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N-doped carbon nanotubes for liquid-phase C=C bond hydrogenation

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ABSTRACT

The introduction of foreign elements inside the channel of carbon nanotubes could lead to a significant modification of the intrinsic properties of these nanomaterials. Nitrogen atoms entering in the graphene sheets as substitute of carbon could modify in a large extend the acido-basic properties and also adsorption of the nanotube itself. Depending on the synthesis conditions, i.e. nature of the N-source, temperature and C-to-N atomic ratio, various N-doped carbon nanotubes can be synthesized with different surface properties. The aim of the present work is to report the synthesis of N-doped CNTs using a common nitrogen source precursor namely ammonia (NH_3) with C_2H_6 as carbon source. The as-synthesized N-CNTs were subsequently employed as catalyst support in the liquid-phase hydrogenation of cinnamaldehyde using palladium as an active phase.

1. Introduction

Catalysis has been closely linked to the development of our society for more than 100 years and continues to be so today [1]. The development of new catalysts or supports is generally associated with processes covering several domains of research, from molecular chemistry to transport phenomena and solid-state studies with the ultimate goal of developing more economical processes with lower environmental impact. Today, one of the most focused research field is the understanding of the catalytic steps at the nanoscopic scale in order to design and optimize new generation of catalysts with better activity and selectivity. The over-increasing development in the field of one-dimensional (1D) materials, i.e. carbon nanotubes, give an opportunity for scientists to study catalytic reactions on a very simple nanoscopic reactor, with active phase deposited inside or on the carbon nanotube and to build a relationship between the catalyst microstructure and its catalytic performance. Since then, a large number of studies have been published in the worldwide literature covering several catalytic applications either in the gas-phase or in the liquid-phase reactions. The 1D shape of these new materials along with their high aspect ratio, i.e. high length-to-diameter ratio, allows one to explore the confinement effect on the catalytic activity and selectivity where the casted material intrinsic properties are strongly modified by the surrounding wall of the support [2]. Several reports have recently dealt with the unusual flow pattern of fluid through this confined space [3,4] which opens a new exploratory field of investigation within the field of nanomaterials. However, the potential use of these 1D carbon materials also rely on the different possibilities to introduce dopant into the graphene structure which in turn, can lead to significant modifications of either the acido-basicity or the electronic properties of the materials. In the wake of the carbon nanotube discovery several research projects were aimed at the study of chemical modification by introducing new functional groups into or onto the carbon surface. Theoretical studies seem to indicate that these nanomaterials hold several promises for numerous potential applications which could trigger unexpected results compared to those usually obtained on traditional catalysts nowadays.

The introduction of foreign elements inside the carbon nanotube walls could lead to a significant alteration of their intrinsic properties and in turn, their catalytic activity and selectivity as well. Among these different doped carbon nanotubes the most studied are the N-doped carbon nanotubes which, despite the large number of research effort devoted, are still in their infancy and progresses are still needed to complete the understanding [5]. Nitrogen-doped carbon nanotubes show many properties that are markedly different from their undoped counterparts. Nitrogen atoms entering in the graphene sheets as substitutes of carbon could also modify in a great manner the adsorption strength of the nanotube towards foreign elements. The incorporation of nitrogen atoms in carbon nanostructures also

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enhance their mechanical and electric properties [6–8] as observed for N-CNT film electrodes that exhibits a drastic activity increase compared to non-doped electrodes in the oxidation of dihydroxyphenylacetic acid. Depending to the synthesis conditions, i.e. nature of the N-source, temperature and C-to-N atomic ratio, and the nature of the catalyst, various N-doped carbon nanotubes with different microstructures can be synthesized with controlled surface properties [9–21]. The presence of N-decoration on the carbon nanotube wall could also modify the electronic and chemical interactions with the deposited active phase which can, in turn, greatly modify the overall catalytic activity and selectivity as well. Indeed, the introduction of dopant can change in a great extend the electronic state of the carbon nanotube which is chemically inert into a chemically active surface. Nitrogen-doped carbon nanotubes are less thermally stable than their pure carbon counterparts and could also have higher oxidative reactivity [22,23].

