Carbon nanotubes were produced in large amounts by catalytic decomposition of acetylene over a Co incorporated zeolite NaY support. Purification of multi-wall nanotubes was required in order to eliminate catalyst and amorphous carbon produced by thermal decomposition of hydrocarbon. First, separation of nanotubes and catalyst particles was carried out by hydrofluoric acid treatment. Then, two ways of removing amorphous carbon were studied: permanganate oxidation and air oxidation. The quality of nanotubes was characterized by means of transmission electron microscopy and the yield of pure nanotubes was quantitatively determined. Changes caused by treatment of the nanotubes were investigated by high resolution electron microscopy and a comparison was made between the nanotubes produced by this method and those synthesized by an arc discharge process after oxidation treatment.

The behaviour of the nanotubes after purification is investigated: it is interesting to explore how low temperature (600 °C) catalytically or arc discharge produced carbon nanotubes behaved towards oxidative treatments. Using high resolution transmission electron microscopy, some comparisons of the changes caused by purification of nanotubes are made.

2 Experimental

2.1 Nanotubes preparation

2.1.1 Catalytic synthesis. Carbon nanotubes were produced by catalytic decomposition of acetylene over supported catalyst Co/zeolite NaY containing about 2.5 wt.% of metal. The catalyst was prepared by the impregnation method described earlier, the catalyst was synthesised by impregnation of zeolite (PQ Zeolites B. V.) with an aqueous solution of cobalt salt [Co(H₃C–CO₂)₂·4H₂O, Riedel-de Haën] in the appropriate concentration to obtain 2.5 wt.% of metal. Finally, it was dried in air at 140 °C for 18 h.

The synthesis of nanotubes was carried out in a fixed-bed flow reactor (quartz tube of 50 mm diameter, 80 mm in length in a Carbolite horizontal reactor) at 600 °C with a reaction time of 60 min. The reaction parameters used for the preparation were acetylene flow 20 ml min⁻¹, nitrogen flow 110 ml min⁻¹ (gas flows measured at STP conditions) and amount of catalyst 1.5 g.

After reaction, the carbon deposit yield was calculated as follows:

\[
\text{carbon yield (\%)} = 100\left(\frac{m_{\text{tot}} - m_{\text{cat}}}{m_{\text{cat}}}\right)
\]

Where \(m_{\text{cat}}\) is the initial amount of catalyst and \(m_{\text{tot}}\) is the total weight of the sample after reaction. The quality of the nanotubes was characterized by means of transmission electron microscopy (TEM) (Philips CM 20 and Jeol CX 200) (Fig. 1).
Fig. 1 Low and high magnification transmission electron microscope images of carbon nanotubes produced by decomposition of acetylene at 600 °C over a Co/NaY catalyst. (A) Low resolution image of crude carbon nanotubes sample. High resolution image (B) of a catalytic particle encapsulated at the tip of a tube and (C) of a tube with closed tip (without catalytic particles).

2.1.2 Arc discharge synthesis. Multi-wall carbon nanotubes were made by evaporating pure graphite (40 min) under an inert gas atmosphere (helium, 660 mbar). The principle is to create a plasma between two graphite rods used as electrodes applying a current (100 A) through the electrodes and controlling the voltage (30 V) during the process. The deposit core obtained in this way contains about one third polyhedral graphitic nanoparticles (and sometimes amorphous carbon), and two-thirds multi-wall nanotubes. These nanotubes and their impurities (nanoparticles and amorphous carbon) can be seen in Fig. 2.

2.2 Purification processes

2.2.1 Separation of the carbon nanotubes from the metal/zeolite catalyst by HF treatment. The HF dissolution procedure fully removed the zeolitic support following:

\[
\begin{align*}
\text{Na}_3\text{Al}_{13}\text{Si}_{39}\text{O}_{139}(\text{H}_2\text{O})_{235} + 768 \text{ HF} & \rightarrow \\
139 \text{ SiF}_4 + 53 \text{ Al}^{3+} + 53 \text{ Na}^+ + 212 \text{ F}^- + 619 \text{ H}_2\text{O}
\end{align*}
\]

A crude sample containing 0.8269 g of carbon deposit and 4.5188 g of NaY zeolite was put in a plastic container under vigorous stirring and 250 ml of 40 wt.% aqueous HF solution were added in small fractions causing a release of gaseous SiF_4. The suspension was stirred for 48 h at room temperature, then filtered and the residue was washed with 100 ml of 40 wt.% HF and with 300 ml of distilled water. The residue was then dried for 12 h at 130 °C.

