



Synergism of Co and Mo in the catalytic production of single-wall carbon nanotubes by decomposition of CO

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Abstract

The catalyst composition and operating conditions for the synthesis of single-wall carbon nanotubes (SWNT) from CO decomposition have been systematically varied in order to maximize the selectivity towards SWNT. A simple quantification method based on the standard Temperature Programmed Oxidation (TPO) technique has allowed us to determine the distribution of the different forms of carbonaceous deposits present on the catalysts after the CO decomposition reaction. A synergistic effect between Co and Mo has been observed. When both metals are simultaneously present, particularly when Mo is in excess, the catalyst is very effective. However, when they are separated they are either inactive (Mo alone) or unselective (Co alone). To understand this synergistic effect, X-ray absorption spectroscopy (EXAFS and XANES) has been used to characterize the state of Co and Mo on the catalysts before and after the production of SWNT. © 2001 Published by Elsevier Science Ltd.

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1. Introduction

The fascinating properties of single-wall carbon nanotubes (SWNT) have opened a great number of potential applications for these unique materials. However, the high costs of the current production methods and the difficulty in making them available for large-scale manufacture have slowed down the process of bringing nanotube-based technologies to commercial practice. Following the original arc-discharge method [1,2], other synthesis methods have been investigated, including laser ablation [3,4] and plasma discharge. To develop a cost-effective operation for the manufacture of SWNT a drastic change in the production scale is necessary. The catalytic method for production of nanotubes has been known for a long time, but this method typically results in production of multi-wall carbon nanotubes (MWNT) or carbon nanofibers [5]. In recent years, several researchers have focused their attention to the production of SWNT by catalytic decomposition of carbon-containing molecules

[6–12]. This method is sometimes referred to as chemical vapor deposition [12]. We have recently pointed out that the catalytic decomposition method is suitable for scaling up and for achieving a ‘*controlled production*’ of single-wall nanotubes (SWNT) [13]. By this term we imply the ability to control the selectivity towards SWNT by changing catalyst parameters and operating conditions, combined with the ability to obtain a reliable quantitative measurement of the amount of SWNT produced.

In our previous report [13], we described a simple quantification method of the SWNT produced by catalytic decomposition of CO, which allowed us to conduct a systematic screening of catalyst formulations. This quantification method was based on the standard Temperature Programmed Oxidation (TPO) technique, commonly employed in catalysis research to quantify and investigate the nature of carbonaceous deposits on spent catalysts. In this method, a continuous flow of an oxygen-containing gas is passed over the catalyst containing the carbon deposits while the temperature is linearly increased. Quantification of the CO₂ evolved gives a direct measurement of the amount of carbon that gets oxidized at each temperature.

One has to be careful in using TPO to identify carbon species since the oxidation of carbon is a catalytic process,

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and as such, the peak positions may be affected by the metallic content as well as the amount of carbon on the surface. However, this method appears particularly suitable for the quantification of SWNT in a set of samples of similar composition and comparable carbon contents. In such set of samples, SWNT are oxidized in a relatively narrow temperature range, which lies above the temperature of oxidation of amorphous carbon and below the oxidation of MWNT and graphitic carbon. The position of the oxidation peak corresponding to the SWNT produced on the catalyst was exactly matched with that of pure SWNT obtained from Tubes@Rice (Rice University), mechanically mixed with the same catalyst powder used in the production of nanotubes. In a separate study [14] we have shown that the peak centered in the range 500–530°C corresponds to a first order process, while that at higher temperatures is a zeroth order process. This reaction orders support the assignment of those peaks to SWNT and MWNT, respectively. The oxidation of a single-shell carbon is expected to behave as a first order process, while when there exist a number of layers, and the burning is layer by layer, the process should be of zeroth order [15]. Also, it is well known that the position of oxidation peaks in TPO does not vary with carbon content for first order oxidations, but it shifts to higher temperatures for zeroth order oxidations. Therefore, we would expect that the carbon content will not affect the position of the peak corresponding to SWNT, but it would certainly affect that corresponding to MWNT. This has in fact been verified experimentally [14].

By using this methodology, we demonstrated that Co is not selective for the production of SWNT and Mo is inactive in the temperature range investigated, i.e., 600–800°C. However, bimetallic Co–Mo catalysts with low Co:Mo ratios exhibited a real synergism that resulted in high selectivity towards SWNT. Previous reports [16] have shown improved performances of bimetallic catalysts in comparison to monometallic, but none of the previously investigated systems showed the dramatic synergism exhibited by Co and Mo in the decomposition of CO.

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

2. Experimental

The Co, Mo, and Co–Mo catalysts were prepared by impregnating a silica gel support (SiO_2 , from Aldrich,

70–230 mesh, average pore diameter 6 nm, BET surface area $480 \text{ m}^2 \text{ g}^{-1}$, pore volume $0.75 \text{ cm}^3 \text{ g}^{-1}$), with aqueous solutions of Cobalt Nitrate and/or Ammonium Heptamolybdate to obtain the bi- or monometallic catalysts. The liquid/solid ratio was kept at incipient-wetness conditions, which for this support corresponds to $0.63 \text{ cm}^3 \text{ g}^{-1}$. In all cases, the total metal content was kept at 6 wt%. The bimetallic catalyst was prepared with a Co:Mo molar ratio of 1:2. The catalysts were first dried in air at room temperature, then in oven at 80°C, and finally calcined in flowing air at 500°C. A Micromeritics ASAP 2010 adsorption apparatus was used to obtain the BET surface area, pore volume, and pore size of the supports and catalysts.

