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Syntheses of CNTs over several iron-supported catalysts: influence of the metallic precursors

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Abstract

This paper describes the synthesis of carbon nanotubes by the catalytic decomposition of acetylene at 700 °C over several Fe/silica catalysts in a thermobalance. Characterization of the catalysts was performed by chemical analyses, N_2 adsorption isotherms, X-ray diffraction, temperature-programmed reduction and CO volumetric chemisorption. The carbon products were mainly characterized by transmission electron microscopy. It was found a high influence of the iron precursor used in the synthesis of the catalysts on the final reaction yield and on the characteristics of the carbon products obtained.

Keywords: Carbon nanotubes; Carbon nanofibers; Acetylene decomposition; Iron catalysts

1. Introduction

Since carbon nanotubes (CNTs) discovery in 1991 by Ijima [1], a significant research activity has emerged around this subject, in order to elucidate the unique structural, electrical, mechanical and chemical properties of this novel material [2–5]. Nowadays the main problems encountered are the scalability and reproducibility of synthesis and consequently the full potential of CNTs for applications will not be realized until their growth can be further optimized and controlled [6].

Among the often used synthetic methods, i.e. arc-discharge evaporation [7], laser ablation of graphite [8] and chemical vapour deposition (CVD) [9], the CVD method was reported to be the most selective in the carbon nanotube formation meanwhile arc-discharge and laser ablation lead to mixtures of carbon materials [9–13]. The control of the nanotube structure with CVD method can be realized by regulating the reaction parameters and catalyst composition as well as by modifying the nanomorphology of the catalysts with dispersion of metals on supports [8,9].

Typically carbon nanotubes have been synthesized using supported Fe, Co or Ni catalysts in reaction with a large amount of hydrocarbons [3,4]. It is difficult to select the best conditions because there are many parameters affecting this reaction, and the lack of systematic studies in bibliography makes these experiments even more complicated. In a previous paper [6] we justified the advantages of using iron–silica catalysts prepared by a sol–gel method, and acetylene as carbon precursor. We showed up that the synthesis of CNTs is directly dependent on the catalyst composition and metallic particle size, and the catalysts with a lower iron content and particle size resulted in a higher yield and quality of CNTs. In this way it seems that it is necessary to design carefully the catalysts to obtain a selective reaction to CNTs.

In the last years some good results obtained in CNTs synthesis by the pyrolysis of iron organic precursors like Fe(phthalocyanine), ferrocene or $Fe(CO)_5$ were published [14–18]. Rao and co-workers [14] reported the synthesis of SWNTs by the pyrolysis of $Fe(CO)_5$ and acetylene, and concluded that the organometallic precursors give rise to very fine metal particles, which are essential for the synthesis of such CNTs. The use of iron-phthalocyanine was reported to be a novel method for the synthesis of aligned CNTs over a quartz substrate, using the appropriate reaction conditions [15,16]. Coville and co-workers [17] described the use of

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$Fe(CO)_5$ and pentane, developing a method to generate small particles via decomposition of this organometallic precursor in gas phase. Recently, Lee et al. [18] studied the influence of reaction temperature on the synthesis of aligned CNTs using ferrocene and acetylene as carbon source, concluding that the size of the catalytic particle limits the diameter of the growing tube. Then, we can admit that the main advantage of this pyrolysis CVD method, with the organometallic precursors, is the formation of small iron particle sizes, favouring the synthesis of homogeneous CNTs. However, the catalyst properties can be better controlled by the use of a support, but there are no works in bibliography using iron-supported catalysts from organometallic precursors with these objectives.

In this paper carbon nanotubes have been synthesized by the catalytic decomposition of acetylene, over several iron-supported catalysts in a thermobalance at a temperature of 700 °C. The main objective of this work has been to study the influence of several iron precursors, inorganic and organometallic, on the activity of the catalysts prepared and on the morphology of the carbonaceous products.