The aim of the present work is to report the synthesis of N-doped CNTs using a most common nitrogen source precursor namely ammonia (NH_3) while the carbon source was C_2H_6 according to the previous works [24]. The as-synthesized N-doped CNTs were further extensively characterized by several techniques including zeta potential, specific surface area measurements by BET method, X-ray photoelectron spectroscopy, and scanning and transmission electron microscopy. The N-doped CNTs were subsequently employed as catalyst support in the liquid-phase hydrogenation of cinnamaldehyde using palladium as an active phase. The results were compared with those obtained on undoped CNTs. The present work is not aimed to answer all the questions that arise from the N-doped carbon nanotube material but to put some additional understanding and results on the use of these hybrid materials in the field of catalysis, where improvements on the activity and the selectivity are still needed regarding the stringent legislations concerning environmental safety for chemical processes.

2. Experimental

The bulk N-doped carbon nanotubes were synthesized by a chemical vapor deposition (CVD) using a mixture of C_2H_6/H_2 and ammonia at temperature around 680 °C over an alumina-supported iron catalyst. Nitrogen source was provided by ammonia which was co-fed into the reactant mixture with different concentrations. This procedure is derived from the classical CVD synthesis described in previous results [24].

The as-synthesized materials morphology was examined by means of a scanning electron microscope (SEM, JSM-6700F) while the microstructure of the material was analyzed by a transmission electron microscope (TEM, Topcon 002B-UHR working at an acceleration voltage of 200 kV with a point-to-point resolution of 0.18 nm). The nature of the surface functional groups on the CNT surface was determined by X-ray photoelectron spectroscopy (XPS) using a XPS system from VG instruments operating with Al Kα radiation. The specific surface area measurements were carried out on a Tristar Micromeritics sorptometer using nitrogen as adsorbent at liquid nitrogen temperature. Before measurement the sample was outgassed at 300 °C for 3 h in order to desorb impurities and moisture on its surface. Zeta potential measurements and pH titrations were carried out on a Nanozetasizer from Malvern instruments. Each sample was previously ultrasonicated for 20 min before analysis.

The catalysts for the selective hydrogenation of cinnamaldehyde were then prepared through an incipient wetness impregnation method using palladium nitrate as metal precursor. Further calcinations and reductions were performed to achieve a loading of 10 wt.% of metallic palladium: after overnight drying at 100 °C, the catalysts were calcinated in air for 2 h at 250 °C and then reduced under H_2 flow (100 cm^3/min) for 2 h at 400 °C. The hydrogenation of cinnamaldehyde was performed using 800 mg of the as-prepared catalysts. Catalytic reaction was performed with 10 mL of cinnamaldehyde diluted in 500 mL of dioxane, at 80 °C, with H_2 bubbling at a flow of 50 cm^3/min and stirring of 1000 rpm. The evolution of the reaction was observed by analysis of the liquid-phase using GC (Varian 3800) with a FID detector. The CNTs used were doped with 4 at.% of nitrogen. Reference catalysts based on palladium supported on CNTs (lab-synthesized multi-wall carbon nanotubes with capped ends impregnated by the same procedure at 10 wt.%) and on activated charcoal (commercial catalyst from Aldrich) were also tested for comparison.

3. Results and discussion

3.1. Catalyst characterizations

The N-doped CNTs were homogeneous with diameter ranging between 40 and 60 nm and length up to several hundred micrometers according to the SEM observation (Fig. 1). The high degree of entanglement in the sample can be attributed to the relatively low synthesis temperature which could introduce topologic defects into the graphene sheets similar to the one that are observed on the N-free carbon nanotubes synthesized by the CVD method. This curved morphology could also be attributed to the presence of nitrogen atoms inside the carbon structure. It is expected that nitrogen atoms will be more stable than carbon in

