New catalytic phenomena on nanostructured (fibers and tubes) catalysts

Marc J. Ledoux,* Ricardo Vieira, Cuong Pham-Huu, and Nicolas Keller

ECPM/ULP/CNRS, Ecole Européenne de Chimie, Polymères et Matériaux de Strasbourg, ELCASS, European Laboratory for Catalysis and Surface Sciences (CNRS-MPG), UMR 7515-L.M.S.P.C, Laboratoire des Matériaux, Surfaces et Procédés pour la Catalyse, Université Louis Pasteur, 25, rue Becquerel, 67087 Strasbourg cedex 2, France

Abstract

The recent development of new catalytic syntheses of carbon or carbide nanostructures has enabled the production of large amounts of these materials. Consequently, it is now possible to use them as supports for active phases in novel catalytic reactions and processes. New phenomena at the surface or inside these structures open up the way to unexpected applications. We shall first present the latest methods of preparation of these nanomaterials and their characterization and then provide some examples of applications in the fields of catalysis for synthesis of chemicals and catalysis applied to environmental remediation.
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1. Introduction

The existence of carbon nanofilaments (called tubes if hollow and fibers if filled) has been recognized since the first tests for natural gas steam-reforming in the 1920s, where these materials were considered as poisons for the desired reactions. Several researchers showed their nature; the first was probably Robertson [1]. When Iijima [2] published his work on the synthesis of fullerenes, he also provided proof of the existence of filaments mixed with the C_{60} and definitely convinced other researchers to invest in this new family of nanomaterials. But at that time two important drawbacks limited the use of these materials for catalytic applications: the relatively low yield obtained by physical synthetic routes (arc-discharge or laser ablation) and the high amount of impurities accompanying the desired products, such as soot and other carbon structures. The chemical route of synthesis, catalytic in essence, could overcome these obstacles. The most recent review published on the subject by De Jong and Geus [3] summarizes the different aspects of this catalytic synthesis acknowledging the pioneering work of Baker's group [4] and of their own group [5]. It is clear that Ni, Fe, and Co are the three metals, pure or alloyed, which can catalytically decompose gaseous carbon sources

(CO and hydrocarbons) at moderate temperatures and build the carbon nanostructures. The different mechanisms of growth [6] and the thermodynamics of the process are well discussed in this review.

Until now far less work has been devoted to the catalytic application of carbon nanofilaments. Baker's group was probably the first to publish an article where carbon fibers were used as support for an active phase—i.e., Fe and FeCu, to study the ethylene hydrogenation [7]. Other experiments published by the same group [8] led the authors to suggest that the specific properties, mainly a much higher activity when compared to catalysts prepared with conventional supports, were due to a strong interaction between the growing metal particle during its reduction and the graphene basal or edge sites, leading to faceted metal particles exposing new specific catalytic sites. A metal-support electronic interaction was not considered in these studies as it was by Planeix et al. [9] with Ru particles supported on rather mixed carbon structures obtained by arc-discharge according to the published TEM pictures, to explain the high selectivity observed in the partial hydrogenation of cinnamaldehyde. Then Geus's group [10] and Bessel et al. [11] extensively studied the hydrogenation of nitrobenzene into aniline by supporting Pd on well-characterized different carbon nanostructures and compared their properties with Pd supported on activated charcoal, the work horse of catalytic hydrogenation in the liquid phase. They found a significant increase in activity for the Pd supported on carbon nanofibers but they did

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* Corresponding author.
  E-mail address: ledoux@cournot.u-strasbg.fr (M.J. Ledoux).

not provide an explanation for this result. Two recent articles report [12,13] the use of carbon nanofibers as support for Pt or Ru–Pt in a direct methanol fuel cell anode. This anode showed a much better performance than an unsupported Pt–Ru colloid.

Based on this pioneering work, we have developed and improved the catalytic route of the synthesis of carbon nanostructures [14], invented new composite materials to support these nanostructures [15], used these nanostructures as starting material for the synthesis of SiC nanotubes [16], and then, explored many fields in catalysis (oxidation [16], hydrogenation [17], ODH [18], and decomposition [15]), where new concepts have been proposed and particularly the discovery of a confinement effect when tubes were employed. This led us to noncatalytic applications of these hollow nanostructures using them as nanoreactors [19]. This short review will illustrate this research and provide new perspectives for this fascinating field where new nanomaterials can bring new answers to old problems dealing with environmental protection or sustainable development.

2. Catalytic preparation of nanofibers and multiwalled nanotubes

2.1. Multiwalled nanotubes of carbon

It is well known from the pioneering work cited earlier that only Fe or Co can provide nanotubes while Ni leads to nanofibers; for nanotubes we will only report the use of

Fe at this stage. Parameters other than the nature of the catalytic metal play a significant role in the constitution of the final material. The support is important because of the mechanism of formation via a dissolution of carbon in the metal [6,20–22]; a too strong or a too weak interaction with the support can modify the exposed faces of the metal particles and consequently change the process of formation. The dispersion of the metal will determine the diameters of the final tube (external and internal). This is an important parameter as it is possible to tune the size of the tubes according to requirements. The best supports seem to be either silica or carbon in different forms. Finally, the reacting mixture, the source of carbon, has not been as extensively studied as the other parameters. We found that hydrocarbons, and particularly ethane, are better than other sources, such as CO, the presence of hydrogen is necessary, and the ratio of hydrogen to ethane is a key parameter for the high yield production of nanofilaments. The amount of hydrogen in contact with the metal particle during the filament growing process (tubes or fibers) probably regulates the flow of carbon entering into the metal; the H/C ratio is thus critical. This is also why ethane seems to be better than other hydrocarbons as it may contribute to this H/C ratio— hydrogen coming from the hydrocarbon possibly having a different role than hydrogen provided by dihydrogen present in the gas phase, the latter probably avoiding the formation of undesired turbostratic coke, which would kill the activity of the catalyst.

