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High crystallinity multi wall carbon nanotubes synthesized by inductive heating CCVD

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Carbon nanotubes were synthesized by CCVD with inductive heating from acetylene on a Fe-Co/CaO catalyst obtained from the thermal decomposition of the Fe:Co:$CaCO_3$ catalyst in nitrogen, previous to the growth process. MWCNTs were synthesized at 750, 850 and 950 °C and characterized by TEM, TGA and Raman Spectroscopy. The nanotubes presented a ratio of the outer to inner diameters between 2 to 3, and 90 % of all them have diameter values ranging from 5-25 nm, with an aspect ratio in the order of hundreds. As the reaction temperature increased, the synthesis efficiencies decreased and the amount of metallic nanoparticles encapsulated inside the nanotubes increased.

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1. Introduction

Due to their unique physical and chemical properties, carbon nanotubes, both single walls (SWCNTs), multi walls (MWCNTs), have found an increased number of applications in various fields ranging from physics, chemistry, electronics, and biology. Their synthesis by Catalytic Chemical Vapor Deposition (CCVD) allows a direct control of their corresponding structure and morphology by the adjustement of the synthesis parameter (catalyst system, hydrocarbon type, carrier gas, temperature, etc.). The catalysts have an important role in the synthesis process, since their composition is controlled by the method and chemistry of preparation affects, the selectivity and the efficiency of the catalytic reaction [1]. Furthermore, they should be easily removable during the purification process without destroying the crystallinity and the morphology of the nanotubes. In this sense, many studies have focused on the utilization of the alkaline earth carbonates [2-6] and their corresponding oxides (Mg, Ca) [7,8] as catalytic suport because they are soluble in mineral diluted acids. In this paper, the focus was to structurally and morphologically characterize the carbon nanotubes synthesized from acetylene on the Fe:Co:CaO catalyst, obtained by *in situ* thermal decomposition of the Fe:Co:$CaCO_3$ catalyst previous to the growth process by the inductive heating (IH) assisted CCVD process [9,6]. The results indicate the successfull use of novel CaO supported catalyst systems that generate high quality multiwall carbon nanotubes with narrow diameter distributions and high crystallinity. Another significant highlight of this work is the ability to grow carbon nanotubes that have transitional metal nanoparticles incorporated in their lumens in various ratios. Such materials have significant novel applications in the area of electromagnetic shielding, radar evasion, nanoelectronics, etc.

2. Experimental details

First, the Fe:Co:$CaCO_3$ (2.5:2.5:95 wt %) catalyst (noted through this study as **$CaCO_3$**) was prepared as previously reported in the literature [3]. The distilled water solutions of the $Fe(NO_3)_3{\cdot}9H_2O$ and $Co(CH_3COO)_2{\cdot}4H_2O$ salts were poured over a $CaCO_3$ suspension in water under continuos stirring. The pH of the salution was maintained constant at 7-7.5 by adding ammonia solution (25 %). The solvent was evaporated on a steam bath under continuous stirring and the resulting solid matter was further dried overnight at 125 °C and powdered in a mortar.

For carbon nanotubes growth, 150 mg of the Fe:Co:$CaCO_3$ catalyst were uniformly dispersed onto a graphite susceptor and introduced into the quartz reactor (2cm diameter and 80 cm length) positioned in the middle of a water-cooled copper coil connected to a high frequency generator (5 kW, 1.9 MHz). A nitrogen flow of 200ml/min was introduced into the reactor for 15 minutes to remove the air, followed by inductive heating at 850 °C for 30 minutes in order to allow the calcium carbonate to decompose into CaO and CO_2. The resulting catalyst was Fe:Co:CaO (4.3:4.3:91.4 wt %) (noted through this study as **CaO**). Once this process was completed the temperature of the susceptor was adjusted to the desired reaction temperature (750, 850 and 950 °C) followed by the administration of acetylene (3 ml/min) for 30 minutes. The final product was cooled into nitrogen flow. For comparison there were also synthesized carbon nanotubes on the **$CaCO_3$** at 750 °C and identical flow conditions for nitrogen and acetylene.The removal of the catalyst from the final product was done by ultrasonication in HCl (1:1) for

30 minutes, washing with distilled water, and drying overnight at 120 °C.