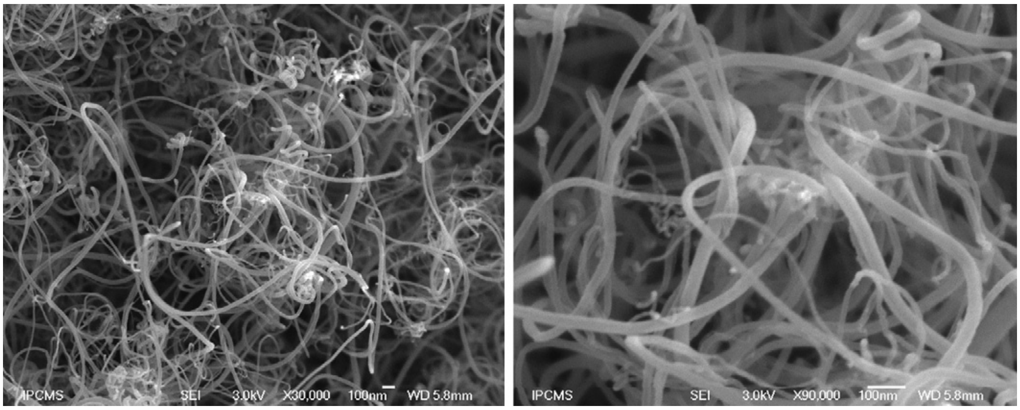

Fig. 1. SEM micrographs of the N-doped carbon nanotubes with a relatively homogeneous diameter, i.e. 40–60 nm, and high aspect ratio. The selectivity towards carbon nanotubes was extremely high as almost no nanoparticles were observed among the sample.

