

Structured silica reactor with aligned carbon nanotubes as catalyst support for liquid-phase reaction

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Abstract

Scaling up and macronization of carbone nanomaterials open a new era for their industrial applications. Here we report the synthesis of aligned and strongly attached multi-walled carbon nanotubes on the wall of a silica reactor, which can be efficiently used as a catalyst support in liquid-phase reactions. The electronic microscopy (SEM and MEB) analysis techniques were used to characterize the morphology and the microstructure of the as-synthesized catalyst support. The probe reaction used was the liquid-phase hydrogenation of a C=C bond using palladium as an active phase. The great advantage of using such a structured reactor was the avoidance of catalyst-product separation which is generally encountered with liquid-phase reactions and the high reactant-structured phase contact surface due to the nanoscopic size of the support.

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1. Introduction

Since their discovery in 1991 by Iijima [1] carbon nanotubes have received an increasing scientific interest because of their exceptional physical properties [2–6]. The most promising route to generate carbon nanotubes is catalytic chemical vapor deposition (CCVD) based on the low temperature decomposition of a mixture of gaseous carbon source with or without hydrogen on a catalyst [7–10]. For nanotechnology devices the development of synthesis methods to form macroscopic and organized carbon nanotubes are needed. Aligned multi-walled carbon nanotubes produced by catalytic chemical vapor deposition (CCVD) methods have been received an increasing scientific interest during the last decade [11–15]. Recently, pioneering works have been published by both Maruyama's group [16,17] and Resasco's group [18] on the vertical growth of aligned single-walled carbon nanotubes on a macroscopic flat substrate by direct decomposition of gaseous hydrocarbons on a Co–Mo catalyst. From these

results, one should expect that the scaling up and the macronization of these carbon nanomaterials have been well controlled and should allow the opening of a new era for their industrial applications. However, to date, these aligned carbon nanotubes samples have been employed mainly in the electronic or filtration fields while almost no catalytic application has been reported on these structured carbon nanomaterials.

It is thought that the combination of a nanoscopic size and high external surface area (due to the nanoscopic size of the tube) of these aligned carbon nanotubes material could allow the use of nanoscopic materials in the structured reactor field, which favor the heat and mass transfer along with the easy recovery of the catalyst and products at the end of the test. It is expected that specific properties could be observed using these nanomaterials, especially in the heterogeneous catalysis field, compared to those usually encountered with traditional catalysts, i.e. powders, grains or extrudates. The biggest advantage of using these nanostructured materials relies on their high external surface area which could dramatically increase the contact surface between the reactants and the active sites and significantly reduce the diffusion problems, especially in liquid-phase reaction medium.

α,β -Unsaturated aldehydes are involved in several important chemical processes, from polymers to fine chemicals [19]. The C=C hydrogenation product formed from cinnamaldehyde has

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recently been reported to be an important intermediate in the preparation of pharmaceuticals used in the treatment of HIV [20]. Despite the relatively large number of research devoted to catalyst development for the selective hydrogenation of cinnamaldehyde [21,22], selectivity remains an important issue that need to be improved.

Recent work carried out in our laboratory have shown that the selectivity towards the C=C bond hydrogenated product could be significantly improved, i.e. ca. 80%, when using carbon nanostructured materials, i.e. nanotubes and/or nanofibers, as catalyst support compared to about 50% on the Pd/activated charcoal catalyst [23,24]. The high external surface area, the absence of any micropores combined with the low acidity of the support was advanced to explain the observed results. The presence of a conductive support could also modify in a significant manner the electronic and structural properties of the supported metal; however a clear explanation is not yet established.

The aim of the present article is to report the synthesis of aligned and strongly attached multi-walled carbon nanotubes on the inner wall of a silica reactor which can be efficiently used as a catalyst support in liquid-phase reactions. The probe reaction used was the liquid-phase hydrogenation of a C=C bond using palladium as an active phase. The great advantage of using such a structured reactor was the avoidance of catalyst-product separation as generally encountered with liquid-phase reactions and the high reactant-active phase contact surface due to the nanoscopic size of the support.