The efficiency of the reaction is defined as per cent ratio between the mass of product obtained after purification and the initial mass of catalyst.

The morphology of the nanotubes was studied by scanning electron microscopy (SEM), transmission electron microscopy (TEM) (FEI Tecnai F30 STEM). For this analysis, carbon nanotubes were dispersed in 2-propanol and ultrasonicated for 10 min. A few drops of the suspension were deposited on the TEM grid, then dried and evacuated before analysis. Raman scattering studies of the CNTs were performed at room temperature using Horiba Jobin Yvon LabRam HR800 equipped with a charge-coupled detector, a spectrometer with a grating of 600 lines/mm and a He-Ne laser (633 nm) and Ar+ (514 nm) as excitation sources. The laser beam intensity measured at the sample was kept at 5 mW. The microscope focused the incident beam to a spot size of <0.01 mm^2 and the backscattered light was collected 180° from the direction of incidence. Raman shifts were calibrated with a silicon wafer at a peak of 521 cm^{-1} Thermogravimetrical analysis (TGA Mettler Toledo 815e) were done in airflow (150 ml/min) and a heating rate of 5 deg /min.

Surface analysis measurements (Micromeritics ASAP 2020) were performed on the catalysts before and after the thermal treatment in order to understant the surface modifications that were induced.

3. Results and discussions

Thermogravmetric analysis was used to determine the decomposition mass for the $CaCO_3$ support and the time that is required for a complete decomposition. Figure 1 shows TGA curve for the **$CaCO_3$** catalyst and its corresponding thermal decomposition curve.

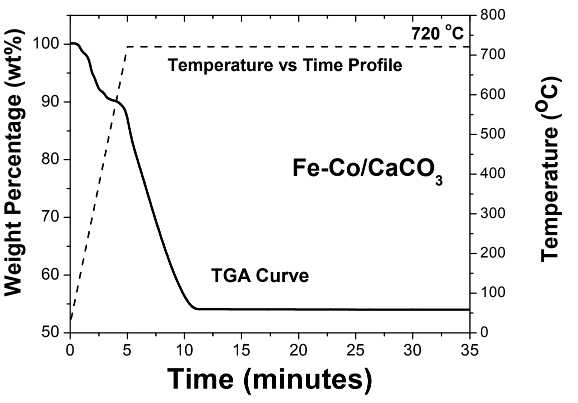

*Fig. 1. The weight loss profile and the temperature curve of **$CaCO_3$** versus time.*

The analysis of the thermogravimetrical analsys data indicates that at 720 °C after aproximately 12 minutes the entire amount of $CaCO_3$ is completely decomposed. The total relative mass loss is 46 % of the initial value, which indicates that out of 100 mg of $CaCO_3$ support only 54 mg will be available to support the new catalyst Fe:Co:CaO. Therefore, the *in-situ* treatment at 850 °C for 30 minutes of the **$CaCO_3$** catalyst before the carbon nanotube synthesis process should be enough to completely generate the **CaO** supported catalyst. The BET surface areas measured by krypton adsorption for the two catalysts are 6.2 m^2/g for **$CaCO_3$** and 6.3 m^2/g for **CaO** respectively. The overall reaction efficiencies were: 28 % at 750 °C, 19 % at 850 °C and 12 % at 950 °C. Figure 2 shows the low resolution TEM pictures after purification of the nanotubes synthesized out of acetylene at 750 °C over the **$CaCO_3$** catalyst and at 750, 850 andi 950 °C over the **CaO** catalyst**.**

