

# Catalytic activity of Fe, Co and Fe/Co supported on Ca and Mg oxides, hydroxides and carbonates in the synthesis of carbon nanotubes

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## Abstract

Catalytic chemical vapour deposition (CCVD) is one of the methods used for large scale production of carbon nanotubes (CNT). In this paper the results of the experiments conducted to study the role of Ca and Mg oxides, hydroxides and carbonates as supports for iron, cobalt and a mixture of iron-cobalt catalysts, in the production of CNT by CCVD method are reported. Acetylene and ethylene were used as the two different sources of carbon and N<sub>2</sub> as the carrier gas. The syntheses reactions were conducted at 700 °C under ambient pressure in a horizontal tubular furnace.

Almost all the support-catalyst mixtures were found to be active in the formation of CNT. The quantity and quality of the tubes produced in different synthesis reactions were however, significantly different. Out of the several supported catalysts used calcium carbonate and magnesium oxide were found to give the best yield of carbon deposit when they were used as supports for a mixture of cobalt and iron. The yield of carbon deposit was found to be very poor when these supports had only Fe. Cobalt on the otherhand showed better activity than iron. A simple method of purification of crude carbon deposit is also described. The density and the quality of nanotubes were analysed by TEM. The CNT produced were found to be multiwall in nature.

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**Keywords:** MWCT; CCVD; Ca and Mg salt supports; Fe/Co catalysts

## 1. Introduction

It is not an exaggeration when it is mentioned that one of the active fields of research in the area of nanotechnology at present is synthesis, characterisation and applications of carbon nanotubes (CNT) [1–7]. These small pipes of carbon which have a big future, were first observed by Sumio Iijima in 1991 in Japan [8]. These nanometer size materials can thought to be arising from rolling of graphene sheet/s into a cylindrical form. Soon after discovery, extensive research efforts on these tubular graphite structures revealed that CNT are the materials of great interest from fundamental point of view as well as for future applications in the areas of hydrogen

storage [9–11], electronics [12], catalysis [13–15], polymer science [16–18], etc.

CNT were first observed in arc discharge method, which was originally used for the production of fullerenes. Due to their fascinating properties and potential applications in several technological fields attempts have been made to synthesise CNT by different methods [19–20]. Pyrolysis of hydrocarbons over metal catalysts supported on an ‘inert’ material proved to be one of the potential methods for large scale production of CNT. Several supports and transition metal/s combinations have been investigated for their activity in the synthesis of CNT under different experimental conditions [21–25]. The quantity and quality of CNT produced in this method has been found to depend on the type of the catalyst, nature of the support, carbon source and the reaction temperature, etc. The research work in this area is in good

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progress and aimed at finding an economical method of production of larger quantities of purified CNT. The present work involves the study of the role of various calcium and magnesium based salts as supports for iron, cobalt and iron–cobalt mixture catalysts in the synthesis of pure CNT in large scale.

## 2. Experimental

### 2.1. Preparation of support-catalyst mixtures

The supports that were used include CaO, Ca(OH)<sub>2</sub>, CaCO<sub>3</sub>, MgO (all vel.Belgium), MgCO<sub>3</sub>, Mg(OH)<sub>2</sub>·4H<sub>2</sub>O (Alfa Aesar). The metal salts used as the source of Fe and Co catalysts were Fe(NO<sub>3</sub>)<sub>3</sub>·9H<sub>2</sub>O (Acros organics), and Co(NO<sub>3</sub>)<sub>2</sub>·6H<sub>2</sub>O (vel.Belgium).

The support-catalyst mixtures were prepared by wet impregnation method [26]. A calculated quantity of the metal salt/s was ground into a fine powder and dispersed in a few drops of water. A required amount of the support material was added to the metal salt/s paste and mixed well to get a homogeneous mixture of the support and the salt/s paste. This mixture was dried in an air oven at 120 °C for 12 h, cooled and ground well to obtain a fine powder of support-catalyst mixture. The support and the metal salt/s were mixed in a proportion such that the weight of the support was 95 and that of the metal was 5. When a mixture of two metals was taken the salts of the metals were mixed to get 2.5 atomic weight percent each of the metal. In each experiment about 20 g of support-catalyst mixture was prepared. Henceforth the support-catalyst mixture is represented simply as the catalyst.

