

Studies of LaNiO_3 used as a precursor for catalytic carbon nanotubes growth

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Received 17 May 2006; received in revised form 4 October 2006; accepted 10 October 2006
Available online 14 October 2006

Abstract

The growth of the carbon nanotubes is carried out on nickel containing catalysts. A fine distribution of metal nanoparticles is obtained by the reduction *in situ* of a perovskite phase. The LaNiO_3 perovskite is synthesized by three different methods in order to compare the nature of the tubes obtained after CH_4 -CVD. These structures are analyzed by DRX, H_2 -TPR and SEM before catalytic test. After CVD, the internal diameter of the tubes is constant no matter the method of preparation of the perovskite and the external diameter depends on the distribution of the metallic particles. The homogeneous distribution of the CNT is related to the homogeneous distribution of the metallic particles obtained after reduction under methane.

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Keywords: Perovskite; MWNT; CVD; SEM; Mass spectrometry

1. Introduction

Carbon nanotubes have been the center of interest since their discovery by Iijima in 1991 [1] for many reasons due to their one-dimensional carbon nanostructures [2,3]. Due to the persistent and resilient nature of sp^2 C network, CNTs possess high mechanical strength as well as flexibility [4]. The morphologies of nanotubes depend on the specific growth conditions. Catalytic growth as a method of synthesis of nanotubes provides a large variety of forms: straight filaments, as well as bent and helically wound tubes [5]. In most cases, the production of nanotubes is based on the catalytic decomposition of carbon-containing gases on metal nanoparticles dispersed on a support. The nanotube diameter appears to be governed by the size of the catalytically active particles. The length of the tubes depends mainly on the reaction time. Various hypothetical mechanisms have been proposed to explain the growth of nanotubes produced by decomposition of hydrocarbons on active metals [6]. For the catalytic method, it is crucial to select an effective catalyst with the appropriate size of active metal.

Mixed metal oxides as perovskites have been recently investigated as the precursor of catalyst [7]. The size of the active transition metallic particles may be controlled by changing the reduction conditions. Liang et al. [8] and Li et al. [9] have used La_2NiO_4 as catalyst precursor for CNTs growth. The growth of nanotubes was obtained by catalytic decomposition of CH_4 over Ni-nanoparticles from the pre-reduced oxide. Different methods of preparation of perovskite are known in solid chemistry as grinding–milling of solids, co-precipitation, sol–gel and resin methods.

The objectives of this work are the synthesis and characterisations of LaNiO_3 prepared by three different resin methods called: citrate, Pechini and propionate. The nature of the CNTs produced by CH_4 -CVD are investigated as a function of the method of perovskite's preparation. The studied parameters measured by HR-MET will be the internal and external diameters, the length and the variety of tubes.

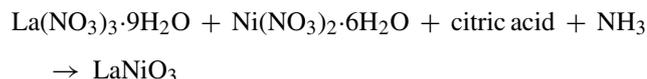
2. Experimental

2.1. Preparation of the LaNiO_3

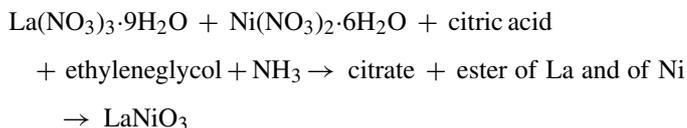
Two types of sources were used to introduce the metallic elements: nitrate salts $\text{Ni}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$ and $\text{La}(\text{NO}_3)_3 \cdot 9\text{H}_2\text{O}$. The initial compounds are more than 99% pure (Strem).

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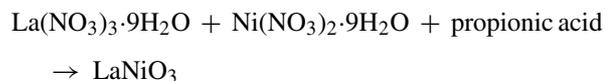
In the citrate method the aqueous solution of nitrates were mixed with an aqueous solution of citric acid in order to obtain metallic citrates. Ammonia is introduced to favour the transformation of citric acid to citrate. The solvent is removed by evaporation until the formation of resin. The resin undergoes a thermal treatment at 400 °C to break up the intermediate citrate complexes and then a treatment at 900 °C for one night in order to form LaNiO₃:



The Pechini's method follows the same steps of preparation as the citrate method apart from the ethylene glycol addition. The aqueous solutions of the two nitrate salts were mixed with an aqueous solution of citric acid and ethylene glycol. The solution is heated and ammonia is added. The resin undergoes a thermal treatment at 400 °C to break up the intermediate citrate complexes and then a treatment at 900 °C for one night in order to form LaNiO₃:



In the propionate method the salts were dissolved in hot propionic acid [10]. The solvent was evaporated until formation of resin. Nitrates species are eliminated as reddish-brown nitrous oxide gases during the elimination of propionic acid. The thermal treatment of 900 °C for one night is also preceded by a step of thermal treatment at 400 °C to break up the metal propionates:



2.2. Characterisation of the LaNiO₃ and synthesis of carbon nanotubes

The X-ray diffraction (XRD) experiments were performed on a D5000 Siemens diffractometer using the Cu K α radiation ($\lambda = 0.15406$ nm). The scattering intensities were measured over an angular range of $10 < 2\theta < 90$ for all the samples with a step-size (2θ) of 0.02° and a step time of 2 s. The diffraction patterns have been indexed by comparison with the JCPDS files (joint committee on powder diffraction standards). The mean particle size was calculated by the Debye–Scherrer's relation. *Temperature programmed reduction (TPR) under H₂* was performed on a 50 mg sample placed in a U-shaped quartz tube (6.6 mm i.d.), the temperature was increased from 25 to 650 °C with a slope of $15^\circ\text{C min}^{-1}$. The reducing mixture was 3% hydrogen in helium (50 mL min^{-1}). Hydrogen consumption was quantified by a TC detector after scavenging of the obtained water. *Temperature programmed reduction (TPR) under CH₄ and CVD* was performed to reduce the oxide and to produce carbon tubes in the same time. A sample of 50 mg was placed in a U-shaped quartz tube (6.6 mm i.d.), the temperature was increased from

