

# Optimization of catalytic production and purification of buckytubes

A. Fonseca<sup>a</sup>, K. Hernadi<sup>a</sup>, J. B. Nagy<sup>a,\*</sup>, D. Bernaerts<sup>b</sup>, A.A. Lucas<sup>a</sup>

<sup>a</sup> *Institute for Studies in Interface Sciences, Facultés Universitaires Notre-Dame de la Paix, 61 rue de Bruxelles, B-5000 Namur, Belgium*

<sup>b</sup> *EMAT, University of Antwerp (RUCA), Groenenborgerlaan 171, B-2020 Antwerp, Belgium*

## Abstract

Carbon nanotubes were produced in large amounts by catalytic decomposition of acetylene in the presence of supported Co and Fe catalysts. The influence of various parameters such as the way of catalyst preparation, the nature of the support, the size of active metal particles, and the reaction conditions on the buckytube formation was studied. The process was optimized towards the large-scale production of buckytubes having the same diameters as the fullerene nanotubes obtained from the arc-discharge method. The separation of the buckytubes from the catalyst was also achieved.

*Keywords:* Buckytubes; Carbon nanotubes; Catalytic synthesis; Silica support; Zeolite support; Co-catalyst; Fe-catalyst

## 1. Introduction

Filaments were observed already in 1953 during the investigation of carbon deposit in the brickwork of blast furnaces [1]. Since that time many papers dealing with carbon filaments formed on transition metal catalysts have explored the prevention of coke formation because of its effect on deactivating the catalysts [2–4]. However, as a result of technological interest [5–10], the catalytic growth of graphitic carbon nanofibers during the decomposition of hydrocarbons in the presence of metals, which were either supported or unsupported, has been widely studied during the last years [11,12]. The main goal of these studies was to avoid the formation of filamentous carbon which strongly poisons the catalyst. More recently, carbon tubules of

nanometer dimensions have been found as a by-product in arc-discharge production of fullerenes [13–16], or in plasma decomposition of hydrocarbons [17]. Their calculated properties such as the high-mechanical strength [18], and their remarkable electronic structure [19] allow to envisage a wide range of potential usage.

In this paper we present a detailed description of the synthesis and purification of the nanotubes of various diameters, lengths and structures. The synthesis was performed by catalytic decomposition of acetylene on various well-dispersed transition metal catalysts.

## 2. Experimental

Catalysts were tested in the decomposition of acetylene at 700°C. Transition metal catalysts

\* Corresponding author.

on  $\text{SiO}_2$  were obtained by ion-adsorption precipitation on silica gel and those dispersed on zeolites were prepared by porous impregnation or by ion exchange.

### 2.1. pH controlled ion-adsorption precipitation on silica gel

As a first step of the catalyst preparation, 1.056 g of  $\text{Co}(\text{H}_3\text{C}-\text{CO}_2)_2 \cdot 4\text{H}_2\text{O}$  (Riedel-de Haën) was dissolved in 60 ml of distilled water for each of the six samples. Then the six solutions were set to different pH values. The pH of the original Co-acetate solution was 7.0, and acetic acid or ammonia solution was used to set the pH of the solutions to 4, 5, 6, 8, 9, respectively. Above pH 7 the colour of the solution turned to blue, and at pH 9 a slight precipitation was also observed.

After this, 2.0 g of silica ('Silica Gel 60', Merck, particle size: 15–40  $\mu\text{m}$ ) was added to each sample and they were stirred occasionally. After two days the samples were filtered on a Büchner funnel and washed with  $2 \times 50$  ml of distilled water and dried at  $100^\circ\text{C}$ . This procedure was followed by calcination in air at  $450^\circ\text{C}$  for 4.5 h. After this treatment the colour of the samples varied from light blue to olive, and to dark grey with increasing pH. A portion (0.4 g) of each sample was hydrogenated, which was carried out in  $\text{H}_2/\text{N}_2$  ( $\text{H}_2$  flow: 35 ml/min;  $\text{N}_2$  flow: 75 ml/min) at  $650^\circ\text{C}$  for 8 h.