2. Experimental methods

Several Fe/silica catalysts were prepared by impregnation in the rotatory evaporator. The iron precursors employed were $Fe(NO_3)_3{\cdot}9H_2O$, 1 and 5 wt.% Fe(n), $Fe(CO)_5$, 1 wt.% Fe(c) and Fe(phthalocyanine), 1 wt.% Fe(pc). A commercial silica gel (480 m^2/g), from Fluka, was used as support. About 50 g of silica was mixed with 500 ml of an ethanolic solution of the metal precursor (in the exact amount to get the required iron percentages). The final solution was evaporated at 30–40 °C under vacuum until the solid was dried. Another iron catalyst was prepared, 1 wt.% Fe(D-P), following the deposition–precipitation method reported in [19]. The iron-nitrate catalysts were dried both at 110 °C for 22 h to remove completely the solvent and then calcined at 450 °C for 16 h in air atmosphere. The iron–pentacarbonyl and phthalocyanine catalysts were used in reaction as prepared to avoid structure modifications of the ligands.

The iron contents (wt.%) for the different catalysts were analysed in an inductively coupled plasma-atomic emission spectrometer (ICP-AES), Perkin-Elmer mod. 3300 DV. Their surface areas were calculated by the conventional BET method, from the N_2 adsorption isotherms at 77 K, determined using a Micromeritics mod. ASAP 2010/TRISTAR 3000 apparatus.

The X-ray diffraction (XRD) patterns for the prepared catalysts were recorded in an X-ray Diffractometer Seifert mod. XRD 3000P, using Cu Kα radiation and a graphite monochromator.

Temperature-programmed reduction (TPR) experiments were carried in a quartz micro-tubular reactor, where about 300 mg of the sample was charged. The reduction was carried out in a gas mixture 10% of H_2 in He, in a total gas flow of 20 ml/min. The sample was heated from room temperature at 5 °C/min until 800 °C. The H_2 consumption and the decomposition products were analysed with a Varian 3400 chromatograph equipped with an automatic sampling valve and a thermal conductivity detector (TCD).

The CO chemisorption measurements were performed in a conventional volumetric system at room temperature. The samples were statically reduced in situ by pulses of H_2 until 400 and 500 °C using a heating ramp of 10 °C/min, keeping the samples at these temperatures during 2 h. After vacuum at reduction temperature for 2 h more, the samples were cooled down until room temperature. Several pulses of CO were then introduced, in order to determine the chemisorption capacity of the sample. Every pulse of CO was left until stabilization of the pressure meter, occurred after about 30 min in every case, and the final pressure value was then taken.

CNTs were synthesized by the catalytic acetylene decomposition, over the iron-supported catalysts previously described, in a thermobalance, C.I. Electronic, at the temperature of 700 °C. About 100 mg of the catalyst was retained on a quartz basket located inside the thermobalance. The catalyst was heated, in a mixture N_2/H_2 (100/100 ml/min), from room temperature to 700 °C, with a heating ramp of 10 °C/min. After 120 min more under these conditions, acetylene was introduced in a reaction mixture of 7% of acetylene in N_2, total gas flow of 500 ml/min, during 120 min. After this time the reactor was cooled down to room temperature in N_2 atmosphere. The reaction yield was followed by weight gain in the thermobalance. The final product was obtained as a light and electrostatic black solid. The transmission electron microscopy (TEM) studies were carried out in a JEOL JEM-2000 FX microscope at 200 kV. The samples were prepared by ultrasonic dispersal in an acetone solution, placed on a copper grid.

3. Results and discussion

The results of the chemical analysis of the samples and their BET surface area are described in Table 1.

The X-ray diffraction (XRD) patterns showed the catalysts exist as amorphous, both the calcined and the non-calcined catalysts, so that it was not possible to determine the iron crystalline species present in the fresh samples.

Table 1
Chemical analysis and BET surface area of the prepared catalysts, and TEM metal particle sizes after treatment

Catalyst	Fe contents (wt.%)	S_{BET} (m^2/g)	TEM metal particle size (nm)
5 wt.% Fe (n)	4.83	443	15–23
1 wt.% Fe (n)	1.03	479	<7
1 wt.% Fe (pc)	0.82	435	11–23
1 wt.% Fe (c)	1.09	486	7–23
1 wt.% Fe (D-P)	0.94	486	15–70