25 to 650 °C with a slope of $15^\circ\text{C min}^{-1}$. The reducing mixture was CH₄ in helium (with a flow of 2.85 and 35 mL min^{-1} , respectively). The gases coming out were analyzed by mass spectrometry. Prior to any measurement, the mass spectrometer is calibrated by introducing a known amount of carbon monoxide, carbon dioxide, methane and hydrogen. A typical measurement consists in the following steps: (i) the catalyst is positioned in the central hot zone of the reactor; (ii) the reaction mixture, methane in helium, is introduced; (iii) once the flow is stabilised, the temperature is increased and the record of the exhaust gas composition begins; (iv) after 1 h at 600 °C the CH₄ is stopped and the reactor is ventilated with helium. *The SEM analyses* have been performed on a JEOL JSM-6700 F scanning microscope. A very thin carbon deposit was used to improve the conductivity of the sample. *Transmission Electron Microscopy (TEM)* analyses were performed using a TOPCON EM 002-B apparatus. *BET surface area* has been determined on SA 3100 Coulter sorptometer at 77 K. The visualisation of the structure was made by the *CaRIne software*, which allows rebuilding the elementary cell and the crystal starting from the space group, the cell parameters and the position of the atoms. This software provided by Divergent S.A. is a tool for research and teaching.

3. Results and discussion

Perovskites, of the general stoichiometry ABO₃ where A is a trivalent rare earth metal ion and B is a trivalent first row transition metal ion [11]. Norman and Morris [12] reported diffraction patterns were Rietveld refined using the trigonal space group, *R-3C*, and crystallographic parameters for the LaNiO₃ system. For the modelling of the structure, the rhombohedral structure was used with the cell parameters ($a = 5.4412$, $b = 5.4389$ and $c = 13.1715$, $\alpha = \beta = 90^\circ$ and $\gamma = 119.8573^\circ$) and the atomic positions of the ions in the unit cell given in [13]. The corresponding representation is given in Fig. 1. The ions Ni³⁺ are in a per-

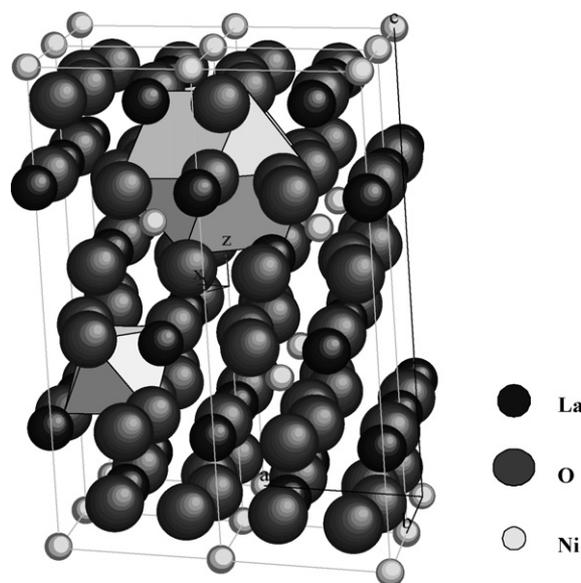


Fig. 1. The structure of LaNiO₃ obtained with the parameters proposed by Norman and Morris [12].

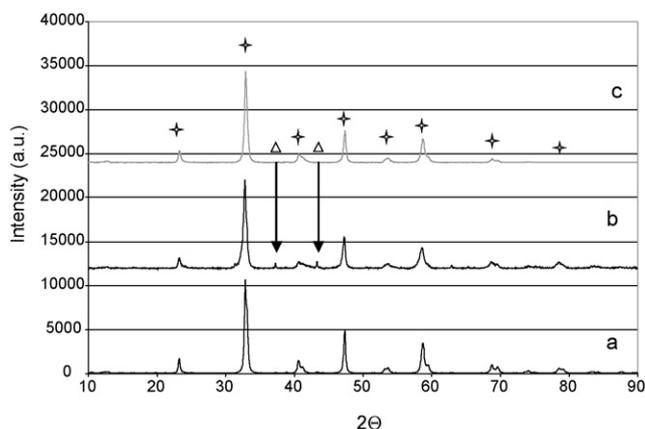


Fig. 2. XRD of LaNiO_3 prepared by (a) citrate method; (b) Pechini's method; (c) propionate method after a treatment at 900°C .

fect hexagonal environment, the La^{3+} ions are in a deformed environment of 12O^{2-} .

3.1. Characterizations of the perovskite

The XRD diagrams of LaNiO_3 prepared by the three different methods were compared after calcination at 900°C in Fig. 2. In each case, mainly the perovskite phase is obtained. In the case of the Pechini's method a low amount of NiO is detected. The average size of crystallites of free NiO is estimated at 11.3 nm . The mean crystallite diameters for the perovskite, calculated by Scherrer's equation, are found to be 21 , 16 and 18 nm for the citrate, Pechini and propionate methods, respectively. The XRD analysis seems to indicate that the three methods of preparation allow a nearly identical formation of the perovskite. It could be considered that the three used methods are able to produce the catalytic solids. It must be noted that the production of a unique crystalline phase is one of the necessary conditions to obtain a controlled size of carbon nanotubes.

These structures were compared to the modelised structure and the rebuilt diffractogram using the software is given in Fig. 3. It is found that the experimental diffractograms are in good agreement with the XRD data. According to [13] the Rietveld analysis indicates a deficiency in lanthanum and oxygen in the structure.