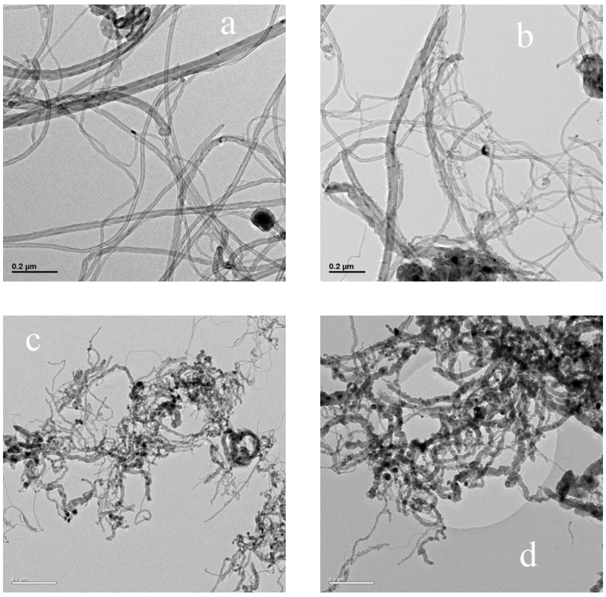

*Fig. 2. Low magnification TEM pictures for the MWCNTs synthesized with acetylene as carbon source at 750 °C over **$CaCO_3$** (a), and 750°C (b), 850°C (c), 950°C (d) over **CaO**, respectively. The bar represents 0.2 µm for a and b and 0.5 µm for c and d.*

The analysis of the TEM data indicates that generally the nanotubes have exterior diameters ranging from 10 to 60 nm, and lenghts in the range of hundreds of nanometers. It was also observed that the amount of metallic nanoparticles entrapped inside the nanotubes synthesized on the **CaO** catalyst (Fig. 2 b,c,d) after purification increased proportionally with the temperature of reaction.

Fig. 3 presents the exterior diameter distribution for the nanotubes synthesized 750 °C over the **$CaCO_3$** (a) and **CaO** (b) catalysts. The diagrams were obtained by analysing the low and high resolution TEM images of over 100 nanotubes for each case.

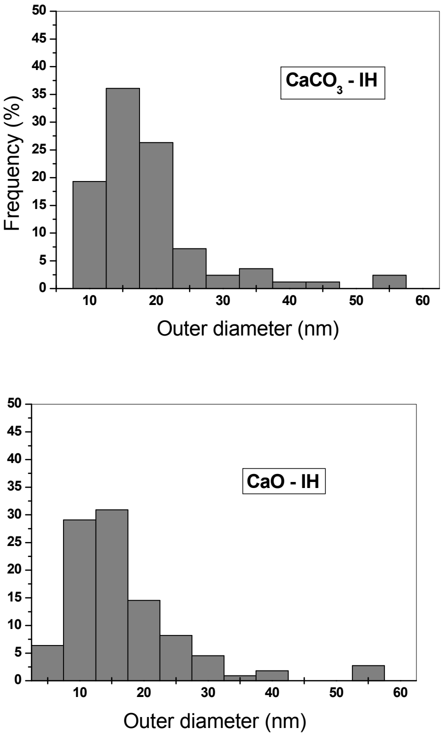

*Fig. 3.Exterior diameter distribution diagrames for the MWCNTs synthesized 750 ^{o}C over the **CaCO$_3$** (a) and **CaO** (b) catalysts.*

It was observed that aproximately 90 % of all the nanotubes have exterior diameters ranging from 5 to 25 nm.

Figure 4 presents the high resolution TEM (HR-TEM) pictures for the nanotubes grown on the **CaO** catalyst at the following reaction temepratures: 750 ^{o}C (a), 850 ^{o}C (b), and 950 ^{o}C (c).