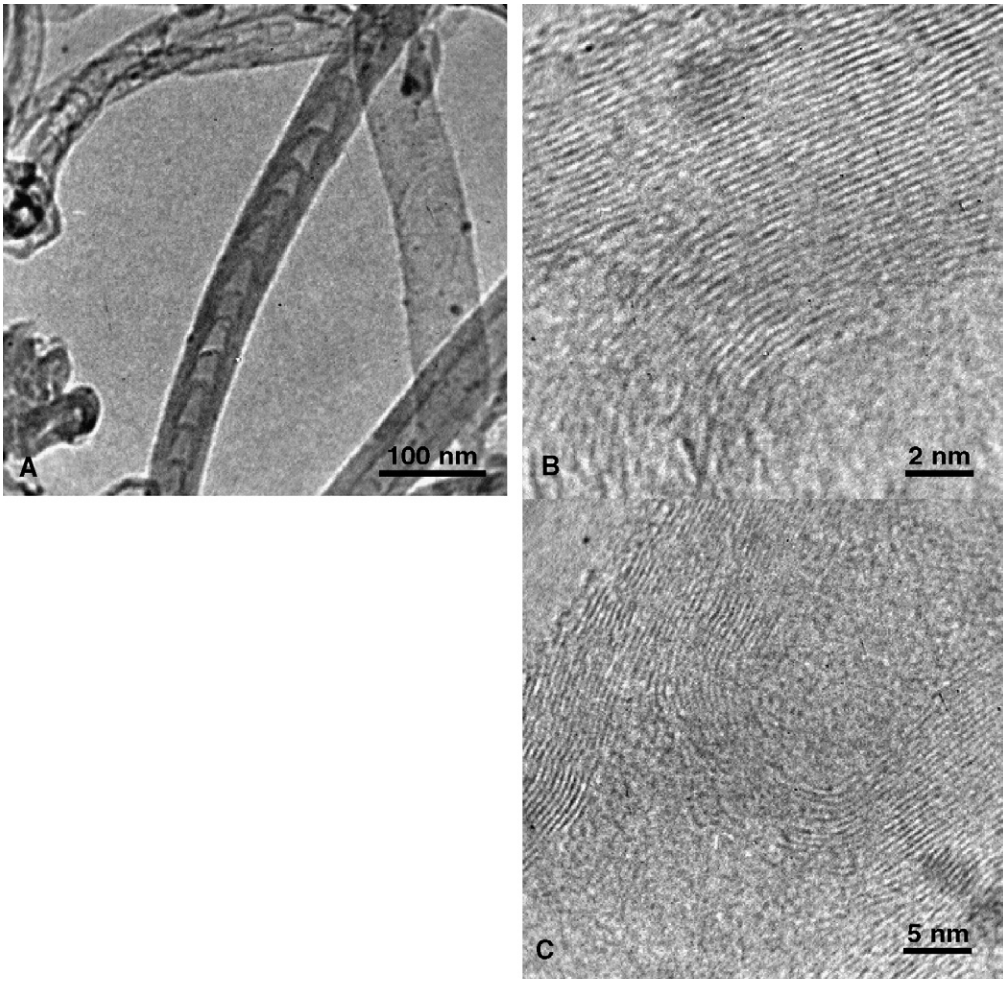

Fig. 2. (A) TEM micrograph of the N-doped CNTs showing the presence of periodical arches along the tube axis. (B and C) High-resolution TEM micrographs showing details of the graphene planes microstructure along the tube wall and on the tube–arch connection. It is noteworthy that the tube surface was quite clean and almost no amorphous carbon layer was observed.

regions of high curvature, i.e. next to the arch region or in the coiled tube. Miyamoto et al. [25] have reported that N substitution helped to stabilize curved sheets of graphite. It is noteworthy that the selectivity towards carbon nanotubes was extremely high as almost no nanoparticles or soot was observed among the product.

TEM analysis revealed that the introduction of nitrogen into the reactants led to the formation of periodical arches along the tube axis (Fig. 2). Similar results have already been reported by de Jong and co-workers [14] during the synthesis of N-doped CNTs on an iron-based catalyst. The authors have also reported that the N-doped CNT microstructure was extremely sensitive to the nature of the growth catalyst, i.e. using Co or Ni catalysts the N-doped CNT were straight and no arches were observed along the channel unlikely to what is observed with iron-based catalysts. Conventional nanotube growth models cannot explain the regular internal “bamboo” cavities of nitrogen-doped carbon nanotubes. An alternative growth model has been proposed by Terrones et al. [26] on the co-based growth catalyst. In the presence of nitrogen atoms the curvatures of the formed graphene layers was modified and thus, lead to the ejection of the metal catalyst particle out from the graphene layer. This growth process with metal ejection was repeated again and thus ended to the formation of a nanotube with periodical arches along the growth axis. This model was supported by the observation that a decrease in the catalyst particle size decreased the bamboo periodicity [27]. It is noteworthy that such growth model is not universally applicable since modifying the nature of the growth catalyst could end up with a different carbon nanotube microstructure. The solubility of the nitrogen atoms inside the catalyst particle could also play an important role on the final microstructure of the formed carbon nanotubes. The arches formation could also be linked to the presence of nitrogen atoms inside the curvature region. Indeed, unlike carbon, nitrogen can adopt stable pyramidal bonding configurations as in the molecule NH_3, where its two remaining valence electrons occupy a shared sp^3 orbital.

High-resolution TEM micrograph also indicates the relatively high graphitization of the N-doped nanotube wall and the almost absence of amorphous carbon layers on the topmost surface of the nanotubes. Such improved graphitization could be attributed to the solid composition within the catalyst particle in the presence of nitrogen. Direct relationship between the presence of nitrogen in the reactant and the graphitization enhancement has not yet been established and work is still ongoing to get more details about such relationship. However, the absence of amorphous carbon on the outer walls of the CNTs can be explained by the etching effect of the $NH_2^{\bullet}$ radicals formed during the growth process.

The specific surface area determined by means of the BET method indicates that the introduction of nitrogen into the graphene sheets does not alter the material surface area which was still high at around 100–120 $m^2\,g^{-1}$. The specific surface area is

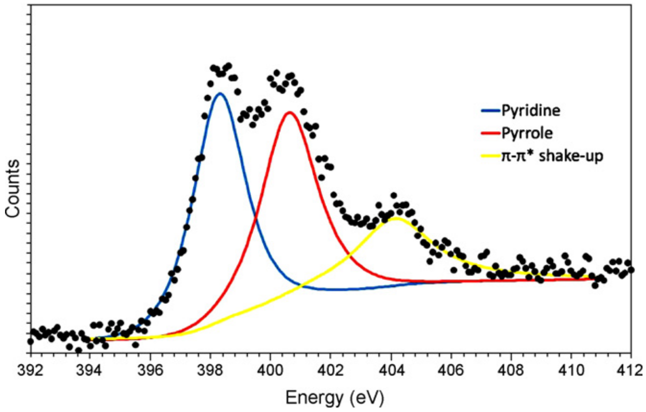

Fig. 3. XPS N 1s spectrum showing the presence of several nitrogen-based species on the N-doped CNTs.