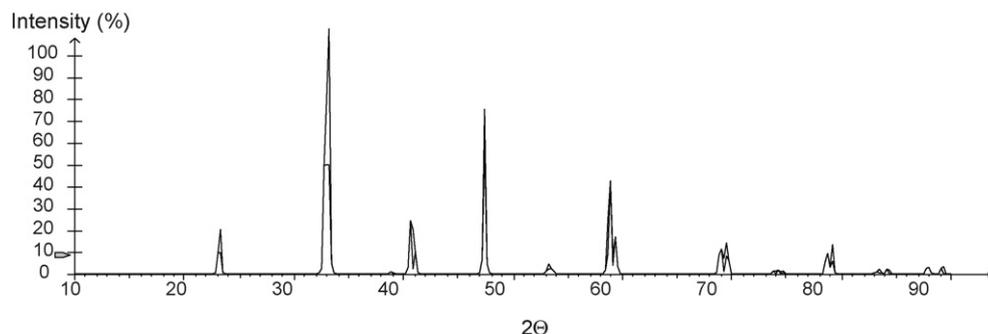


Fig. 3. Corresponding diffractogram obtained by the modelling of the structure LaNiO_3 with the space group $R-3C$.

SEM-micrographs of all the samples prepared by the three methods are shown in Fig. 4a–d. The mean particle size was estimated by visual inspection of the SEM-micrographs. The estimated mean particle sizes were in the range of $50\text{--}100\text{ nm}$ for citrate method and from 30 to 100 nm for the two other methods. The primary crystal sizes for LaNiO_3 are in accordance with XRD results, however, there is a tendency to agglomerate the initial nanoparticles to larger particles. For example the citrate sample present larger areas of cubic crystals stuck one to the other by several faces. The statistical estimation of this sample results in one or two free faces of six possible faces. The SEM images of LaNiO_3 sample prepared by propionate and Pechini's methods show small, rather monodispersed particles (Fig. 4c and d). Propionate presents more or less the same morphological aspect as the citrate one. However the catalyst grains are less geometrical compared to the citrate and Pechini's method samples.

3.2. H_2 -TPR and DRX after partial and total TPR

The reductibility of prepared samples of LaNiO_3 is investigated by H_2 -TPR and the results are presented in Fig. 5. Under these H_2 -TPR conditions the La^{3+} ions are non-reducible, so the observed H_2 consumption is ascribed only to the reduction of Ni^{2+} or Ni^{3+} ions. For all the samples, two reduction zones can be distinguished at low and high temperature. The low temperature zone presents a large asymmetrical peak of H_2 consumption, a multiple step Ni^{2+} or Ni^{3+} reduction more complex than that proposed by Provendier [10]. The reduction of the citrate sample results in the most definite profile at lowest temperature—an intense peak centered at 415°C followed by a small peak at 450°C . This kind of reduction profile has been found for LaCoO_3 by Hansteen et al. [14]. The sample prepared by Pechini's method exhibits only one large reduction peak in the low temperature zone centered at 435°C . It seems that the small quantity of free NiO found for this sample by XRD does not influence the reductibility of perovskite, which is confirmed also by the high temperature peak (575°C) at exactly the same temperature as for citrate sample. The sample prepared by propionate method presents wide low temperature peak at 440°C which is closer to the Pechini's method sample. However this sample shows a high temperature reduction at 555°C , slightly lower temperature than the others. For all samples the second

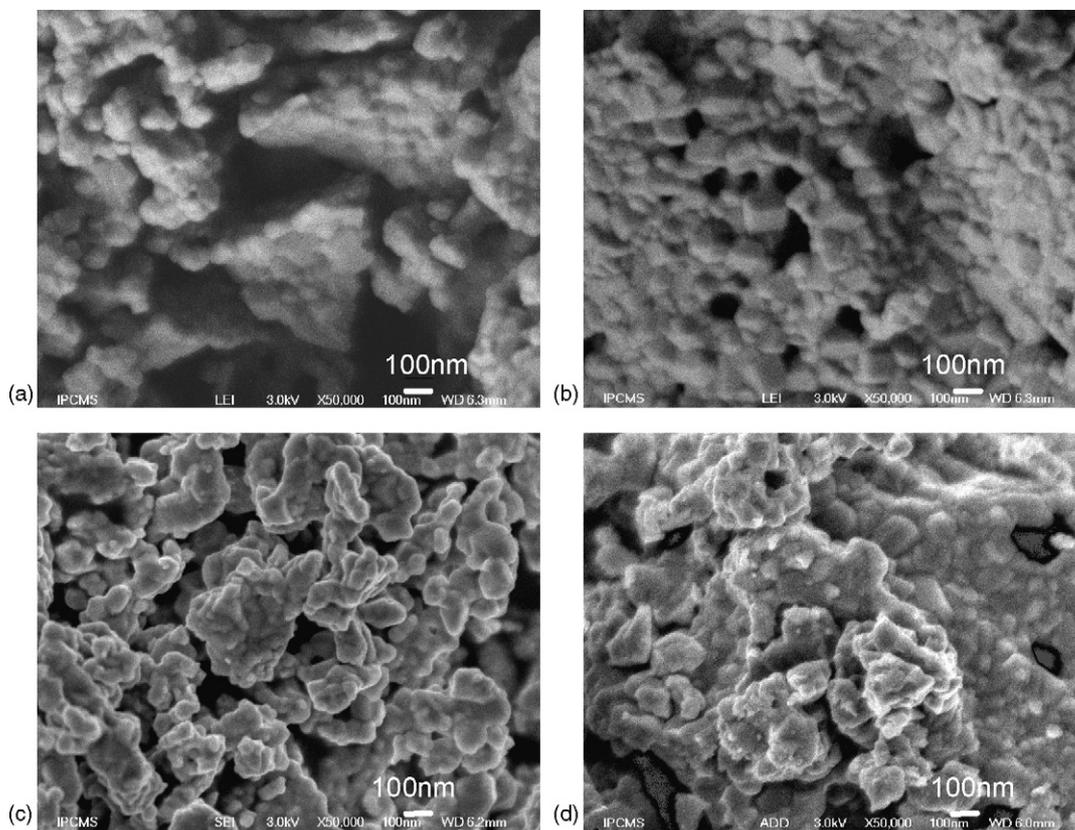


Fig. 4. SEM of LaNiO_3 prepared by the citrate method (a) fairly dense zone, (b) very dense zone in mode LEI, (c) prepared by the Pechini's method and (d) propionate method with an enlarging of 50,000 in mode SEI.

high temperature zone presents very symmetrical peak of H_2 consumption suggesting a quick one-step reduction.

