Synthesis of carbon nanotubes from acetylene on the FeCoMgO catalytic system obtained by ball milling

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Abstract. Highly crystalline multi wall carbon nanotubes have been synthesized by RF-CVD from acetylene at 850°C over a Fe:Co:MgO catalyst. The catalytic system was obtained by mixing for 100 h Fe, Co and MgO powders in a ball milling device under petroleum ether environment, followed by oxidation in air at 500°C for 24 h. Most of the nanotubes had external diameters in order of dozens of nm and lengths of microns, resulting in an aspect ration of over 1000. Their external to internal diameter ratio varied between 2.5 and 3.

1. Introduction

Given their remarkable electric, mechanic, and optical properties, the carbon nanotubes are continuously more attractive for various advanced applications. For the synthesis of carbon nanotubes, there are currently employed three major methods: electric arc discharge [1], laser ablation [2], and chemical vapour deposition [3]. Until now, the CVD method is the mostly commonly used because it allows the control of the morphological properties of the nanotubes by modifying the reaction parameters. This process is based on the pyrolysis of various gaseous hydrocarbons (C₂H₂, CH₄, C₂H₄), carbon monoxide CO or liquid (alcohols, benzene, hexane), typically between 700-1000°C over a catalytic system [4, 5]. The type of nanotubes (SW or MW), diameter, chirality, or the synthesis yield are very sensitive to the type, composition and the structure of the catalyst used in the reaction. Generally, the catalyst used for the growth of carbon nanotubes are mono or bi-metallic of transitional metals Fe, Co, Ni, or Mo on various inorganic supports MgO, Al₂O₃, SiO₂, usually obtained by impregnation [6] and co-precipitation [7]. It has also been previously reported the use of hydrogen uptaking alloys such as AB₂ (Zr-based), AB₃ (Mm-based) [8], or LaNi₅ [9].

In this contribution, we present the synthesis of multi wall carbon nanotubes from acetylene at 850°C over the Fe:Co:MgO (2.5:2.5:95 % wt) catalyst, which was obtained by mixing Fe, Co, and Mg powders in a ball milling device for 100 h. The mixing process was done under petroleum ether, followed by an oxidation in air at 500°C for 24 h. Previous studies [10] showed that by employing the
same synthesis conditions on Fe:Co:MgO (2.5:2.5:95 % wt) catalyst, obtained by impregnation, favours the formation of single-wall carbon nanotubes.

2. Experimental Details

2.1. Catalyst Preparation
The catalyst, Fe:Co:MgO (2.5:2.5:95 % wt), used in this report was obtained in two steps as follows: First the powders Mg (purity 99%, particle size < 125 µm), Fe (purity 99%, particle size < 63 µm) and Co (purity 98.5%, particle size < 45 µm) have been mixed together in a Fritsch type „Pulverized 6“ ball milling device. This process was done in a stainless steel bowl with steel balls of 2, 4, and 8 mm in diameter, having the balls-powders ratio of 5.5-1. The mixing of powder was realized for 100 h, and at an angular rotation of 400 rot/min, under petroleum ether which ensures a good homogeneity and prevents the agglomeration of powder. The loading process and the sample collection was accomplished under an inert environment of argon in a glove box. The second step, the mixture was oxidized in air at 500°C for 24 h. The final product was a grey puffy powder and was characterized by measuring its surface area BET (Micromeritics ASAP 2020), scanning electron microscopy (SEM) (JEOL 7000F) and X-ray diffraction (Bruker D8 Discovery).

2.2. Carbon nanotubes synthesis
The carbon nanotubes growth was done by RF-CVD, which was previously described [11] at 850°C using acetylene as the carbon source. 100 mg of catalyst powder have been placed in a graphite susceptor located in the center of a water-cooled quartz tubing with a diameter of 30 mm. The reactor was rinsed with argon (100 ml/min ) for 10 min and was heated up to 500°C for 15 min, in order to desorb the gases present on the graphite surface. Ultimately, the temperature was raised to 850°C followed by the administration of acetylene (2 ml/min ) for 10 min. The cooling was done in argon flow until the reactor reached the room temperature.

To remove the catalyst, the final product was sonicated in HCl (1:1) for 1 h and kept in acid for 4 days. Finally after filtration, the product was washed with distilled water and dried at 120°C overnight. The nanotubes were characterized by SEM, Transmission Electron Microscopy (TEM) (JEOL-2100F TEM), thermogravimetric analysis (TGA) (Mettler Toledo TGA/SDTA 851e).