The same procedure was used to prepare the Fe/ $\text{SiO}_2$  (ion-adsorption precipitation) catalyst, except for the starting material that was basic iron acetate ( $\text{HO}-\text{Fe}(\text{H}_3\text{C}-\text{CO}_2)_2$ ) (INC Pharmaceuticals), and the fact that the pH of the solution was set to 7 only before filtration.

### 2.2. Porous impregnation and ion exchange on zeolites

For the catalyst preparation, different methods (impregnation, ion exchange) using zeolite support (NaY, Union Carbide) were applied. For both impregnation and ion exchange, Co-

(Fe-)acetate solution was used in the catalyst preparation procedure. Catalyst samples were calcined at  $450^\circ\text{C}$  for 4.5 h. The final Co(Fe) content of the impregnated samples was about 2.5 wt.%.

### 2.3. Catalytic decomposition of acetylene at $700^\circ\text{C}$

For the characterization of the catalyst samples, decomposition of acetylene was studied in a fixed-bed flow reactor (quartz tube of 14 mm in diameter in a Stanton Redcroft horizontal oven) at  $700^\circ\text{C}$  with a time of contacting with acetylene (reaction time) of 30 min. Each reaction was carried out using the same flow of acetylene (8 ml/min, Alphagas) and nitrogen (75 ml/min, Alphagas) and a catalyst amount of approx. 30 mg. The exact amount of carbon deposit formed during the reaction was determined by weighting and the reproducibility was within 3%.

### 2.4. Identification of carbon deposit

The nature of the carbon deposit on the catalyst surface was characterized by transmission electron microscopy (TEM: Philips XL 20 and JEOL 200 CX, 200 kV). For the sample preparation a Rh–Cu grid was dipped in a glue solution (50 cm of tape -- Scotch; 19 mm -- suspended in 100 ml of  $\text{CHCl}_3$ , followed by filtering). Using this glued grid, we could investigate a representative sample of the catalyst and product together.

The presence of zeolite Y in different samples was checked by classical X-ray powder diffraction (Philips P.W. 1349/30 diffractometer).

### 2.5. Purification procedure of buckytubes

The purification of the nanotubes requires their separation from both the catalyst and the amorphous carbon.

### 2.5.1. Separation of the buckytubes from the catalyst

The separation of the buckytubes from the catalyst was achieved by two different methods:

— in one of the purification procedures, 50% HF (UCB, Vel) was used in order to dissolve catalyst particles. After the treatment, the samples were filtered (pore size of 0.2  $\mu\text{m}$ ), and washed with distilled water [20,21];

-- The second treatment required firstly dissolving Co- (or Fe-)particles from the sample because the nanotubes were bonded to the surface of the catalyst support via these particles. For this purpose diluted  $\text{HNO}_3$  was found to be the best, since it was able to dissolve the cobalt (iron) derivatives from the surface. The samples were kept in the acidic solution (30% nitric acid) for 4 h, then they were filtered, washed with distilled water and finally with acetone. Samples, obtained by this method, were used for further ultrasound treatment (sonifier BRUNER, model 250 with adjustable output power up to 200 Watts). A mixture of n-hexane, acetone and iso-propanol in the volume ratio of 1:1:1 gave the best results for separating the nanotubes from the support during the sonication. The nanotube samples were sonicated for 10 min at 40% of output power then they were left to settle down for 20 min, and that was followed by decantation. This 20-min sedimen-

tation seemed to be sufficient for the separation of the nanotubes and the catalyst support particles. This treatment was repeated five times and the liquid phases were collected together. After evaporating the solvent, the black, very fluffy, and light product was collected.

While the former method was effective for samples with zeolite support, the latter one was mainly used for silica-supported products, since silica covered by carbon can hardly be dissolved in HF.

