Influence of the Metal and Support in the Synthesis of Carbon Nanotubes by Chemical Vapor Deposition

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Carbon Nanotubes (CNTs) are usually synthesized by the chemical vapor deposition (CVD) of hydrocarbons over metal – inorganic oxide support systems. We have studied semi-quantitatively, the CVD of carbon from acetylene on (1) Fe_2O_3-MoO_3 / MgO, (2) CoO-MoO_3 / MgO, (3) Fe_2O_3-MoO_3 / graphite and (4) Cs_2O / MgO. We find that both the nature of the metal (Fe or Co) and the support (MgO or graphite) influence significantly, the yield of CNTs (vis-à-vis amorphous and graphitic carbon), and the nature of the CNTs formed. More CNTs were formed when Co rather than Fe was used. Also, MgO was a superior support compared to graphite.

Keywords: Carbon Nanotubes (CNT), Chemical Vapor Deposition (CVD), Influence of metal, Influence of support in CNT formation.

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1. Introduction

Carbon Nanotubes [1] are nano-scale structures formed by self assembly. They possess excellent chemical and physical properties [2][3] that make them promising candidates for various applications ranging from electronics [4] to drug delivery [5]. CNT synthesis has been carried out by three methods namely, arc discharge [6], laser ablation [7] and CVD [8][9].

There are certain steps in nanotube formation that require the catalytic role of the metal [10]. Metals like Fe, Co and Ni, which form eutectic compound with carbon [11], are widely used in preference to other metals. The support used for the metals will influence the dispersion and electronic state of the metal and thereby the concentration and the type of nanotubes formed. In this communication, the influence of metal (Fe, Co and Cs) and support (MgO and graphite, rather than the usual oxide or zeolite support) on CNT formation is reported. Special emphasis is placed on the quantitative aspects of CNT formation; this latter information is lacking in most of the published results in this field [6-10].

2. Experimental

2.1 Catalyst Preparation

The catalyst samples (500 mg) were prepared by combustion method [12]. Fe_2O_3 – MoO_3 and CoO – MoO_3 catalysts (3 wt.% supported over MgO with Fe or Co : Mo = 9:1) were prepared by mixing $Fe(NO_3)_3.9H_2O$, $(NH_4)_6Mo_7O_{24}.4H_2O$, $Mg(NO_3)_2.6H_2O$ (GR, Merck, India) stoichiometrically followed by the addition of calculated quantity of citric acid (Loba Chemie, 99.5%). The weight ratio of $Mg(NO_3)_2$ to citric acid was 1:1.2. The mixture was ground thoroughly and made into a paste-like material with a few drops of distilled water. It was then burnt directly in a pre-heated muffle furnace at 450 ^{O}C for 10 min. The resultant mass was ground well and calcined at 550 ^{O}C for 5 h. Cs_2O / MgO catalyst was prepared by the same method from $CsNO_3$ (Merck, India), $Mg(NO_3)_2.6H_2O$ and citric acid.

Fe_2O_3 – MoO_3 catalyst (3 wt.% over graphite with Fe or Co:Mo = 9:1) was prepared by dry impregnation. Commercially available graphite rods were made into fine powder in a rotary spindle and soaked in conc. HNO_3 for 24 h to remove any metal impurity and subjected to heat treatment at 400 ^{O}C for 5 h to activate the powdered graphite. Calculated quantities of $Fe(NO_3)_3.9H_2O$, $(NH_4)_6Mo_7O_{24}.4H_2O$ were dissolved in about 10 mL demineralised water and the slurry was thoroughly mixed with graphite and grounded well at 80 ^{O}C. The solvent was removed by drying and calcined at 450 ^{O}C for 5 h.

2.2 CNT Synthesis and Purification

Carbon Nanotube growth was carried out by CVD using the prepared catalysts with the aid of conditioning catalyst, MoO_3 / MgO, prepared by controlled co-precipitation using NH_3 solution, which is reported to act as carbon sink during the CVD and thus control the feed-rate of the carbon to the active catalyst [13]. The CVD was carried out in an automated horizontal qaurtz tube furnace (FirstNano) operated with the ET2000 software to control the reaction temperature, reaction time and the flow rate of gases. In a typical experiment, the catalyst, taken in a 7 cm long quartz boat, was heated to 850 ^{O}C from room temperature in 13 min with a constant argon purge of 1000 sccm. At 850 ^{O}C, the flow rate of argon was stepped up to 2000 sccm along with an acetylene flow of 100 sccm for 20 min after which, the reactor was allowed to cool to room temperature with 1000 sccm flow of argon.

