Synthesis of Multiwall Carbon Nanotubes by Inductive Heating CCVD

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Abstract

The CCVD syntheses of MWCNTs from acetylene on Fe:Co:$CaCO_3$ and Fe:Co:CaO were performed using two different methods of heating: outer furnace and inductive heating. The comparative analysis of the MWCNTs obtained by the two methods show that the tubes grown in inductive heating have smaller diameters (5-25 nm), with fewer walls and aspect ratio of the order of hundreds. The ratio of outer to inner diameter (od/id) is ranging between 2 and 2.5. Inductively assisted CCVD is a very attractive method because of the major advantages that it presents, like low energetic consumption, thinner, well crystallized and more uniform tubes.

Keywords: A. Carbon nanotubes; B. Chemical vapor deposition, Induction heating

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Introduction

In the last 14 years since the discovery of the carbon nanotubes [1], they became a key component of nanotechnology [2], being currently among the most intensively studied materials.

Among the synthesis methods of carbon nanotubes, the catalytic chemical vapor deposition (CCVD) is the most commonly used, due its versatility in the growth morphology control of the carbon nanostructures by monitoring the reaction conditions (catalysts, temperature, composition and flow rate of the carrier gas, and hydrocarbons, etc). It is considered as the most promising method for large-scale production of carbon nanostructures.

Following the growth process by CCVD method, the carbon nanotubes have to be purified in order to remove the catalyst particles and the carbon byproducts without destroying the morphology of the nanotubes. In the last years the attention has been focused on finding performant catalysts for high quality production of carbon nanotubes, able to allow the removal of both the metal nanoparticles and the oxide support in a single purification step, generally by dissolution in diluted acids. Much progress has been made using Co_3O_4/MgO [3] and Fe:Co/$CaCO_3$ [4] catalysts.

The increasing need for carbon nanotubes (both SWCNTs and MWCNTs) resulted in the development of techniques for scale–up the continuous synthesis by CCVD [4] and of new high-yield catalysts [5-7].

The synthesis of carbon nanotubes by inductively assisted CCVD has lower energetic consumption and the overall reaction time is significantly reduced with direct impact on the final production price of the nanotubes. In inductive heating the heat transfer flows from the susceptor to the catalyst which are in direct contact and requires a smaller number of intermediary steps compared with the resistive heating in outer furnace. The thermal fluctuations for the inductively enhanced CCVD are much smaller and the temperature can be

controlled more accurately. The inductive heating was used for carbon fibers production [8] and for susceptor heating in laser ablation SWNTs synthesis [9]. Lupu et al. reported for the first time the growth of carbon nanotubes (SWCNTs and MWCNTs) and carbon nanofibers by inductive heating while using a number of catalysts and different carbon sources [10,11]. Later, this method was used to produce SWCNTs by the catalytic decomposition of alcohol on a bimetallic catalyst of Fe/Co on zeolite support [12].

This paper reports experimental results for MWCNTs synthesis by inductive heating assisted CCVD. A catalyst reported by Couteau et al [4] was selected for our experiments, using the same conditions, for a comparative study of the outer furnace and induction heating effects and also of the catalyst support ($CaCO_3$ and CaO) effects.

Experimental

The Fe:Co/$CaCO_3$ catalyst was prepared as described in the literature [4] by impregnation. $Fe(NO_3)_3 \cdot 9H_2O$ and $Co(CH_3COO)_2 \cdot 4H_2O$ salts were dissolved in distilled water followed by the introduction of $CaCO_3$ under continuous stirring. During the preparation of the catalyst, the pH was kept constant at 7.2 by adding NH_4OH. The ratios of $Fe(NO_3)_3 \cdot 9H_2O$, $Co(CH_3COO)_2 \cdot 4H_2O$, and $CaCO_3$ were those corresponding to final composition Fe:Co/$CaCO_3$ = 2.5:2.5:95 wt % (further referred to as $CaCO_3$). The solvent was evaporated on a water bath the result product was dried over night at 130 °C followed by grinding into a mortar.

The Fe:Co/CaO catalyst was obtained by thermal decomposition of Fe:Co/$CaCO_3$ catalyst at 830 °C with the final result Fe:Co/CaO = 4.3:4.3:91.4 wt.% (further referred to as CaO).