### 2.5.2. Separation of the buckytubes from the amorphous carbon

The  $\text{KMnO}_4/\text{H}_2\text{SO}_4$  aq. oxidation of the amorphous carbon yields pure carbon nanotubes with open tips:

100 mg (8.326 mmoles of carbon) of carbon nanotubes obtained after HF aq. dissolution of the residual Co/zeolite Y (impregnation) catalyst (sample of Fig. 6c) are introduced in a 3-necked flask fitted with a magnetic stirrer and a reflux condenser topped by an addition funnel. 25 ml of 0.5 M sulfuric acid is added to the flask and the solution is heated to reflux. 877.2 mg (5.550 mmoles) of  $\text{KMnO}_4$  dissolved in 25 ml of 0.5 M sulfuric acid is then added dropwise to the mixture and the reflux is prolonged for 5 more hours. The mixture is then cooled down and filtered through an HPLC filter (Gelman FP-200; pore size 0.2  $\mu\text{m}$ ). The precipitate is washed with 50 ml of 1 M hydrochloric acid and then with 25 ml of concentrated hydrochloric acid to dissolve the  $\text{MnO}_2$ . Afterwards the precipitate is washed with 50 ml of water, collected and dried at 100°C for 18 h. The yield of purified nanotubes is 23 mg (23%).

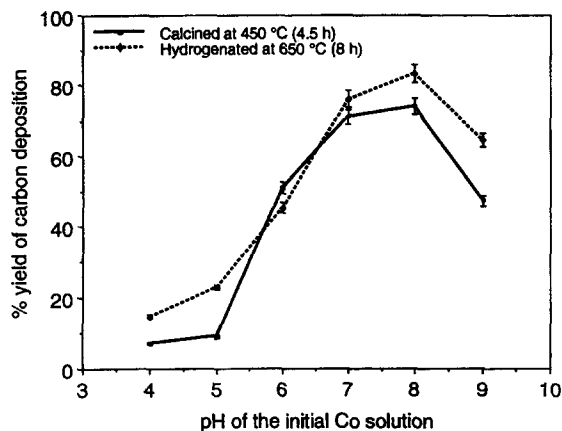


Fig. 1. Yields of carbon deposition over different Co/ $\text{SiO}_2$  catalysts as a function of the pH of the original Co solution.

## 3. Results and discussion

Catalytic hydrocarbon conversion for carbon deposit can be used for the production of nanotubes. The nature of the deposited carbon, e.g., the graphitic structure of the buckytubes strongly depends on the experimental parameters.

### 3.1. Effect of the pH on the preparation of silica-supported catalysts

At 450°C the thermal decomposition of Co-acetate takes place and gives CoO. In Fig. 1 carbon yields of acetylene decomposition over different Co/silica catalyst samples are given. The highest activity was observed in the presence of catalyst prepared from the Co-acetate solution of pH 8, both for the original and the hydrogenated samples. It is interesting to note that according to Fig. 1, there is no significant difference between catalysts prepared from solutions of pH 7 and pH 8. Otherwise decreasing or increasing the pH of the initial Co-acetate solutions result in a reduced carbon yield.

A large amount of carbon nanotubes of graphitic structure was formed over the catalyst prepared from Co-acetate solution of pH 8 (Fig. 2a). According to TEM observations (Fig. 2a), the main component of the product was carbon nanotubes having quite regular diameter and only a very small amount of amorphous carbon was found. The average value of the outer (inner) diameter is 20–30 nm (5–10 nm). The length of the nanotubes was found to be in the order of magnitude of 10  $\mu\text{m}$  for a 30-min reaction, and that of the longest ones was about 60  $\mu\text{m}$ . Helices, in relatively high percentage were also observed over Co/silica (pH 8).

For the catalyst prepared from Co-acetate solution of pH 9, the quality has been found also very good, similar to the previous one. The only difference observed by electron microscopy was the definitely higher amount of helices.

While the activities of the catalysts prepared from solutions of pH 7 and 8 were about the same (Fig. 1), there was a significant difference between the qualities of carbon deposit formed on them. The composition of the product obtained over the catalyst of pH 7 was more heterogeneous, while in the case of samples of pH 8 and 9, all catalyst particles were covered by regular carbon nanotubes after the reaction. On the catalyst of pH 7, much less particles