2. Experimental

The structured reactor consisted of a cylindrical (20 mm, inner diameter, 200 mm, length) silica reactor housed inside another silica reactor located in a horizontal furnace. The aligned carbon nanotubes film was grown by injecting a mixture of ferrocene/toluene and argon into the decomposition zone and nanotubes growth maintained at 800 °C according to the results reported by Ayajan's group [2]. The synthesis was carried out for 4 h and then the reactor temperature was cooled to room temperature under an argon flow. The resulting solid was discharged from the reactor at room temperature without any precaution. The average growth rate, calculated from the carbon nanotubes thickness and the synthesis time, is typically 5 $\mu\text{m min}^{-1}$.

The silica reactor containing Pd/CNTs (18 mg of Pd) was fixed onto a magnetic stirrer device which was immersed into a solution of dioxane (500 ml) containing 5 vol.% of cinnamaldehyde (25 ml). The hydrogen flow (50 ml min^{-1}) was continuously bubbled through the solution at room temperature during 30 min in order to remove the dissolved oxygen in the solution. The structured silica reactor with carbon nanotubes was stirred at different speeds. The carbon nanotubes were strongly attached to the silica wall as no fine formation was observed during the first hour of stirring. The reactor temperature was increased from room temperature to 80 °C and the reaction was continuously monitored by gas chromatography.

SEM was carried out on a Jeol JSM-6700F working at 3 kV accelerated voltage, equipped with a CCD camera. The sample was previously coated with gold and then deposited on a standard

aluminum holder for observation. TEM was carried out on a Topcon 002B microscope working under 200 kV accelerated voltage and with a point-to-point resolution of 0.17 nm. The samples were dispersed in ethanol in an ultrasonic bath and then a drop was deposited on a perforated carbon coated copper grid for examination.

3. Results and discussion

After synthesis the surface of the silica tube was covered by a dense and homogeneous layer of aligned carbon nanotubes on both sides of the silica reactor with various thicknesses depending on the synthesis time. Low magnification SEM micrographs show the aligned carbon nanotubes with a thickness approaching almost 1200 μm (Fig. 1A). High magnification SEM micrographs show that the carbon nanotubes exhibit a highly anisotropic orientation along the growth axis despite the fact that the alignment varies slightly along the tube height. The base and the middle of the carpet consisted of carbon nanotubes well aligned along the growth axis (Fig. 1B). The alignment was less perfect when approaching the top of the carpet and the carbon nanotubes adopt a wave-like structure. The average diameter of the formed carbon nanotubes was around 60 nm. Statistical

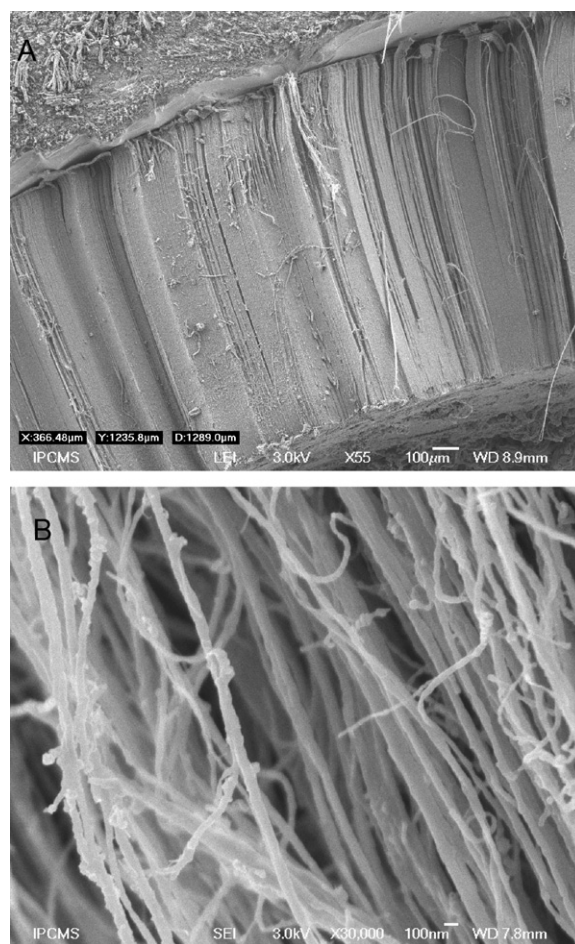


Fig. 1. (A) Sheet of parallel carbon nanotubes forest with a height of 1200 μm grows on the inner surface of the silica reactor. (B) High magnification SEM micrograph showing the perfect alignment of the tube and the average diameter.