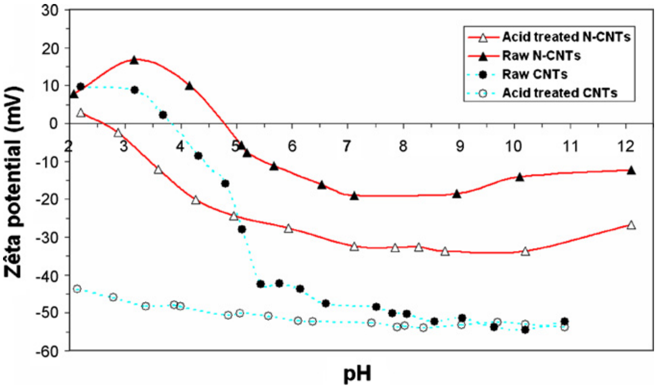

Fig. 4. Zeta potential as a function of the pH for pure and acid purified N-CNTs. For comparison, CNT results are also reported in the same figure.

mainly coming from the nanoscopic size of the material and no ink-bottled pores which are usually encountered with traditional supports were observed. Such result is extremely interesting for catalytic uses, and especially in the case of trickle-bed, where the ink-bottled pores could be filled by the liquid and thus, become inaccessible to the reactants. Preliminary experiments carried out in the laboratory also highlighted the relatively high sensitivity of the N-doped surface area as a function of the nature of the reactants, i.e. synthesis carried out in the presence of C_2H_6–NH_3 and Ar led to solid with specific surface area approaching 220 $m^2 g^{-1}$ whereas in the presence of H_2 the surface area was decreased of about twice. The reason for such modification has not yet been determined but an effect of least graphitization due to impurities in argon may be put forward to explain this alteration.

The combination of elemental analysis and XPS characterization indicated that the nitrogen distribution was homogeneous throughout the material at around 7 at.%. XPS N 1s spectrum (Fig. 3) indicates the presence of at least three nitrogen species on the material which exhibit three strong and distinct peaks at 398.6, 400.9 and 404.2 eV. These XPS peaks could be assigned to the pyridinic nitrogen (BE at 398.6 eV) [28–29], to pyrolic or quaternary nitrogen (BE at 400.9 eV) [29] and to adsorbed nitrogen, nitrogen oxides or to a π–π* shake-up satellite peak (BE between 401 and 405 eV) [16,30–31]. The sharpness of the two main peaks located at low binding energy could be attributed to the homogeneous dispersion of the nitrogen species on the carbon nanotubes surface with low C–N functionalities, otherwise a higher degree of overlapping should be expected on the N 1s spectrum [12]. These results are also consistent with previous articles from the literature concerning the XPS analysis of N-doped CNTs [32].

Zeta potential analysis allows one to access to the acido-basic character of the support which could have an influence on the active phase electronic and microstructural characteristics of the active phase. The zeta potential measurements revealed a significant modification of the surface charge behavior as a function of the pH value when nitrogen was added into the graphene sheets (Fig. 4). The grafting of N-functionalities lead to the formation of basic groups which tend to increase the value of the isoelectric point compared to N-free nanotubes. After acid oxidative washing, the nanotubes get functionalized with oxygenated groups which are increasing the acidity of the CNT surface. As a result, the isoelectric point of both species (N-CNTs and CNTs) is shifted to the acid region of pH. The zeta potential values obtained for our samples are consistent with previous results in the literature [33,34].

However, the introduction of nitrogen into the carbon structure seems to have almost no influence on the palladium phase dispersion compared to the one obtained for N-free carbon nanotubes. Representative TEM micrographs of the Pd/N-CNT and Pd/CNT catalysts prepared using Pd(nitrate) are presented in Fig. 5. From statistical analysis, the mean particle size was reported to be around 5 nm for both samples, the only significant difference being the absence of Pd nanoparticles inside the N-doped CNTs due to the presence of carbonaceous arches. High-resolution TEM observations of the metal microstructure or shape are ongoing in order to check if any modification would occur by introducing nitrogen atoms into the graphite plane.