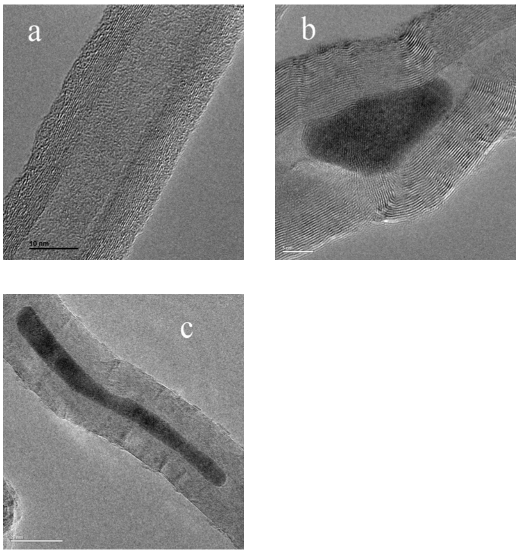

*Fig 4. HR-TEM pictures of the MWCNTs synthesized on **CaO** catalyst at 750 ^{o}C (a), 850 ^{o}C (b) and 950 ^{o}C (c) (the bar represents 10 nm for (a), 5 nm for (b) and 20 nm for (c)).*

The pictures shown in Figure 4 indicate that there are no depositions of amorphous carbon on the nanotubes surfaces, that the graphitic layers are well ordered and equi-distanced, and following the exterior profile of the nanotubes, especially for those grown at 850^{o}C (Fig. 4 b). Analyzing over 100 nanotubes indicated that the ratios of the exterior to interior diameters (OD/ID) range between 2-3, values that are in good agreement with those obtained during other synthesis processes that used inductive heating assisted CCVD [6]. The metal nanoparticles encapsulated inside the nanotubes were found to have spherical, ellipsoidal, pyramidal, and cyllindrical shapes with dimensions that vary from 3 to hundreds of nm.

The quality and overall purity after purification of the nanotubes synthesized from acetylene on the **CaO** catalyst were assesed by both TGA and Raman Spectroscopy.

Thermogravimetric curves of the samples synthesized over the **CaO** catalyst, and which were performed in air in the temperature range of 25 to 850 ^{o}C, are shown in Fig. 5.

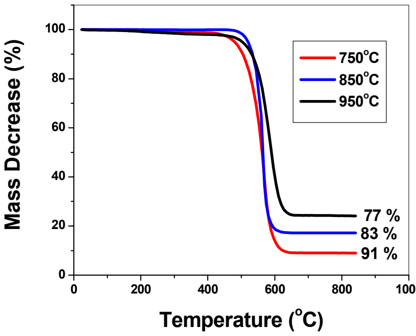

*Fig. 5. The TGA curves for the MWCNTs synthesized over the **CaO** catalyst at 750, 850 and 950 ^{o}C..*

The TGA curves (Fig. 5) indicate the existence of a single mass loss profile for all reaction temperatures, which indicates that all the analyzed nanotube samples are composed of a single type of carbonic form. [10,11]. The purity of the nanotubes determined from the TGA curves (mass that thermally decomposes) decreases linearly with the increase of the reaction temperature: 91 % for 750 ^{o}C, 83 % for 850 ^{o}C and 77 % for 950 ^{o}C.

Since all nanotube samples were exposed to identical purification processes, the purity differences can be explained by the fact that the remains after burning off the carbonic product are the metal nanoparticles encasulated inside the nanotubes and which were unreached by the acid during the purification process. These observations are in very good corelations with the low and high resolution TEM pictures.

Raman Spectroscopy is a powerful, fast, and non-destructive tool for the characterization of carbon nanotubes without sample preparation [11,12]. Generally the Raman spectroscopy does provide very accurate and reliable information of the graphitic materials, that incude: morphological and structural properties and crystallinity. Given the weaker Raman signal of the oxidized metal impurities as compared to the signal geneated by the carbonaceous materials, it is possible to use this analytical technique to characterize carbon nanotubes both before and after purification.