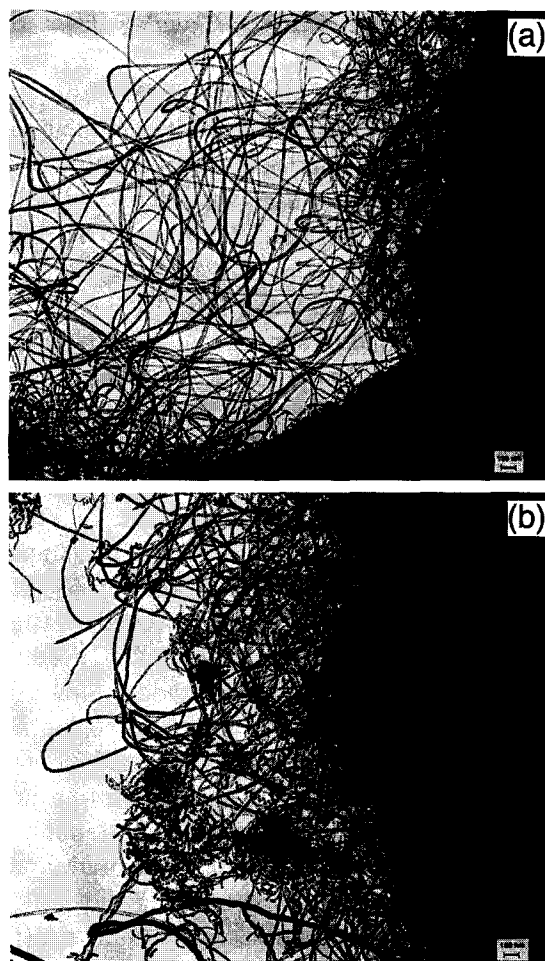


Fig. 2. Low-magnification electron microscopic images of carbon nanotubes obtained in the decomposition of acetylene at 700°C over: (a) Co/SiO<sub>2</sub> calcined at 450°C during 4.5 h; (b) catalyst as in (a) but reduced under H<sub>2</sub> during 8 h at 650°C.

were covered by well-graphitized tubes, while the relative amount of irregular tubes and fibres increased considerably.

The surface of the catalyst samples prepared from Co-acetate solution of lower pH (pH 6, 5 and 4), is mostly covered by amorphous carbon and fibres. On Co/silica of pH 4, concomitant to the decreasing amount of carbon deposit, only a very few soot-like bunches were observed by TEM.

As a conclusion of the effect of the pH on the catalyst preparation: pH 8 or 9 is recommended for the ion-adsorption precipitation solutions de-

pending on the desired shape of the nanotubes (straight or helical).

### 3.2. Effect of the prereduction treatment on silica-supported catalysts

Making a comparison between the original and the hydrogenated samples, it can be concluded that the latter ones yield carbon deposit in a somewhat higher amount (Fig. 1). However, significant difference was observed in the quality of the carbon deposit, especially for the samples of pH 8 and 9 (Fig. 2). While over the original catalysts almost no amorphous carbon, soot, fibres were found, the amount of these 'by-products' was significantly higher on the hydrogenated samples (Fig. 2b). Especially the amount of thick tubes and fibres (over 50 nm in diameter) increased.

The catalyst samples, calcined at 450°C, should contain well-dispersed Co-oxide particles on the silica support mainly in the inner pores, while the calcined and hydrogenated samples contain cobalt particles in reduced form. Nevertheless, reduction alone does not explain the higher catalytic activity leading to a higher carbon yield or the appearance of amorphous carbon and thick fibres, since the reactant acetylene itself is also able to reduce the catalyst under the reaction conditions. According to our previous results [12,23], the diameter of the carbon nanotubes growing on a Co/silica particle depends mainly on the dispersion of the catalyst. During the hydrogenation treatment the catalyst was exposed to high temperature for a long time (compared to the average reaction time of 30 min). As a consequence cobalt particles had a chance to migrate from the inner pores to the outer surface and to assemble, thus reducing dispersion. These particles outside the pores can be reached by the reactant molecules more easily, which gives an explanation for the higher catalytic activity. At the same time increasing particle size can result in the higher amount of amorphous carbon and thick tubes

obtained over the hydrogenated catalyst samples.

Since acetylene is able to reduce CoO particles to a required extent and form the active sites in situ at the beginning of the acetylene decomposition, it seems that hydrogenation has only disadvantageous effects on the performance of the catalysts. The most selective catalyst can be obtained during the induction period of the reaction. It can be concluded that catalyst samples calcined at 450°C for 4.5 h give better results in nanotube production than the other ones which were reduced in advance.