3.2. Hydrogenation tests

The N-doped CNTs were used as catalyst support for palladium in the liquid-phase hydrogenation of cinnamaldehyde and the results were compared with different Pd/CNT catalysts, i.e. Pd/N-free CNTs and Pd/activated charcoal.

According to the observed results, the most effective catalyst in term of activity (expressed as conversion) is the commercial one: this is probably due to the high specific surface area (typically 1000–1500 $m^2 g^{-1}$) of the support that favors the adsorption process. On the other hand, the N-free catalysts exhibit lower hydrogenation conversion regardless the particle size. From the results one can state that the active phase particle size, within a certain range of value, only have a small influence on the hydrogenation catalytic activity. Such results were in line with the literature results as usually hydrogenation activity is not a structure-sensitive reaction, i.e. activity-particle size dependent. On the contrary, a large activity improvement was observed on the N-doped catalyst taken into account the similar reaction conditions. The conversion was almost doubled and became close to the one observed for the commercial catalyst indicating that the introduction of N atoms into the graphite structure led to a dramatic modification of the metal surface adsorption and in turn, of the overall C═C bond hydrogenation activity. For now the explanations concerning such activity improvement are not still well defined but electronic interaction which could modify the surface or microstructure of the active phase seem to be the most appropriate causes to explain the activity change for the N-doped catalyst. High-resolution spatial analysis by TEM will be performed in order to have access to such possible modifications of the active phase and to correlate the structure–activity relationship.

The catalytic results clearly show an improvement in terms of selectivity towards the C═C bond hydrogenation on the Pd