The amount of H_2 consumed in the range $415\text{--}440^\circ\text{C}$ for LaNiO_3 sample can be attributed to the reduction of Ni^{3+} to Ni^{2+} occurring at the surface as well as in the bulk. Subsequently, the reduction peak at around 570°C was assigned to the reduction of Ni^{2+} to metallic nickel. The relative ratio of second peak to the first one was calculated as 1.7, 2.0 and 2.2 for the citrate, Pechini's and propionate methods, respectively. These values are close to 2 the quantitative analysis correlates well with the H_2 consumption – for the first peak: reduction of Ni^{3+} to Ni^{2+}

– for the second peak: reduction of Ni^{2+} to Ni^0 . The size of metallic particles calculated by XRD of the three samples after total reduction at 650°C and partial reduction at 480°C are presented in Table 1.

In all the cases, after total reduction the LaNiO_3 structure was destroyed and nickel metal deposited on lanthanum oxide was obtained. After partial reduction, the formation of $\text{La}_2\text{Ni}_2\text{O}_5$ is observed by XRD, which confirms that the reduction goes through two distinct stages. In the case of the Pechini's sample, the presence of nickel metal observed even before H_2 -TPR; by XRD becomes larger. The mean crystallite diameter for $\text{La}_2\text{Ni}_2\text{O}_5$, calculated by Scherrer's equation is found to be close to those obtained for LaNiO_3 . The average crystallite diameter for La_2O_3 remains in the same order of magnitude for the three methods and comparable with that of the starting structure. It

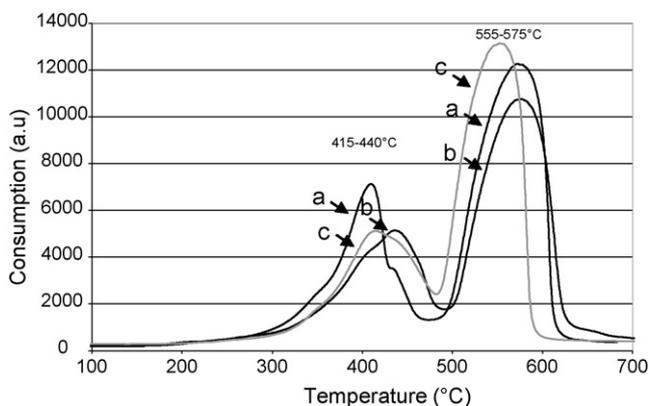


Fig. 5. H_2 -TPR of LaNiO_3 after a treatment at 900°C : (a) citrate method; (b) Pechini's method; (c) propionate method.

Table 1
Phases and mean crystallite diameters of $\text{La}_2\text{Ni}_2\text{O}_5$, La_2O_3 and Ni obtained by XRD after partial or total reduction

Method	Citrate	Pechini	Propionate
Phases obtained after total reduction	$\text{La}_2\text{O}_3 + \text{Ni}$	$\text{La}_2\text{O}_3 + \text{Ni}$	$\text{La}_2\text{O}_3 + \text{Ni}$
Size of La_2O_3	13 nm	17 nm	16 nm
Size of Ni	–	16 nm	14 nm
Phase obtained after partial reduction	$\text{La}_2\text{Ni}_2\text{O}_5$	$\text{La}_2\text{Ni}_2\text{O}_5$	$\text{La}_2\text{Ni}_2\text{O}_5$
Size of $\text{La}_2\text{Ni}_2\text{O}_5$	16 nm	16 nm	19 nm
Ni and size of Ni	No	Yes, 21 nm	No

could be supposed that nickel was reduced without modifying construction completely.

Hansteen et al. [14] showed that $\text{La}_2\text{Co}_2\text{O}_5$ oxidizes via $\text{La}_3\text{Co}_3\text{O}_8$ to LaCoO_3 . The reported study of intermediate cobalt structures suggests the presence of anion vacancies which allows the diffusion and fast reaction with oxygen through the volume. The anion vacancy ordering is well known for the oxygen deficient perovskites ($\text{AMO}_{3-\delta}$) and results in superstructures where the cationic sublattice of the perovskite is essentially unchanged. The co-ordination of few or all metal atoms decreases the symmetry from octahedral to typically tetrahedral or square planar, e.g., $\text{La}_2\text{Co}_2\text{O}_5$ and $\text{La}_2\text{Ni}_2\text{O}_5$ [13]. The type of oxygen vacancy ordering strongly depends on the nature of transition element. Reduction of perovskite type oxides leads to loss of oxygen, which is connected with the formation of oxygen vacancies. Strong similarities exist between the structure LaCoO_3 and LaNiO_3 on the one hand, and $\text{La}_2\text{Co}_2\text{O}_5$ and $\text{La}_2\text{Ni}_2\text{O}_5$ on the other hand. The TPR results can be seen as the reverse mechanism of the oxidation of $\text{La}_2\text{Ni}_2\text{O}_5$ and the reduction via $\text{La}_2\text{Ni}_2\text{O}_5$ and perhaps by $\text{La}_3\text{Ni}_3\text{O}_8$ until the metallic nickel on La_2O_3 are proposed.