3. Results and Discussions
Figure 1a shows the SEM image of the catalytic system after oxidation. From the SEM analysis, it can be observed the presence of particles with dimensions of less than 3-4 µm, of irregular shapes with a sponge-like appearance. The X-Ray analysis indicating the presence of various phases and their relative concentrations (Rietveld refinement) are presented in figure 1b and table 1.

![Figure 1. SEM image (a) and the X-Ray diffraction spectrum (b) of the catalyst powder after its oxidation at 500°C.](image)
Table 1. The structural phases present in the catalyst system and their relative concentrations as analyzed by X-Ray diffraction studies.

| Identified Phases                  | Identification of the figure 1b | Relative Concentration (%) |
|------------------------------------|---------------------------------|-----------------------------|
| MgO                                | *                               | 70.4%                       |
| (MgO)_{0.91}(FeO)_{0.09}           | ^                               | 20.5%                       |
| CoO                                | $                               | 6.8%                        |
| CoFeOx                             | !                               | 2.9%                        |
| (MgO)_{0.239}(FeO)_{0.761}         | #                               | 3.8%                        |
| (Mg_{0.19}Co_{0.81})(Mg_{0.68}Co_{1.32})O_{4} | +                              | 2.4%                        |

The BET surface area analysis performed by using nitrogen adsorption at 77K was of 68.84 m^2/g. The total volume of the pores was of 0.27 cm^3/g, with an average pore diameter of 162 Å.

Figure 2 presents the thermogravimetric analysis curves of the „as prepared” and the acid purified carbon nanotubes products. The measurements were done in air flow (150 ml/min) at a heating rate of 5°C/min. Based on the „as prepared” TGA curve it was determined a reaction efficiency of 16%. The purified nanotubes TGA curve shows the presence of two distinctive domains, first from 250 to 375°C corresponding to a mass loss of 3.5% attributed to the burning of the amorphous carbon mass [12], and the second one of 93% in the 400 and 680°C range representing the thermal mass loss of the crystalline graphitic structures of the nanotubes. Figure 2 inset shows the differential thermal analysis (DTA) curve for the purified nanotubes indicating a thermal desintegration temperature of 528.2°C.

Figure 2. TGA curves for the „as prepared” (black curve) and „purified” (red curve) carbon nanotube samples. The inset presents the DTA analysis of the purified nanotubes.

The SEM image of the „as prepared” carbon nanotubes is presented in figure 3a. This image indicates the presence of a high density of entangled multi wall carbon nanotubes which covers uniformly the catalyst particles. The Nanotubes have lengths of douzens of µm and diameters in the order of douzens of nm, which results in an aspect ratio of ~ 1000. Low resolution TEM image of a carbon nanotube with a diameter of 12 nm and the visible length of about 1 µm is presented in figure 3a. Both the images presented in figures 3a and b indicate a high diameter uniformity for the studied nanotubes.

Figure 4 a and b represent the high magnification TEM images of two nanotubes with external diameters (D_{ext}) of 25.5 nm and 13.2 nm, respectively. The internal diameters (D_{int}) for the two nanotubes were of 10.5 nm and 4.2 nm. Also it was observed that the nanotubes have a relatively low number of highly crystalline graphitic walls with an inter-wall distance of 0.34 - 0.35 nm. Also the nanotubes present a small amount of amorphous carbon over their external surfaces, fact also confirmed by the thermogravimetric analysis studies. In figure 4a the arrow indicates a catalyst particle of a spherical shape with an diameter of 5 nm encapsulated within a 3 wall nanotube (D_{ext} = 6.5 nm and D_{int} = 5 nm). The D_{ext}/D_{int} ratio of over 50 analyzed nanotubes ranges between 2.5 and 3.0.
Figure 3. SEM images of the „as prepared” carbon nanotubes (a) and a low magnification TEM image of a single nanotube with a diameter of 12 nm and of an approximate length of 1 µm.

Figure 4. High magnification TEM images of two carbon nanotubes after the removal of the metallic catalyst.

4. Conclusions
Multi wall carbon nanotubes have been synthesized from acetylene over the Fe:Co:MgO (2.5:2.5:95 % wt) catalyst at 850°C by RF-CCVD. The catalyst was obtained by mixing Fe, Co and Mg powders in a ball milling device for 100 h and the final mixture was oxidized in air at 500°C for 24 h. The majority of the nanotubes had external diameters in the range of dozens of nm, lengths of dozens of µm with an „aspect ratio” of over 1000, a $D_{\text{ex}}/D_{\text{int}}$ ratio of 2.5-3 and a high degree of crystallinity.

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