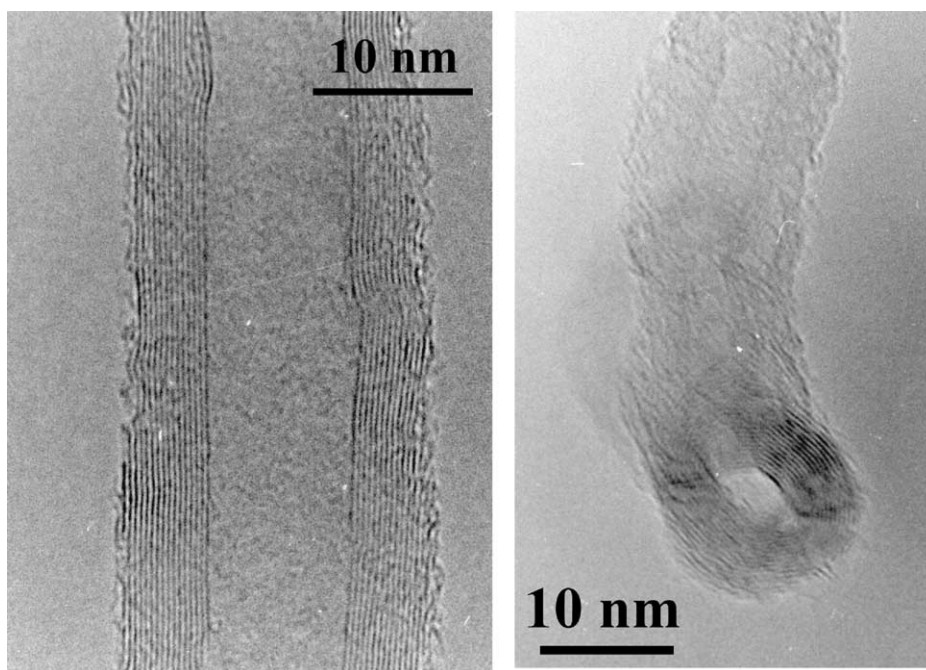Fig. 1 shows an example of carbon multiwalled nanotubes prepared under the following conditions: 20% Fe/SiO$_2$,

Fig. 1. Multiwalled carbon nanotubes obtained on Fe/SiO$_2$ catalyst (with an average length of several micrometers). Twelve to 14 graphene cylinders can be observed with a very smooth internal surface and relatively disordered last external graphene layers. The mouth of a 17–18 walled tube is shown in the photo on the right.
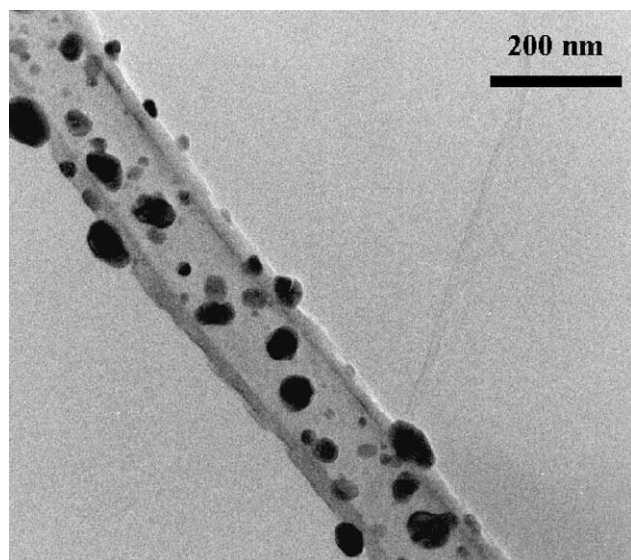
Fig. 2. Ni particles supported on the outside surface of carbon nanotubes.

50/70 H$_2$/ethane ratio, a yield of 6 g per gram of Fe per day of highly pure nanotubes obtained after purification [16]. A one-day process of purification, ultrasound, biphasic separation from the catalyst and drying, followed by an aqua regia treatment under reflux for one night to dissolve the last traces of Fe, was used.

2.2. Carbon nanofibers

Many different routes have been tested to obtain the purest material with the largest yield. As expected Ni was the best metal and ethane the best carburizing gas. Twenty seven percent Ni/SiO$_2$ treated at 650 °C under the same conditions as those for the Fe catalyst for nanotubes gave after purification 16 g per gram of Ni per day of highly pure herring bone shaped fibers with a distribution in diameter varying from 10 to 100 nm, centered around 30 nm. To improve the yield and avoid the purification step another system was tested. Multiwalled large nanotubes provided by Applied Sciences Ltd. (Ohio, USA) were impregnated with a Ni salt in order to obtain 20 wt% of Ni. Using a specific procedure already reported [14] after reduction by pure hydrogen most of the Ni was located on the outer surface of the tube (see Fig. 2). This material was an outstanding catalyst providing such a yield that further purification was not necessary. The best yield, 1700 g per gram of Ni per day, was obtained at 650 °C with a mixture of 40/100 H$_2$/ethane. A mixture of herring bone and "pile of plates" fibers were observed, this structure depending on the shape of the Ni particles; Fig. 3 shows an example of a "pile of plates" nanofiber.