3.3. CH_4 -CVD and DRX after test: evolution of LaNiO_3

Gommes et al. [15] presented a kinetic study of carbon nanotubes production by the use of a mass spectrometer. *In situ* monitoring of the different species in effluent gas during the CNTs growth process could provide precious information for understanding the reduction of LaNiO_3 under methane and the CNTs growth in detail. Fig. 6 represents the profiles of variations of relative intensity for 5 m/z selected corresponding to the consumption of CH_4 and the formation of H_2 , H_2O , CO , CO_2 in time on stream for the citrate sample. All the experiments are undertaken under the same conditions. It is observed that the temperature of 600°C is necessary in all the cases to have a reaction between methane and perovskite. For all samples, the reduction begins with a CH_4 consumption which is converted over the oxide into CO_2 , H_2O , CO and H_2 . The first formed

Table 2

Ratios of calibrated gases obtained by MS and compared with the data obtained according to the equation of reduction

Method	Given by the equation	Citrate	Pechini	Propionate
CO/CO_2 ratio	1.36	1.50	1.20	1.33
$\text{H}_2/(\text{CO} + \text{CO}_2)$ ratio	1.85	4.10	4.36	1.86
H_2/CH_4 ratio	1.85	0.84	1.17	0.43
$\text{CH}_4/(\text{CO} + \text{CO}_2)$ ratio	1.00	4.90	3.73	4.28

product is CO_2 which presents the narrowest peak. CO and H_2 are formed in two steps. This indicates the decrease of available oxygen during the reduction. The reduction proceeds in two stages and the carbonaceous deposit is formed as soon as the active sites are available, confirmed by accompanied production of H_2 in time on stream.

By considering the nature of produced a degree of reduction of Ni^{3+} from the perovskite structure could be established. The total transformation (Ni^{3+} to Ni^0) is given by the equation as follows:

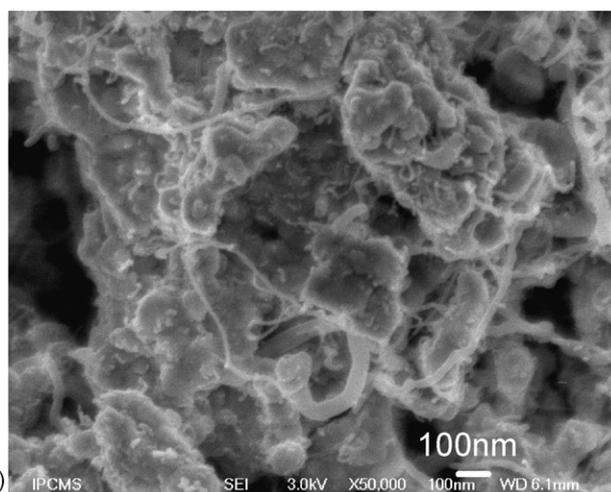
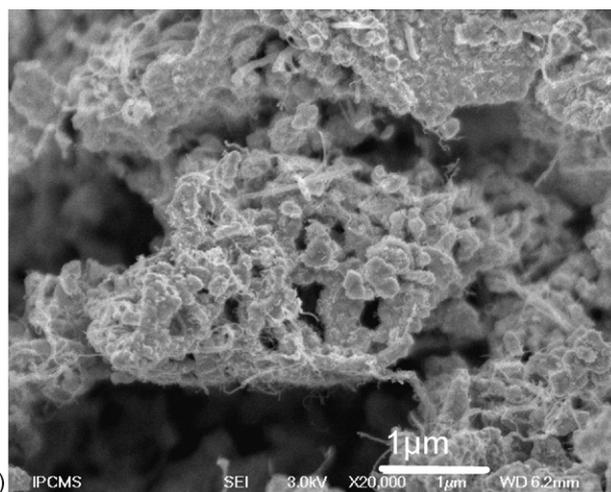
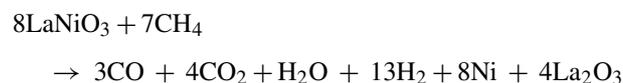


Fig. 7. SEM of LaNiO_3 prepared by the citrate method after CH_4 -CVD with an enlarging of (a) 20,000 and (b) 50,000 in mode SEI.

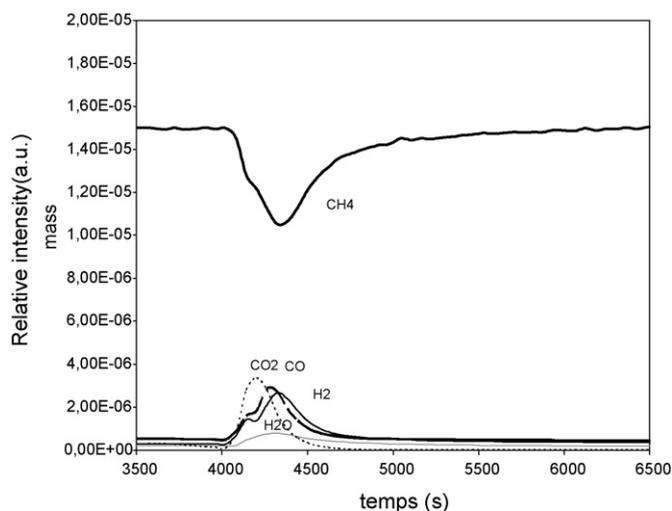


Fig. 6. CH_4 -CVD of LaNiO_3 prepared by citrate method.