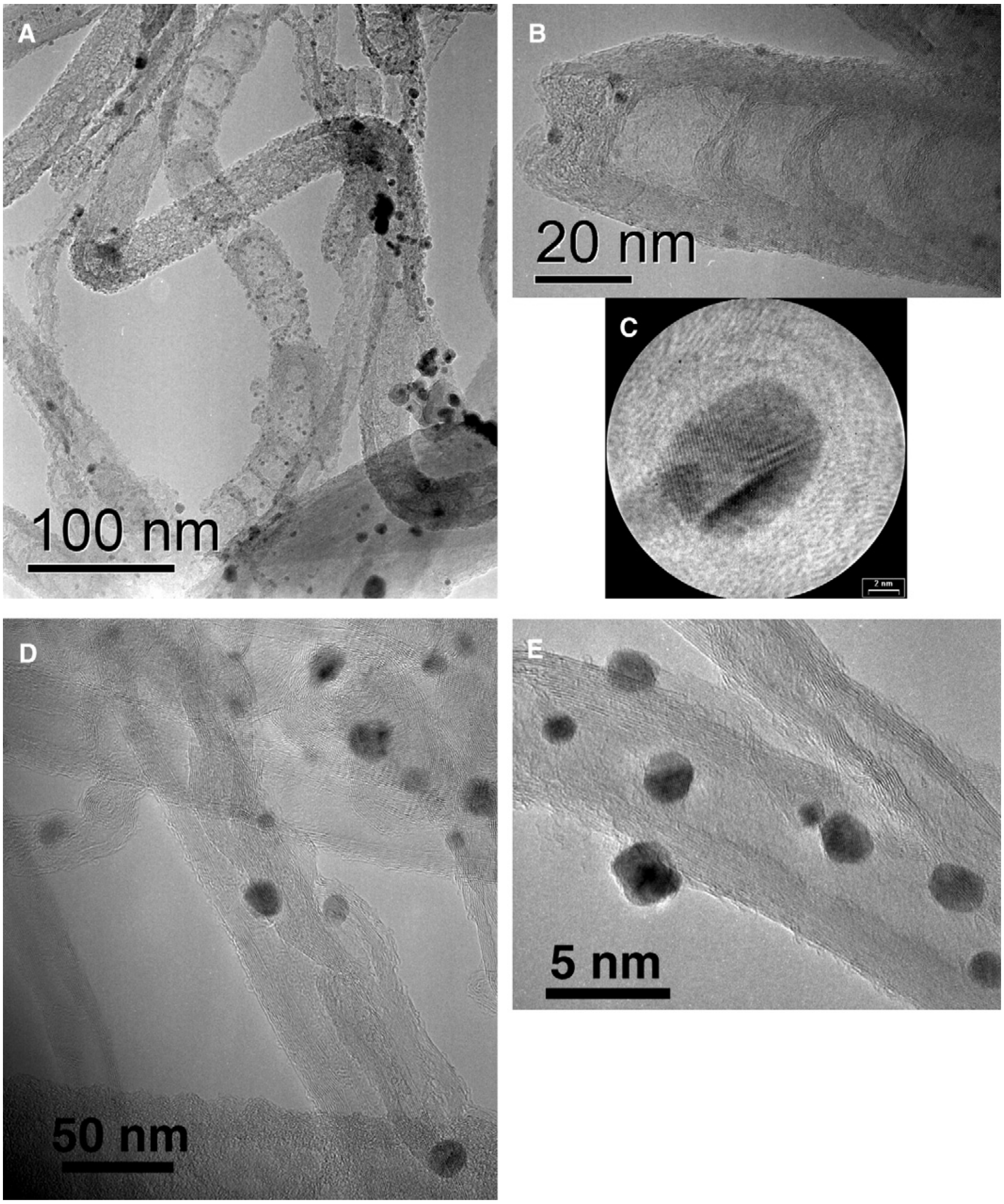

Fig. 5. TEM micrographs of the Pd supported on the N-doped carbon nanotubes (A–C) and on N-free carbon nanotubes (D and E) with different magnifications showing the evenly presence of the palladium particles on the tube surface. Low magnification TEM micrograph seems to indicate that the particles size distribution was broader in the case of undoped carbon nanotubes than on N-doped ones. However, the mean particle size remains the same for both samples, showing that the dispersion is more homogeneous in the case of N-doped carbon nanotubes.

supported on CNT and N-doped CNT prepared with the nitrate precursor salt taking into account similar reaction conditions, i.e. 80 and 90%, respectively, instead of less than 60% for the two others (Fig. 6).

Concerning the selectivity into hydrocinnamaldehyde (HCAL), the best one was obtained for the N-CNT catalyst, followed by the CNT catalyst and the AC one. The selectivities of the CNT- and N-CNT-based catalysts were stable, 80% and 90% respectively, whereas the one of the AC catalyst was diminishing with increasing conversion going from 60% to 20%. These differences could be explained by the increase of the electronic density coming from the electron pair of the nitrogen atoms. Moreover, in spite of its high specific surface area, the AC-based catalyst exhibits low selectivity into hydrocinnamaldehyde and the main formed product is the phenylpropanol (PP) which is obtained after total hydrogenation of the C=C and C=O bonds of the cinnamaldehyde. The low selectivity of the commercial catalyst comes from the presence of microporosity in the activated carbon that unfavors the partially hydrogenated products desorption (due to diffusion limitations or steric effects). The presence of acidic sites on the activated charcoal could also participate to the primary hydrogenation selectivity loss. On the contrary, the better selectivity of the nanotubes based catalysts could be explained by the easy desorption of the products from the surface catalytic sites and the absence of microporosity [35]. The higher C=C bond hydrogenation selectivity observed on the N-doped catalyst could also be linked to the pronounced basic character of the support. The role of the basicity on the hydrogenation selectivity will be deeply investigated and will be reported soon.