### 2.2. Production of nanotubes

Carbon nanotubes synthesis reactions were carried out in a horizontal furnace. About 0.5 or 1.0 g of the catalyst, spread

on a quartz boat was introduced into the furnace preheated to 700 °C in a flow of nitrogen (300 ml/min). After 10 min the hydrocarbon gas (acetylene or ethylene) was made to pass over the catalyst bed at a rate of 30 ml/min for 60 min. The hydrocarbon gas flow was stopped; the product on the quartz boat was cooled to room temperature while nitrogen flow was on. The weight of the carbon deposited along with the catalyst was noted. The percentage of carbon deposit (C%) obtained in each reaction was determined using the following relationship:

$$C\% = \frac{w_3 - (w_1 - w_2)}{w_1 - w_2} \times 100 \quad (1)$$

where  $w_1$  is the initial weight of the catalyst,  $w_2$  the weight loss of the catalyst at the reaction temperature, and  $w_3$  the weight of the carbon deposit and the catalyst.

The weight of the catalyst at the reaction temperature ( $w_1 - w_2$ ) is less than the weight taken initially ( $w_1$ ). In order to find this decrease in weight of the catalyst at the reaction temperature, about 0.5 g of exactly weighed catalyst ( $w_1$ ) was calcined at 700 °C for 60 min, under N<sub>2</sub> flow. From the weight of the catalyst after calcination the loss of weight was calculated.

### 2.3. Purification of carbon deposit

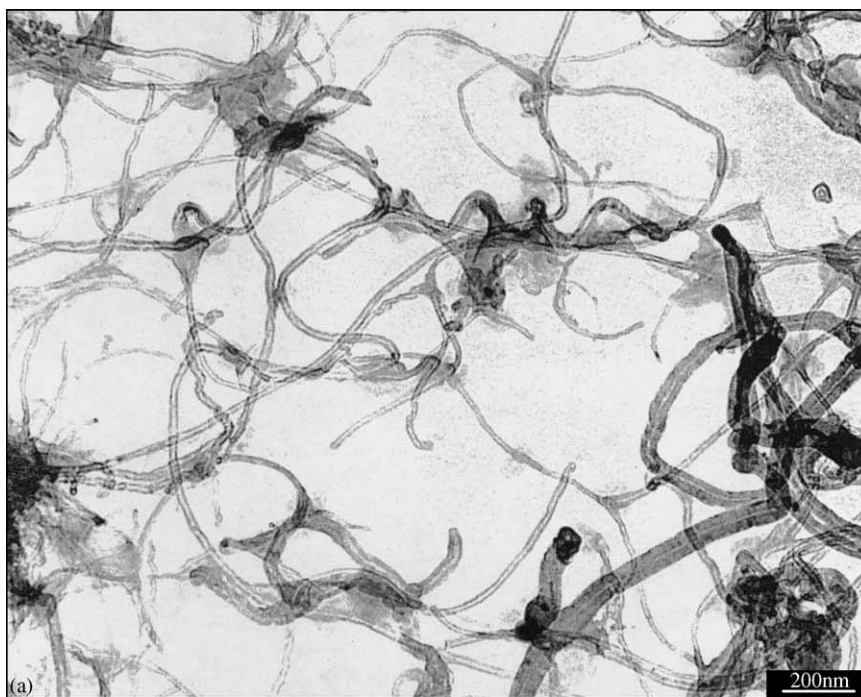
About 20 g of carbon deposit was synthesized from each of the several reactions conducted under similar conditions using the catalyst which gave highest percentage of carbon deposit. The as synthesized carbon deposit was treated with 200 ml of concentrated HCl and stirred over night. The solid was filtered, washed free from chloride ions and dried at 120 °C in a hot air oven for 24 h. The relative percentages of Ca, Mg, Fe, Co contents in the crude and the purified samples were analyzed by proton induced X-ray emission (PIXE) and proton induced gamma ray emission (PIGE) experiments to record the purity of the carbon deposit before and after HCl treatment.

