New organometallic precursor catalysts applied to MWCNT synthesis by spray-pirolysis

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During the last years the carbon nanotubes field and the nanostructured materials have been widely developed [1–3]. Since 1991, lijima [4] presented the first evidences of the car- bon nanotubes, numerous papers have been reported in this area, such as, diameter and wall thickness evaluation (single or multiple) [5-7], growth mechanism [8], alignment charac- teristics [9–11], electron emission properties [12–14], nanode-vices [15,16], theoretical predictions [17] and potential applications [18]. Single-wall nanotubes and multi-wall car- bon nanotube (MWCNTs) present attractive chemical, elec- trical and mechanical properties for electronic, catalytic and electrochemical applications. Their potential applications include field emitters [19], gas storage and separation [20] nanoprobes [21], chemical sensors [22], high strength composites [23] and fuel cells [24-26]. The techniques widely used to produce high-quality MWCNTs are laser ablation [27], electric arc discharge [28] and chemical vapor deposition (CVD) [29,30] which provide the appropriate conditions for MWCNTs synthesis. The laser ablation and arc discharge methods are difficult to scale-up the nanotubes production to industrial level; however the CVD method present better results to obtain MWCNTs to scaleup with less impurities and using relatively low temperature. The spray-pirolysis is a modification of CVD method, therefore large-scale produc- tion of MWCNTs can be



obtained at lowest cost.

Transition metals (e.g. Fe, Co and Ni) are the most com- mon catalysts used as precursors for carbon nanotubes (CNTs) growth [31]. Solid organometalocenes (such as ferrocene, cobaltocene and nickelocene) are widely used as catalysts materials because of liberate metal particles in situ to enhance the CNTs growth [32]. Ferrocene had been demonstrated as good catalyst for high-quality MWCNTs synthesis by CVD at 625–775 °C [33] and at 600 °C using 12.4 MPa [34].

This work present the synthesis and characterization of novel organometallic complex [(Pentyl)4N]3FeBr3Cl3 which is used as precursor of Fe-catalysts to obtain MWCNTs. This novel precursor catalyst was prepared in aqueous solution with (Pentyl)4NBr and FeCl3. The precursor solu- tion is dissolved on toluene and decomposed by spray- pyrolysis into vycor tube at 900 °C [35] to form MWCNTs. The interest of this work concerns with the possibility to define the basis to develop new catalyst for CNT synthesis. The results of this work open a new route to obtain volatile compounds, compatible with carbon-source molecules and some new precursor which could be cheaper and to be able to induce different properties to CNT than those obtained by conventional method.

Experimental methods

Iron chloride hydrate (FeCl3 Æ 6H2O, 2 g, 7.39 mmol, Sigma, 98%) was dissolved in 10 ml of distilled water. A second solution (100 ml) was prepared with tetrapentylam- monium bromide 8.4 g (6.48 mmol) (Pentyl)4NBr (Aldrich, 99%) and water–isopropanol (2:1) at 70 °C. Both solution were mixed and stirred at the same temperature for 30 min. An oil compound was formed and it was kept undisturbed



by 2 h in cold bath. The oil compound was turned to semisolid compound and separated of solution. The brown semisolid precipitated ([(Pen)4N]3FeBr3Cl3) was characterized by FTIR and UV spectroscopy. The compound stoichiometry was determinate by TGA–DTA analysis.

The FTIR spectrum was obtained using a Nicolete Magna-IR 750 Fourier Transform Spectrophotometer, using a KBr pellet. An Electronic (UV–vis) spectrum was recorded with a Perkin–Elmer Lambda 10 UV spectropho- tometer using isopropanol as solvent. Differential thermal analysis (DTA) and thermogravimetric analysis (TGA) of the organometallic precursor were made simultaneously with TA Instrument SDT 2960 DTA–TGA equipment under a dry nitrogen flow from 293 to 1073 K at heating rate of 10 K/min.

The spraying system to carbon nanotubes synthesis is illustrated in Fig. 1. A vycor tubing was attached to a pneu- matic system, which was used as a solution atomizer. The overall tube dimensions were an internal diameter of



Fig. 2. FT-IR spectra for [(Pentyl)₄N]₃FeCl₃Br₃ using KBr pellet.