For the production of nanotubes, 100–500 mg of calcined catalyst was placed in a horizontal quartz tubular reactor, heated in H_2 up to 500°C, and then in He up to 700°C. Subsequently, CO was introduced at the same temperature, at a flow-rate of $100 \text{ cm}^3 \text{ min}^{-1}$ and kept under these conditions for a given period of time, which ranged from 3 to 60 min. A combination of transmission electron microscopy (TEM), Raman spectroscopy and temperature programmed oxidation (TPO) techniques was used to characterize the carbon species produced during the reaction period. The TEM images were obtained in a JEOL 2000FX-TEM. For these observations, the samples were prepared by sonicating in methanol for 10 min followed by deposition of a few drops of the resulting suspension on the TEM grid. The laser Raman spectra were obtained in a JASCO TRS-600SZ-P single monochromator spectrophotometer, equipped with a CCD (charge-couple device) with the detector cooled to about 153 K with liquid nitrogen. The excitation source was the 514.5 nm Spectra 9000 Photometrics Ar ion laser. All the spectra were recorded with the samples under ambient conditions. TPO measurements were conducted by passing a continuous flow of 5% O_2 in He over the catalyst containing the carbon deposits, while the temperature was linearly increased at a rate of $12^\circ\text{C min}^{-1}$. The evolution of CO_2 produced by the oxidation of the carbon species was monitored by a MKS mass spectrometer. Quantification of the evolved CO_2 was achieved by calibrating with 100 μl pulses of pure CO_2 and oxidation of known amounts of graphite. No CO was observed during any of the TPO experiments.

X-ray absorption (EXAFS/XANES) data were obtained at the National Synchrotron Light Source (NSLS) at Brookhaven National Laboratory, Upton, New York using beam line X-18b equipped with a Si (111) crystal monochromator. The X-ray ring at the NSLS has energy of 2.5 GeV and a ring current of 80–220 mA. The samples were investigated as fresh samples after an initial treatment in H_2 (500°C)/He (700°C) and as spent samples after different reaction periods for the production of carbon nanotubes. In both cases, they were not exposed to the air, but directly transferred from the reaction chamber to a He

glove bag, where they were wrapped in Kapton tape and stored in He-purged sealed vessels. The EXAFS experiments were conducted in a stainless steel sample cell at liquid nitrogen temperature. Six scans were recorded for each sample. The average spectrum was obtained by adding the six scans. The pre-edge background was subtracted by using power series curves. Subsequently, the post-edge background was removed using a cubic spline routine. The spectra were normalized by dividing by the height of the absorption edge. To obtain structural parameters, theoretical references for Co–Co, Co–O, Mo–O, Mo–C and Mo–Mo bonds were obtained by using the FEFF and FEFFIT fitting programs from the University of Washington [17–19]. In this routine, the Debye Waller factors for each bond type (σ), the edge energy difference (ΔE_o), 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%.

3. Results

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

Table 1 summarizes some of the data, as calculated from the TPO profiles. The quantification of the different forms

of carbon was done by fitting the entire profiles with gaussian–lorentzian mixtures. The peak centered at about 500–530°C represents the carbon in the form of SWNT. It must be noted that the shape and position of a TPO peak may vary when the catalyst composition changes, and may also vary depending on the kinetics of the oxidation process and the amount of carbon on the surface. However, in this case, all the samples were analogous and the amounts of carbon were also similar. Therefore, the position of the TPO peaks for each carbon species did not greatly vary. Moreover, as mentioned above, our current studies have shown that the oxidation of SWNT is a first order process, while that of the MWNT or carbon nanofibers is initially a zeroth order process. Therefore, we do not expect a shift in the position of the peak corresponding to SWNT, even for different carbon concentrations. On the other hand, the peak at higher temperatures corresponding to graphitic carbon structures is expected to shift to higher temperatures as the amount of carbon increases.

The data in Table 1 shows that the monometallic Co catalyst was unselective, while the monometallic Mo was almost inactive in the temperature range investigated. Similarly, an unsupported Mo₂C sample was also shown to be inactive. Physical mixtures of a Co catalyst with monometallic Mo catalyst or an unsupported Mo₂C resulted in the same production as the Co catalyst alone.

3.1. Effect of reaction temperature on the production of nanotubes

To study the effect of varying the operating temperature on the yield and selectivity to SWNT, we conducted the decomposition of CO over two Co–Mo/SiO₂ catalysts for 60 min at temperatures ranging from 600 to 800°C. Fig. 1 illustrates the TPO profiles obtained on the Co:Mo (1:1) at 600, 700, and 800°C. The fittings of each TPO profile, using Gaussian–Lorentzian mixture curves are included in the Fig. 1. As described in the previous work [13], the

Table 1
Yield and selectivities to SWNT obtained by decomposition of CO on Co:Mo catalysts as calculated by TPO^a

Catalyst	Operating temperature	Reaction conditions	Total Carbon yield (%)	Selectivity to SWNT (%)
Co	700°C	1 h, 50% CO	1.8	7
Mo	700°C	1 h, 50% CO	0.6	0
Co:Mo (1:1)	600°C	1 h, 50% CO	2.7	25.8
	700°C	1 h, 50% CO	1.7	62.5
	800°C	1 h, 50% CO	1.0	86.6
Co:Mo (1:1)	600°C	30', 20% CO	1.38	43
	700°C	30', 20% CO	0.55	61
	800°C	30', 20% CO	0.33	39
Co:Mo (1:2)	700°C	1 h, 50% CO	1.5	88
Co:Mo (2:1)	700°C	1 h, 50% CO	2.2	57
Co:Mo (1:4)	700°C	1 h, 50% CO	1.6	96

^a Yield is defined as the percent weight of carbon deposited per total catalyst weight. Similarly, selectivity is defined as the percent of carbon products deposited on the catalyst that is in the form of SWNT.