2.3. Carbon fibers/carbon felt composite

The preceding results inspired us to imagine a new composite material which would exhibit all the properties of
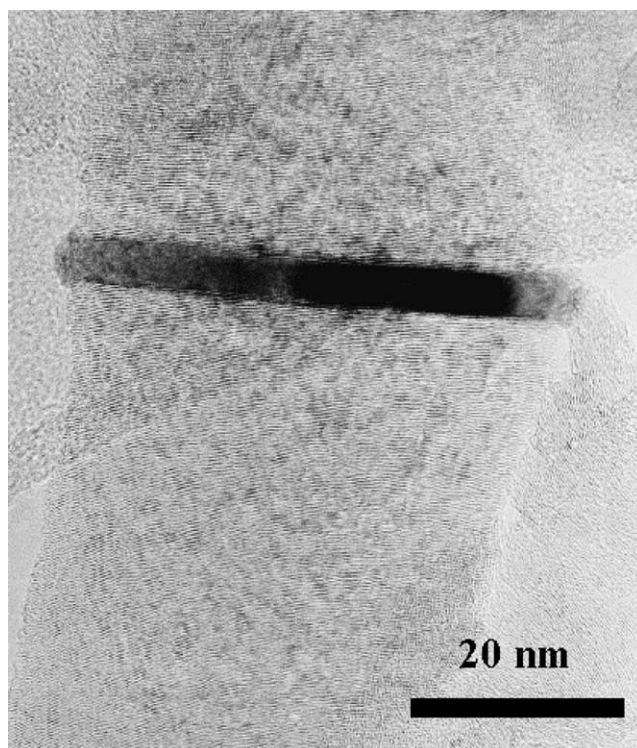

Fig. 3. "Pile of plates" carbon nanofiber growing on both sides of its mother Ni particle.

strength, dispersive ability, and surface properties of carbon nanofibers but not their main drawback, which is the too fine powder shape which greatly complicates their use in a catalytic reactor, fixed bed or slurry. A very small amount of Ni (1 wt%) was deposited on the microfibers of a carbon felt (1 m^2/g), macroscopically shaped as desired [15]. After reduction to Ni metal by an hydrogen flow the material was submitted to a flow of H$_2$/ethane (5/1) at 700 °C. When the weight increase reached 100%, the reaction was stopped and the new support (95 m^2/g) was ready for further impregnation and catalytic use. In Fig. 4 one can observe a small part of the initial microfiber surrounded by a glove of entangled nanofibers; by increasing the resolution of the microscope, the herring bone nature of these fibers can be clearly observed. Such a material was able to support more than 3500 times its own weight, while maintaining its high specific surface area and lightness. This new strength and rigidity could be explained by the growth of nanofibers in and out of the microfibers from the very small Ni particles, in this way providing a formidable glue without closure of the felt structure.

2.4. Nanotubes of silicon carbide

Some years ago [23–25] we developed a new synthetic concept for β-SiC that we called "shape memory synthesis" based on the fact that the macroscopic shape of a carbon form was maintained after reaction with SiO vapor and transformation of C into SiC. This method was adapted
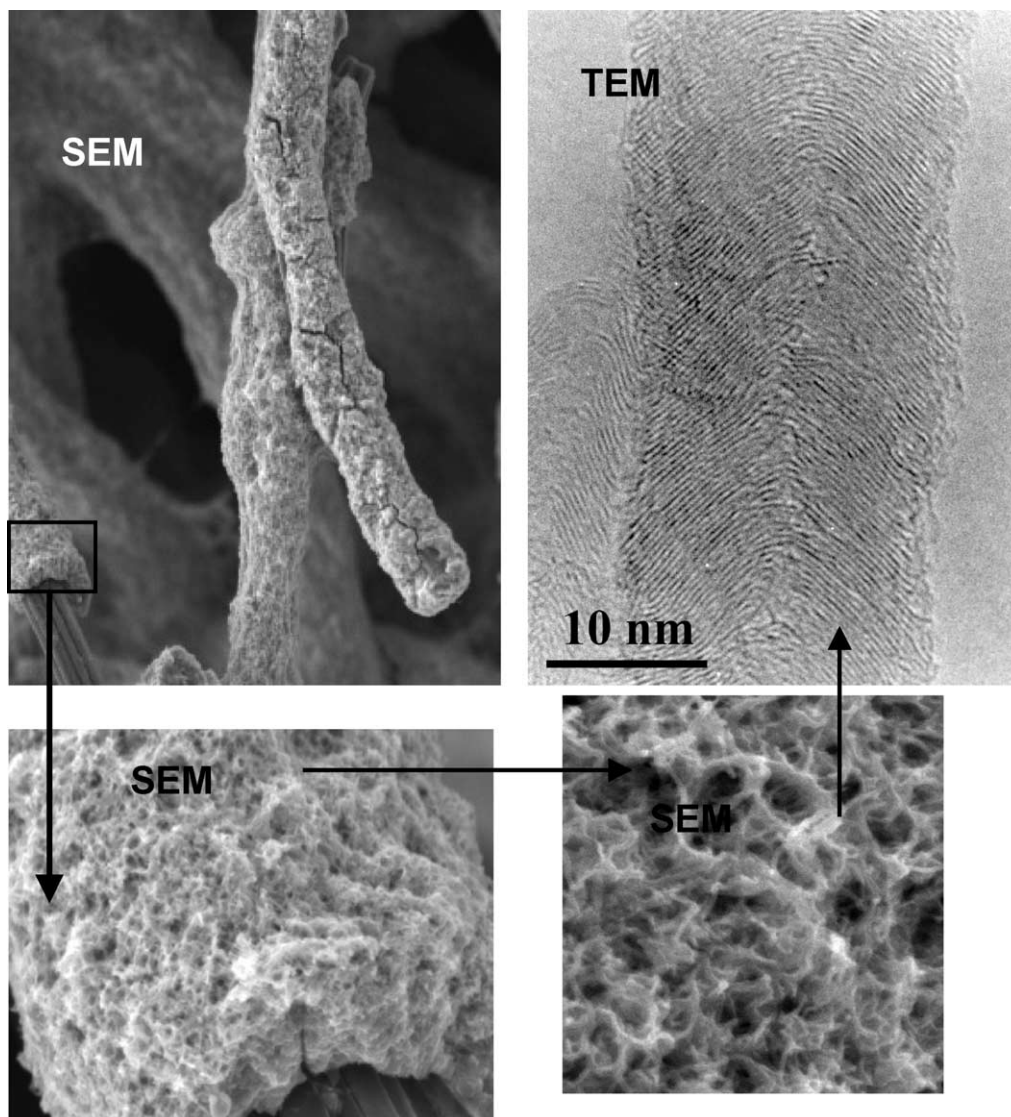
Fig. 4. Felt of carbon microfibers (visible at the bottom left of the top left photo) covered with a strong layer of solid carbon nanofibers (hering bone shape) anchored in the carbon fibers of the felt.

to nanotubes and nanofibers of carbon as starting material and as long as the diameter of the carbon multiwalled nanotube was large enough it was possible to obtain their reprint in β-SiC; see Fig. 5. The carbon nanotubes were not stable enough for the synthesis of smaller sized structures with only SiC powder being obtained after reaction; in order to produce SiC nanotubes with small diameters, less than 100 nm (see Fig. 6), the use of carbon nanofibers was required. These syntheses were already published in detail [16].