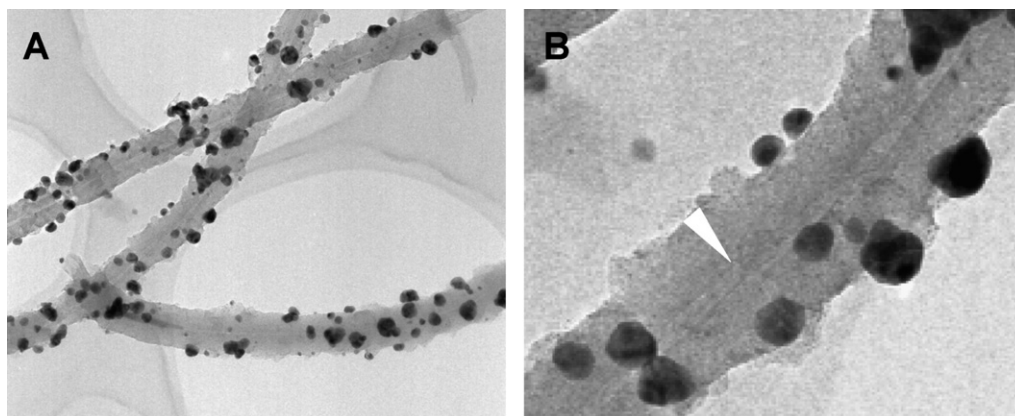


Fig. 2. (A) TEM micrographs of the palladium supported on carbon nanotubes catalyst with different magnifications. Note the relatively narrow channel of the carbon nanotubes synthesized by ferrocene pyrolysis (indicated by arrow in B).

SEM observation reveals that the carbon nanotubes were grown almost perpendicularly to the silica surface.

The silica contained carbon nanotubes layer was purified by heating in an aqueous solution of HNO_3 at 80°C overnight in order to remove as much as possible of the iron catalyst. It is noteworthy that the carbon nanotubes anchorage on the silica wall was extremely strong as no tubes loss has been observed during the acidic treatment and sonication. During the treatment in boiling nitric acid, oxygen-containing surface groups were incorporated according to the XPS spectra, where a large amount of oxygenated groups (CO- , COO- , etc.) was detected on the carbon nanotubes surface (not shown). The presence of these oxygenate groups will modify the hydrophobic and inert character of the material and thus, render it more suitable to be used as catalyst support material [25]. The decrease of the hydrophobic character by introduction of the oxygen-containing surface groups will increase the wettability of the support surface by the impregnated solution and provide the anchorage sites for the active phase precursor and the active phase itself after thermal treatment on the carbon nanotubes surface.

The microstructure of the as-synthesized carbon nanotubes, after acidic treatment, was also observed by TEM. Low magnification TEM micrographs confirm the parallel orientation of the as-synthesized carbon nanotubes despite the grinding and sonication for preparing the sample for the TEM observation (not shown). TEM results also confirm the extremely homogeneous diameter of the formed CNTs, ca. 60 nm, with a length greater than several hundred micrometers leading to an aspect ratio (length-to-diameter ratio) of more than 5000.

The purified sample was further impregnated with an aqueous solution of palladium nitrate. Part of the attached carbon nanotubes containing palladium particles was removed from the silica reactor wall for TEM analysis. The TEM micrograph demonstrates the formation of homogeneous and small palladium particles on the surface of the carbon nanotubes (Fig. 2). The palladium particles randomly decorate the surface of the carbon nanotubes according to the TEM micrograph in Fig. 2A. The average palladium particle size deduced from statistical TEM analysis ranged between 10 and 15 nm. TEM observation indicates that the metal has a well-defined geometrical

shapes which bears witness to the existence of metal–support interactions.