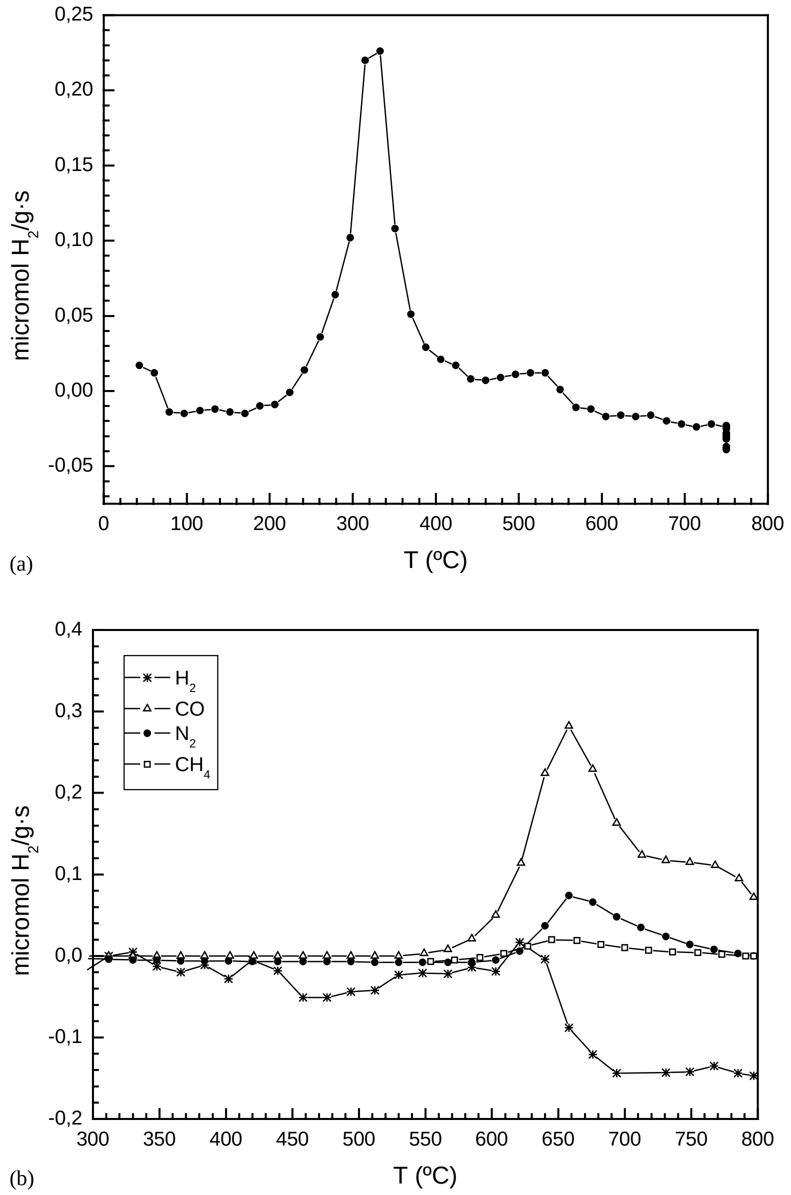


Fig. 1. (a) TPR result obtained for 5 wt.% Fe(n) catalyst and (b) TPR for 1 wt.% Fe(pc).

The TPR experiments gave little information about the iron reduction in the catalysts. Fig. 1 displays the TPR profiles of the 5 wt.% Fe(n) and 1 wt.% Fe(pc) catalysts. It can be observed a high H_2 consumption for the 5 wt.% Fe(n) at about 300 °C (Fig. 1a). A low hydrogen consumption was also observed at higher temperatures (450–550 °C), but the complete reduction to metallic iron species was not certain as it was calculated from the integration of the TPR peak area. The TPR profile of 1 wt.% Fe(n) (not included here for the sake of brevity) did not show any clear peak related with any reduction step of the iron species to metallic iron, probably due to the low metal content of this catalyst. In the case of 1 wt.% Fe(c) it was not previously expected to observe any hydrogen consumption, due to the presence of metallic iron in the precursor employed for the synthesis of this catalyst. Anyway, this complex is light sensitive, so it should have been partially oxidized, and some hydrogen consumption should be observed at temperatures around 300–400 °C. However, no hydrogen consumption due to metal reduction was observed in the TPR curve (not shown). In the case of the 1 wt.% Fe(pc) (Fig. 1b), it was clearly observed the decomposition of the phthalocyanine complex at temperatures around 650 °C. It was obtained a small H_2 consumption and the subsequent production of CO, N_2 and small amounts of CH_4 and H_2 at this temperature. The production of CO from the fragmentation of this ligand, with no oxygen in the molecular formulae, points up a high interaction of the phthalocyanine rings with the hydroxyl groups of the silica support. The small hydrogen consumption observed in this sample at 650 °C could be related both to the fragmentation of the ligand and/or to the iron reduction from the originally Fe(II) in the complex. The Fe(pc) sample was studied after the TPR experiment by XRD, in order to detect a possible iron carbide in the sample residue, but the pattern obtained just showed amorphous phases and no carbide could be observed.