The MWCNTs were synthesized on $CaCO_3$ and CaO catalysts by CCVD method in a fixed-bed flow reactor by decomposing acetylene at 720 °C in both outer furnace (OF) and inductively heated (IH) regime.

100 mg of catalyst were placed in a graphite boat, which was inserted in a quartz tube (28 mm inner diameter and 1 m length) and heated at the reaction temperature in nitrogen flow (200 ml/min). When the boat reached reaction temperature, acetylene was introduced (3.3 ml/min); the reaction time was 30 min for all the experiments after which acetylene flow was stopped and the sample cooled in nitrogen flow.

For inductive heating the outer furnace was replaced by a nine-coil inductor of 45 mm inner diameter and 80 mm length connected to a high frequency generator (1.3 MHz). The inductive heating ensured a very uniform heating of the susceptor (the same boat used in outer furnace technique) and the temperature was monitored with an optical pyrometer.

In some experiments the $CaCO_3$ catalyst was activated prior to the CCVD synthesis (further referred to as $CaCO_3 + H_2$). The activation was done "in situ" at 400 °C by a mixture of nitrogen (200 ml/min) and hydrogen (18 ml/min) for 30 min. After the activation time, the hydrogen flow was stopped and the temperature was raised to 720 °C and acetylene flow started for CCVD synthesis.

To produce the CaO catalyst, 150 mg of $CaCO_3$ catalyst was placed in the susceptor, heated inductively at 830 °C in nitrogen for 30 minutes, followed by the adjustment of the temperature to 720 °C and the introduction of acetylene

The scheme of the experimental se-up used for producing the carbon nanotubes by CCVD method with inductive heating is shown in Fig. 1.

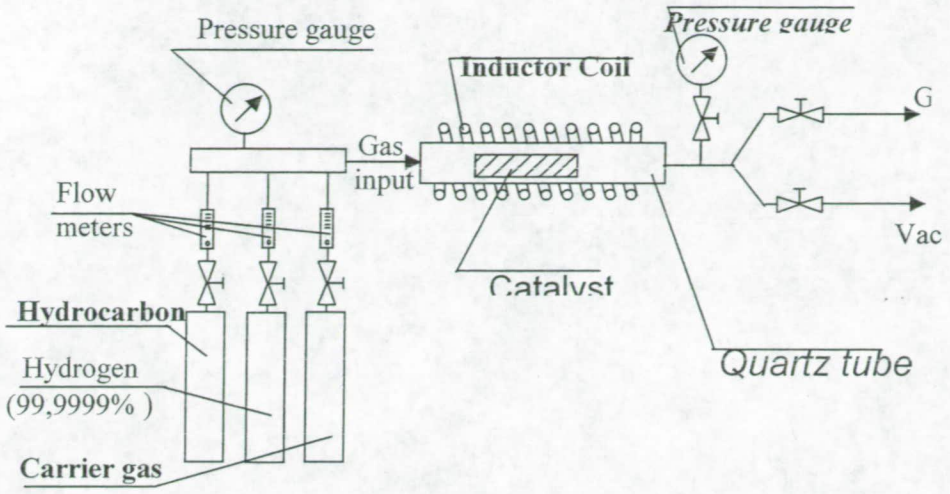


Fig.1. Scheme of the experimental se-up for inductive heating assisted CCVD syntheses of carbon nanotubes.

The products were purified by sonication in HNO_3 (30 %) for 30 min, filtered, washed with distilled water and dried at 130 °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.

For the catalysts characterization several techniques were used thermogravimetric analysis (TGA) (Mettler Toledo 815e), SEM and X – Ray diffraction (DRON 2).

The morphology of the carbon nanotubes was analyzed by High Resolution Transmission Electron Microscopy (FEI Tecnai F30 STEM).

Results and Discussions

The thermal decomposition curve of the $CaCO_3$ catalyst, Fig. 2, show several stages: the weight loss in the range 100-150 °C corresponding adsorbed water, the decomposition of the acetates at 250-350 °C and the drastic weight loss between 680-800 °C due to the decomposition of calcium carbonate into calcium oxide and carbon dioxide [4]. The total

weight loss is 45.7% of the initial mass. The three stages of mass decrease are more visible in the first order derivative curve.

