Catalytic effect of Fe, Ni, Co and Mo on the CNTs production.

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Abstract. In this work a chemical vapour deposition (CVD) process was implemented and automatized for the synthesis of carbon nanotubes (CNTs). Looking the possibility to make an extensive use of biogas, and also for decreasing the costs of the process, methane was used as carbon source. Different CNT structures were obtained using Fe, Ni, Co and also Mo nanoparticles, supported on silica-gel as catalyst for CNT’s growing. The number of walls, the morphological effects and efficiency of the process showed dependency on the catalyst type. Cobalt helps the growing of CNTs with fewer layers, compared with Ni, Fe and Mo. Low quality structures are mainly obtained with Fe nanoparticles. Cobalt promotes small diameters in carbon nanotubes and Ni promotes the best quality and yielding during the CVD process.

1. Introduction

Facing the market of nano-materials, one of the main kinds which are increasingly used for different technologies are the CNTs. Due to excellent structural, physical, electrical and mechanical properties, CNTs have stimulated the development of new technologies unimaginable some decades ago. This has become the subject of studies focused on exploring the use of CNTs in various areas [1]. The CNT applications can enable nano-scale molecular levels, which have also generated great enthusiasm in the scientific community and a revolution in modern materials science [2]. Currently is possible to find a variety of studies about CNTs, ranging from structural and physicochemical properties, synthesis to surface modifications [3, 4]. Despite this vast literature, the knowledge obtained on the CNTs are just the prelude of its potential.

Historically, CNTs have been obtained by different methods; including: chemical vapor deposition (CVD), solvothermal (several synthetic strategies have been employed without using transition metal catalyst. Templates, precursors and hydro or solvothermal methods, using binary and complex metal
oxides, chalcogenides, and carbides can be implemented), electrochemical (deposition from organic solutions at room temperature, with formation and growth stimulated by transition metal catalyst, such as iron and/or nickel), or hydrothermal methods (hydrothermal synthesis using polyethylene/water mixtures in the presence of nickel at 700-800° C under 60-100 MPa pressure), as well as arc discharge (soot formed from graphite electrodes during arc discharge), reactive milling (ball-milling and annealing or a pressure-vapor-condenser), laser ablation (a pulsed-laser vaporizes a graphite target in a high-temperature reactor as an inert gas is blend into the chamber), plasma forming (plasma growth at low temperatures) and HiPCO (continuous flow high-pressure carbon monoxide) [5-7].

Although all the methods for nanotube synthesis and processing are still under continuous development, the most common synthesis method is the hydrocarbon pyrolysis process, also known as carbon vapor deposition (CVD). For CNTs production, it is usually known as thermal CVD or catalytic CVD, to distinguish it from many other kinds of CVD used for various purposes [8]. CVD is an economically and industrially viable process due to the facility to scale. In this process, CNTs can grow from catalyst particles using batch or continuous processes such as a fluidized bed. Thermal decomposition of a hydrocarbon vapor is achieved in the presence of the metal catalyst. As a carbon source it is possible to use different hydrocarbons compounds, including biogas, allowing a proper kinetic for the production of CNTs [9] and the modulation of the nanotube diameter [10-11].

The catalysts used for the production of CNTs are usually transition metals supported on silica [12], mesoporous silica (MCM-41, MCM 48, SBA-15), [13], calcium carbonate, zeolites [14] or magnesium oxide [15]. All types of catalysts have been studied with the aim of increasing the productivity of CNTs, for improving their properties and modulate their structures. In this work a CVD process was used for the synthesis of CNTs, using different silica-supported catalysts, like Fe, Ni, Co and Mo. The sol-gel method was used for the synthesis of supported metal catalysts.