Table 1

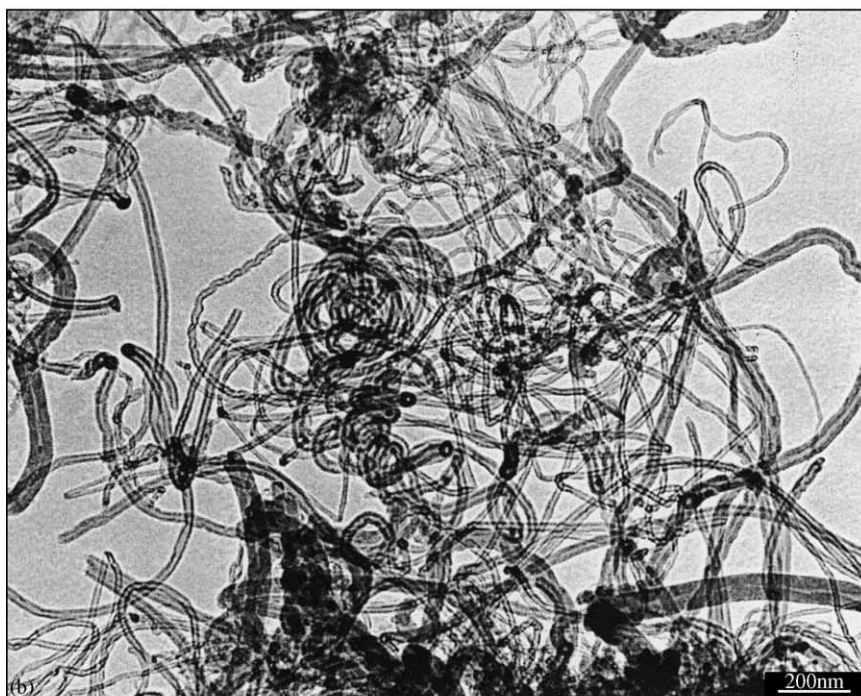
The catalysts used and the physical appearance and yield (wt.%) of the as synthesized carbon deposit in CCVD of acetylene

A	CaO–Fe/Co	CaO–Co	CaO–Fe	MgO–Fe/Co	MgO–Co	MgO–Fe
B	Very spongy	Spongy	Not spongy	Spongy	Not spongy	Fine powder
C	57 (71)	41.3 (58)	– (1.7)	229 (238)	23.7 (28)	16.1 (23.2)
D	++	+	–	+++	–	–
A	Ca(OH) <sub>2</sub> –Fe/Co	Ca(OH) <sub>2</sub> –Co	Ca(OH) <sub>2</sub> –Fe	Mg(OH) <sub>2</sub> –Fe/Co	Mg(OH) <sub>2</sub> –Co	Mg(OH) <sub>2</sub> –Fe
B	Spongy	Little spongy	Not spongy	Spongy	Not spongy	Not spongy
C	154.5 (163.9)	41.0 (76.7)	3(–)	169 (166.9)	62.6 (41)	59.28 (59.3)
D	++	++	–	+++	+	–
A	CaCO <sub>3</sub> –Fe/Co	CaCO <sub>3</sub> –Co	CaCO <sub>3</sub> –Fe	MgCO <sub>3</sub> –Fe/Co	MgCO <sub>3</sub> –Co	MgCO <sub>3</sub> –Fe
B	Very spongy voluminous	Very spongy	Not spongy	Spongy	Not spongy	Not spongy
C	358.67 (192.3)	70.54 (54.2)	11.7 (14.5)	167 (105)	44.37 (73.3)	30.12 (44.2)
D	+++	++	–	+++	+	+

A: catalyst; B: appearance of the carbon deposit; C: weight % yield of carbon deposit per 0.5 g of catalyst (within brackets for 1 g of the catalyst); D: density of carbon nanotubes (+++) very good; (++) good (+) low and (–) nil; reaction conditions: acetylene flow 30 ml/min; nitrogen flow 300 ml/min and time of the reaction 60 min; reaction temperature –700 °C.



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Fig. 1. Low resolution TEM pictures of carbon nanotubes produced by the pyrolysis of acetylene using Fe/Co supported on calcium salts: (a) CaO–Fe/Co; (b) Ca(OH)<sub>2</sub>–Fe/Co; (c) CaCO<sub>3</sub>–Fe/Co.