Since their syntheses these four families of materials have been extensively studied in our laboratory or in collaboration with the Fritz–Haber Institute (FHI) of Berlin, as catalysts or as support for catalysis for numerous conventional or new reactions presenting difficulties such as mass transfer problems, too small concentrations of reactants (thus kinetically limited), poor selectivity, or very high mechanical stress.

3. Reactions using nanofibers or nanotubes as catalytic materials

3.1. Carbon nanotubes as catalysts for selective ethylbenzene oxydihydrogenation, ODH, into styrene

This work was conducted at the FHI [18], where only one of us was directly involved, the Strasbourg contribution being mainly to provide the catalytic material. The authors demonstrated that carbon black (soot) can be an efficient catalyst for the ethylbenzene (Φ–CH$_2$–CH$_3$) ODH, with selectivity into styrene (Φ–CH=CH$_2$) as high as a conventional Fe-based catalyst. However, the main drawback is the combustion of the catalyst because of the presence of air in the reacting gas at the reaction temperature of 550 °C. The use of graphite stabilized the system because it burns at temperatures higher than 550 °C. The mechanism proposed by
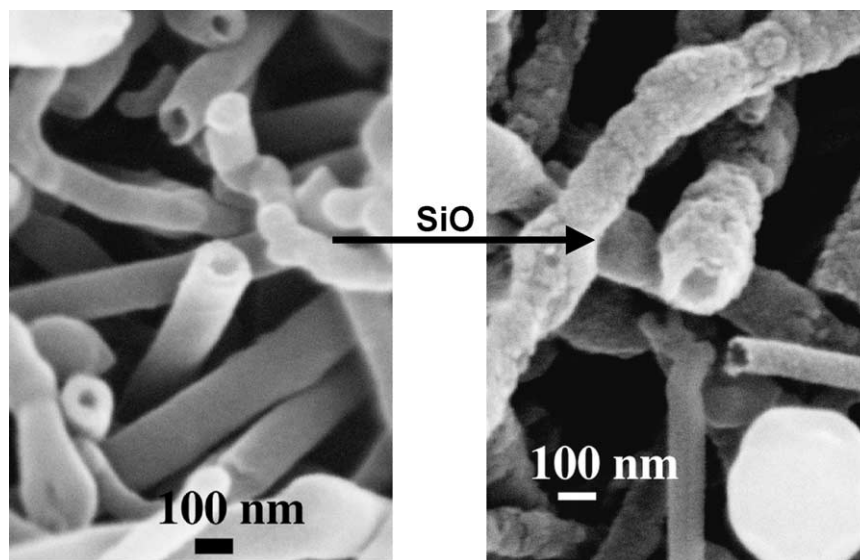
Fig. 5. SiC nanotubes (right) obtained from carbon nanotubes (left).

the authors, close to the concept introduced by Mars and van Krevelen [26] in partial oxidation reactions, involves adsorption and dissociation of dioxygen on the basal planes of the graphite, then diffusion of the oxygen radicals toward specific sites located on the prismatic edges of the graphitic material, where these radicals extract the two hydrogen atoms of the ethyl branch, forming two hydroxyl groups bonded to the carbon. The sites are then regenerated by dehydration and formation of steam. One can expect when conventional graphite is replaced by carbon nanotubes that an increase in

the volumetric density of these active sites will occur while keeping the stability of the catalyst high, because carbon nanotubes are at least as stable as bulk graphite. The tests to check this hypothesis are illustrated in Fig. 7 and confirm that soot works but burns, that graphite is stable, and that carbon nanotubes are stable and the most efficient [27].

3.2. Liquid phase selective hydrogenation of cinnamaldehyde

The hydrogenation of cinnamaldehyde (Φ–CH=CH–CHO) on conventional Pd supported on activated carbon is not selective and both the C=C and the C=O double bonds are hydrogenated to give the saturated corresponding alcohol (Φ–CH$_2$–CH$_2$–CHOH), 60% at total conversion,
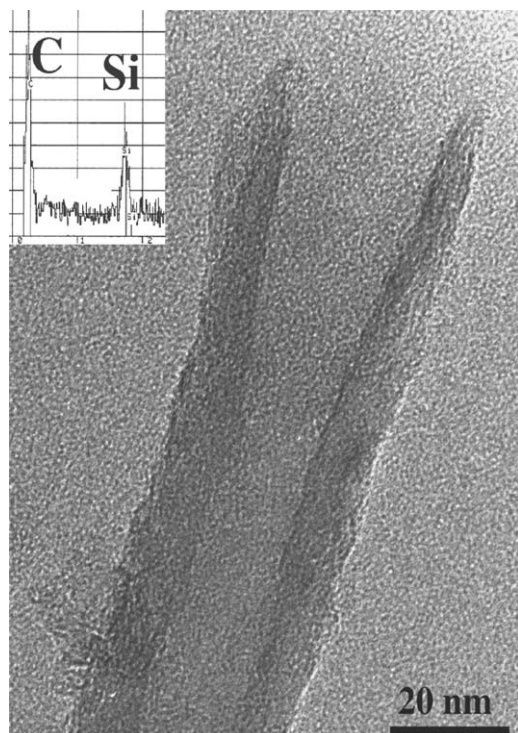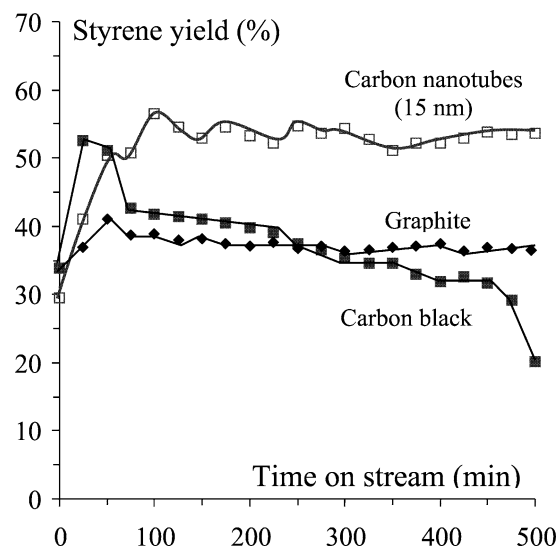