From this general equation, the quantity of methane necessary for the full reduction of Ni^{3+} to Ni^0 could be established. It is 1.78×10^{-3} mol. The ratios between the produced gases and methane (CO/CO_2 , $\text{H}_2/(\text{CO}/\text{CO}_2)$, H_2/CH_4 , $\text{CH}_4/(\text{CO}/\text{CO}_2)$) are compared to the theoretical values in Table 2.

After calibrating the known amounts of gases by SM, it could be observed that the ratio related to the reduction only, namely CO/CO_2 ratio is close to the value found by the suggested equation for all the samples. However the production of H_2 is larger than the calculated amount and it suggests that the phenomenon of decomposition of methane to H_2 and carbon also takes place. Compared to the other methods, the propionic method produces more water and less CO (figure not shown). As the quantity of methane consumed for Ni reduction is known by the equation [1], the quantity of CH_4 transformed to carbon deposits could be also calculated. The values of 79%, 73% and 77% of CH_4 for the citrate, Pechini's and propionate samples, respectively, are transformed into the carbonaceous deposit. For all the samples the XRD show the destruction of LaNiO_3 structure to totally reduced nickel and lanthanum oxide after the CH_4 -CVD at 600°C . The mean crystalline diameters of Ni obtained by XRD are 15, 18 and

11.5 nm for citrate, Pechini's and propionate methods, respectively.

3.4. SEM and MET after test CH_4 -CVD: nanotubes growth

For the CNT formation mechanism the following steps have been proposed [16]: (i) methane decomposition at the surface of the nickel crystallite; (ii) formation of surface carbide in the reaction zone; (iii) carbon diffusion into the crystal volume; (iv) carbon release, after some over-saturation, at the Ni surface. When using a defined structure oxide, it is necessary to reduce the nickel at the first place. The advantage is that in LaNiO_3 the initial nickel structure is very homogeneously dispersed in volume. It could be distinguished by the nanotubes distribution on the catalyst, its distribution in sizes, length and form. To have first idea on it, the samples were studied by SEM after CH_4 -CVD. Figs. 7–9 show the examples, at two different magnifications of the nanotubes grown at 600°C for the three samples. Generally the morphology of the initial system is preserved, especially for the citrate sample. The obtained Ni on La_2O_3 shows tendency to agglomerate but the shape and organisation of the grains is similar to those of LaNiO_3 . The formation of the nanotubes is

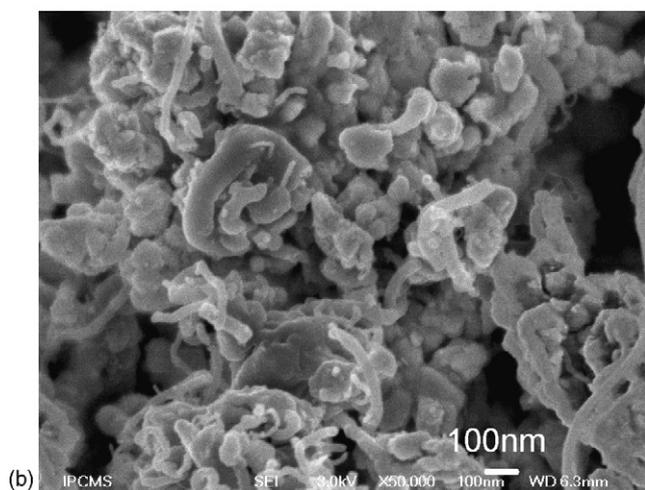
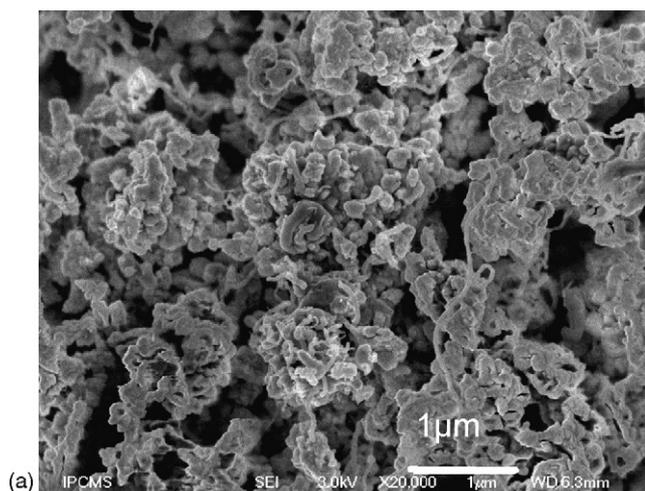


Fig. 8. SEM of LaNiO_3 prepared by the Pechini's method after CH_4 -CVD with an enlarging of (a) 20,000 and (b) 50,000 in mode SEI.

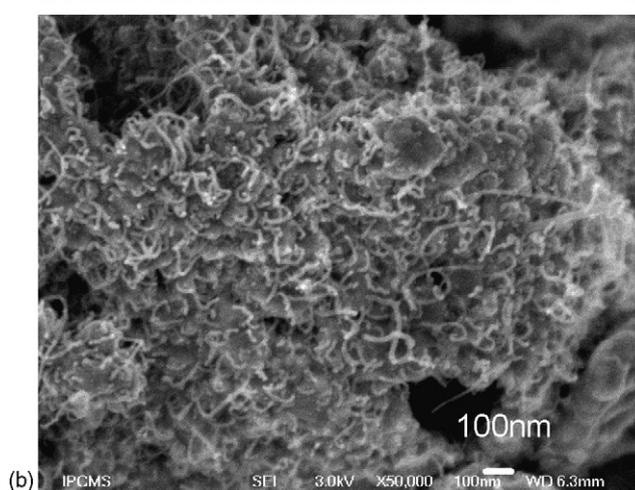
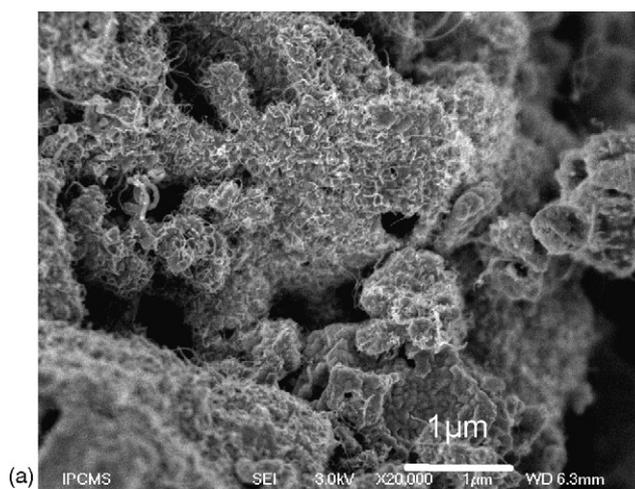