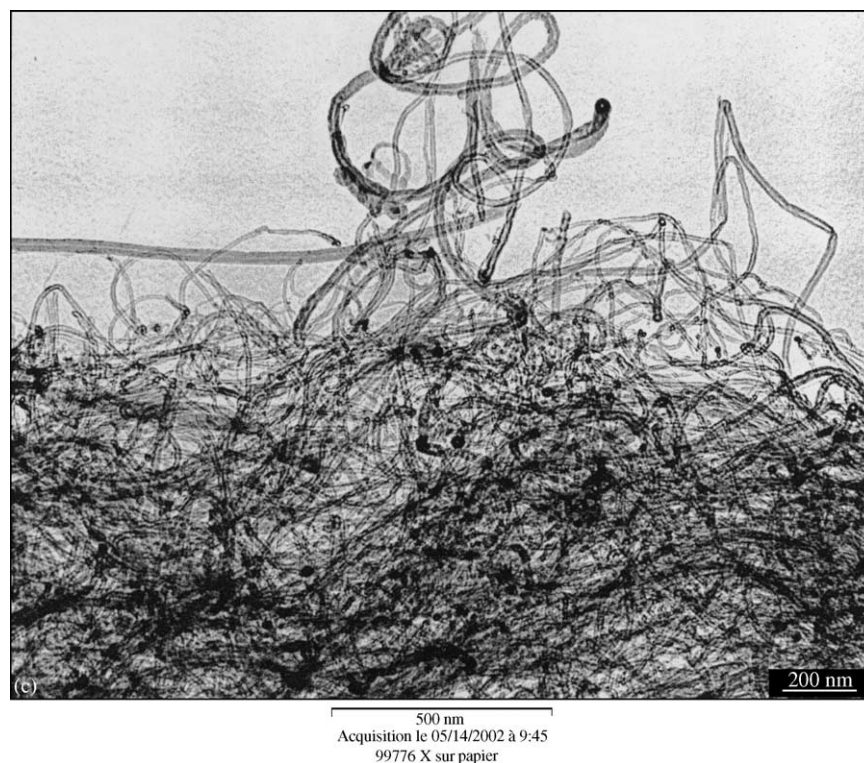


Fig. 1. (Continued).

#### 2.4. Characterization of nanotubes

The nature and density of carbon nanotubes in the carbon deposit obtained from all the synthesis reactions as well as the carbon deposit obtained after HCl treatment were analyzed by using transmission electron microscope (TEM). The samples for TEM analysis were prepared by gluing the sample on a Cu/Rh grid using a solution of scotch tape in chloroform.

### 3. Results and discussion

The catalysts obtained after drying at 120 °C were fine powders and not hygroscopic. Though the catalysts were associated with only either Fe or Co or Fe/Co they exhibited different colors. For instance all the cobalt containing supports did not have the same colors but showed different shades of pink to gray. Fe and Fe/Co containing samples also exhibited the same property. This indicates that the coordination sphere of the metal ions was different when associated with different supports. Therefore, at the first instance these observations indicate that metal ion-support interactions in different catalysts used in the present investigation were different.

The experiments conducted to determine the percentage weight loss of the catalysts revealed that these materials lost about 18–55% of their initial weight under the flow of nitrogen at 700 °C, i.e., the temperature condition chosen for CNT production. These corrected values of weights of the catalysts were used to calculate the exact amount of the carbon deposit

obtained on the catalyst. In the following discussion an attempt has been made to explain the observed results based on