### 3.3. Effect of the catalyst support on the activity

While the best silica-supported catalyst is the one prepared by ion-adsorption precipitation (Fig. 3a), the Co/zeolite Y prepared by ion exchange was found to be inactive in the formation of carbon nanotubes. However, zeolite supported catalysts made by impregnation showed high activity, the nanotubes being formed on the external surfaces of the zeolite exclusively.

According to the electron microscopic observations (Fig. 3b) Co/zeolite (prepared by the impregnation method) is able to produce regular buckytubes with the average diameter of 20–30 nm and with a length of about 10  $\mu\text{m}$ . On the high resolution images of carbon nanotubes produced over Co/Y catalyst (Fig. 4), it was observed that the tubes are regular, not covered by amorphous carbon, and their walls are well-graphitized [22]. Formation of regular helices was also observed. The straight cylindrical tube of Fig. 4a is composed of 16 concentric tubes. The inner diameter is 8 nm and the outer diameter is equal to 18 nm corresponding to the sum of the inner diameter and  $30 \times 0.34$  nm, where 0.34 nm is the graphite inter layer distance. Fig. 4b shows a peculiar phenomenon, where the inner tube is closed, while the outer part has continued to grow. The closing was realised using five membered rings in the structure, the presence of which can be noted by the break in

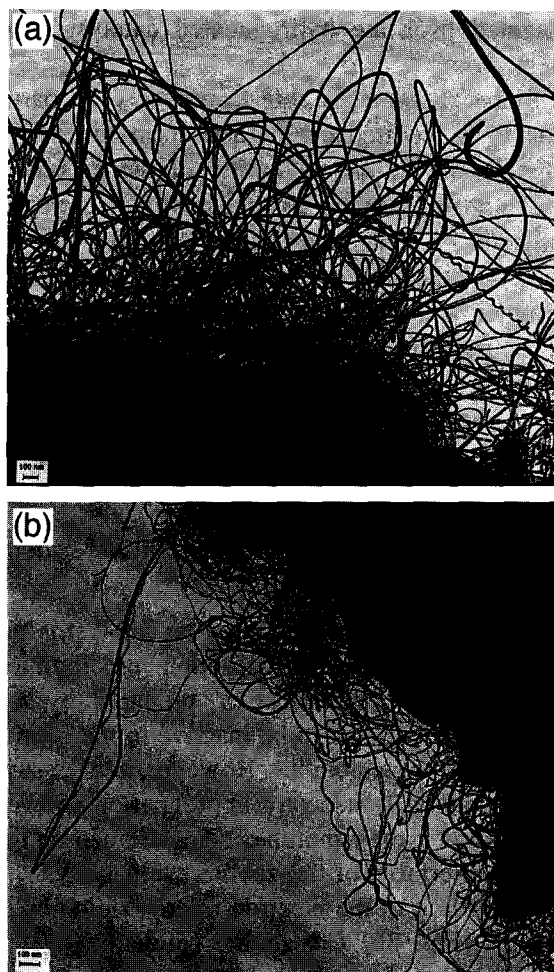


Fig. 3. Low-magnification electron microscopic images of carbon nanotubes obtained in the decomposition of acetylene at 700°C over: (a) Co/SiO<sub>2</sub> (ion-adsorption precipitation); (b) Co/zeolite Y (impregnation).