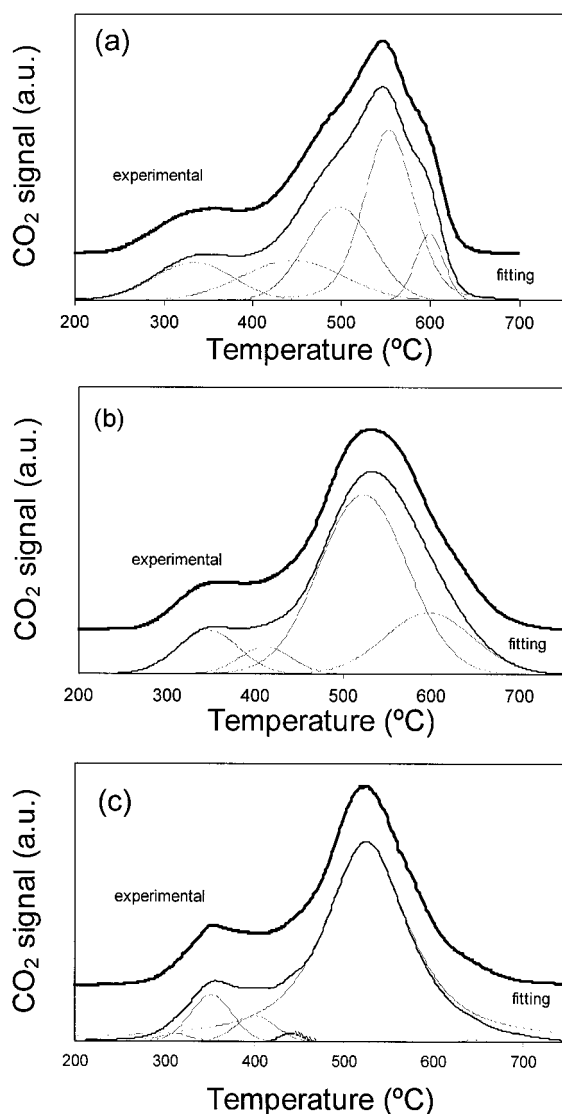


Fig. 1. Temperature programmed oxidation (TPO) of the carbonaceous species present in Co:Mo/SiO₂ catalysts after decomposition of 50% CO/He for 60 min at reactions temperatures (a) TR=600°C, (b) TR=700°C, and (c) TR=800°C (experimental TPO—heavier line, Gaussian–Lorentzian fitting—lighter line).

oxidation of SWNT on this type of catalysts under the particular TPO conditions used in this work has a maximum around 510°C. The position of maximum rate of oxidation of SWNT was confirmed using purified SWNT from Tubes@Rice. When compared at 700°C, the Co:Mo (1:2) catalyst was more selective than the Co:Mo (1:1), exhibiting lower contributions in the area of amorphous carbon (centered at around 330°C) as well as MWNT and graphite (centered at around 590 and 620°C, respectively).

As shown in the TPOs of Fig. 1 and summarized in

Table 1, the amount of carbon deposited on the Co:Mo (1:1) catalyst over the 60 min period increased with decreasing operating temperature. We ascribe this trend to the complex temperature dependence of both the rate of carbon deposition, which increases with temperature, and the rate of catalyst deactivation, which also increases with temperature. Therefore, the low carbon yield observed at 800°C is most probably due to a rapid deactivation of the catalyst, which counterbalances the rapid rate of CO decomposition. At 600°C, the amount of carbon deposited is significantly higher than at higher temperatures. However, the selectivity towards SWNT is much lower. It is clearly seen that the TPO of the sample reacted at 600°C exhibited a significant amount of amorphous carbon (centered at around 330°C) as well as MWNT, and perhaps some graphitic carbon, represented by the intense peak and shoulder at 556 and 610°C, respectively. The TEM observations of these samples are shown in Fig. 2, and agree very well with the TPO results. The Co:Mo (1:1) sample reacted at 600°C showed the presence of MWNT with external diameters of about 18 nm and wall thickness of around 6 nm. By contrast, the samples reacted at 700°C and 800°C showed mostly SWNT. The high-magnification TEM pictures of these two samples exhibited the presence of the typical rope-like bundles, which are similar to the structures grown by other methods [20]. Thin layers of amorphous carbon cover the SWNT bundles, which exhibited very uniform individual diameters of about 1 nm. The presence of SWNT on the sample treated at 700°C was further confirmed by Raman spectroscopy, conducted at room temperature and using 514.5 nm excitation. The spectra for the reference and the sample after reaction at 700°C are shown in Fig. 3. They both exhibit the typical doublet lines due to the ‘graphite-like’ tangential modes in the range 1550–1590 cm⁻¹, previously observed for purified SWNT [21]. In addition, a broad D-band is observed in the region of 1300–1350 cm⁻¹. This band is due to disordered carbon and has been previously observed with MWNT and polycrystalline graphite [22]. The sample reacted at 600°C is also included in Fig. 3. In good agreement with the TEM observations and the TPO profiles, the presence of disordered carbon is clearly seen by the intense D-band appearing in the region of 1300–1350 cm⁻¹. Clearly, the TPO cannot differentiate between MWNT and carbon nanofibers, because they all burn in the same temperature range and exhibit a zeroth order behavior. However, the TEM clearly shows that the tubes produced at 600°C are hollow in their core and their walls are multilayer having the basal plane parallel to the tube axis, which are characteristic features of MWNT.

3.2. Effect of CO concentration on the production of nanotubes

It was observed that not only the temperature, but also the concentration of CO in the gas phase has a profound