After the CVD experiment, the solid sample containing both the catalyst as well as the carbon deposit (the latter containing the carbon nanotubes as well as amorphous and graphitic carbon) was soaked in 1:1 aqueous solution of HNO_3 for 24 h at room temperature to dissolve the metal and MgO impurities. This acid-treatment was repeated twice and the sample was filtered, washed several times with distilled water till the pH of the filtrate was 7.0 and dried.

The dried sample was analyzed by Scanning Electron Microscope (SEM Leica 440). Thermo-gravimetric studies in air were performed with a Diamond TG-DTA system (Perkin Elmer Instruments). The samples were then burnt at 350 ^{O}C to remove the deposits of amorphous carbon. Transmission Electron Microscope (TEM) pictures of these purified samples were taken with a JEOL 1200EX microscope with tungsten electron source. The Raman Spectra of the samples were recorded using an integrated Laser Raman and photoluminescence instrument with UV coated deep depletion CCD camera. The spectra were obtained following an exposition time of 50 sec per step with an argon ion laser (20 mW) and standard Si calibration 519.726 cm $^{-1}$.

3. Results and Discussions

3.1 Role of Metal and Support

Cs / MgO did not yield any nanotubes (Figure 1 (a)). The catalytic role of a transition metal is (apparently) necessary for the nanotube growth. The Fe-Mo catalyst supported on graphite gave a very low yield of CNTs (Figures 1 (b-c)) in contrast to about 50 % yield from Fe-Mo catalysts supported over MgO.

This suggests that in addition to the metal, the nature of the support material also plays an important role in the formation of CNTs.