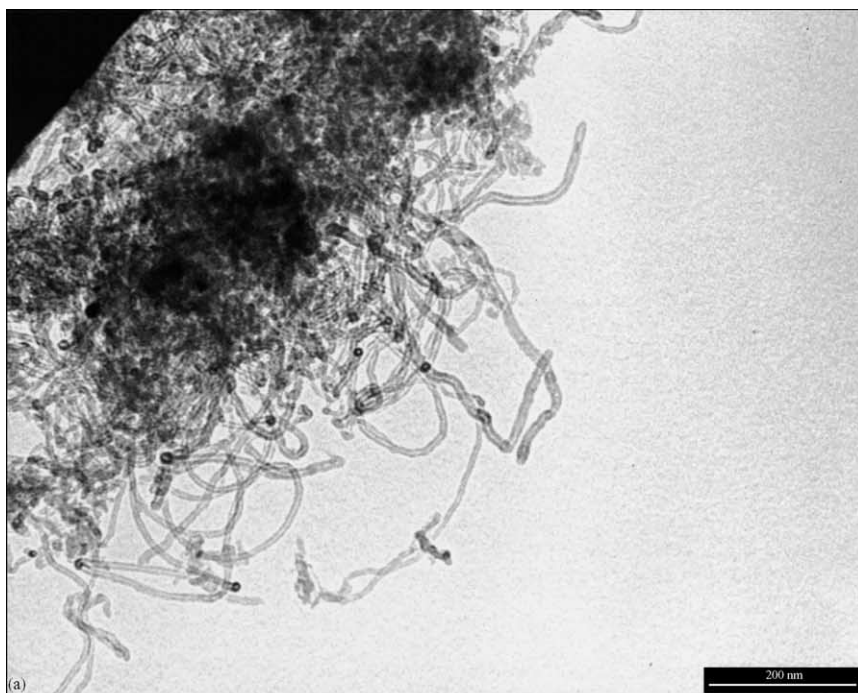
- the difference in the physical appearance and the percentage yield of the as synthesised carbon deposit;
- the density and quality of CNT in the carbon deposit.

These observations were used to explain the relative catalytic activity of various catalysts and hence identify the best catalyst for the production of CNT in large scale.

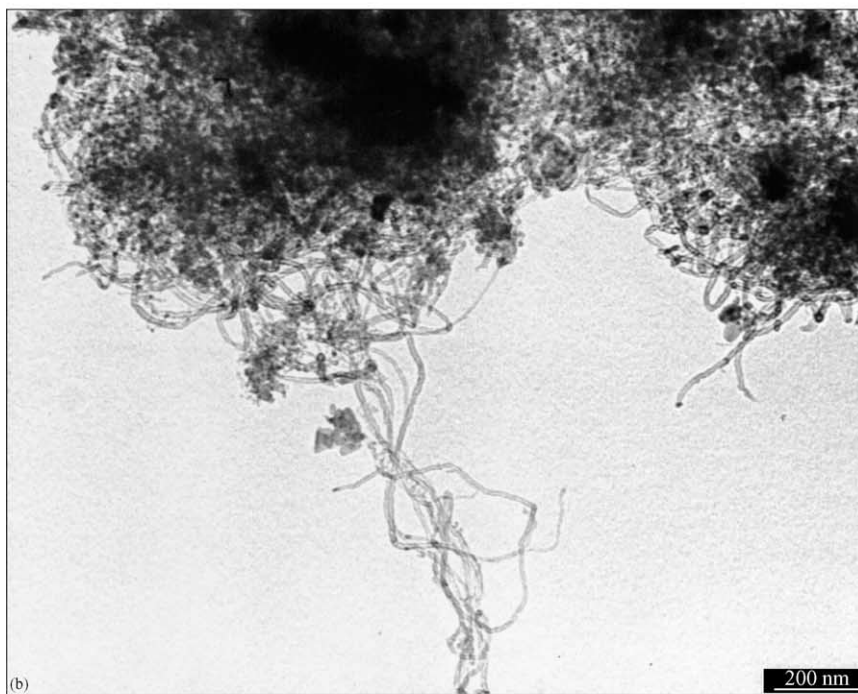
#### 3.1. Physical appearance and the yield of as synthesized carbon deposit

The as synthesized carbon deposit was black in all the cases but the texture was distinctly different. In some cases the carbon deposit was obtained as a very soft and spongy material whereas in a few other cases it was like a fine rough powder. The physical appearance of the carbon deposit along with the catalysts used is indicated in Table 1. From the difference in texture of the carbon deposit obtained from different syntheses, one can get at the first instance an idea if a particular catalyst was active for CNT production or not. In general we have observed that when the carbon deposit appeared spongy the catalyst was good for CNT production. On the otherhand when the deposit remained powdery but turned only black, activity for the CNT formation was negligible.