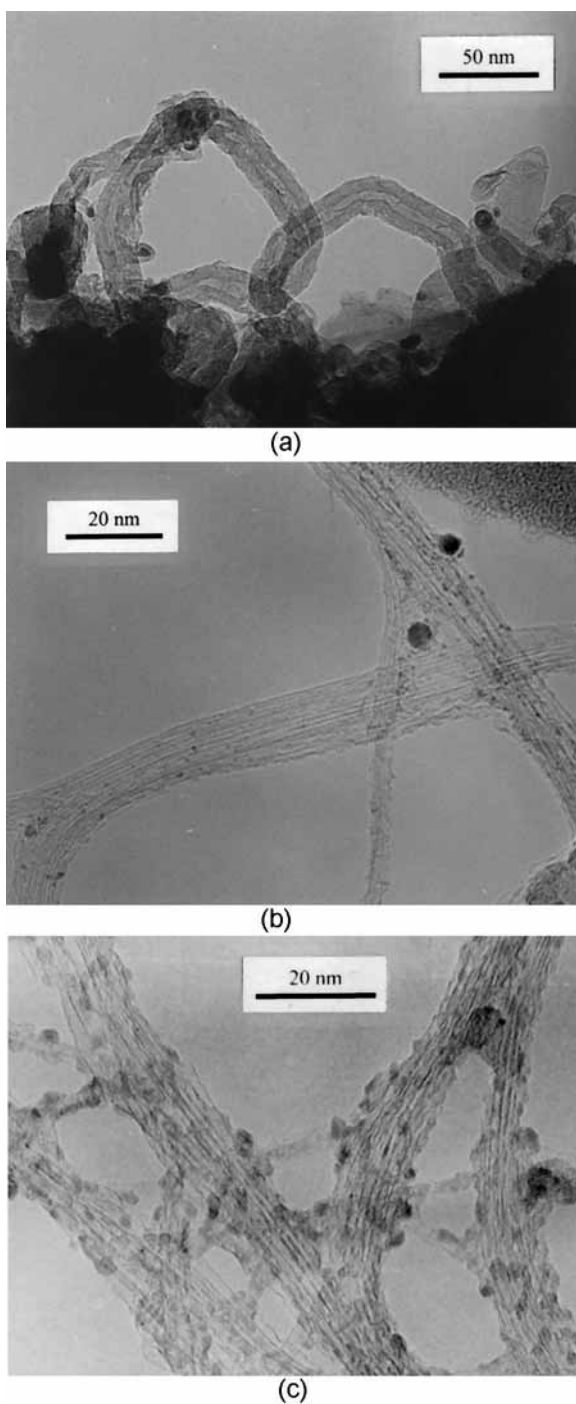


Fig. 2. TEM images showing SWNT and MWNT produced by decomposition of 50% CO/He on a Co:Mo/SiO₂ (Co:Mo=1:1) catalyst for 60 min at various temperatures. (a) 600°C; (b) 700°C; (c) 800°C.

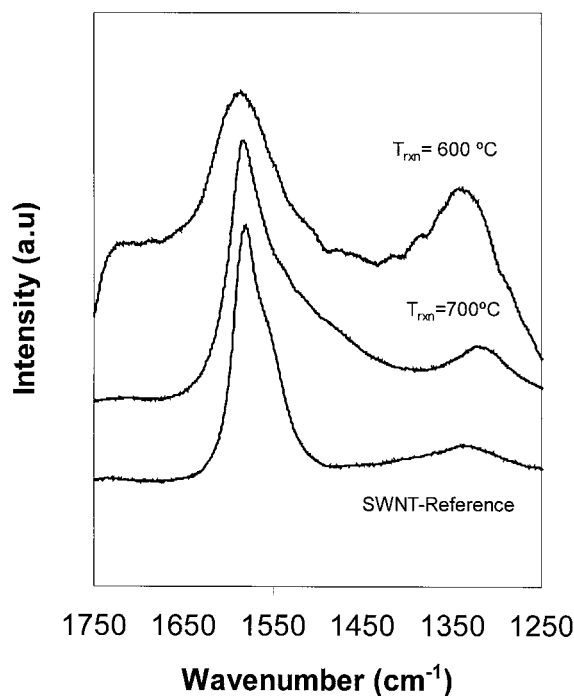


Fig. 3. The Raman spectra of SWNT reference (from Carbolex Inc.), deposited carbon on Co:Mo/SiO₂ catalyst (Co:Mo=1:1) after CO decomposition at 700°C, and deposited carbon on Co:Mo/SiO₂ catalyst (Co:Mo=1:1) after CO decomposition at 600°C.

effect on the rate of formation of SWNT. Fig. 4 shows the TPO of samples treated for 60 min at 700°C on the Co:Mo (1:1) catalyst with varying CO concentration in the gas phase. From the position of the TPO peak, it can be concluded that at low CO concentrations, the main form of carbon deposited at 700°C was amorphous. Only when the CO concentration increased, the SWNT began to dominate. The weak shoulders observed at 550°C and 600°C correspond to small amounts of MWNT, which were also observed by TEM.

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

3.3. Effect of reaction time on the production of nanotubes

One of the important considerations in the design of a

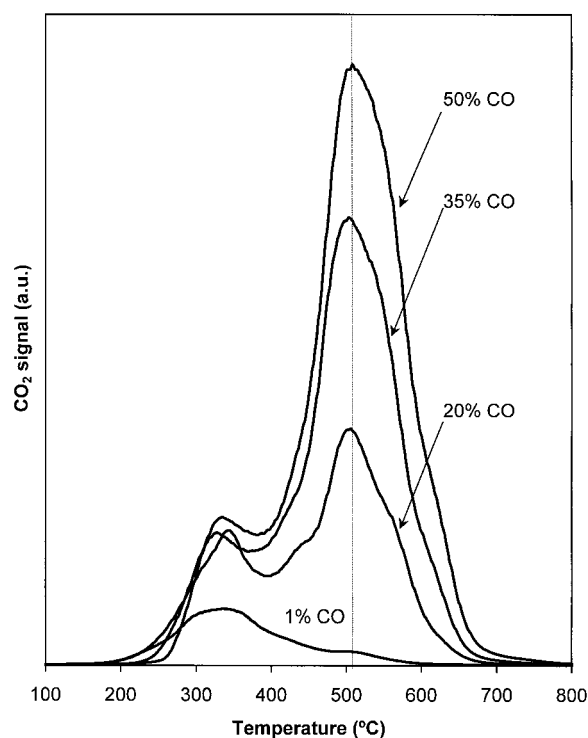


Fig. 4. Temperature programmed oxidation (TPO) of the carbonaceous species present in a Co:Mo/SiO₂ catalyst (Co:Mo=1:1) after CO decomposition at 700°C for 60 min with varying CO concentrations.