2.2.2 Elimination of amorphous carbon from carbon nanotubes. 2.2.2.1 Oxidation in air at 500 °C. This purification method is very simple: the crude sample containing nanotubes and amorphous carbon reacts with oxygen (from air) to form

Fig. 2 Low and high magnification transmission electron microscope images of carbon nanotubes produced by arc discharge. (A) Low magnification image showing the general aspect of the nanotubes with the nanoparticles (as impurities). (B) High resolution image of polyhedral graphitic nanoparticles. (C) High resolution image of a nanotube (21 graphitic layers, inner and outer diameter 4.5–18.6 nm).
carbon dioxide or carbon monoxide if the temperature is high enough to induce the reaction:

\[ \text{C} + \text{O}_2 \rightarrow \text{CO}_2 \]
\[ 2\text{C} + \text{O}_2 \rightarrow 2\text{CO} \]

100 mg of carbon deposit obtained after HF(aq) dissolution of the catalyst support were oxidized in air at 500 °C, using an air flow of 12 ml min⁻¹ (quartz tubular reactor of 14 mm diameter) for 210 min.

2.2.2.2 Oxidation by potassium permanganate in acidic solution. The oxidation reaction of potassium permanganate in acidic solution to remove the amorphous carbon contamination proceeds as follows:

\[ 3\text{C} + 4\text{KMnO}_4 + 4\text{H}^+ \rightarrow 4\text{MnO}_2 + 3\text{CO}_2 + 4\text{K}^+ + 2\text{H}_2\text{O} \]

100 mg (8.324 mM) of carbon deposit obtained after HF(aq) dissolution of the catalyst were introduced to 50 ml of 0.5 M sulfuric acid and 526.3 mg (3.330 mM) of KMnO₄ in a flask fitted with a magnetic stirrer and a reflux condenser. The flask was heated to 80 °C in an oil bath. When the colour of the mixture changed (the purple colour of potassium permanganate in acidic solution disappeared when the MnO$_4^-$ was reduced to MnO$_2$), the reaction was prolonged for a further 1 h at the same temperature. The mixture was then cooled and filtered through an HPLC filter. The precipitate was washed with 50 ml of concentrated hydrochloric acid and then with 25 ml of 0.5 M hydrochloric acid to dissolve the MnO$_2$. Finally, the precipitate was washed with 50 ml of water, collected and dried at 140 °C for 12 h.

3 Results and discussion

3.1 Catalytic nanotube synthesis

The cobalt impregnated NaY zeolite catalyst is an effective catalyst for the catalytic formation of carbon nanotubes (Fig. 1A). Cobalt particles on the outer surface of the catalyst deposited by impregnation are responsible for this activity. The carbon deposit yield was around 18%, which is not very high, but the quality, characterized by electron microscopy (Fig. 1) was very good. The nanotubes were not covered by a high temperature (around 750 °C).

The carbon loss variation was investigated for the nanotubes produced catalytically versus reaction temperature for given reaction times of 210 and 300 min (Fig. 5A). This figure shows that the efficiency of air oxidation increases with increasing reaction temperature resulting in significant carbon loss at 500 °C (up to 90% carbon loss for 300 min reaction). Finally, the extent of oxidation rate after 300 min is greater than for 210 min at the same reaction temperature; this is why the second important parameter is the reaction temperature.