Thus, from the observations made on the physical appearance of the carbon deposit obtained from different catalysts



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Fig. 2. Low resolution TEM pictures of carbon nanotubes produced by the pyrolysis of acetylene using Fe/Co supported on magnesium salts: (a) MgO–Fe/Co; (b) Mg(OH)<sub>2</sub>–Fe/Co; (c) MgCO<sub>3</sub>–Fe/Co.

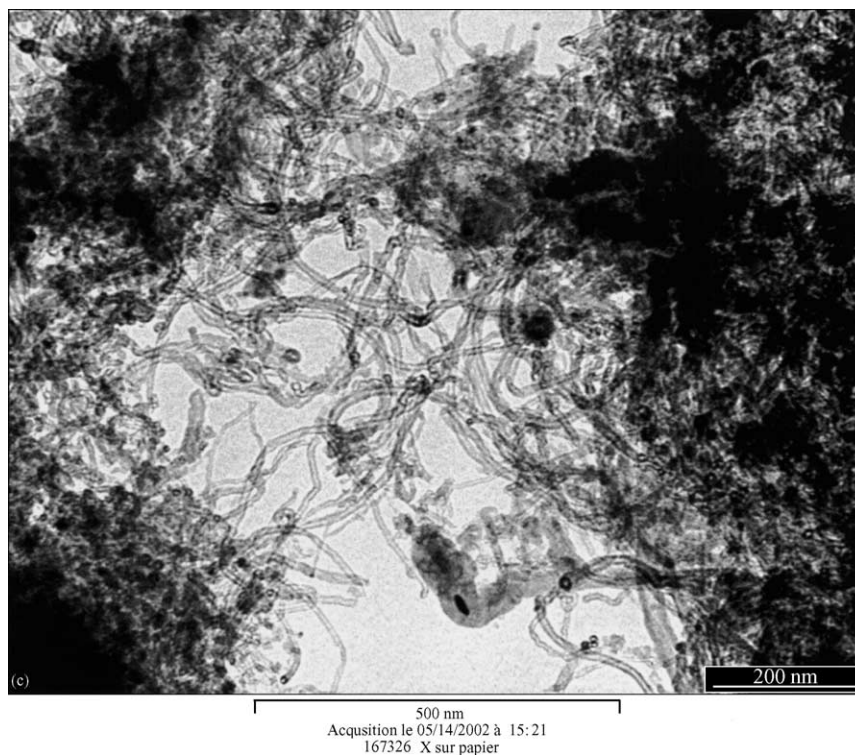


Fig. 2. (Continued).

(Table 1) the following inferences can be drawn, regarding the yield of carbon deposit:

- a mixture of Fe and Co was more active than the individual metals irrespective of the kind of support;
- Fe on calcium salt supports and Fe as well as Co on magnesium salt supports did not show good activity;
- a mixture of Fe/Co on calcium salt supports exhibited higher catalytic activity than on magnesium salt supports;
- Fe/Co on  $\text{CaCO}_3$  was found to be the best catalyst for the production of good quantities of carbon deposit.

On a given type of calcium and magnesium salt supports the catalytic activity of the metal ions towards carbon deposit was found to vary in the same order, i.e.,  $\text{Fe/Co} > \text{Co} > \text{Fe}$ . As far as the different calcium supports were concerned Fe/Co– $\text{CaCO}_3$  produced highest yield of carbon deposit (358%) whereas among magnesium supports Fe/Co–MgO was found to be the best (229% of carbon deposit).

The weight percentages of carbon deposit obtained from various calcium and magnesium based catalysts are given in Table 1. It was not possible to generalize whether calcium salts serve as better supports than the corresponding magne-

sium salts or vice versa for a given metal ion in their activity for the formation of good quantity of carbon deposit. For instance Fe/Co on CaO resulted only 57% of carbon deposit whereas on MgO these metals gave 230% of carbon deposit. Further cobalt alone either on calcium or magnesium supports showed more or less same activity. However, iron alone on magnesium salt supports showed much better activity than on calcium salt supports. From these observations it can be inferred that the nature of the support, the catalyst and most importantly the type of interaction between the metal and the support had a great influence on the yield of the carbon deposit from CCVD method.