The CO chemisorption measurements showed a low chemisorption capacity of the catalysts. This behaviour is related with a strong interaction between the iron and the silica support, which could make more difficult the iron reduction at 400 and 500 °C. In fact it was observed a higher chemisorption over the reduced catalyst at 500 °C than over the reduced one at 400 °C, which confirms that the reduction is more favoured at higher temperatures, probably due to the support–metal interactions. Because of experimental limitation, we could not measure the chemisorption capacity of the catalysts reduced at 700 °C, so the complete catalysts characterization with the iron particle size determination was calculated after reaction by studying the sample by TEM (see Table 1).

The thermogravimetric data took out from the thermobalance in the synthesis of CNTs are shown in Fig. 2. The 5 wt.% Fe(n) was the most active catalyst for acetylene decomposition, showing a carbon deposition yield close to 50 wt.%. This latter is probably due to its highest metal content. Anyway the most important differences were observed among the catalysts from different precursors and same iron contents of 1 wt.%. The rate of acetylene decomposition over those catalysts was Fe(n) > Fe(pc) > Fe(c) > Fe(D-P). A blank experiment with clean SiO_2 was also carried out, in order to show that the carbon yield obtained after the 2 h of reaction was only due to the metal activity in the catalysts. Actually, the silica showed to be almost inactive in this reaction (see Fig. 2). These differences are remarkable not only in the carbon deposition yield, but also in the physical characteristics of the carbon products obtained and studied by TEM. These TEM analyses confirmed the formation of CNTs and other carbonaceous species such as carbon nanofibers (CNFs), carbon capsules of metal particles and amorphous carbon.

Table 2
Physical characteristics of the CNTs observed in TEM images

Catalyst	CNTs external diameter (nm)	CNTs internal diameter (nm)
5 wt.% Fe (n)	11–19	7–8
1 wt.% Fe (n)	6–12	4
1 wt.% Fe (pc)	8–11	<7
1 wt.% Fe (c)	8–14	5–6
1 wt.% Fe (D-P)	15–20	<7

The 5 wt.% Fe(n) catalyst was active for the synthesis of CNTs, as it is shown in Fig. 3a. Anyway, it was also found that the formation of carbon capsules of metal particles. The CNTs showed many defects on their structure and high heterogeneity of diameters (see Table 2). The reaction with the 1 wt.% Fe(n) catalyst produced small diameters and scarce CNTs as it is shown in Fig. 3b. The CNTs were homogeneous in sizes (see Table 2) but it was found high amounts of amorphous carbon (not showed). It was not found carbon capsules of metal particles, nor CNFs. This sample was not very selective to CNTs, due to the scarce CNTs observed, and the high carbon deposition observed in Fig. 2 should be related to high deposition of amorphous carbon. The products obtained with the 1 wt.% Fe(pc) are showed in Fig. 3c. The CNTs were very homogeneous in sizes, opened and clean. No carbon capsules of metal particles, CNFs or