Fig. 6. SiC nanotubes obtained from carbon nanofibers.

Fig. 7. Ethylbenzene ODH into styrene (550 °C, WHSV = 3, O$_2$/ethylbenzene = 3).
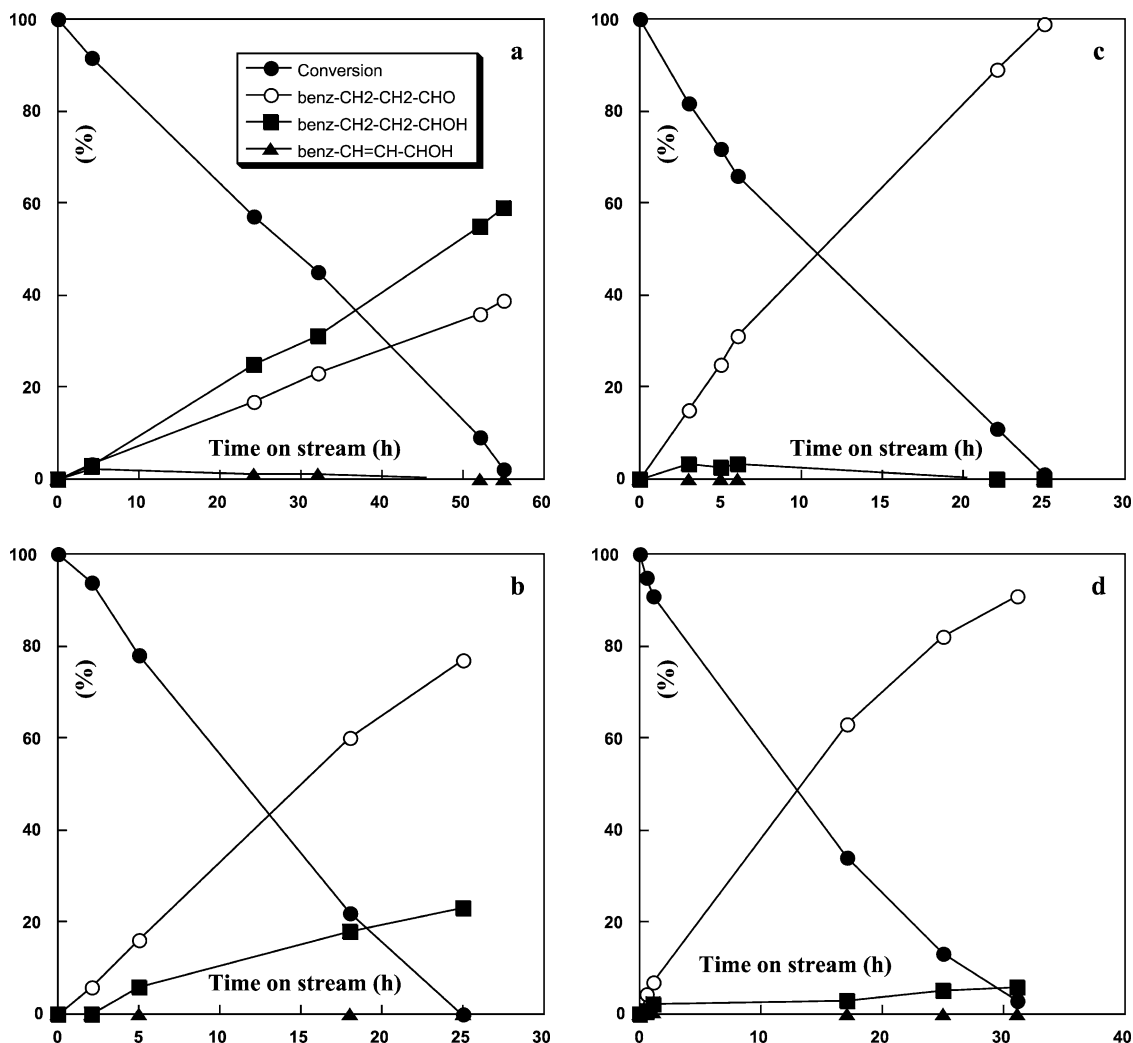
Fig. 8. (a) Cinnamaldehyde hydrogenation on Pd/activated charcoal; (b) on Pd inside carbon nanotubes. (c) Cinnamaldehyde hydrogenation on Pd/SiC nanotubes; (d) on Pd supported on carbon nanofibers.