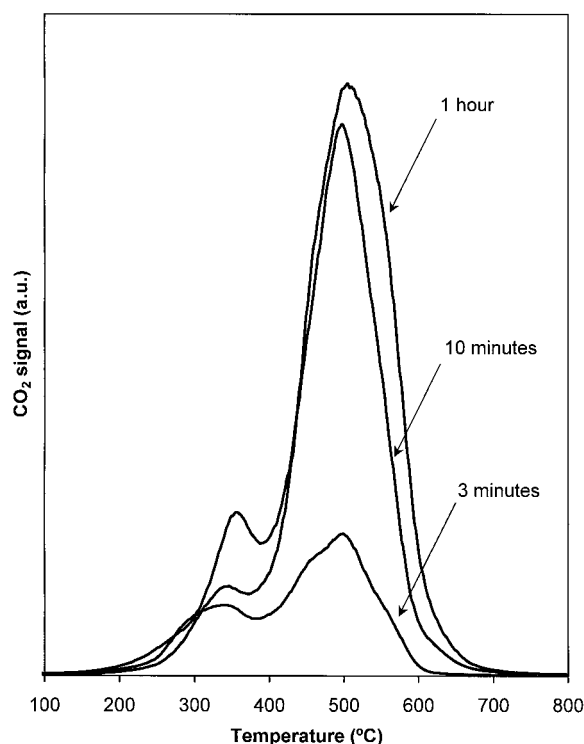


Fig. 5. Temperature programmed oxidation (TPO) of the carbonaceous species present in a Co:Mo/SiO₂ catalyst (Co:Mo=1:1) after decomposition of 50% CO/He at 700°C during different periods of time.

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

3.4. Characterization of the state of Co during the production of SWNT

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

Table 2

Surface area, pore volume, and pore size of various catalysts and supports as determined by nitrogen adsorption (BET) at liquid nitrogen temperature

Sample	BET area ($\text{m}^2 \text{g}^{-1}$)	Single point total pore volume ($\text{cm}^3 \text{g}^{-1}$)	Average pore radius by BET (nm)
SiO ₂ support Calcined 500°C	480	0.75	3.1
SiO ₂ support Calcined 800°C	450	0.71	3.1
Co:Mo (1:2) on SiO ₂ Fresh catalyst	427	0.67	3.1
Pretreated at 700°C, in He Co:Mo (1:2) on SiO ₂	427	0.67	3.1
Spent catalyst, 3 min 700°C, 50% CO	421	0.67	3.1
Co:Mo (1:2) on SiO ₂ Spent catalyst, 30 min 700°C, 50% CO	421	0.67	3.1

3.5. Characterization of the state of Mo during the production of SWNT

The characterization of the state of Mo was conducted on the K edge of Mo ($E_0=20\,000$ eV) both, on the fresh pretreated catalyst and after reaction. The near-edge spectra and EXAFS data are shown in Fig. 8 and 9, respectively. The XANES of the fresh Co:Mo (1:2) catalyst pretreated at 700°C can be compared to that of bulk MoO₃,

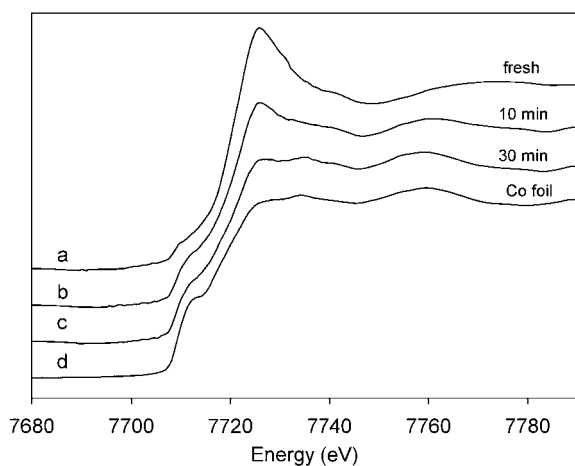


Fig. 6. Near edge spectra XANES obtained at the K edge of Co ($E_0=7,709$ eV) on a fresh Co:Mo/SiO₂ catalyst (Co:Mo=1:2), pretreated in H₂(500°C)/He(700°C), and after the growth of carbon nanotubes by decomposition of 50% CO/He at 700°C for reaction periods of 10 and 30 min. The XANES of a Co foil is included for comparison.

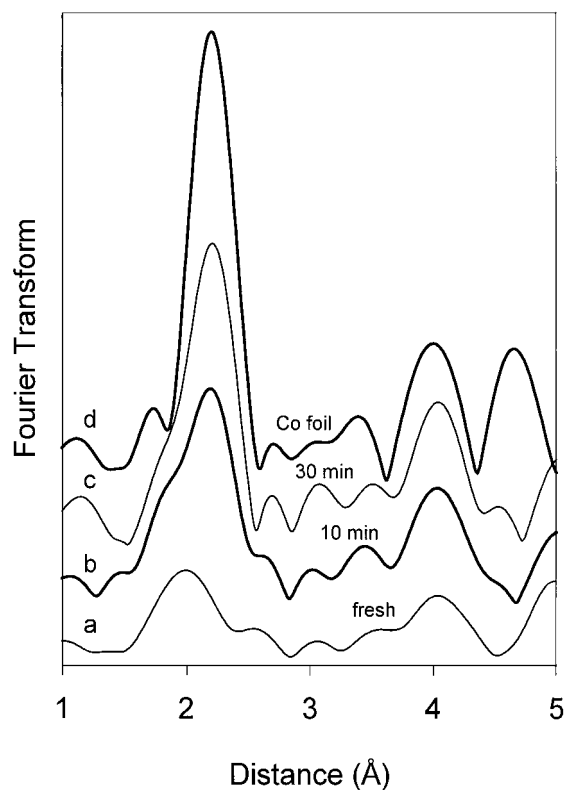


Fig. 7. Fourier transforms of the k^3 EXAFS data obtained at the K edge of Co for a fresh Co:Mo/SiO₂ catalyst (Co:Mo=1:2), pretreated in H₂(500°C)/He(700°C), and after the growth of carbon nanotubes by decomposition of 50% CO/He at 700°C for reaction periods of 10 and 30 min. The EXAFS data of a Co foil is included for comparison.