From TEM observations, trapped metal particles can be present (Fig. 1B) or not (Fig. 1C) on the nanotube tips. These differences between tubes in a crude sample can be explained by the growth mechanism. Cobalt particles were involved in this mechanism and played a role in determining the cross section of the tubes. Two growth modes, namely “tip growth” or “base growth”, can occur either simultaneously or successively, depending on the particle-support interactions. This explains the presence or absence of metal particles in the nanotubes.

3.2 Purification processes

3.2.1 Separation of carbon nanotubes from the metal/zeolite catalyst by HF treatment. The weight loss after HF treatment was exactly 100% of the zeolitic support quantity present in the initial crude sample. Moreover, the filtrate collected after this treatment presented a pink colour typical of an octahedral cobalt (II) solution, which means that the particles of Co (in various oxide and metal forms) were also dissolved in the HF.

Analyses of the solid residue by X-ray diffraction and $^{27}$Al NMR confirmed total elimination of the zeolitic support. A low resolution TEM image of the carbon material residue after HF treatment shows aggregates of amorphous carbon (dark spots in the image) and carbon nanotubes (Fig. 4). These aggregates were released from the inner pores of the NaY zeolite during the treatment. Hence, it was necessary to remove the amorphous carbon to obtain pure carbon nanotubes samples.

3.2.2 Elimination of amorphous carbon from the carbon nanotubes. 3.2.2.1 Oxidation in air at 500 °C. Different parameters have been investigated to optimize the purification in the case of carbon nanotubes produced by the catalytic process. The first parameter was the reaction temperature: it was shown previously for nanotubes synthesized by the arc discharge process that in order to initiate these oxidation reactions, it was necessary to heat the carbon material at a high temperature (around 750 °C).1

The carbon loss variation was investigated for the nanotubes produced catalytically versus reaction temperature for given reaction times of 210 and 300 min (Fig. 5A). This figure shows that the efficiency of air oxidation increases with increasing reaction temperature resulting in significant carbon loss at 500 °C (up to 90% carbon loss for 300 min reaction). Finally, the extent of oxidation rate after 300 min is greater than for 210 min at the same reaction temperature; this is why the second important parameter is the reaction time.

Fig. 5B presents the carbon loss variation versus reaction time at 500 °C. We can observe for the two different samples, A and B, produced under the same experimental conditions described above, that the shape of the curve is identical: this curve has a slope discontinuity in the carbon loss versus reaction time. The two different slopes (S and N) crossing at
around 55% carbon loss may indicate the oxidation rates of amorphous carbon (slope S for soot) and of nanotubes (slope N for nanotubes). Slope S is very high compared to slope N, meaning that the amorphous carbon is more easily oxidized than the carbon nanotubes. It is then possible to purify the nanotubes produced by catalytic process using air oxidation. Moreover, the maximum yield of pure carbon nanotubes at 500 °C could be equal to 45% (crossing of slopes around 55%).

Pure carbon nanotubes were obtained with 27% yield using 12 ml min$^{-1}$ of air flow for 210 min at 500 °C. They are visible in the electron microscope images (Fig. 6): the low magnification image of these nanotubes (Fig. 6A) does not show any dark spots meaning that all aggregates of amorphous carbon have been removed by this treatment. Moreover, the tubes obtained after the air oxidation have open tips (Fig. 6B). The opening of nanotube tips caused by this treatment increases with the reaction time. Note that the images represent typical examples characteristic of the majority of the nanotubes.

### 3.2.2.2 Oxidation by potassium permanganate in acidic solution

The purification procedure to obtain pure carbon nanotubes at 40% yield using KMnO$_4$/H$_2$SO$_4$ has been reported by Hiura et al.$^4$ for nanotubes produced by the arc discharge process. For nanotubes produced catalytically, some modifications are required from the procedure described, principally with respect to the reaction temperature. If the procedure described is strictly applied, no selectivity is observed between the nanotubes and the amorphous carbon oxidation.

The lowest reaction temperature (70–80 °C) required to purify nanotubes produced catalytically allows one to increase the selectivity of the oxidation reaction. However, the purification yield in our case is practically the same (38–39%).