and the saturated aldehyde (Φ–CH$_2$–CH$_2$–CHO), 40% at total conversion. The unsaturated alcohol (Φ–CH=CH–CHOH) was only found as negligible traces (Fig. 8a). Pd was then impregnated inside carbon nanotubes (mean internal diameter of 180 nm) (Fig. 9a) or inside SiC nanotubes, and these two catalysts were tested under conditions identical to the Pd/activated charcoal (stirred liquid phase, bubbling hydrogen, solid catalyst, 80 °C, 40 ml of dioxane the solvent, 0.26 g of cinnamaldehyde, and 1.05 mg of Pd). On Pd/carbon NTs (Fig. 8b) one observed a very significant acceleration of the reaction rate (total conversion in 25 h instead of 55 h), meaning a better mass transfer (the usual limitation with conventional catalyst in liquid phase), and a strong improvement of the selectivity, 80% of saturated aldehyde against 20% of total hydrogenation. On Pd/SiC NTs (Fig. 8c), the same acceleration rate was found but now the selectivity reached 100% for the saturated aldehyde. One could expect at this stage that a confinement effect due to the location of the active metal inside the tubes would be responsible for the new selectivity. However, when

Pd was impregnated on carbon nanofibers (herring bone shape) (Fig. 9b) the same improvement in selectivity and in reaction rate (Fig. 8d) was found [17], meaning that an hypothesis other than confinement should be put forward. Before finding and proving another explanation, one should retain the concept proposed by Baker et al.; i.e., faceted metal particles are induced by a specific interaction between the surface of the nanostructure and the metal particle during its crystallization, providing new specific reaction sites that were absent on conventional metal particles grown on conventional supports. The results of careful examination of the shape of the Pd particles in Figs. 9a and 9b do not contradict this concept as many of these particles seem to be faceted instead of the usual spherical shape, but this should be confirmed by a more in-depth study. However, a confinement effect for the catalyst using nanotubes cannot be excluded and the fact that the catalyst supported on nanofibers also exhibits a strong increase in selectivity and activity (not as high as on the nanotubes!) could be a coincidence.
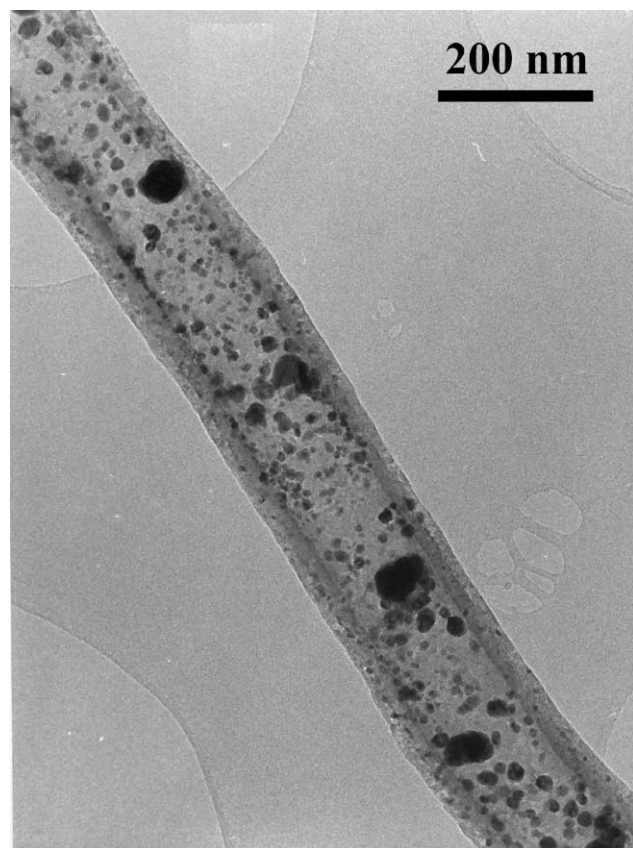
(a)
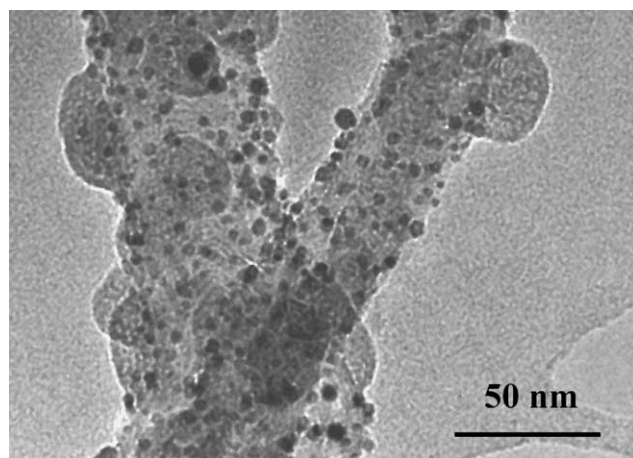
(b)

Fig. 9. (a) Pd inside carbon nanotubes; (b) Pd supported on carbon nanofibers (the bubbles are due to solvent intercalated between the graphene planes and extracted by the electron beam under vacuum).

3.3. Catalytic decomposition of hydrazine on Ir supported on carbon nanofibers/carbon felt composite

Usually satellites have slightly unstable trajectories around the Earth due to the attraction of other planets or to other phenomena, such as solar wind, and require regular impulsions to be replaced on their nominal position. These impulsions are generally provided by small jet engines using hydrazine (N_2H_4) for fuel and its catalytic decomposition into hydrogen and nitrogen as the source of energy (with minimum formation of NH_3). This decomposition should start as fast as possible to spare the very precious fuel (directly responsible for the activity life of the satellite), at the lowest possible temperature, and liberate the highest energy, i.e., the highest pressure, in the shortest time in order to provide the highest initial thrust. Obviously it should be light, as for everything sent into space and should have a good stability, at least equal to the life of the satellite. The commercial catalyst used up to now is Ir supported on alumina at high loading, about 35 wt%. The explosive decomposition of hydrazine, particularly inside the pores of the support, can seriously damage the integrity of the material because of the pressure and temperature shock. In addition the propagation of the explosion in this porous material absorbs a significant fraction of the pressure overshoot and consequently negatively affects the yield of the initial thrust.