### 3.2. TEM analysis for the density and nature of the CNT in the carbon deposit

TEM analysis of the as synthesized carbon deposits using various catalysts revealed that the density and the nature of carbon nanotubes produced were different in each case (Table 1).

The general observation made from the results in Table 1 is that Fe/Co on  $\text{CaCO}_3$  and on all the magnesium salt

Table 2

The yield of carbon deposit (wt.%) obtained on various Ca and Mg salts supported Fe, Co, Fe/Co catalysts from CCVD of ethylene

CaO–Fe/Co	76.6	CaO–Co	55.5	CaO–Fe	17.5	MgO–Fe/Co	109.7	MgO–Co	8.0	MgO–Fe	10.5
Ca(OH) <sub>2</sub> –Fe/Co	124.4	Ca(OH) <sub>2</sub> –Co	38.5	Ca(OH) <sub>2</sub> –Fe	19.3	Mg(OH) <sub>2</sub> –Fe/Co	77.1	Mg(OH) <sub>2</sub> –Co	16.3	Mg(OH) <sub>2</sub> –Fe	33.0
CaCO <sub>3</sub> –Fe/Co	184	CaCO <sub>3</sub> –Co	49.0	CaCO <sub>3</sub> –Fe		MgCO <sub>3</sub> –Fe/Co	80	MgCO <sub>3</sub> –Co	9.0	MgCO <sub>3</sub> –Fe	17.6

supports exhibited a good density of CNT in the carbon deposit. Cobalt on  $\text{Ca}(\text{OH})_2$  as well as on  $\text{CaCO}_3$  exhibited moderately good activity for CNT formation. All other catalysts, however, exhibited very low or no activity at all. Thus, if one is interested in the synthesis of large quantities of carbon nanotubes probably Fe/Co supported on  $\text{CaCO}_3$  or MgO are the best. It should be noted that high percentage of spongy carbon deposit not necessarily indicate that the catalyst associated is active for the formation of good density of CNT, because the carbon deposit may also be associated with other forms of carbon such as amorphous carbon and carbon fibers along with the required CNT. Low resolution TEM analysis of HCl washed carbon deposit revealed that the number of walls of the CNT was in the range of 2–20. The average inner and outer diameter of the CNT was found to be 4.8 and 10.1 nm, respectively.

PIXE and PIGE analysis of the crude and the HCl treated carbon deposits revealed that the latter samples were associated with relatively negligible amounts of the support as well as the catalyst particles. Thus, a mere HCl treatment of the crude carbon deposit obtained by this method followed by a simple air oxidation would yield pure nanotubes.

### 3.3. Carbon deposit from ethylene

Comparison of physical appearance of as synthesized carbon deposit from ethylene with that of acetylene indicated that former produced grayish, smoother and lighter deposit than the latter. A tarry viscous liquid that was deposited at exist end of the reactor when acetylene gas was used, was absent with ethylene. The percentage weight of carbon deposit obtained with various calcium and magnesium salt supported Fe and/or Co catalysts, when ethylene was used, as the carbon source is presented in Table 2. Even with ethylene, a mixture of iron and cobalt produced highest percentage of carbon deposit on all the calcium and magnesium based supports in particular  $\text{CaCO}_3$  was found to be the best. The percentage of carbon deposit on calcium salt-based supports in general was more than on the magnesium based supports. It was also noticed that iron exhibited better activity than cobalt on magnesium supports whereas this trend was reversed in the case of calcium supports. TEM observations revealed that the carbon nanotubes obtained from ethylene pyrolysis are also multi-walled in nature. These tubes appeared longer probably due to this; therefore the carbon deposit was smooth and lighter than that obtained from acetylene.

A few representative TEM pictures of CNT obtained from various catalysts are presented in Figs. 1 and 2.

## 4. Conclusion

We have demonstrated in the present work that the multi-walled carbon nanotubes may be synthesized in large quantities by CCVD method using Fe/Co catalysts supported on

magnesium and calcium salts. The nature and yield of the nanotubes generated however are greatly influenced by the nature of the metal support interactions and the source of carbon. Simple HCl treatment of the as synthesized carbon deposits would easily separate the support and the catalyst particles from it resulting pure carbon nanotubes.

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