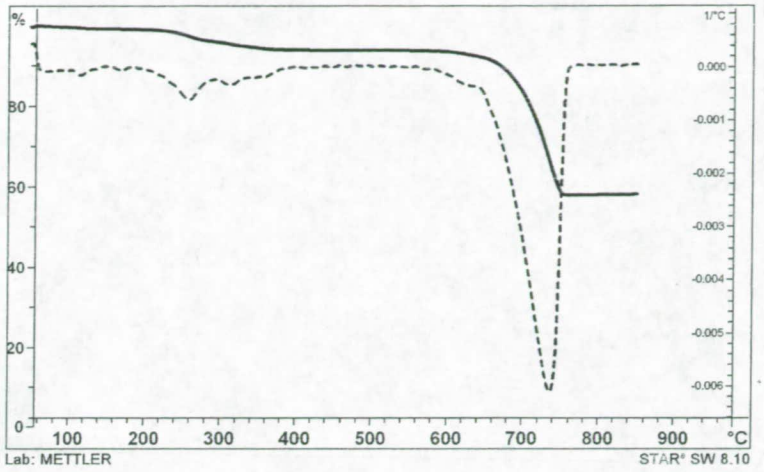
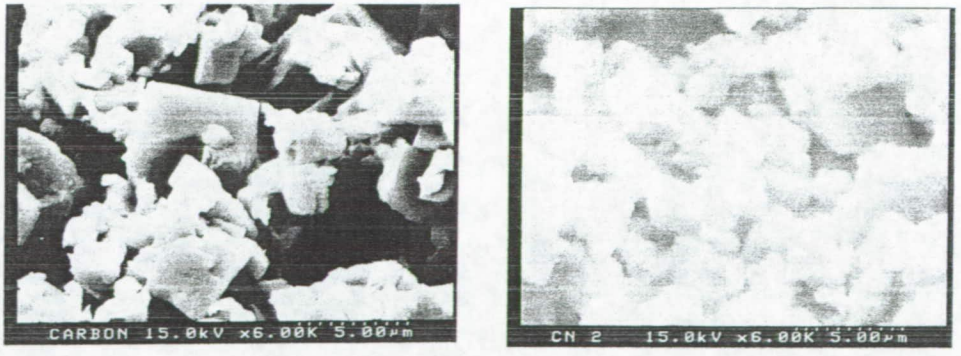


Fig.2. The thermal decomposition curve of the $CaCO_3$ catalyst along with its first derivative curve.

Fig.3 presents the SEM images of the $CaCO_3$ catalyst and the CaO catalyst. It can be observed that they have sponge-type morphologies but for the CaO catalyst the holes are smaller and more frequent. The $CaCO_3$ catalyst (Fig. 3a) shows particles between 600-5000 nm with flat and smooth surfaces. The CaO catalyst (Fig. 3b) exhibits particles in the same range of dimensions with rough surfaces.



a) b)

Fig.3. SEM images of the $CaCO_3$ (a) and CaO (b) catalysts

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.

Figure 4 shows the powder X-ray spectrum for the CaO catalyst. The spectral lines correspond only to a CaO support and the catalytic metals are present in an oxidized state as Fe_3O_4 and Co_3O_4, as identified by the corresponding spectral lines. The spectral peak corresponding to a diffraction angle of $2\theta \approx 51^\circ$ is attributed to the spinel $CaFe_2O_4$ formed most probably due to the thermal treatment.

The peaks corresponding to the Fe_3O_4 and Co_3O_4 compounds were approximated based on a generalized Fermi distribution that describes their degree of asymmetry and the calculation for the integral widths for the peaks were done by solving the Fourier deconvolution equation [13,14].

For both $CaCO_3$ and CaO catalysts, the average dimensions of the Fe_3O_4 and Co_3O_4 crystallites corresponding to each identified diffraction peak were obtained by using the Scherer equation and range between 41–47 nm for Fe_3O_4 and between 10–36 nm for Co_3O_4,