Raman spectra (over the spectral domain 1000 to 3000 cm^{-1}) obtained at two excitation wavelengths (514 nm and 633 nm), of the nanotubes synthesized on the **CaO** catalyst at 750, 850 and 950 ^{o}C, are presented in Figure 6. The spectra show all the characteristic bands corresponding to MWCNTs: D band (between 1305 and 1330 cm^{-1}) is associated to the vacancies, defects, and carbonic impurities (amorphous carbon, glassy carbon, etc) that destroy the symetry, G band (between 1500 and 1600 cm^{-1}) coresponding to the splitting of the E_{2g} stretching mode for graphite, and 2D band, which is the second harmonic of he D band (between 2450 – 2650 cm^{-1}) and is associated to the degree of crystallinity of the graphitic layers [13,14]. The ratio between the intensities of the G to the D bands (I_G/I_D) gives information regarding the purity of the carbon nanotubes relative to the presence of other graphitic products (high value = high purity). Alternatively, the ratio between the intensities of the G and 2D bands, (I_G/I_{2D}), also indicates the level of quality and crystallinity of the carbon nanotubes (low value = increased crystallinity) [10].

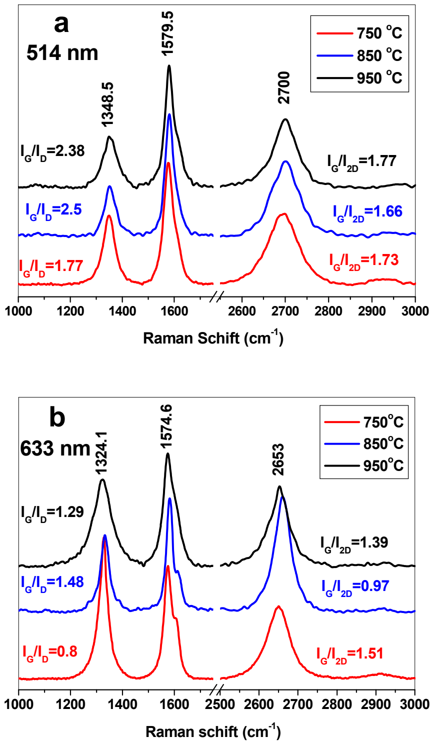

Fig. 6. Raman Spectra of the corresponding carbon nanotubes synthesized over the ***CaO*** *catalyst at 750, 850 and 950 ^{o}C for two laser excitations 51 4 nm (a) and 633 nm (b).*

The Raman spectroscopy data and the I_G/I_D şi I_G/I_{2D} ratios as specified in Figure 6 (a and b) and as previously shown by others [18], indicate that for both excitation wavelengths (514 and 633 respectively), the highest values (I_G/I_D=2.5, I_G/I_{2D}= 1.66 at 514 nm and I_G/I_D=1.48, I_G/I_{2D}= 0.97 at 633 nm) are obtained for the nanotubes synthesized at 850 ^{o}C. Although all the samples were found to present high quality and crystallinity, the synthesis temperature that generated the highest crystallinity nanotubes was 850 ^{o}C. Therefore, although the synthesis efficiencies varied linearly with the growth temperature, the quality of the coresponding nanotubes did not present the same trend. These results are in excellent correlation with the HR-TEM images (Fig 4b) and with other research reports that showed the existence of a window of temperature for the nanotube synthesis [15].

4. Conclusions

Multi wall carbon nanotubes were synthesized by the inductive heating - assisted CCVD method (1.9 MHz) from acetylene on a Fe:Co:CaO catalyst that was obtained by *in-situ* thermal decomposition of the Fe:CoCaCO_3 catalyst.

The characterization of the corresponding carbon nanotubes by TEM, TGA and Raman Spectroscopy indicated that: (1) the reaction efficiency decreases as the synthesis temperature increase, (2) 90% of the nanotubes have the exterior diameters ranging between 5 to 25 nm, (3) the amount (both quantity, size, and numbers) of the entrapped metal nanoparticles inside the carbon nanotubes increased significantly with the reaction temperature, (4) no amourphous carbon was noticed on the surface of the nanotubes, (5) the outer to inner diameter ratios ranged between 2 to 3, (6) the reaction temperature that generated the nanotubes with the highest crystallinity was found to be 850 ^{o}C

The growth of carbon nanotubes with high quality and high content of encapsulated ferromagnetic nanoparticles is of high importance due to their potential use as doping nano-materials in advanced composites with applications electromagnetic shields, nanoelectronics, radar evasion, and electrostatic charge dissipation.

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