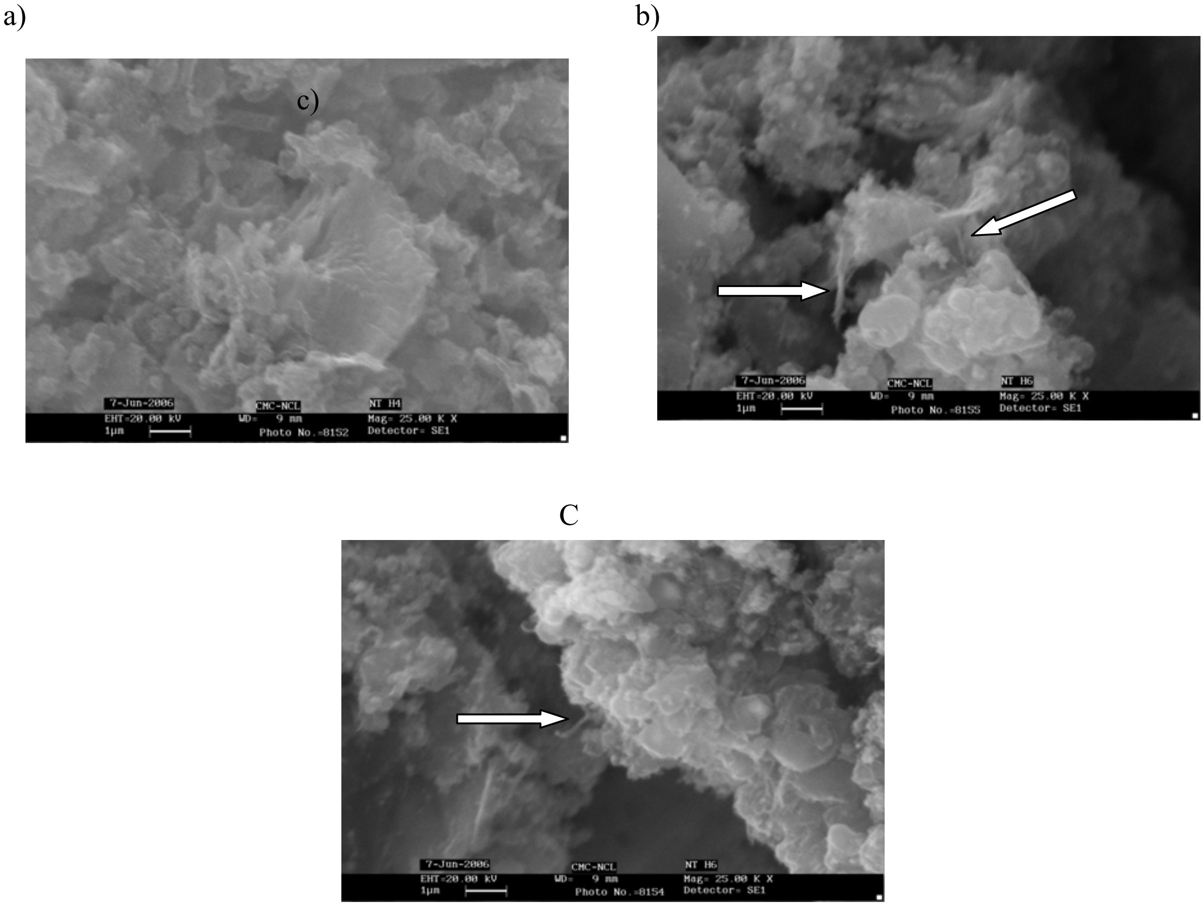


Figure 1 (SEM Images of Cs / MgO Catalyst after CVD (a), CNTs grown over Fe-Mo / graphite (b,c)

3.3 Quantifying the Carbon Yields

The total carbon deposited in each CVD experiment was calculated [14] as follows:

$$Total\ \ carbon\ deposit\ \% = [\ (W_{product} - W_{Catalyst})\ /\ W_{Catalyst}\ ]\ *\ 100$$

where $W_{product}$ is the total weight of the carbon deposit plus the catalyst after the reaction and $W_{Catalyst}$ represents the weight of catalyst alone before the reaction. The carbon deposit values are shown in Table 1.

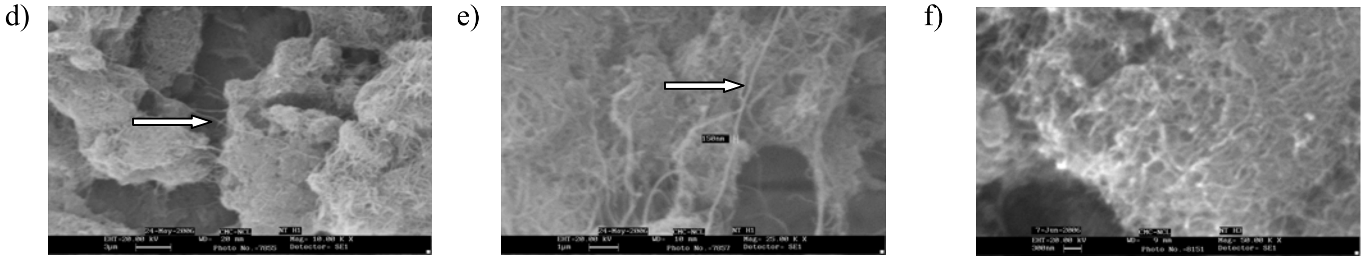
For a reaction time of 20 minutes during the CVD (with a constant 100 sccm flow of acetylene at 850 ^{O}C) 0.616 g of acetylene containing 0.568 g carbon would enter the reaction chamber, which is responsible for the 25 mg and 70 mg of the carbon deposition per 100 mg of Fe–Mo / MgO and Co–Mo / MgO catalysts, respectively. Assuming a linear relationship between the amount of carbon passed and the amount deposited over a given amount of the catalyst, we conclude that 4.4% and 12.3% of the total carbon passed has been deposited per 100 mg of the Fe-Mo / MgO and Co-Mo / MgO catalysts respectively.

Table 1: Influence of the metal in % carbon yield during the CVD

Catalyst used	Weight of Catalyst (mg)	Weight of Product + Catalyst (mg)	Carbon yield (%)	Weight of product after acid treatment (mg)	Weight of product after air oxidation (mg)
Fe-Mo / MgO	250	312	25	60	45
Co-Mo / MgO	100	170	70	63	26