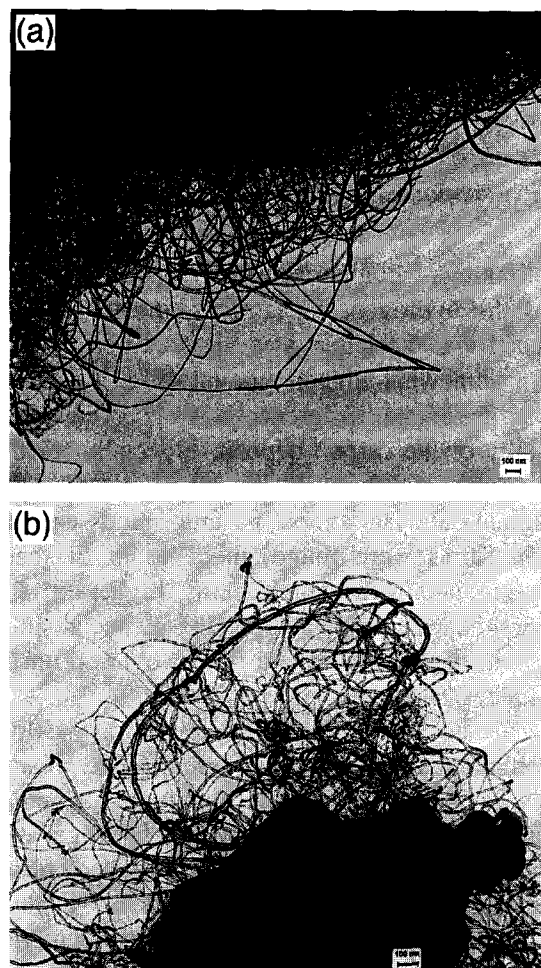


Fig. 5. Low magnification electron microscopic images of carbon nanotubes obtained in the decomposition of acetylene at 700°C over: (a) Fe/SiO<sub>2</sub> (ion-adsorption precipitation); (b) Fe/zeolite Y (impregnation).

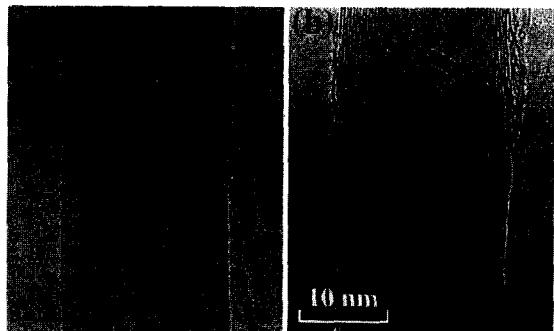


Fig. 4. High resolution images of carbon nanotubes (produced over Co/zeolite Y; impregnation) after the second HF aq. treatment.

the curvature [23]. This once again emphasizes the fullerenic nature of the nanotubes.

#### 3.4. Effect of the transition metal on the activity

Carbon nanotubes produced on Fe/silica (made by ion-adsorption precipitation) can be seen on Fig. 5a. According to the electron microscopic observations, all catalyst particles are covered by carbon nanotubes of similar diameter. Some helices were also observed. The average value of the outer diameter is approximately 10–15 nm and that of the inner diameter is 5–8

nm. The structure of their wall, observed at high resolution images, is graphitic and the macroscopic appearance of the material can be described with a 'spongy' texture. It is very fluffy, light and easily charged electrostatically. The tubes stick to glassy surfaces very strongly. Taking advantage of the latter property, after simply removing the catalyst bed, a pretty large amount (approx. 3 wt.%) of almost pure carbon nanotube was stuck on the bottom and could be collected by scraping from the quartz boat. This

material contains only a small amount of silica support and is free of amorphous carbon.

Comparing activities of Fe/SiO<sub>2</sub> prepared by ion-adsorption precipitation (Fig. 5a) and that of Fe/zeolite Y prepared by impregnation (Fig. 5b), it is concluded that the silica-supported catalyst is much more active (117 wt.% and 48 wt.% carbon deposit, respectively). As a general rule, much more carbon is deposited on silica compared to zeolite Y.