Fig. 3. UV/Visible absorption spectra of the $[({\sf Pentyl})_4N]_3{\sf FeCl}_3{\sf Br}_3$ obtained at 298 K dissolved in isopropyl alcohol solution.



Fig. 1. Schematic of the spray pyrolysis system for the MWCNTs synthesis.

temperature controller (±1 K). The solution feed time was kept constant during 15 min for all experiments. Twenty- five milliliters of [(Pen)₄]₃FeBr₃Cl₃ oil dissolved in toluene (99.5%, Fluka) were placed in the nebulizer container. Argon (99.99%, Praxair) was used as carrier gas; the flow rate was regulated by mass flow controller at 83.33 cm³/ seg. The mixture argon/[(Pen)₄]₃FeBr₃Cl₃/toluene entered without



previous heating to the vycor tubing after furnace temperature was stable. The MWCNTs were taken off from the tubing for electronic microscopy and XRD characterization.

A JEOL JSM5800 LV scanning electron microscope (SEM) was used to perform morphological of MWCNTs. Several areas were analyzed at different magnifications. Transmission electron micrographs were obtained in a side entry CM-200. Analytical transmission electron micro- scope (TEM) operating at 200 kV equipped with EDX Prime and electron energy loss spectroscopy (EELS) Gatan

Digipeels 766. The specimen for TEM were prepared by dispersing in acetone and ultrasonic for 2 min, the drop of suspension was put onto holey carbon Cu grid, and was allowed to dry. The X-ray diffraction (XRD) study were obtained in a X-Pert MPD Phillips Diffractometer equipped with a curved graphite monocromator using Cu Ka radiation (k = 1.54056 Ű), operating at 43 kV and 30 mÅ.

Results and discussion

This work propose a high-yield method for the easy and novel preparation of [(Pentyl)4N]3FeCl3Br3 as iron precur- sor catalyst to produce MWCNTs. This preparation involves the reaction in aqueous-isopropanol solution of (Pentyl)4NBr with stoichiometric amount of FeCl3. The reaction engages an acid–basic interaction as show in Reac- tion (1).

$$3(\text{Pen})_4 \text{NBr} + \text{FeCl}_3 \rightarrow [(\text{Pen})_4 \text{N}]_3 \text{FeCl}_3 \text{Br}_3$$
 (1)



Determinant	$\{[CH_3(CH_2)_4]_4N\}_3FeCl_3Br_3$
T ₁ (K)	150
$T_2(\mathbf{K})$	450
Δw_1 , wt% (experimental)	83
Δw_1 , wt% (calculated) assuming loss	83.4
Lost reactive	$[CH_3(CH_2)_4]_3N + {[CH_3(CH_2)_4]_3N}_2ClBr + Cl_2$
$T_3(\mathbf{K})$	670
Δw_2 , wt% (experimental)	11.5
Δw_2 , wt% (calculated) assuming loss	12.3
Lost reactive	Br ₂
$\sum \Delta w$, wt% (experimental)	94.5
Residual, wt% (experimental)	5.5
Residual, wt% (calculated), assuming residual as Fe	4.3

Table 1 DTA-TGA results for the {[CH₃(CH₂)₄]₄N}₃FeCl₃Br₃ precursor catalyst under Nitrogen Atmosphere



Fig. 4. DTA-TGA curve of the [(Pentyl)₄N]₃FeCl₃Br₃ decomposition.







Fig. 5. Scanning electron micrographs of the MWCNTs formed (a) low magnification, (b) high magnification.





Fig. 6. Transmission electron micrographs of the MWCNTs formed.

