectra were obtained at room temperature after each subsequent in-situ oxidation steps at 400°C and 500°C and 600°C, under the same conditions used in the TPO experiments. Figure A.4b shows the Raman spectrum obtained in each case. It can be observed that the relative intensity of the D band is much stronger for this sample than for any of the other samples investigated. This clearly reveals the low selectivity of the particular catalyst used in this sample. In addition, there are other interesting changes in the Raman spectra that deserve further consideration. First, the relative area of the D band in each spectra changes after each subsequent oxidation step. This behavior is illustrated in Figure A.3b, which shows for the unselective catalyst a clear decrease on the D band contribution after the first oxidation step (400°C). As previously stated, below this temperature amorphous carbon species are oxidized and, therefore this first oxidation step should eliminate most of the amorphous carbon present in the material, consequently, a

decrease in intensity of the D band in the Raman spectrum is observed. A different behavior is observed after the oxidation step at 500°C. In this case, an enhancement in the contribution of the D band to the overall spectra is observed. Evidently this behavior cannot be attributed to the presence of amorphous carbon in the sample, since all amorphous carbon species have been removed below this temperature. The enhancement in the D band should therefore be ascribed to a decrease in the amount of ordered forms of carbons in the sample. As mentioned above, SWNT are oxidized at a temperature below the oxidation threshold of MWNT and graphite. In fact, the intensity of the D band in the Raman spectra suggests that even after oxidation at 400°C the sample is composed of SWNT and other forms of disordered carbon. All these together points to a decrease on the amount of SWNT and an increase on the relative amount of MWNT and (or) graphite in the sample after the 500°C oxidation step, which in turn would be responsible for the increase of the intensity of the D band [20]. Finally, after the oxidation at 600°C, most of the carbonaceous species have been oxidized as shown by the TPO profile. Moreover, the low intensity of the bands in the Raman spectrum is consistent with a small amount of refractory graphite still present in the sample.

ACKNOWLEDGEMENTS

This research was conducted with financial support from the Department of Energy, Office of Basic Energy Sciences (grant No. DE-FG03-02ER15345) and the Oklahoma Center for the Advancement of Science and Technology (OCAST). I would like to thank Francisco Pompeo for providing the purified CVD-SWNT samples, and to the members of the NASA Johnson Space Center Nanotube Project for providing the HipCO raw and purified samples.

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