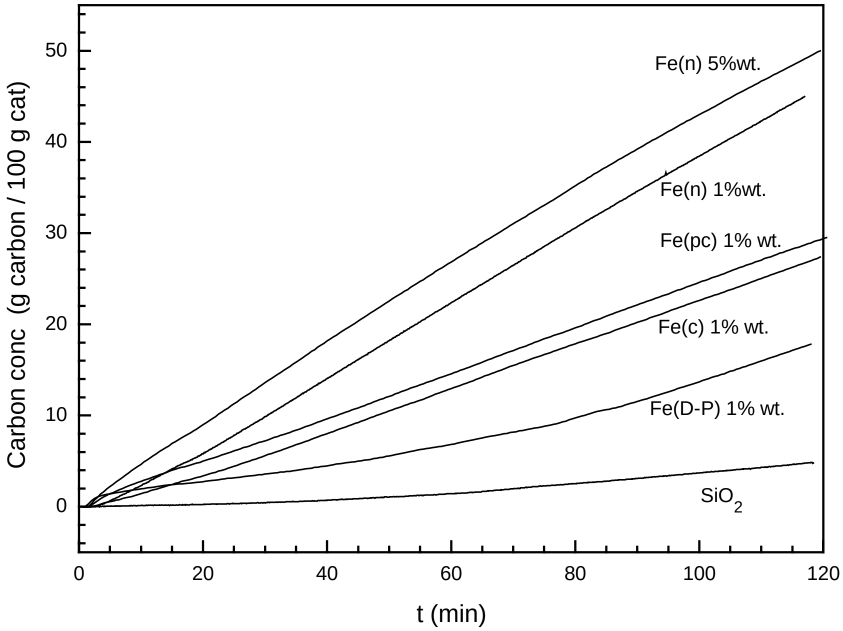


Fig. 2. Carbon deposition, from C_2H_2 decomposition, in a reaction mixture of 7% of acetylene in N_2 at 973 K, over the prepared catalysts.

amorphous carbon were observed in this sample, so this catalyst seemed to be very selective to CNTs formation. Hueng et al. [15] and Li et al. [16] have obtained a high control in the carbon structures got after the pyrolysis of iron (II) phthalocyanine at temperatures between 800 and 1100 °C. Anyway it was not found in the bibliography any paper referred to supported catalysts from iron phthalocyanine. The catalyst from 1 wt.% Fe(c) showed to be active for CNTs production in reaction (see Fig. 3d), but it was also produced CNFs and many carbon capsules of metal particles. The CNTs were very heterogeneous in sizes and showed many defects in the internal and external walls. These observations do not agree with the results of Rao and co-workers [14] and Coville and co-workers [17], probably because they synthesize CNTs by the pyrolysis of the iron pentacarbonyl. In those cases it was reported that $Fe(CO)_5$ allowed the formation of small metal particles, and so, the synthesis of CNTs would be favoured. However, in our case the TEM observations revealed a heterogeneous size distribution of the metallic particles obtained by deposition of the iron pentacarbonyl on the surface of the silica. TEM images of the carbon products synthesized from 1 wt.% Fe(D-P) (see Fig. 3e) showed up that this sample was not very selective to CNTs. Very big carbon capsules of metal particles and also CNFs were observed. The scarce CNTs were heterogeneous in sizes, so we can conclude that D-P method does not seem to be optimal to prepare dispersed iron-supported catalysts.

In Table 2 it is presented a resume of the external and internal diameters of the CNTs measured from TEM images. It is remarkable that the internal diameter of the CNTs could give us an idea about the iron particle size after reduction treatments before reaction with acetylene. However, it is also important to note that CNTs grow up from a narrow range of metal particle sizes, therefore the homogeneity of the sample determine the quality of the carbon products. In this way we could conclude that the catalyst 1 wt.% Fe(D-P) presents high amounts of carbon capsules of metal particles of different sizes, as observed in the picture (Fig. 3e), because of the high heterogeneity in particles sizes.

From data in Table 2 we observed that CNTs from 5 wt.% Fe(n) showed the highest internal diameter, but with not large differences from the other catalysts. The external diameters are directly related with the number of CNTs walls, and it seemed to be clearly a function of the catalyst