We have impregnated (wet impregnation of a solution of salt in water) the carbon fibers/carbon felt composite with 30 wt% of Ir and tested in a comparative manner the commercial alumina supported material with this new catalyst [15]. The measurements of the pressure release as a function of time are reported in Fig. 10. It is clear that the gain in initial pressure was remarkable, with, however, a slight time lag of 1/10 of a second. The stability was then tested by shooting 20 pulses in a row, only waiting for the system to cool to room temperature between each shoot. This was a very severe test as, usually, a shoot takes place only once a day leaving plenty of time for the catalyst to release the stress. The commercial catalyst was severely affected after such a treatment while the composite supported Ir was even more active than after one shoot, presenting no apparent physical attrition or damage; even the dispersion of Ir was still very high for such a high loading and severe treatment (see photos in Fig. 11). The high dispersion was certainly due to the strong interaction between the prismatic sites of the carbon nanofibers and the metal, the high initial pressure to the total absence of micropores and the mechanical strength to both this absence of pores and the elasticity of the material working like a shock absorber [28].

3.4. H_2S oxidation by air into S and water at low temperature, 60 °C

This is an important industrial reaction for the protection of the environment, used to clean the tail gas of sulfur plants containing up to 1% of H_2S, released as SO_2 after combustion. The use of SiC as a support for the Ni sulfide active phase has been a great improvement in this process compared to conventional alumina or alumina doped supports [29,30]. When extrudates of β-SiC are replaced by SiC nanotubes as support we have observed a strong increase in the rate of reaction, not to mention the large increase
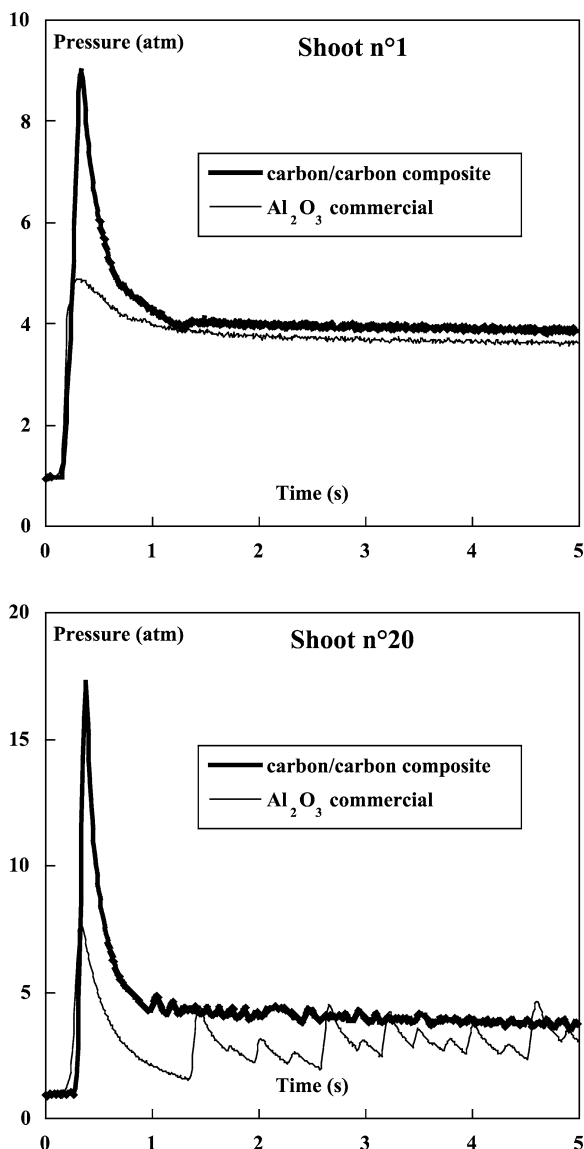
Fig. 10. Decomposition of hydrazine on Ir/carbone composite—30 wt% and Ir/Al$_2$O$_3$—35 wt%, first and 20th shoots.

Table 1

Catalyst	Relative rate
NiS$_2$ supported on bulk β-SiC, average pore diam. 20 nm	1
NiS$_2$ supported in β-SiC microtubes, internal diam. 15 μm	1
NiS$_2$ supported in β-SiC nanotubes, internal diam. 90 nm	> 4
NiS$_2$ supported in β-SiC nanotubes, internal diam. 15 nm	> 4
NiS$_2$ supported in carbon nanotubes, internal diam. 90 nm	> 4

in favor of surface cleaning (see the role of hydrophilic and hydrophobic parts of the surface for this cleaning process in [25]). The rate of reaction could be expressed as a function of only the partial pressure of H$_2$S because all the other parameters remained constant: $r = K \times [\mathrm{H_2S}]^{\alpha}$ ($\alpha = 1$ for this reaction [31]). As the macroscopic partial pressure of H$_2$S was kept constant for all the supports, one must make the hypothesis that a nanocondensation or a nanocapillarity phenomenon artificially increased the partial pressure of H$_2$S inside the nanotubes where the active sites were located. Mass transfer problems can be excluded from this gas phase reaction as all precautions were taken by varying the flow and checking the absence of nonkinetic behaviors. One could not totally exclude the explanation which was used above for the hydrogenation of cinnamaldehyde, i.e., the presence of faceted crystals of active phase, but here there is no significant difference in the nature of the surface between the bulk β-SiC and the SiC 90 nm nanotubes according to the TEM studies, and Ni sulfide particles are much "softer" than metal particles such as Pd and can probably be easily reconstructed during the reaction, consequently losing any hypothetical specific shape built during their formation.