Table 3
Structural parameters of the Co–Mo/SiO₂ catalyst (Co:Mo=1:2) after different reaction periods, as obtained from the EXAFS data analysis^a

Sample	Sample treatment	Edge (M)	ΔE_0	σ	N_{M-M}	N_{M-O}	N_{M-C}	R (Å)	r factor
Co:Mo (1:2)	Spent 3 min	Co	4.2	0.0068	5.8	–	–	2.470	0.043
				0.0025	–	2.2	–	2.050	
Co:Mo (1:2)	Spent 10 min	Co	8.0	0.0075	8.2	–	–	2.490	0.034
				0.004	–	2.6	–	2.075	
Co:Mo (1:2)	Spent 30 min	Co	9.4	0.0065	9.2	–	–	2.498	0.020
				0.0003	–	1.1	–	2.070	
Mo ₂ C	Reference (as received)	Mo	6.6	0.0063	11.6	–	–	2.97	0.022
				0.0106	–	–	5.8	2.08	
Co:Mo (1:2)	Spent 30 min	Mo	7.1	0.0075	6.7	–	–	2.98	0.038
				0.0075	–	–	3.3	2.09	
				0.0039	–	0.9	–	1.68	

^a In the table, ΔE_0 represents the energy shift, σ is the Debye–Waller factor, N_{M-M} , N_{M-O} and N_{M-C} are the coordination numbers between the metals (Co or Mo) with another metal atom, oxygen atom, and carbon atom respectively. R (Å) is the coordination distance for each respective bond, and the r factor is a measurement of the fit quality.

which is the Mo species that one would expect if large Mo oxide aggregates were present [23]. In fact, the near-edge spectrum of the fresh catalyst is similar, but not exactly identical to that of MoO₃. It is well established that supported Mo oxide can exhibit different structures and states of aggregation depending on the Mo loading, thermal treatment, and type of support investigated. An investigation of Co–Mo catalysts supported on silica [24] has shown that, depending on the Co:Mo ratio, the form of preparation, and the thermal treatment, oxide species such as MoO₃, Co₃O₄ and CoMoO₄ can coexist on the samples. Some features in these XANES spectra can be used to

describe the state of Mo in the catalyst. For example, the pre-edge feature clearly observed for MoO₃ is due to a 1s→4d bound state transition [25], which is formally forbidden. However, it can become allowed by mixing of d-states with p-orbitals of the ligand. This mixing is very effective in compounds with tetrahedral geometry, such as Na₂MoO₄, and in those cases a strong pre-edge feature appears. When the geometry is octahedral, the transition is not allowed, but in MoO₃, the octahedral is distorted, and as a result, a small pre-edge feature is observed. In the fresh catalyst pretreated at 700°C, the pre-edge feature is very small, indicating a less distorted octahedral configura-

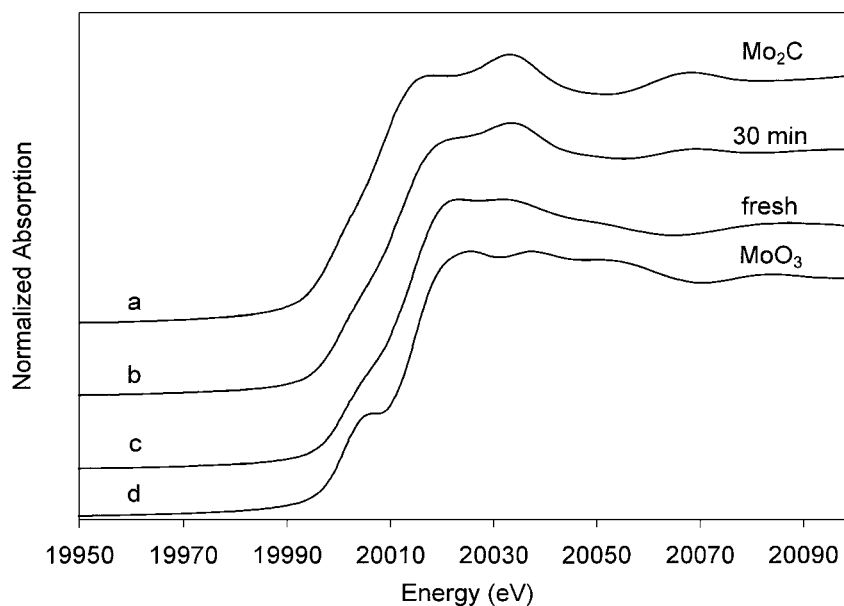


Fig. 8. Near edge spectra XANES obtained at the K edge of Mo ($E_0=20\,000$ eV) on a fresh Co:Mo/SiO₂ catalyst (Co:Mo=1:2), pretreated in H₂(500°C)/He(700°C), and after the growth of carbon nanotubes by decomposition of 50% CO/He at 700°C for 30 min. The XANES of MoO₃ and Mo₂C are included for comparison.

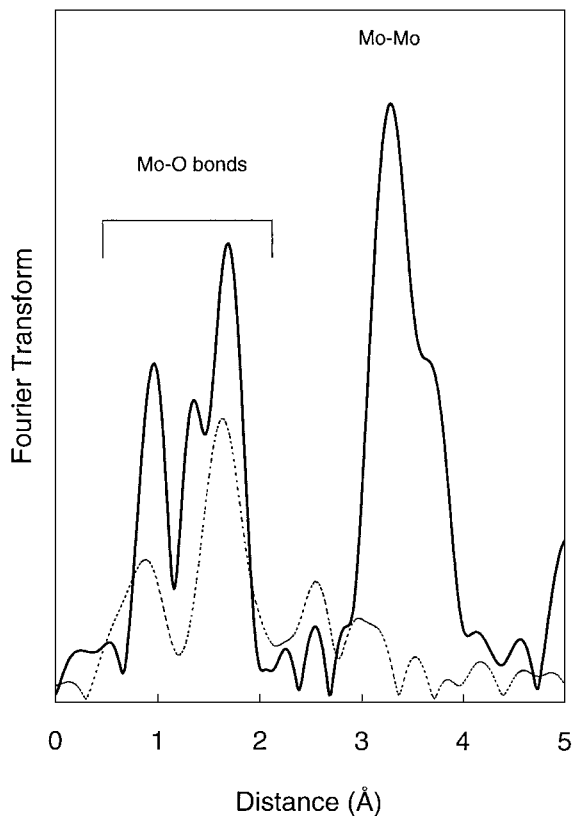


Fig. 9. Fourier transforms of the k^3 EXAFS data obtained at the K edge of Mo for a fresh Co:Mo/SiO₂ catalyst (Co:Mo=1:2), pretreated in H₂ (500°C)/He (700°C) (dashed line) compared to a MoO₃ reference (solid line).