Fig. 9. SEM of LaNiO_3 prepared by the propionate method after CH_4 -CVD with an enlarging of (a) 20,000 and (b) 50,000 in mode SEI.

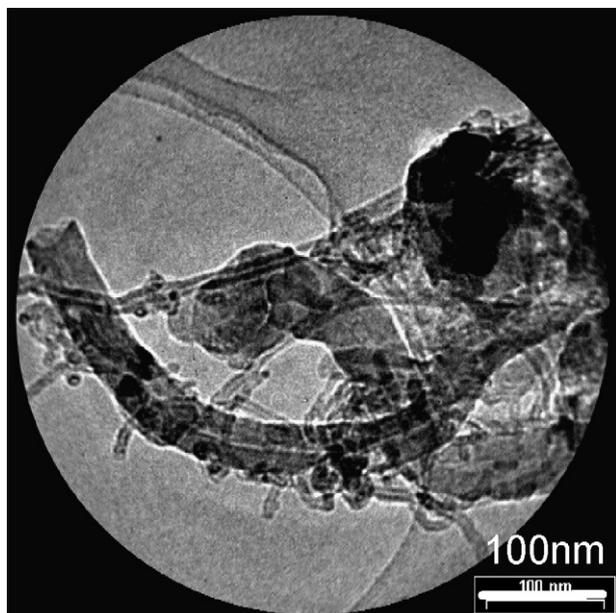


Fig. 10. TEM of LaNiO_3 prepared by the citrate method after CH_4 -CVD with an enlarging of 23,000.

possible on this catalyst in big quantity as shown by the nanotubes starters on the surface. The distribution of these tubes observed by SEM seems relatively heterogeneous in spite of the single formation of the phase perovskite at the beginning. For the Pechini's method, the morphology of the catalytic sample is preserved. A few large tubes are visible and the surface of the catalyst is not covered by the small tube starters as for the prepared citrate and propionate samples. This implies that for citrate and Pechini's samples, the quantity of CH_4 transformed into C and estimated by SM is mainly used for the growth of the largest tubes. In the case of propionate sample, the surface is completely covered by short and fine nanotubes with uniform sizes and the support is not visible. The catalytic system appears less geometrical than its LaNiO_3 precursor.

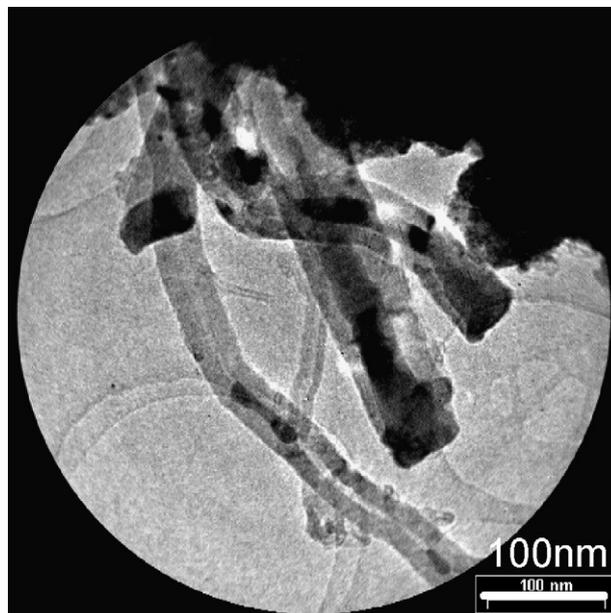


Fig. 11. TEM of LaNiO_3 prepared by the Pechini's method after CH_4 -CVD with an enlarging of 23,000.

The analysis of the samples after CH_4 -CVD continue with TEM in order to study particularly the nanotubes (Figs. 10–12a and b). Three parameters were studied for each method, namely: the external and internal diameters of the tubes as well as their length. The results are reported in Tables 3–5.

The measurements of the tubes formed on citrate sample show a majority of fine tubes with external diameter in agreement with the size of the nickel particles found by XDR after CH_4 -CVD (15 nm). Sixty-five percent of these tubes were formed with rather important length (about 20 times their external diameter). The larger the tubes are, the longer they are but the length to external diameter ratio is relatively constant (TEM 10).