The activity of Fe/zeolite Y (Fig. 5b) is

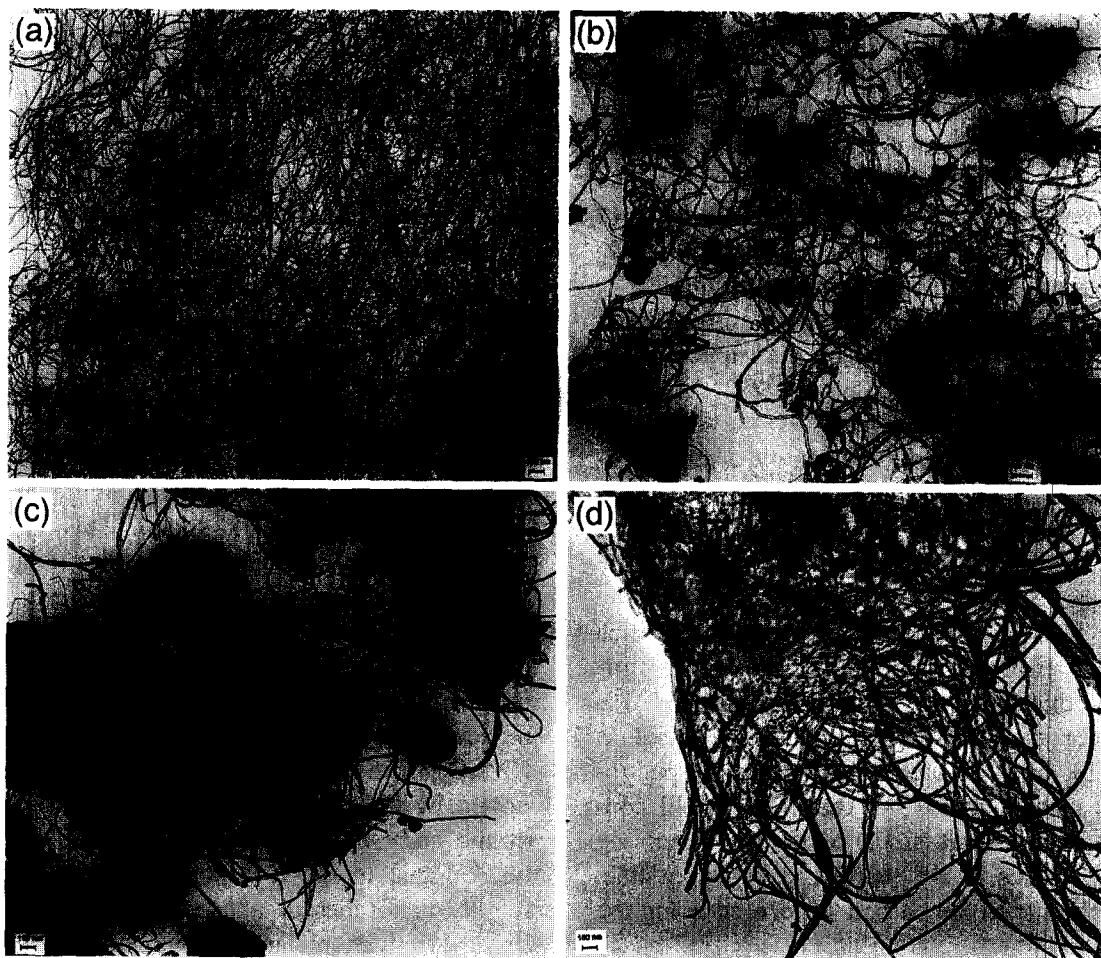


Fig. 6. Low magnification electron microscopic images of carbon nanotubes obtained in the decomposition of acetylene at 700°C, over different catalysts, followed by different purification procedures. (a) Fe/SiO<sub>2</sub> (ion-adsorption precipitation). The nanotubes were collected by scraping from the bottom of the quartz boat after reaction. (b) Co/SiO<sub>2</sub> (ion-adsorption precipitation). The nanotubes were removed from the silica support by sonication after nitric acid treatment. (c) Co/zeolite Y (impregnation). The nanotubes were recovered by filtration after dissolution of the catalyst in HF. (d) Co/zeolite Y (impregnation). The catalyst was dissolved in HF aq. and the amorphous carbon was oxidized by KMnO<sub>4</sub>/H<sub>2</sub>SO<sub>4</sub> aq.

higher than that of the corresponding Co/zeolite Y, the amount of weighted carbon deposit is higher. Nevertheless, the quality of the nanotubes (degree of graphitization) is better on the cobalt samples. Very few helices were found on the surface of Fe/zeolite Y and the tubes seem to be more 'crumbled' compared to those 'impetuous' straight tubes observed over Co/zeolite Y (Fig. 3b).

### 3.5. Relations between the support and the yield of the buckytube purification

Up to now, our best nanotube crude samples have been obtained by scraping from the bottom of the quartz boat after reaction using Fe/SiO<sub>2</sub> (ion-adsorption precipitation). A representative TEM image of this material is given in Fig. 6a, where it is possible to see the similarity of the nanotubes in diameter, as well as their different coilings and lengths. Some very small SiO<sub>2</sub> particles are also still present in the sample.

Two other purification methods were applied to the products, depending on the support.