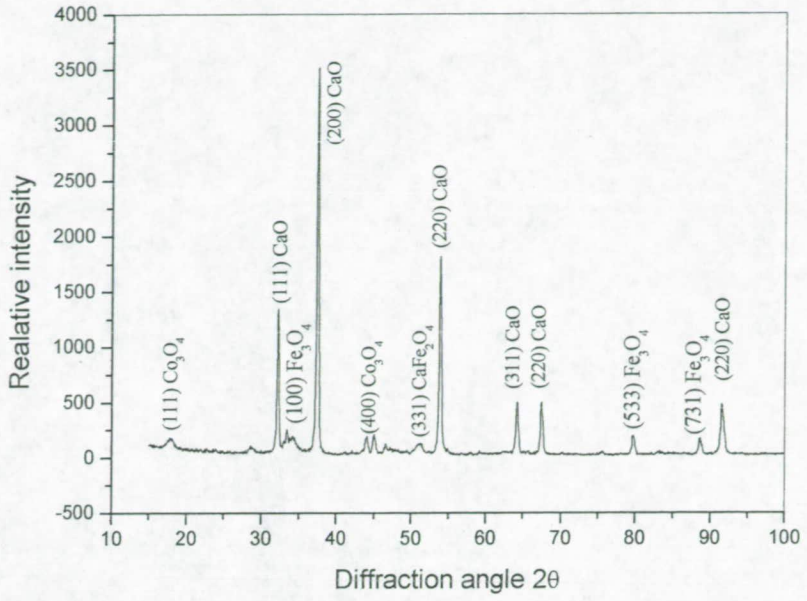


Fig. 4. The X-Ray powder diffraction spectrum for the CaO catalyst

The low magnification TEM images as well as the diameter histograms (each histogram based on the analysis of over 100 individual nanotubes) of the multiwall carbon nanotubes grown on the $CaCO_3$ and CaO in different conditions are shown in Fig.5.

The histogram for the nanotubes grown on $CaCO_3$ catalyst in outer furnace (Fig. 5a) shows the presence of two groups of MWCNTs. The first one comprises the large majority of the nanotubes (~ 86 %) with outer diameter 8-35 nm and the second one much less abundant (~ 14 %) in the range of 40-60 nm outer diameter. These results can be explained by the partial decomposition of the $CaCO_3$ catalyst when the temperature increases from 680 to 720 °C (see Fig.1): in this situation, the nanotubes are grown on a mixture of $CaCO_3$ and CaO supported catalysts, as revealed by diameter distribution histogram.