2. Experimental procedure

2.1. Catalyst preparation
The sol-gel method has been extensively used in the preparation of supported metal catalysts because it typically results in highly homogeneous materials with high degree of metal dispersion [16]. In this sense, catalysts were supported on silica sol-gel with the metal to 50 percent based on silica added. To obtain metallic catalyst supported on high-surface area silica by the sol-gel method, the polymerization of an alkoxy-silane such as tetraethoxysilane (TEOS), also known as tetraethyl orthosilicate, is carried out in the presence of the appropriate metal precursors. In our case, catalyst nanoparticles were prepared from high purity salts of the transition metals: Ni(NO3)2•6H2O, Fe(NO3)3•9H2O, Co(NO3)2•6H2O and (NH4)6Mo7O24•4H2O, from Baker Co [17]. To accelerate the polymerization, an increase in pH can be brought about by addition of a base, which causes a rapid hydrolysis followed by polymerization [18]. Simultaneously with this polymerization process, the metallic ions (Fe, Ni, Co and Mo) precipitate, thus forming a homogeneous and well-dispersed mixture.

2.2. CNTs synthesis
After placing the catalyst inside a quartz tube, a continuous nitrogen flow rate of 1 L/min was passed through the reactor for removing the oxygen. Subsequently, the reduction process was accomplished within at 600° C. The reduction process was kept for 30 minutes in an atmosphere of 90 % v/v of N2 and 10 % v/v of H2. Next, the temperature was increased up to 700° C for the nucleation and growing of CNTs.

2.3. Characterization
The high-resolution images were obtained using a high-resolution transmission electron microscope JEOL JEM-2010, operated at 200 kV and a scanning electron microscopy (SEM) JEOL JSM 5300 operated at 5 kV. Complementary RAMAN spectroscopy was performed, and also thermogravimetric analyses (TGA) for CNTs were carried out in a SW Stare Mettler 8.0 device, with a heating rate of 10 °C/min (25 to 900 °C) in an air atmosphere with flow of 50 ml/min.
3. **Results and discussion**

Raman spectra of CNT samples using different catalysts are presented in Figure 1. Studies carried out by Dresselhaus about Raman spectra for CNT show that the number of defects in graphene layers depends on the ratio \( I_D/I_G \), which must be less than 0.45 for high structure quality of the CNTs [19]. Figure 1a shows the Raman spectra for CNTs-Ni, in which the ratio \( I_D/I_G \) is 0.416, relating a high purity material. The highest purity was obtained in CNTs-Co, with an \( I_D/I_G \) ratio of 0.26. On the other hand, with Fe, and Mo the quality is decreased in a high level (Figures 1c, 1d), mainly with Fe (\( I_D/I_G \approx 1.48 \)). This is due to the low solubility of C in Fe. In order to obtain a better quality, in this case the CVD process must performed to high temperatures (~900°C). In our experiments, for comparison purposes, the temperature was always the same for the different metal-catalyst (~700°C).

According to previous reports [20], the increase of the D band intensity (characteristic peak at ~1350 cm\(^{-1}\)) with decreasing multiwalled carbon nanotubes (MWCNT) content, is a direct result of the addition of carbonaceous by-products. In the same sense, a decrease in the G’ band intensity (characteristic peak at ~2700 cm\(^{-1}\)) is observed as the MWCNT mass fraction decreases. The G' band on Figures 1a and 1b reflects the well-structured carbon walls in the samples with Co and Ni catalyst, while the Figures 1c and 1d (CNTs-Fe and CNTs-Mo), indicate a less ordered structures, due to the carbonaceous by-products.

**Figure 1.** Raman spectra of CNTs grown with (a) Ni, (b) Co, (c) Fe and (d) Mo on silica gel.

FESEM in Figure 2 shows a linear growth of CNTs using Ni as catalyst. The Figure 2a shows that the external diameter distribution of CNTs-Ni ranges from 40 nm to 100 nm. The lengths reached up to several microns (1-7 μm). The tips of these CNTs are closed and contain the catalytic particles enclosed. Figures 2b and 2c show the layers for an isolated CNT. An analysis of the image obtained by HRTEM shown in Figure 2b, lead to conclude that a total of 69 layers and an external diameter of 85.05 nm was obtained (between the layers a gap of ~0.35nm can be calculated in order to obtain the total of layers, according to the methodology developed by Gommes [21] and collaborators, and performing some numerical treatments, through the cross section of the CNTs using the Lambert's law [22]). Also, it is observed that the CNT’s layers are relatively aligned, verifying the structural quality predicted by the \( I_D/I_G \) ratio in Raman spectra (Figure 1).
Figures 3a-3c show CNT-Co. In this case, the number of walls in the samples is less than the rest of catalyst (Fe, Ni, Mo), with a length above 10 μm. Figures 3b and 3c show that the CNTs layers ranged from 4 to 12. Despite the little number of walls, during the CVD process we obtained MWCNT because the number of walls is in average higher than 4 layers. The CNT-Co allows low number of layers as has been reported by S. Porro [23]. Some CNTs have internal diameters less than 10nm and an external diameter less than 50 nm.