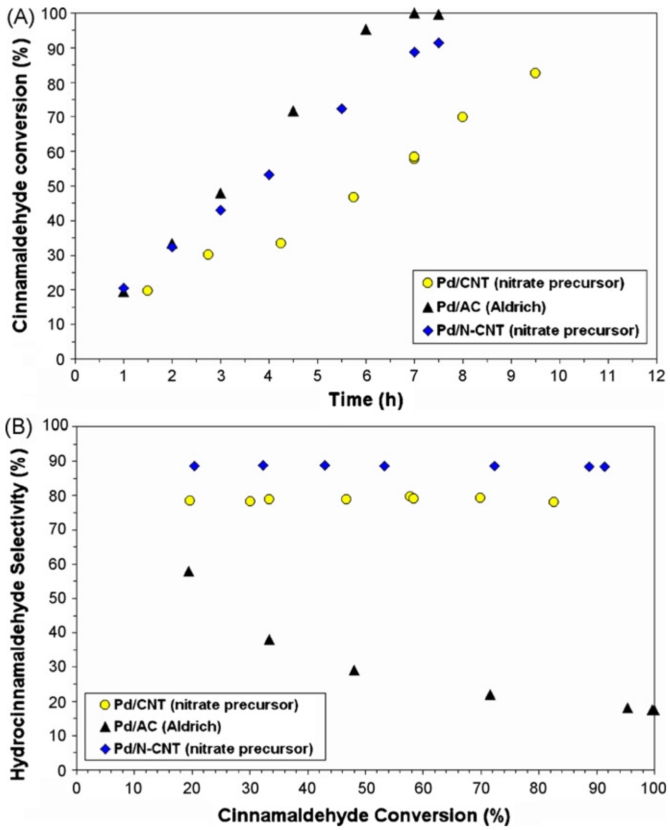

Fig. 6. (A) Cinnamaldehyde conversion as a function of the reaction time. For almost all catalysts, the total conversion is performed within 15 h. (B) HCAL selectivity versus cinnamaldehyde conversion for the different catalysts tested. CNT-based catalysts are all having stable selectivities whereas the commercial catalyst based on palladium supported on AC exhibits a decreasing selectivity with time.

It is also noteworthy that the catalysts exhibit a relatively high stability as neither activity nor selectivity modification has been observed after re-use. The high anchorage of the palladium particles on the support surface seems to prevent palladium loss during the course of the reaction.

4. Conclusion

The synthesis of nitrogen-doped carbon nanotubes has been successfully achieved by direct doping in the CVD procedure. By simply adding ammonia to the reactive atmosphere, N-doped nanotubes with nitrogen content up to 7% were synthesized. The structural properties such as the diameter, the length and the specific surface area were the same than those of undoped CNTs. It is noteworthy that contrary to the undoped carbon nanotubes the channel of the N-doped nanotubes was periodically closed by arches and thus, prevented deposition of the active phase inside the channel during the impregnation process. The introduction of the nitrogen atoms into the graphene plane also modified the basicity of the material as observed by the zeta potential analysis.

The as-synthesized N-CNTs were then tested for the selective hydrogenation of cinnamaldehyde into hydrocinnamaldehyde using palladium as the active phase, and compared to catalysts based on palladium supported on CNT and activated charcoal. Nitrogen atom incorporation led to a significant improvement of the hydrogenation activity compared to those observed on the N-free carbon nanotube catalysts. The activity improvement was attributed to possible electronic or morphologic modifications of the active phase leading to a higher turnover frequency of the catalytic site. Work based on the use of high-resolution TEM analysis and EELS will be performed in order to get more insight about the active phase structural modification in the presence of nitrogen atoms.

The results obtained also highlighted the fact that the selectivity towards the C=C bond hydrogenation was strongly influenced by the active phase particle size. The as-synthesized basic support exhibits a relatively high selectivity towards the C=C bond hydrogenation compared to the one obtained on samples without nitrogen incorporation regardless the slight difference in term of particle size. The C=C bond hydrogenation selectivity observed in the present work on the N-doped catalyst is among the highest that has ever been reported up to now in the literature.

Work is ongoing in order to achieve macroscopic structure consisting in assemblies of N-doped nantotubes, i.e. plate or cylindrical forms. In fact, the hydrogenation of cinnamaldehyde has already been performed using Pd supported over carbon nanofibers/carbon felt [36,37] and aligned carbon nanotubes [38]. The advantages of these macroscopic supports are their direct use as a stirrer, the easy separation of the products, the catalyst which could trigger a significant cost reduction of the process and also prevent waste generation. The N-doped carbon nanotubes with aligned pattern could also be useful in the field of hyperhydrophobic materials with self-cleaning properties as it has reported for the pure carbon nanotubes array in the recent literature [39].

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