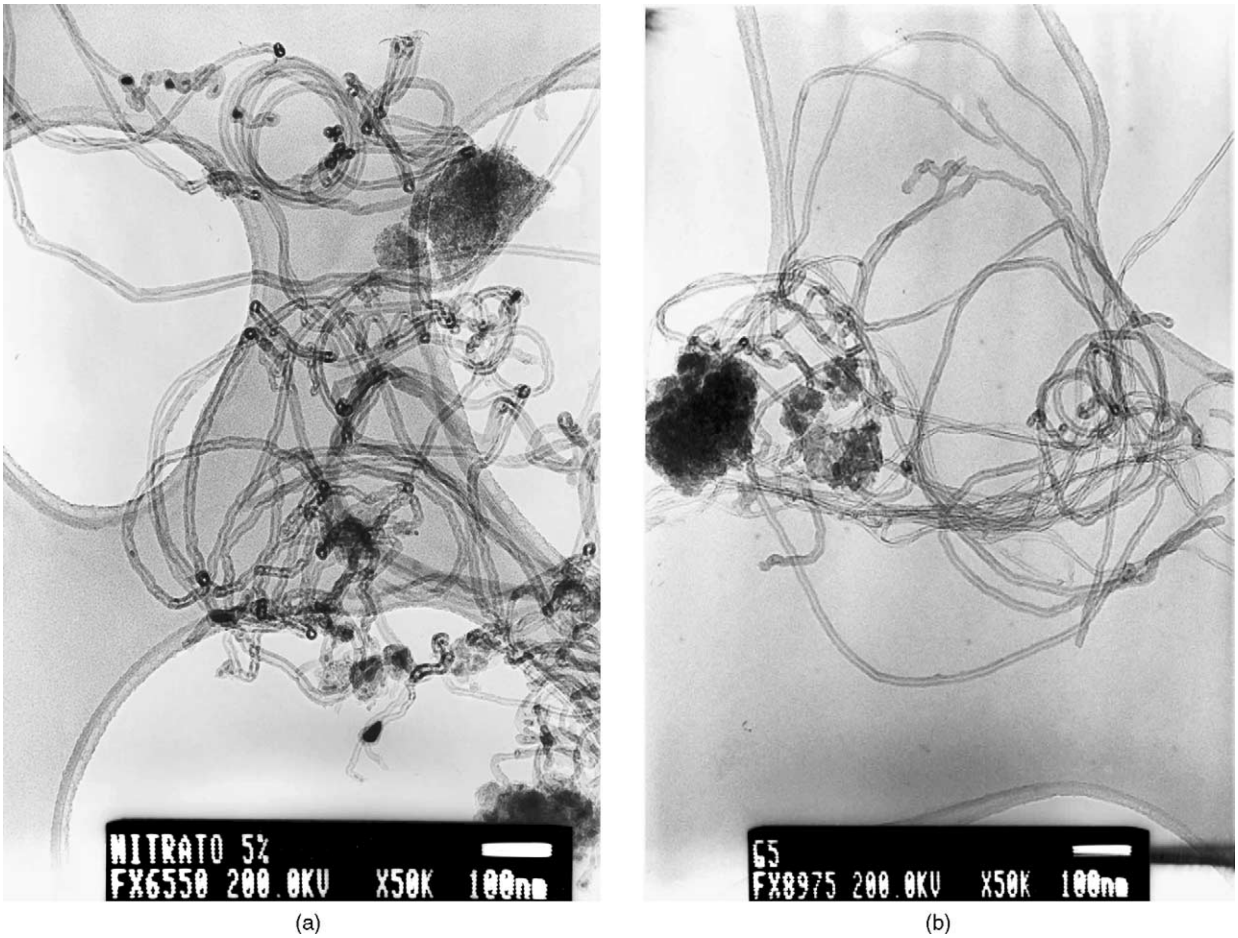
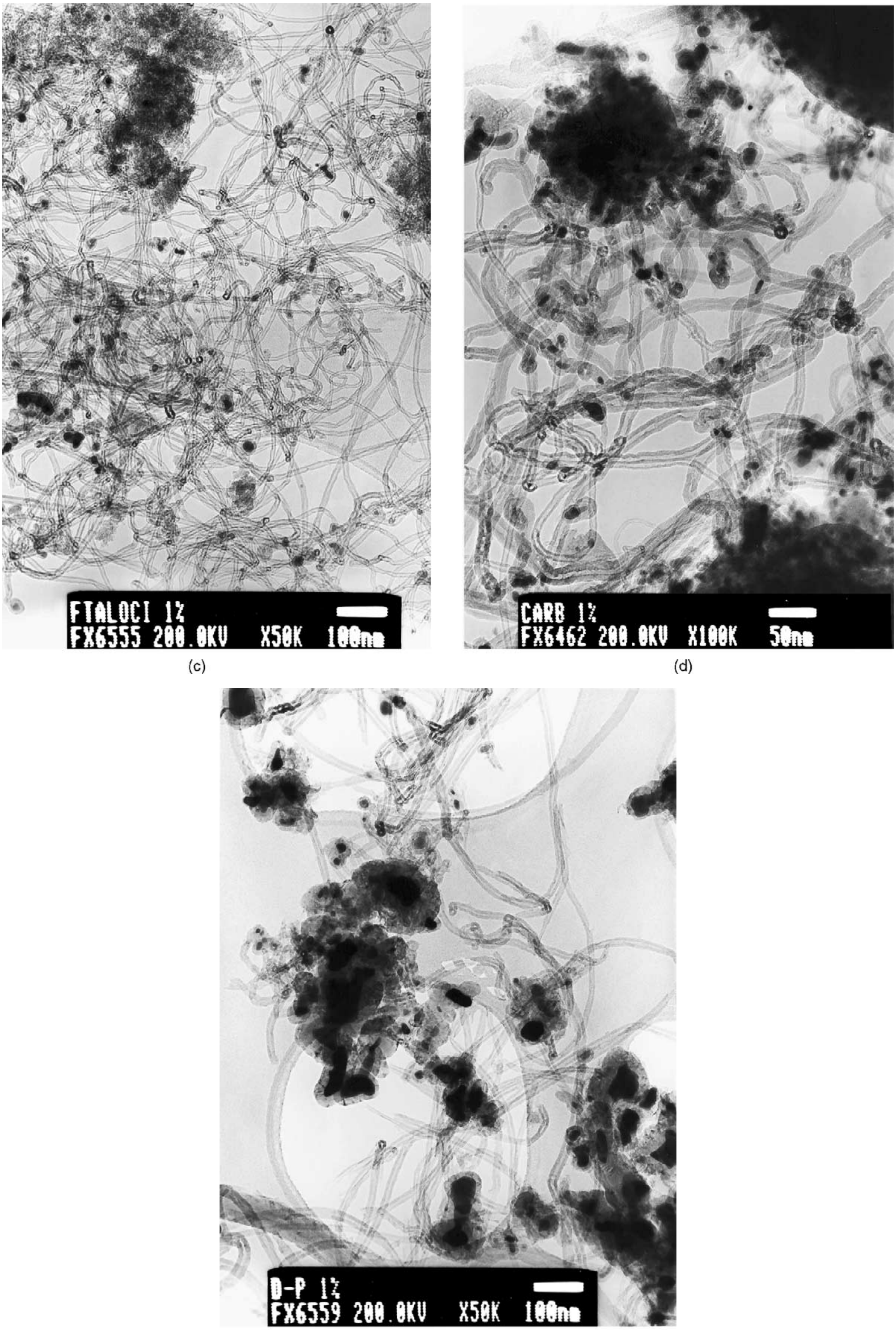