#### 3.5.1. Using silica support

The nitric acid treatment removed the transition metal derivatives liberating the nanotubes from the catalyst surface. Afterwards, the ultrasound treatment was able to take some of the nanotubes into suspension. They were in the liquid phase after decanting the heavy silica particles. However, the yield of nanotubes purified by this method was very low (approx. 1% yield for the nanotube sample represented in Fig. 6b) and -- according to the IR spectroscopic measurements -- the product still contained some small silica particles. Dissolving silica particles in HF seemed to be impossible, probably due to the carbon deposit covering the support.

At this stage of the purification the yield was 1% for the Fe/silica catalyst and somewhat less for the Co/silica.

After the separation from the catalyst particles, the sample still contained a few percent of

amorphous carbon. For removing this contamination, hydrogenation of the sample was carried out at 900°C, for 4.5 h. According to a previous paper [24] this treatment is effective in the elimination of elemental carbon having irregular structure. Comparing reactivity of different carbon structures to hydrogen, it can be concluded that the reaction rate of amorphous carbon is significantly higher, which makes the method suitable for the separation from the graphitic forms. The total yield of the second treatment is about 0.25%, relative to the amount of carbon deposited on the catalyst. Because of difficulties with the sample preparation, no confirmation could be obtained by TEM about their purity.

#### 3.5.2. Applying zeolite Y support

The HF dissolution procedure described in the experimental part was able to fully remove the zeolitic support. This was followed by the disappearance of the characteristic X-ray bands on the powder diffraction pattern spectra. After three HF treatments, the yield of recovered carbon material is 76% of the total amount of carbon deposited on the catalyst. The TEM image of the corresponding product is given on Figs. 4 and 6c. On the figure lots of nanotubes can be seen together with some aggregates of amorphous carbon (dark spots). This kind of sample, produced in gram scale in our laboratory, is actually submitted to different oxidation [23,27–30] and reduction [24] treatments to get rid of the amorphous carbon. As a preliminary result on its oxidation, we obtained pure carbon nanotubes in 23% yield using the KMnO<sub>4</sub>/H<sub>2</sub>SO<sub>4</sub> aq. oxidation procedure reported by Ebbesen et al. [27]. The TEM image of the corresponding product is given on Fig. 6d. On that image it is possible to see lots of regular nanotubes of all shapes and with open tips. Moreover, no amorphous carbon was observed on these nanotubes, the dark spots on Fig. 6d being only due to the superimposition of several nanotubes.

According to our previous observations, most of the amorphous carbon formed inside of the



pores of the supports. The lower amorphous carbon content — liberated by the HF treatment — on zeolite Y compared to silica is probably due to its lower pore diameter. The zeolite channels are blocked at the beginning of the reaction before their pores are filled with soot.

#### 4. Conclusions

It is established, that Co/silica catalysts produced from a Co solution of pH 8, can produce carbon nanotubes of well-graphitized structure with high activity. Since acetylene is able to reduce Co-oxide to a required extent, no further hydrogen treatment is necessary, even more hydrogenation can have unfavourable effects on the catalyst performance.

Catalytic process is a method to synthesize carbon nanotubes of a large variety of forms and lengths up to 60  $\mu\text{m}$ . Straight nanotubes as well as bent and helically wound nanotubes were observed. The latter regular helices of fullerene diameter can be of special interest both from theoretical and practical points of view [25,26].

The catalytic method as it was shown in this study has some advantages over the arc-discharge nanotubes production. First, the yield of nanotubes in the catalytic production is higher than in the arc-discharge. Using the zeolite Y as support, it was possible to optimize the method for the deposition of almost all carbon in the form of tubular filaments. The isolation of nanotubes is also easier in the case of catalytic production, mostly when the support is zeolite. They can be separated from the substrate by the combination of various methods (chemical treatment, sonication).

The high percentage of nanotubes in the product (up to 76% actually isolated with some amorphous carbon from Co/zeolite Y) gives the possibility for their effective purification either by gasification (oxidation or hydrogenation) or by acidic  $\text{KMnO}_4$  oxidation [27].

Carbon deposition from acetylene on zeolite Y catalyst was optimized to give pure nanotubes in 17% global yield after HF aq. dissolution of the zeolite and  $\text{KMnO}_4/\text{H}_2\text{SO}_4$  aq. oxidation of the amorphous carbon.

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