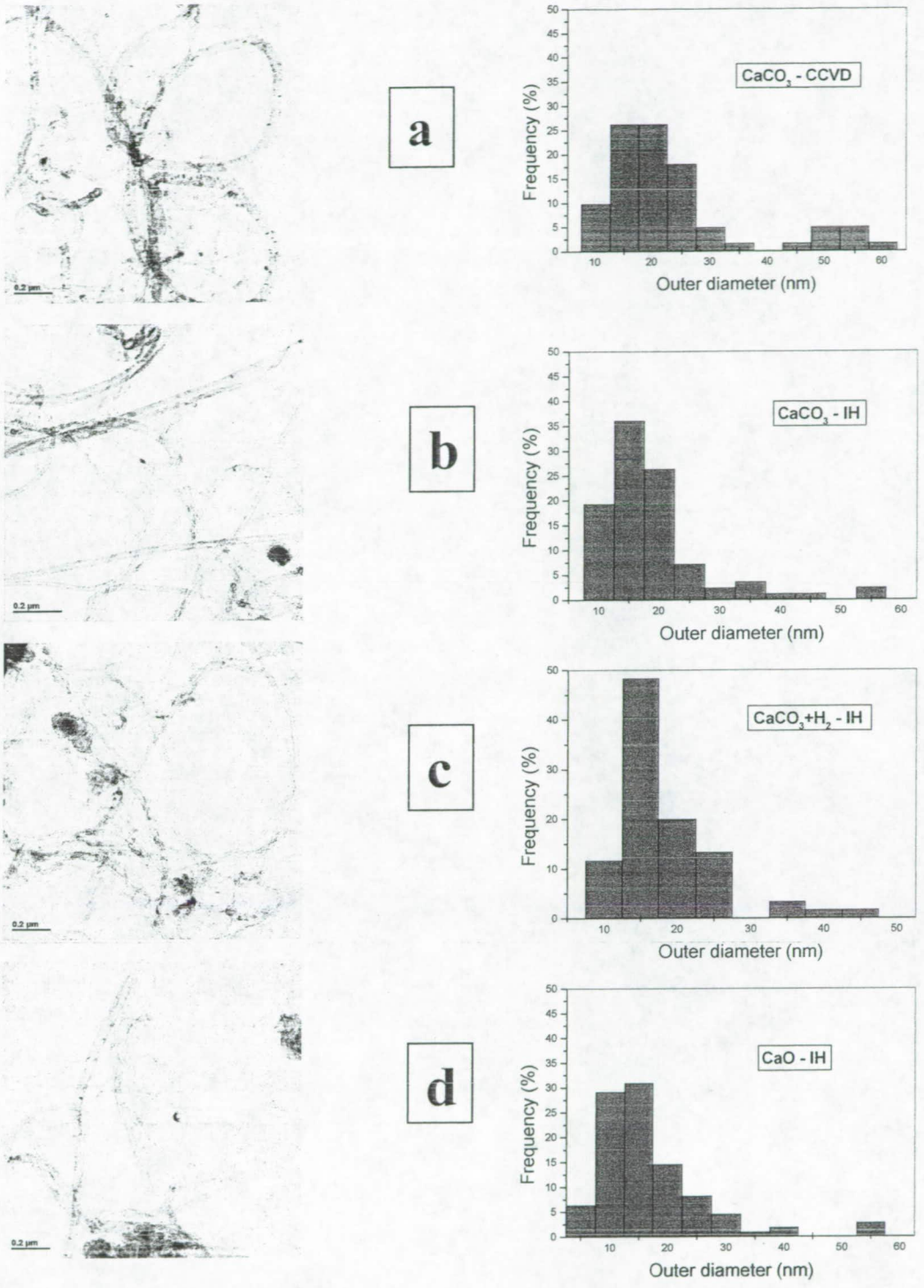


Fig.5. Low resolution TEM images and the diameter histograms for the multi wall carbon nanotubes synthesized from acetylene at 720 °C in different conditions: $CaCO_3$ (OF) (a), $CaCO_3$ (IH) (b), $CaCO_3$+H_2 (IH) (c), and CaO (IH) (d).

Generally, for the nanotubes grown by inductive heating (Fig. 5 b-d), a decrease of the outer diameter is observed (over 90 % of the nanotubes having outer diameters 5-25 nm). Two hypotheses may be imagined:

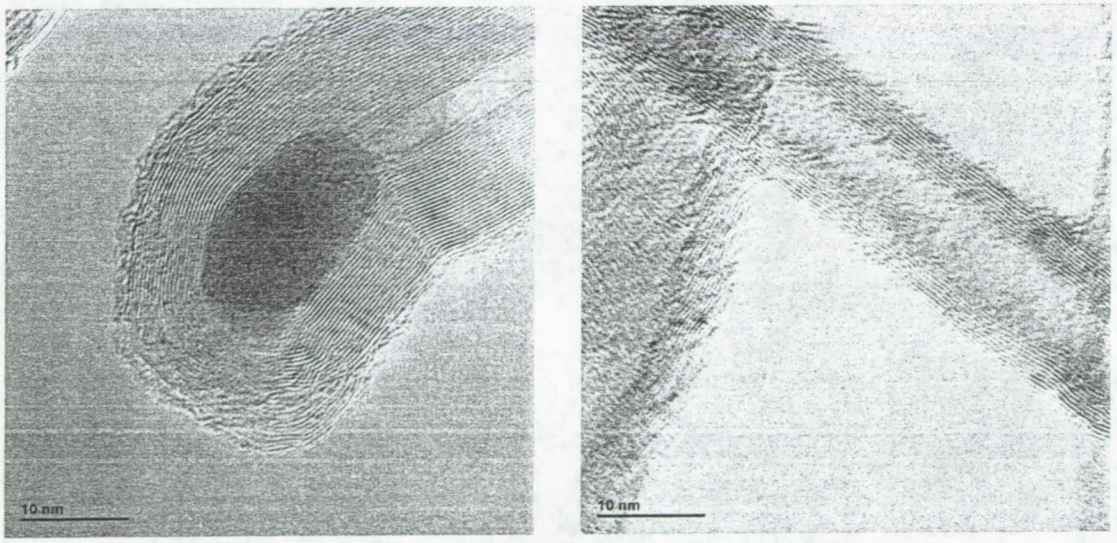
i) The surface diffusion rate of Fe(Co) species on the support increases with temperature resulting in an increase of the nanoparticle catalyst (NP) with increasing annealing time [15]. The carbon nanotubes outer diameter follows the NPs dimension [16-18]. With the inductive heating a much faster heating rate is possible, the reaction temperature is reached in few dozens of seconds. The fast IH, with very short annealing time, does not allow significant increase of NPs average size so that nanotubes of lower outer diameter are obtained.