For the Pechini's sample, the tubes are larger than those of the citrate sample. The distribution is centered at external tubes

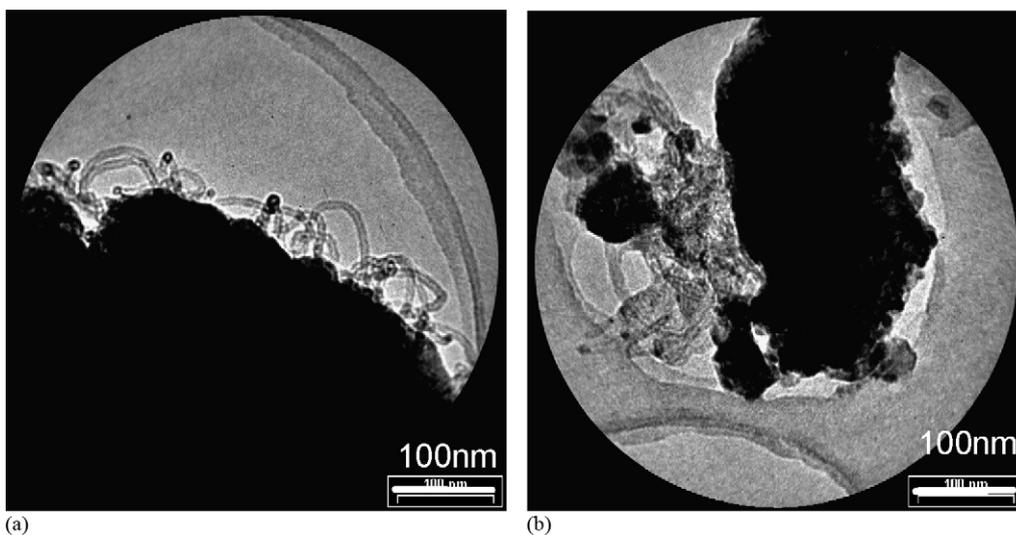


Fig. 12. (a and b) TEM of LaNiO_3 prepared by the propionate method after CH_4 -CVD with an enlarging of 23,000.

Table 3
Characterisations of tubes obtained by CH₄-CVD on LaNiO₃ prepared by citrate method

Method	Citrate		
Percentage of tubes with different external diameter (%)	86	7	7
External tubes diameter (nm)	10–15	16–30	31–50
Internal tubes diameter (nm)	5.5–6	6–6.5	6–6.5
Percentage of tubes with different length (nm)	33% of 40–80, 5% of 81–200, 62% of 201–400	15% of 200–300, 85% of 301–500	>500

Table 4
Characterisations of tubes obtained by CH₄-CVD on LaNiO₃ prepared by Pechini's method

Method	Pechini			
Percentage of tubes with different external diameter (%)	10	76	5	9
External tubes diameter (nm)	10–30	31–50	51–100	>100
Internal tubes diameter (nm)	5.5–6	6–6.5	6–6.5	6–6.5
Percentage of tubes with different length (nm)	50–150	10% of 50–150, 60% of 151–250, 30% of 251–425	400–450	400 to >500

Table 5
Characterisations of tubes obtained by CH₄-CVD on LaNiO₃ prepared by propionate method

Method	Propionate		
Percentage of tubes with different external diameter (%)	95	2	3
External tubes diameter (nm)	7.5–10	10–15	>30
Internal tubes diameter (nm)	5.5–6	6–6.5	6–6.5
Percentage of tubes with different length (nm)	45% of 25–50, 45% of 51–100, 10% of 101–200	200 to >500	>500

diameters between 30 and 50 nm. The tubes appear to be relatively longer and with larger external diameters compared to the CNT obtained by the citrate method (TEM 11). There is no agreement between the value of the diameters of the tubes and the average size of nickel (18 nm) measured by XRD probably because of the presence of small amount of free nickel oxide over the perovskite which is beneficial to the growth of larger tubes. It is the only case in which the presence of some large tubes (external diameter higher than 100 nm) containing migrated nickel in the tubes during the growth is observed.

For the propionate method, TEM confirms the results of the SEM namely the narrower distribution of fine carbon nanotubes (TEM 12a). The external diameter of the tubes is equal to the size of nickel crystallites calculated to XDR (11.5 nm). The amorphous carbon was also observed (TEM 12b).

If one consider the quantity of deposited carbon on the samples the yields of the reactions are as follow: 1.2%, 1.8% and 2.5% for propionate, citrate and Pechini's sample. The quantity of methane used in each reaction constitutes approximately 75% of the total quantity of methane (Table 2). Twenty-five percent of methane was used for structure reduction. So it means that the conversion of methane to solid carbon in the CH₄-CVD was approximately equal to 1%, 1.3% and 2% for propionate, citrate and Pechini's sample.

All these results confirm that the size of carbon nanotubes has a direct relationship with the size of metallic particles. This study shows the great sensitivity of the nature of carbon tubes to the preparation conditions even in the case of definite structures oxides as catalyst precursor. The most interesting method of the synthesis LaNiO₃ perovskite is the propionate method. However this work requires complementary studies to understand deeper the reasons of these distinct evolutions. The observation

of the produced nanotubes shows that the internal diameter is constant for all tubes independently of the size and the length of the tubes as well as the method of preparation of the LaNiO₃ precursor. It seems to indicate the minimal size of metallic nickel obtained after LaNiO₃ reduction by CH₄-CVD for the formation of nanotubes as 5.5–6 nm. It could be suggested that tubes are formed around one tube by building the larger concentric tubes as larger as nickel particles. By taking into account the thickness of a tube and by considering a distance between two plans as a distance of Van der Waals interaction, it could be concluded that the number of concentric tubes in majority formed by CH₄-CVD with 600 °C for LaNiO₃ propionate sample is about 5.

4. Conclusion

This work concerned the use of a structure rich in nickel (La/Ni ratio = 1) as a possible catalyst precursor for multiwalls carbon nanotubes growth. It showed the feasibility of this reaction with narrow distribution of nanotubes and the relationship between distribution of the nickel particles produced by reduction under CH₄. It is observed that the internal diameter is constant for all the catalysts. The variation of the method of preparation has a remarkable effect on the quantity and quality of the nanotubes, which indicates the great sensitivity of the growth of the MWNT with nickel environment.

Acknowledgements

The authors would like to thank the GDRE 2756 for scientific organization. They are indebted to Dr. S. Ivanova and R. Blell for proof reading the manuscript.

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