Figure 2. FESEM (a) and HRTEM (b) images for CNT-Ni. (a) and (b) CNT-Ni and (c) number of layers.
Figure 3. FESEM (a) and HRTEM (b), (c) images for CNT-Co.

Figure 4 shows CNT-Fe with lengths about 4 μm with not high crystallinity, an internal and external diameters of ~12 nm and more than ~40 nm respectively and 57 layers. The growth of CNT-Fe is tangled and disorderly. According to the results obtained by Huang [24], CNT-Fe and CNT-Co present a non-linear growth. It is also common find the catalyst encapsulated inside the CNT, as a result of the growing process and the little chemical interaction between the catalyst and the silica-gel support. In this sense, the equilibrium state of iron oxide phases (α, β) promote the agglomeration of the catalyst nanoparticles and decrease the encapsulation and the introduction of nanoparticles inside the silica support [25].
Figure 4 (a) FESEM image of CNTs-Fe, (b) HTEM of CNT. An iron particle encapsulated in a CNT is observed, (c) Number of layers.

Figure 5 shows the CNT-Mo. The micrographs exhibit the low productivity compared with Ni, Co, and Fe. Besides the matrix of silica gel may cover the metal particles, exposing a little surface area to the carbon precursor gas. The main reason for this scarce production of CNTs is attributed to the little solid-state diffusion of carbon in molybdenum. It was difficult to obtain a high purity in samples, due to the big size of silica clusters (red circle in Figure 5a). The presence of silica during HRTEM analyses inhibits the observation of the numbers of layers due to the electron’s saturation at high voltages (~ 200 kV). Nevertheless, Figure 6 shows the external diameter of CNT-Mo but obtained by FESEM at low voltages. The external diameter ranges between 64.8 to more than 70 nm.

Figure 5 FESEM micrographs of CNT-Mo
J.H. Lehman et-al mentioned that no single metric defines nanotube purity. The naïve definition of pure MWCNTs in bulk refers to multiple MWCNTs, all identical, each consisting of a specified number of carbon atoms [26], but this not real during the production of MWCNTs. In this sense, purity refers to the nature of the MWCNT content. On the other hand, for industrial-scale measurements and batch-to-batch quality control, TGA is arguably the most common and practical tool. TGA analysis for CNT-Co in Figure 7a shows an increase in weight since 200 to 400°C, due the oxidation of catalytic metal nanoparticles. Then, the decomposition of carbon structures, related to the loss of weight, is observed from 480 – 500°C. Because some catalytic nanoparticles, encapsulated inside the tubes, can be released during the carbon’s structures oxidation; a new increase in weight follows until ~600°C. From this point, the decomposition of different carbon structures continues. In other words, the broad temperature gap (~400°C – ~850°C) indicates diverse number and quality for the carbon layers of nanotubes.

Figure 7. TGA obtained in oxidizing atmosphere for CNT-Co (a) and CNT-Ni (b).
4. Conclusion

When the sol-gel method is used for the synthesis of supported metal catalysts, additional parameters related to the chemistry of the metal precursors are also important. In this regard, this work showed that the different metals used as catalysts allowed the growing of carbon nanotubes. The CNT-Ni is more homogeneous and stable than CNTs grown with other catalysts. Cobalt allows modular small diameter sizes (7-40 nm) during the sol-gel synthesis. The CNT-Fe was not very stable. In other words, because the diffusion of carbon in iron is favored with increasing temperature (>700° C), the presence of amorphous carbon is promoted. The Mo catalyst requires temperatures above 800° C for the deposition of CNTs. The silica sol-gel is a catalytic support that allows high surface area for different catalytic metals (i.e. Fe, Ni, Co, Mo) facilitating the synthesis of CNTs at low temperatures, with different morphological characteristics, for different potential applications.

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