ii) The exothermal reaction of carbon graphitization supplies a large amount of thermal energy to the catalyst nanoparticle and since the heat transfer to the low thermal conductivity oxidic support is limited, it could be possible that the metallic nanoparticles are supposed to a melting and reconstruction process [19]. The metallic character of the catalyst nanoparticles can determine an increase of their local temperature, induced by the RF skin currents. Therefore, a temperature difference might be present between the metallic species and the oxidic support of the catalysts that have a lower thermal conductivity and represent a "bottleneck" for the transfer of heat [19]. A higher local temperature can result in a higher growth rate of the nanotubes with smaller diameters as reported in the literature [16, 20, 21].

Though the CaO catalyst was exposed to a 30 minute thermal treatment at 850 ^{o}C, with the possibility of larger metallic particles formation, the diameter distribution of the nanotubes was found to be relatively narrow (5-25 nm) as seen in Fig. 5d. This observation points the second hypothesis as more reliable for the growth of thinner nanotubes in inductively heated CCVD. This effect can be exploited also for other catalyst systems where higher temperatures can be reflected in morphological and structural changes of the catalyst support.

The analysis of the TEM images shows that most of the nanotubes have lengths larger than 2-3 μm, which allows the conclusion that the aspect ratio for these nanotubes is of the order of hundreds. Another characteristic that needs to be observed is the diameter uniformity over the entire length of the nanotubes. Generally there were not observed too many catalyst particles encapsulated; the number of the metallic nanoparticles encapsulated is slightly larger for the $CaCO_3$ catalyst.

Figures 6 present the high resolution TEM pictures for the carbon nanotubes synthesized by inductively heated CCVD on the $CaCO_3$ catalyst without (a) and with (b) hydrogen activation. All the HRTEM images have shown that the inductively grown carbon nanotubes are rather well crystallized with a relatively low number of carbon walls (7 – 12 walls) and with outer to inner diameter ratios (od/id) ranging between 2 and 2.5. The nanotubes grown with IH are generally thinner and have a fewer walls compared with those grown with outer furnace.



a) b)

Fig. 6. HRTEM images of the carbon nanotubes grown on the $CaCO_3$ catalyst without (a) and with (b) prior hydrogen activation

It should be mentioned that no morphological or structural differences were observed between the nanotubes that were grown on catalysts with or without prior hydrogen activation, another reason why this catalyst is suitable for continuous processes since it doesn't require activation.

Synthesis efficiency values relative to the $CaCO_3$ catalyst are presented in Table 1.

Tabel 1. Synthesis efficiency values for multi wall carbon nanotubes grown in different conditions on the $CaCO_3$ and CaO catalysts.

Sinteza	$CaCO_3$ (OF)	$CaCO_3$ (IH)	$CaCO_3$+H_2 (IH)	CaO (IH)
η (%)	87	78	74	26
[% gC/mol Ca]	91.6	82.2	78	27.4

As the surface areas of $CaCO_3$ and CaO are practically the same the much lover yeld for CaO catalyst are consistent with the recent observations of Magrez et al [22] that the evolved CO_2 from $CaCO_3$ during the reaction is directly involved in the growth process for CCVD synthesis.

Conclusions

The MWCNTs were prepared from acetylene at 720 °C on the Fe:Co/$CaCO_3$ and Fe:Co/CaO catalyst by using CCVD with heating with outer furnace and inductive heating using the same reaction conditions as reported by Couteau et al. [4].

The comparison between the MWCNTs characteristics synthesized by outer furnace and inductive heating shows that the inductive heating produces carbon nanotubes of smaller average diameter with fewer walls, and aspect ratio in the range of hundreds.

The comparative analysis of the yield for syntheses on $CaCO_3$ and CaO is in good agreement with recently reported results [22], the participation of CO_2 (resulting from $CaCO_3$ support decomposition) in the growth process via a reaction with acetylene.

The inductively assisted CCVD has some major advantages over the classical CCVD: significantly lower energetic consumption, lower overall reaction time, much faster heating rate, possibility of visual inspection of the reaction, easier implementation of continuous production regime [23].

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