Fig. 7 shows the relation between the molar equivalent of potassium permanganate and the carbon loss (%) for a given temperature (70 °C). Two straight lines with different slopes crossing at around 0.4 KMnO$_4$ molar equivalent are evident in this plot. As for air oxidation (Fig. 5B), the difference between the two slopes indicates the difference in oxidation rates for the amorphous carbon (slope S) and the nanotubes (slope N): amorphous carbon is oxidized faster than nanotubes (slope S higher than slope N). Theoretically, pure nanotubes can be obtained with 0.4 KMnO$_4$ molar equivalent. But experimentally, pure nanotubes are obtained when the carbon loss is higher than 60%; i.e. when 0.3 molar equivalent of potassium permanganate (0.4 molar ratio) or more are used for the reaction (verified by TEM). This molar ratio (0.4) for the tubes produced catalytically is also different from the one given for the nanotubes synthesized by the arc discharge process (1.5 molar ratio of potassium permanganate). These differences can be explained by the reactivity difference between amorphous carbon and the more graphitic nanoparticles present in the sample produced by arc discharge and absent in samples synthesized by catalytic processes.
Fig. 8  Low and high magnification transmission electron microscope images of pure carbon nanotubes obtained after KMnO$_4$ oxidation. (A) Low magnification image of pure nanotubes. (B) High resolution image of damaged nanotubes.

Pure nanotubes obtained after this treatment are shown in Fig. 8: the general aspect of the tubes (without amorphous carbon) is in the low magnification image and the high magnification gives details of damage caused by the oxidative treatment (tips are opened and graphitic layers are damaged where there are structural defects).

3.3  HREM comparison of the modifications caused on nanotubes produced by the catalytic process and those synthesized by the arc discharge technique

Carbon nanotubes produced by the arc discharge process were oxidized by potassium permanganate following the experimental procedure used for nanotubes synthesized catalytically (70 °C, 0.4 molar ratio of KMnO$_4$). First, as expected, graphitic nanoparticles are not removed from the sample: pure nanotubes are not obtained by this treatment as the nanotube tips are closed (Fig. 9A and B). Fig. 9 shows differences in the damage caused by oxidation of the nanotubes produced by the two techniques: after treatment, the nanotubes synthesized by the arc discharge process are not as damaged as the ones produced catalytically. These differences in damage are very visible on the nanotubes tips (closed tips for the nanotubes produced by the arc discharge in comparison with the open tips of nanotubes synthesized catalytically). This fact can be explained by structural differences between the nanotubes produced by the two methods: there are more defects on the tubes produced catalytically, meaning that these nanotubes will be more easily oxidized than the nanotubes produced by the arc discharge process. The nanotubes will be attacked preferentially by the oxidation at defect sites (discontinuity of the turbostratic layers, presence of pentagons, strain...).

4 Conclusions

Carbon nanotubes produced by a catalytic method can be purified by two methods: oxidation in air at high temperature (500 °C) and oxidation in the liquid phase by potassium permanganate at lower temperature. After HF treatment to remove the catalytic support, pure nanotubes are obtained in a 27–40% yield after air and permanganate oxidation, respectively. These nanotubes after purification are damaged and uncapped.

Fig. 9  High magnification transmission electron microscope images of carbon nanotubes after KMnO$_4$ oxidation. (A) and (B) produced by the arc discharge technique, (C) and (D) produced by the catalytic process.
Oxidative treatment by KMnO$_4$ applied to multi-wall nanotubes produced by the arc discharge technique is not effective for purification. But, the principal difference between the nanotubes produced by the two methods is their behaviour with respect to oxidation. As the nanotubes produced by arc discharge are not damaged by oxidation treatments, like those synthesized catalytically, we conclude that the nanotubes produced catalytically contain more defects on their surfaces and tips.

Acknowledgements

J-F.C. and P.P. are grateful to European Commission, TMR contract NAMITECH, ERBFMRX-CT96-0067 (DG12-MIHT) and thank the Belgian Programme on Inter University Poles of Attraction initiated by the Belgian State, Prime Minister’s Office of Science Policy Programming (4/10).

References