tion. The EXAFS data show that the coordination of Mo in the fresh catalyst involves Mo–O bonds, but it is not the same as that of MoO₃ reference. At the same time, it does not exhibit coordination distances in the second shell region, which would indicate the presence of large aggregates. The results indicate that the fresh catalyst contains well-dispersed oxidized Mo species. As mentioned above, these oxidized species may in fact be a combination of oxides and molybdates [24]. Since the pretreatment involves a reduction step, it is possible that in the pretreated catalyst Mo may be in a partially reduced state e.g. Mo(IV).

As illustrated in Fig. 8, after a 30-min reaction period, the near-edge spectrum of Mo showed a drastic change in appearance and became very similar to that of molybdenum carbide, Mo₂C. At the same time, the EXAFS of the used catalyst, shown in Fig. 10, exhibited peaks in the Fourier transform that exactly corresponded with those of the Mo₂C reference. The transformation of oxidized Mo species into Mo carbide during the reaction was indeed very clear, with only a small fraction of unconverted Mo remaining in the catalyst. This conversion can be clearly seen from the EXAFS analysis data of the

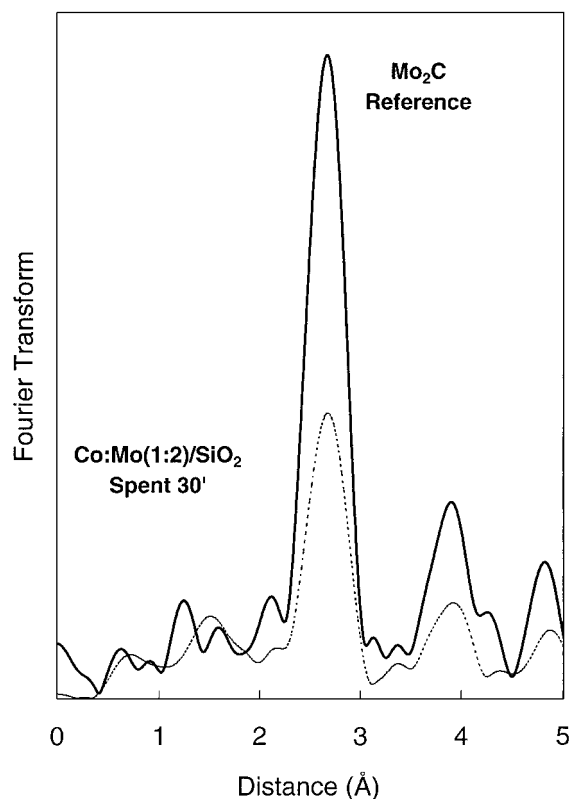


Fig. 10. Fourier transforms of the k^3 EXAFS data obtained at the K edge of Mo for a Co:Mo/SiO₂ catalyst (Co:Mo=1:2) after the growth of carbon nanotubes by decomposition of 50% CO/He at 700°C for 30 min compared to a Mo₂C reference.

spent catalyst summarized in Table 3. The best fit of the experimental data was obtained when the coordination sphere of the Mo was described as composed as Mo–C, Mo–Mo, and Mo–O. This indicates that the conversion to Mo carbide is not complete and a fraction of Mo remains as an oxidized species.

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

4. Discussion

In the first place, it is interesting to note that the growth of carbon nanotubes occurs for a limited period of time, after which the catalyst deactivates and the growth slows

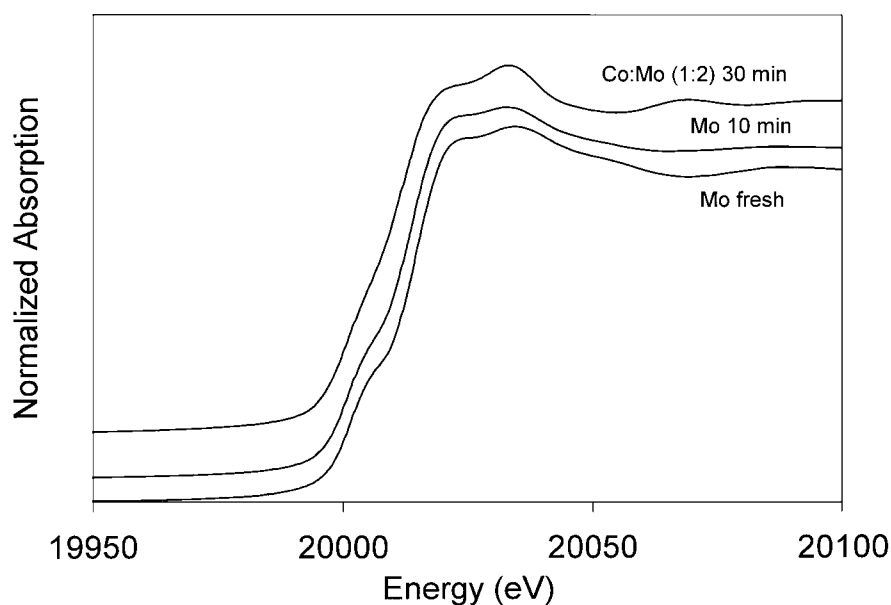


Fig. 11. Near edge spectra XANES obtained at the K edge of Mo ($E_o = 20\,000$ eV) on a fresh Mo/SiO₂ catalyst, pretreated in H₂ (500°C)/He(700°C), and after the growth of carbon nanotubes by decomposition of 50% CO/He at 700°C for 10 min. The XANES of the 30 min spent Co:Mo=1:2 catalyst is included for comparison.