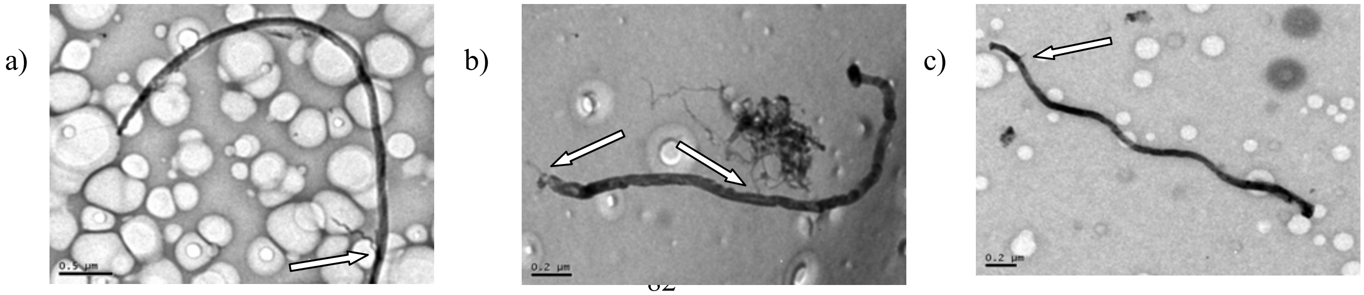
3.3 CNT Characterization

The acid-treated samples were analyzed by SEM for the presence of CNTs. SEM pictures indicate a good yield of nanotubes (of length 10-20 µm as indicated with arrows) with average diameters of 80-150 nm (Figures 2 (d-e)) (Fe-Mo / MgO) and 20-40 nm (Co-Mo / MgO) catalyst (Figure 2(f)).



Figures 2 (d-f)

Figures 3 (d, e, h, i) show the TEM micrographs in which tubes of 2-3 nm diameter are detected (indicated by arrows) though their concentration is lower than that of the thicker tubes. An interesting feature of the TEM pictures is the growth of CNTs from pre-existing CNTS in the system. As shown in Figures 3 (a-c, f, h) with arrows, nanotubes of diameter 2-5 nm (probably Single-Walled or Double-Walled Carbon Nanotubes – SWNTs or DWNTs) appear to have grown as offshoots of a parent nanotube, which perhaps contained encapsulated metal particles during its growth, suggesting the possibility of bi-directional growth of CNTs. There were also some twisted tubes (nanoropes). DWNTs in Figures 3 (e, h) and bundles of SWNTs in Figure 3 (i) are also indicated. CNTs with uniform U-like junctions were also observed (Figure 3(c)).



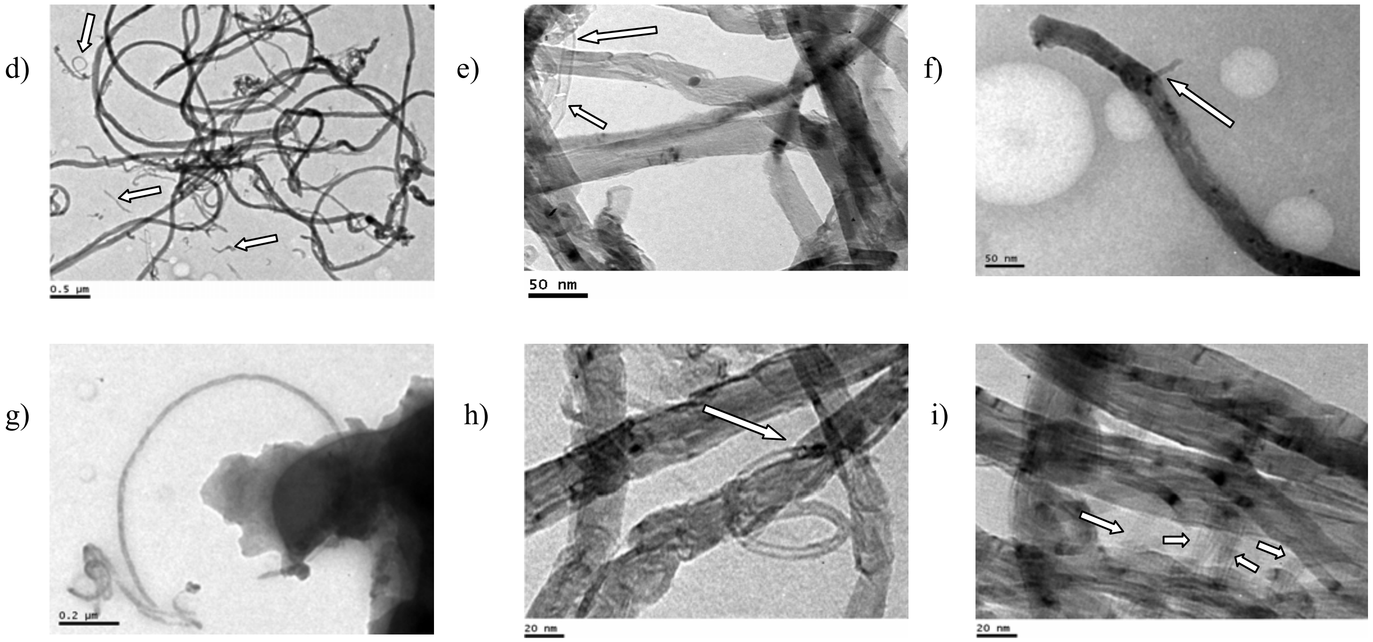


Figure 3 (CNTs grown over Fe-Mo/MgO (a–e) and Co-Mo/MgO (f-i))