Fig. 3. TEM images of the carbonaceous products obtained after reaction over: (a) 5 wt.% Fe(n), (b) 1 wt.% Fe(n), (c) 1 wt.% Fe(pc), (d) 1 wt.% Fe(c) and (d) 1 wt.% Fe(D-P).



(c) (d)

(e)

Fig. 3. (*Continued*).

surface characteristics. The thinner and more homogeneous in size CNTs were produced from 1 wt.% Fe(n), showing external diameters of 6–12 nm and internal ones of 4 nm. The problem with this catalyst is the low selectivity to CNTs. The synthesis with 1 wt.% Fe(pc) produced high amounts of homogeneous CNTs. This homogeneity can indicate a high dispersion of the iron on the silica support due to the effect of the bulky phthalocyanine ligand, which would have favoured the formation of small metal particles after decomposition of the complex under reaction conditions.

4. Conclusions

In this work, we have shown that the CVD method with iron catalysts produces homogeneous CNTs in general, but their structure seem to be highly dependent on the metal content, the iron precursor employed and the preparation conditions of the silica supported catalysts. Several metal precursors and preparation methods were tested in order to determine which would be the optimal conditions to grow high yield and high quality CNTs. Even though the iron-nitrates produced the highest activity in acetylene decomposition, the iron-phthalocyanine produced the best quality CNTs, in quantity, size homogeneity and absence of amorphous carbon. This was related with the characteristics of the phthalocyanine ligand, which could favour high dispersion of iron on the silica support. The impregnation method seemed to allow more homogeneous metallic dispersion on the silica support than the deposition–precipitation (D-P) method. So, we can conclude that the use of iron-phthalocyanine precursor supported on silica by the impregnation method assures the synthesis of CNTs in high yield and high quality.

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