4. Conclusions and perspectives

The best argument in favor of a confinement effect can be found in the most recent development of our work where we used carbon nanotubes as nanoreactors for the synthesis of solid materials such as zeolite or ferrite [19]. Briefly, because this is not catalysis, when carbon nanotubes are dipped in solutions containing the right ingredients for the synthesis of ZSM-5 or of Co ferrite, one can easily avoid the use of hydrothermal conditions (high pressure, temperature, and steam) to obtain nanocrystals of zeolite or ferrite at low temperature and normal pressure directly in the mother liquor, a new form of "chimie douce." The only simple explanation for this strange phenomenon is to consider that the interior of the nanotubes behaves like a small pressurized reactor even if the outside remains at normal pressure. Theoretical studies on the behavior of polar molecules inside small volumes, but not as small as the pores of the zeolites (close to the dynamic diameter of the molecules), should be performed in order to confirm or exclude this concept of confinement. It is possible to imagine that in these small volumes the shocks with the walls could become as significant as the shocks between the molecules themselves and that the usual situation where the energy exchanged with

in sulfur storage capacity of the catalyst, which is another subject [16]. Ni sulfide was in this case located inside the tubes as it was not detectable outside by TEM. Table 1 shows comparative rates of this oxidation reaction when the shape of the support was modified, all other parameters such as metal loading, temperature, and conditions of flow, pressure, and volume being kept identical from one support to the other.

When the support was only micro- or mesoporous or when the tubes had too large an internal diameter, i.e., microtubes, there was no difference in the rate of reaction. As soon as the internal diameter reached the nano range a strong increase (a factor of 4) in reaction rate was observed. The carbon supported material had an unstable rate; only the initial rate was high, and a decrease with time on flow was probably due to the poor hydrophilicity of carbon not
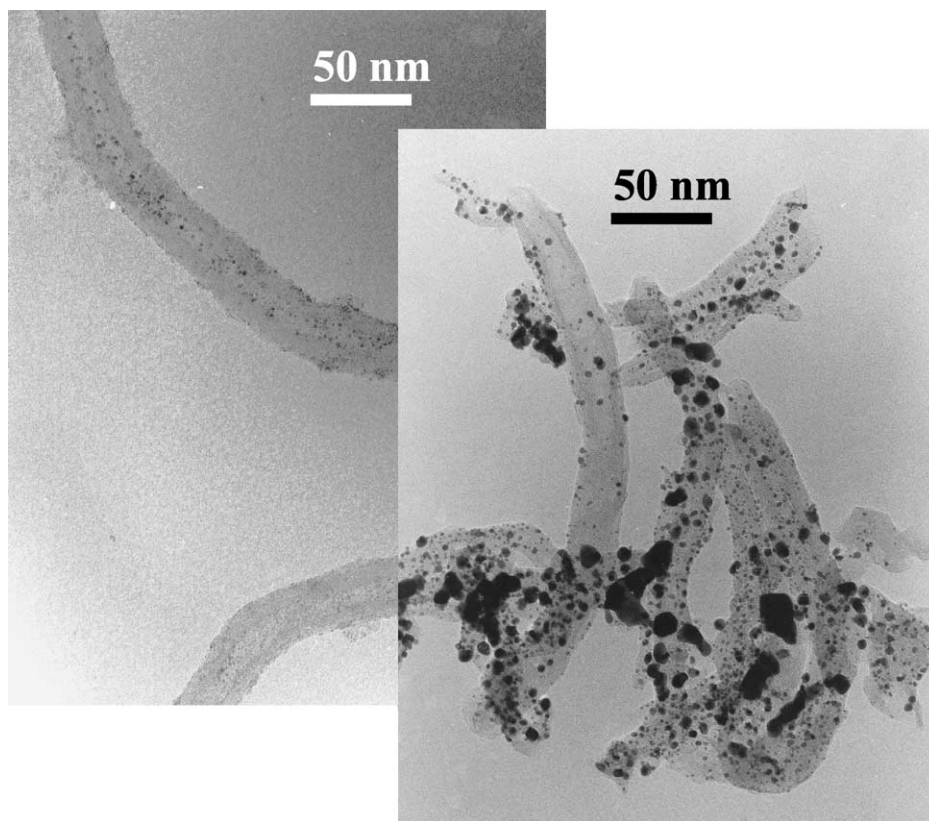
Fig. 11. Ir—30 wt% supported on carbon fibers/carbon felt composite before (left) and after (right) 30 shoots of hydrazine decomposition.

the walls is considered negligible now becomes predominant and modifies the nature of the matter enclosed. "Enclosed" is in fact the wrong word as these phenomena only work in tubes open at both ends. In porous materials where tubes of similar diameters are present but closed at one end no such reaction occurs. The best example is the reaction of H_2S on bulk β-SiC with pores of mean diameter 20 nm and on SiC nanotubes having an internal mean diameter of 15 nm. The reaction is four times faster in the nanotubes.

This example is typical in terms of future development of the use of nanotubes for environmental treatment. Atmospheric pollutants are generally present at very low concentrations and their catalytic destruction is consequently difficult, high reaction rates needing either high concentrations of the reactant or a large amount of catalyst. By artificially increasing the concentration of the molecules which should be destroyed on the active sites, the confinement effect could increase the rate without increasing the amount of catalyst. In addition the possibility of supporting carbon nanostructures on composite systems (carbon felt, metals, etc.) can solve the problem of handling these very dispersed materials in gas phase as well as in liquid phase. In liquid phase particularly, the large surface area without microporosity greatly reduces the negative effect of poor mass transfer. Finally nanostructured catalyst supports, and particularly the carbon nanofibers, can be of great help in the recent development of mini-, micro-, or nanoreactors, which is often limited by diffusion, mass transfer, or other limita-

tions of the same sort. Most of the problems related to the synthesis of large amounts of these nanostructures are now solved or almost solved; a large field of research is open, and not only in catalysis where we are currently working but also in new synthetic methods (chimie douce), electronics, etc. All this confirms the main message of the authors of the NRC report [32] devoted to the future of catalysis 10 years ago placing the development of new catalytic materials at the heart of catalysis; "A materials-focused approach is needed to complement the existing strong efforts on understanding and elucidating catalytic phenomena. More emphasis should be placed on investigation of the optimised design and synthesis of new catalytic materials...."

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