TGA was performed on the acid washed samples for quantitatively estimating the relative content of the CNTs in the carbon deposits (Figures 4 (a-b)). The samples were heated to 800 ^{O}C from room temperature (with a ramp rate of 5 ^{O}C / min) and the loss of weight (%) was recorded. The amount of nanotubes was estimated to be 51% by weight (Fe-Mo / MgO) and 83% by weight (Co-Mo / MgO), whose oxidation started at approximately 500 ^{O}C. Graphite, with oxidation temperature of around 600 ^{O}C was estimated to be 40% (Fe-Mo) and 7% (Co-Mo). The TGA also showed that 2.92% of the Fe-Mo catalyzed nanotube sample was left unburnt at 800 ^{O}C. This is attributed to the remaining metallic and inorganic (MgO) impurities, which was not observed in the Co-Mo sample (Figure 4 (b)), whose acid treatment had resulted in metal-free CNTs.

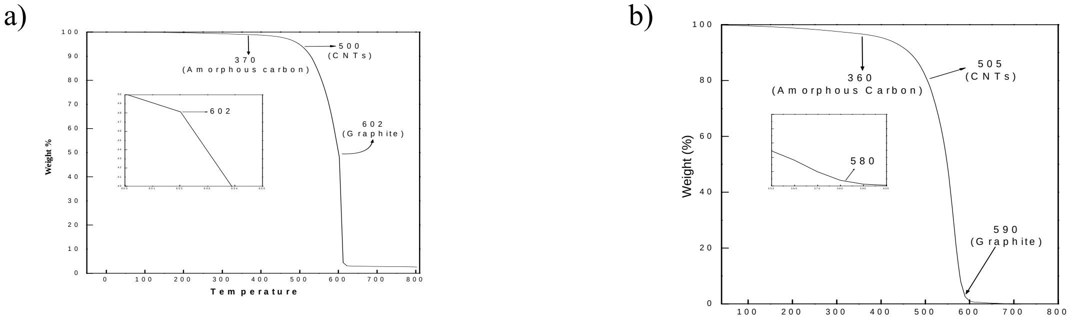


Figure 4 (TGA curves of Fe-Mo / MgO (a) and Co-Mo / MgO (b) catalyzed nanotubes)

Raman spectroscopy was used to estimate the tube diameter from the low frequency Radial Breathing Mode values (ω_{RBM}) [13]. Their presence in our samples confirms that there are nanotubes of diameter about 1 nm (Figures 5 (a-b)). Table 2 presents the diameter of the nanotubes calculated from the expression – $\omega_{RBM} = A / d$ *(nm) + B, where* $A = 234\ cm^{-1}$ *and* $B = 10\ cm^{-1}$ [13] and their corresponding chiralities [15].

The Fe-Mo / MgO yielded CNTs with wider diameter distribution than the Co-Mo / MgO catalyst (Table2). A strong G band at 1580 cm^{-1} (representative of the crystallinity and structural perfection of the nanotubes) [14] and the D band at 1349 cm^{-1} (representative of the defects, imperfections and crystal distortions) [14] are present for both the samples. The ratio of the area of Raman peaks in the low frequency RB Mode to the area of the peaks in the full spectral range was estimated to be 0.06 (Fe-Mo / MgO) and 0.075 (Co-Mo / MgO). This suggests that in the respective samples, 6% and 7.5% of the total nanotube content are those tubes whose diameter was between 0.72 nm – 1.18 nm (Single-Walled or Double-Walled CNTs).