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

This competition between carbon growth and catalyst deactivation seems to play a very important role in determining the resulting structure of the nanotubes. Cassell et al. [26] have observed similar decreases in growth rate at relatively short periods of time. One of the explanations proposed by these authors for growth abatement was the plugging of the catalyst pores by the nanotubes themselves. That may indeed be a factor when there is a large amount of carbon formed. However, in the case of the reaction at 800°C, the amount of carbon formed was very small and as shown by the N₂ adsorption data, pore plugging is not significant. Also, the comparison of heat treatment of the silica at 500 and 800°C showed no difference, indicating that support sintering due to thermal collapse does not occur. Therefore, deactivation by carbon

encapsulation of the metal particles or carbon deposition on the surface appears more likely in this case. It is worth noting that the maximum amount of amorphous carbon by varying the reaction time or CO concentration was quickly reached, in contrast with the formation of SWNT, which was predominant only at longer times and at high CO concentrations. An important observation that may be linked to the deactivation process is the parallel trend observed in the oxidation state of Co with the rate of SWNT growth. XANES/EXAFS showed that oxidized Co was present while the growth rate of SWNT was high. After 30 min in reaction, when the SWNT growth slowed down, all Co became metallic.

The result that we would like to emphasize in this contribution is that the simultaneous presence of Co and Mo results in a more efficient catalyst for the production of SWNT from CO decomposition. Without Mo, Co is active for carbon growth but very unselective. Both TPO and TEM measurements showed the presence of large amounts of MWNT and amorphous carbon. Conversely, without Co, Mo is almost inactive in the temperature range investigated. We must note here that other investigators have reported the formation of SWNT by decomposition of CO on Mo catalysts [8]. However, those studies were conducted at 1200°C and an important difference of our results with those is that we observe formation of bundles of SWNT as opposed to the study conducted at 1200°C, in which the absence of bundles or 'ropes' was reported [8]. Another important difference is that in their case, there was a wide distribution of tube diameters, ranging from 1 to 5

nm. Our TEM observations show a more uniform distribution of diameters at around 1 nm.

The EXAFS/XANES results on the Co:Mo (1:2) may shed some light in the combined action of Co and Mo. These results show that Co suffers a drastic transformation under reaction conditions. Before reaction, but after pre-treatment in H₂ at 500°C and then in He at 700°C, a large fraction of Co is in the oxide state. After 10 min under reaction conditions, a significant growth in metallic Co was observed, although some oxidized Co was still present. After 30 min, the particles were even larger and essentially all the Co became metallic. The pronounced particle growth observed during the reaction was not observed during the treatment in He at the same temperature. It is well known that Co carbide is unstable at 700°C, but it is also known that CO greatly affects the surface of Co causing severe reconstruction [27]. This reconstruction can be associated to the rapid formation and decomposition of unstable carbides.

An important experimental observation to point out is that the formation of Mo carbide under reaction conditions only occurs in the presence of Co. That is, Co may be acting as an activator of CO, thus generating active carbon that would react with Mo and generate the carbide. After this finding we wanted to test the possibility that Mo carbide is the active species. It has been recently proposed that intermediate aromatic species generated on Mo may be the growing units in the production of SWNT [26]. This proposal was based on the idea that Mo carbide is supposedly the active species in the newly discovered aromatization of methane to benzene [28]. However, in that case, the reaction is thought to proceed via C₂ species, which are produced at the Mo carbide and subsequently oligomerize to benzene on the acid sites of the zeolite [29]. Therefore, it is unlikely that such mechanism operates in the growth of SWNT, but it is not unreasonable to consider that Mo carbide may play an important role in the reaction. For example, it is possible that Mo alone is not active for growing SWNT because in the absence of Co it cannot form the carbide, which in turn would be responsible for the formation of SWNT. However, the carbon growth measurement conducted on the pre-formed Mo₂C sample showed no SWNT formation. Therefore, the role of Mo may be that of a moderator of the Co activity rather than as an active species itself.

Likewise, no additional effect was observed when physical mixtures of Mo₂C and Co/SiO₂ or Mo/SiO₂ and Co/SiO₂ were tested. In both cases, the physical mixtures behaved as the sum of the individual parts. Therefore, it is shown that Co and Mo are simultaneously needed and in rather intimate contact. The question that remains is how can Mo inhibit the activity of Co towards the formation of MWNT, which are formed in large quantities in the absence of Mo. As shown in Fig. 7, the cobalt species in the fresh catalyst are in an oxidized state and very highly dispersed. At the same time, Fig. 9 demonstrates that only

Mo–O are present with essentially no Mo–Mo contributions. This results indicates that molybdenum oxides species are present in small domains in comparison to bulk MoO₃. In addition, as shown in Fig. 6 and 8, the oxidized cobalt species become metallic Co while the Mo species are converted to Mo carbide during the reaction with CO. It is reasonable to speculate that one of the roles of molybdenum in the catalyst is the stabilization of small particles of oxidized cobalt species, which are highly selective to the production of SWNT. Without this stabilization, Co species would tend to agglomerate, to get reduced more easily, and to form MWNT and graphite, as it is seen on Co/SiO₂ catalysts.

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

Another important consequence of the characterization results reported here is the demonstration that, under reaction conditions, the mobility of the catalyst components is very high. Therefore, explanations commonly found in the literature [7,8] based on pre-formed nanoscale metal particles, which in turn govern the size of the carbon nanotubes must be reconsidered. As shown here, the Co particles continuously grow in the presence of CO, much more than under He. At the same time, Mo initially in the form of a highly dispersed oxide, becomes carbide. At the high temperatures required to grow carbon nanotubes, one cannot expect that the size of the particles will remain as that of the original preparation.

5. Conclusions

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

- A synergistic effect between Co and Mo has been shown. When both metals are simultaneously present, the catalyst is very selective. When they are separate

they are either inactive (Mo alone) or unselective (Co alone).

- X-ray absorption spectroscopy (EXAFS and XANES) has shown that at the beginning of the reaction, Co is in the oxidic state, but is progressively reduced to the metallic form. During this process, metal particle growth takes place. Simultaneously, Mo is converted to the carbidic form.
- The yield and selectivity to SWNT are a strong function of the reaction temperature and the CO concentration in the gas phase.

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