Fourier transform IR spectrum of [(Pen)₄N]₃FeCl₃Br₃ is shown in Fig. 2. Iron precursor catalyst present stretching bands at wavenumber between 2800 and 3000



cm⁻¹ which are characteristic of C–H and C–C bonds and it can be as- signed to tetrapentylammonium group. The other impor- tant band with strong absorptions at 1466 cm⁻¹ and 1385 cm⁻¹ correspond to the vibrations of Fe–halogen, which are according to similar structures of tetraalkylam- monium iron reported by Do et al. [36]. Fig. 3 shows spec- trum of iron complex prepared in isopropanol solution. The complex exhibits three maximum absorption bands at the visible and UV regions. The bands appeared at

The electronic spectrum is in agree- ment with previously reported for similar iron clusters [37,38] and it can be useful for characterization proposes. The data from the TGA–DTA studies of iron precursor catalyst [(Pentyl)₄N]₃FeCl₃Br₃ are shown in Table 1 and Fig. 4. The weight lost from the thermal decomposition is carried out in two steps. A complicate decomposition pat- tern is proposed, it involve an intermolecular rearrangements and an interaction with neighbor units.

According to Table 1 and Fig. 4, the transition observed for the iron precursor is consistent with the following reac- tions series:

$$\{ [CH_3(CH_2)_4]_4 N \}_3 FeCl_3 Br_3 \rightarrow [CH_3(CH_2)_4]_4 N + \{ [CH_3(CH_2)_4]_4 N \}_2 ClBr + Cl_2 + FeBr_2$$

$$FeBr_2 \rightarrow Br_2 + Fe$$
(2)
(3)

The first step (150–450 °C) is proposed to involve elimina- tion of one molecule of tetrapentylammonium, one mole- cule of tetrapentylammonium BromeCloride and one chloride molecule. The second step, at 450–670 °C suggests the elimination of one bromide molecule. The final residual (wt%) is assuming as iron. As show in Fig. 4, both steps of decomposition are characterized by two endothermic peaks, at 210



and 400 °C.

Fig. 5a and b shows typical SEM images of MWCNTs growth by spray pyrolysis method from iron pentyl precur- sor catalyst [(Pentyl)₄N]₃FeCl₃Br₃. The large quantities of net-like network were observed. The MWCNTs are growth inside the vycor tube surface. The higher magnification micrograph (5b) shows a random distribution of the curved fibrous carbon materials, which clearly illustrate an uni- form diameter distribution. The fibrous are flexible, with length of several micrometers and uniformly distributed. Although SEM images show the fibrous-like structure, TEM micrographs confirm a homogeneous distribution of carbon nanotubes in the entire sample observed, it can be appreciate in Fig. 6.

The transmission electron micrographs of Fig. 6 show hollow cylindrical tubes with nanometric diameter size. The nanotubes sizes suggest the formation of the multi-wall carbon nanotubes with diameters between 20 and 50 nm. The diameter size dispersion is attributed to the strong chemical interaction between the catalyst particles size and the carbon source. However, the mean diameters of the nanotubes are around 30 nm. The MWCNTs can be formed following the tip growth model and depending on the position of the catalyst [39]. Some encapsulated particles of iron inside the nanotubes can be observed. It corre- sponds to the Fe nucleus where the carbon molecules start he growth. The micrographs of 6a show some big parti-cles, they are amorphous carbon which did not react during the nanotubes synthesis process.

The X-ray pattern in Fig. 7 shows some characteristic intensities of the graphite, they match to the nanotubes structure. The intensities shapes in the



pattern are well defined like a crystalline structure. The XRD figure also shows some peaks correspond to the iron oxide and the Fe without reaction present in the surface of the nanotubes materials.



Fig. 7. X-ray diffraction pattern for the MWCNTs synthesized.

Conclusions

A new synthesis method of the organometallic precursor catalyst was found. The FT-IR, and TGA–DTA results con- firm that the complex synthesized was {[CH3(CH2)4]4N}3- FeCI3Br3. The properties of Fe precursor were favorable for the MWCNTs synthesis. MWCNTs were produced relatively easy by spray pyrolysis technique using the orga- nometallic precursor synthesized. Microscopy results show a disorder and multi-wall carbon nanotubes growth with length in the



micrometer order and diameter between 20 and 50 nm. The TEM micrographs and XRD data show the presence of iron inside the nanotubes which help as a nucleation site for the carbon growth.

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