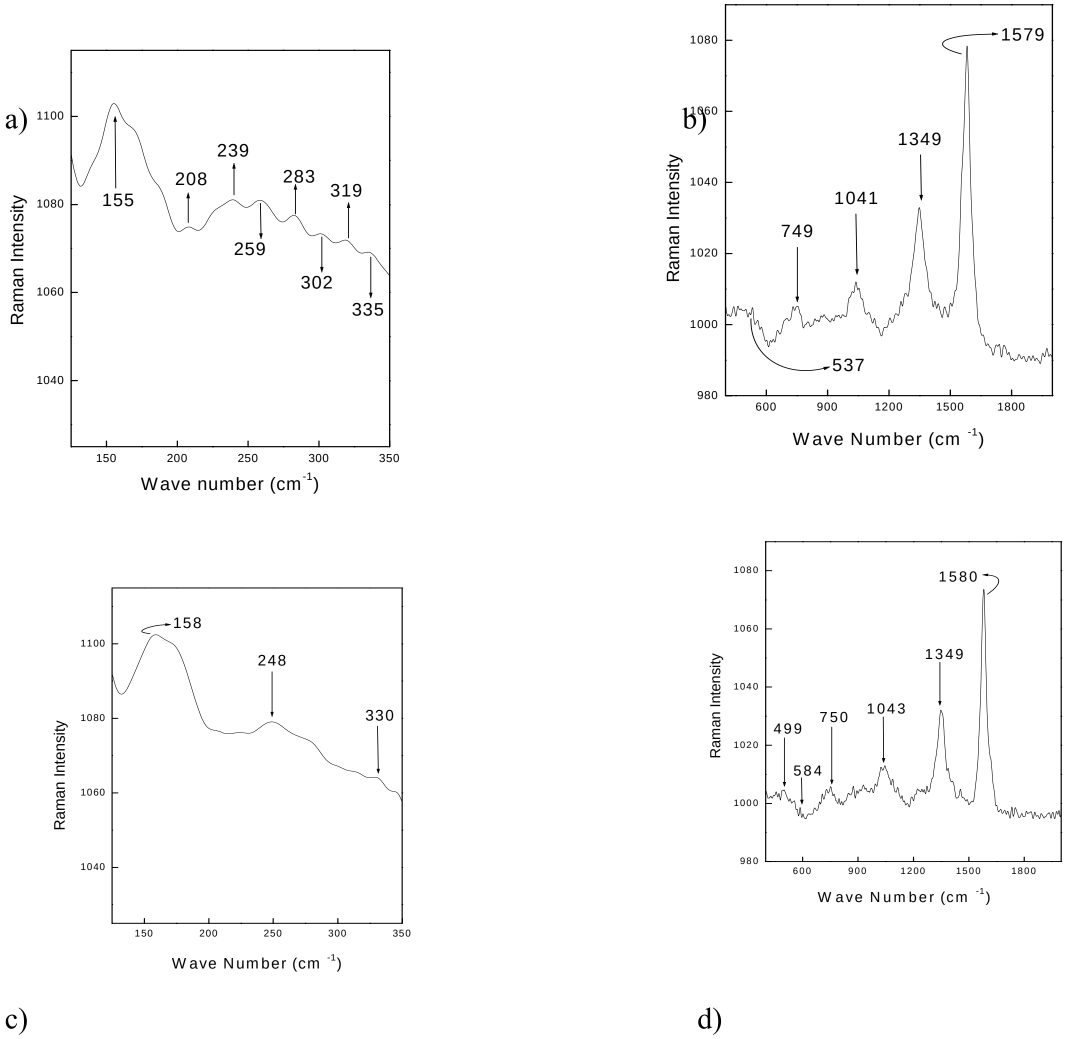


Figure 5 –Raman Spectra of Fe-Mo/MgO (a, b) and Co-Mo/MgO (c,d) catalyzed CNT samples.

Table 2: Structural parameters of CNTs from RBM values of Raman spectra

Catalyst used	ω_{RBM} (cm $^{-1}$)	Diameter-d (nm)	Chirality (n,m)
Fe-Mo / MgO	208	1.18	(10,7)
	239	1.02	(9,6)
	259	0.93	(11,1)
	283	0.85	(7,5)
	302	0.80	(7,4)
	319	0.75	(8,2)
	335	0.72	(6,4)
Co-Mo / MgO	248	0.98	(12,0)
	330	0.73	(6,4)

4. Conclusions

We have examined the influence of the metal and support used in the CVD synthesis of Carbon Nanotubes over Cs / MgO, Fe-MoO$_3$ / MgO, Co-MoO$_3$ / MgO and Fe-MoO$_3$ / graphite. Fe-MoO$_3$ / graphite catalyst gave an extremely low yield of nanotubes. Cs / MgO does not catalyze the nanotube formation under similar experimental conditions. The nanotubes (about 1-3 nm diameter) prepared from Fe-Mo and Co-Mo supported over MgO revealed a possible bi-directional growth of CNTs and formation of uniform U-like junctions.

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