The palladium average particle size observed in the present work was slightly higher than that obtained in previous work. Indeed, earlier results reported in the laboratory on the palladium supported on commercial carbon nanotubes system have demonstrated the high interactions between the deposited palladium particles and the tube surface leading to high palladium dispersion with an average particle size of ca. 5 nm [26,27]. The lower palladium dispersion on the aligned CNTs could be attributed to the higher graphitization of the tubes synthesized at 800°C , with lower surface reactivity despite the presence

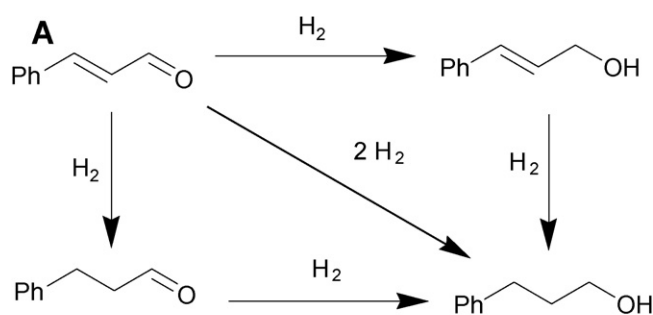


Fig. 3. (A) Simplified reaction pathways of the hydrogenation of cinnamaldehyde. The products reactions are the hydrocinnamaldehyde, the cinnamyl alcohol and the 3-phenyl-1-propanol. (B) Optical image showing the fixation of the catalyst which was subsequently used as stirrer.

of the functional groups as evidenced by XPS analysis (not shown).

The hydrogenation of cinnamaldehyde is a parallel and consecutive reduction of different functional groups present in the same starting substrate, i.e. C=C hydrogenation leading to the formation of the hydrocinnamaldehyde and C=O hydrogenation leading to the formation of the unsaturated alcohol [22,28–30]. The simplified reaction pathway of the hydrogenation of cinnamaldehyde is presented in detail in Fig. 3A.

The silica reactor containing the aligned carbon nanotubes carpet was directly attached to the glass rod and used as a stirrer for the reaction (Fig. 3B). The great advantage of such a system design is the ease in catalyst-products separation and handling of the catalyst compared to traditional powder catalysts, where post-reaction filtration is needed to recover the catalyst from the reaction liquid medium.

The experiments were carried out at least twice in order to check the reproducibility of the catalytic and experiment setup.

The liquid-phase hydrogenation activity obtained at 80 °C on the Pd/aligned-CNTs as a function of time on stream and stirring speed is presented in Fig. 4. According to previous results obtained on the system, the C=C bond hydrogenation was the fastest reaction leading to the formation of hydrocinnamaldehyde. The secondary reaction, i.e. total hydrogenation, also occurred but was several times lower, leading to an extremely high selectivity of hydrocinnamaldehyde of >90% (Fig. 4B). Apparently, on the palladium surface the adsorption occurs mainly through the C=C bond, in good agreement with the literature results [26]. A slight increase in the conversion as a function of time on stream was observed when the stirring speed was increased from 150 to 250 rpm (Fig. 4A). At higher stirring speed, i.e. 350 rpm, almost no activity change was observed.

The extremely high selectivity towards the C=C bond hydrogenation was interesting takes into account the possibility that cinnamaldehyde may be hydrogenated into several compounds. It is noteworthy that cinnamyl alcohol was never observed in any case, indicating that on the palladium supported on carbon nanotubes, the adsorption of the C=O bond is almost lacking.

The difference in the selectivity could be attributed to several factors: (i) the existence of a peculiar metal–support interaction between the palladium metal crystallites and the carbon nanotubes surface, i.e. electronic interaction which in turn modifies the adsorption and selectivity of the products. Generally, the use of a graphitic carbon support has been shown to be very effective for modifying the catalytic properties of the supported metals due to the existence of electronic interactions between the metal and the π -electrons of graphite [31–33]; (ii) the complete absence of any microporosity as found on the activated charcoal or ink-bottled pores in traditional supports and the high external surface area of the carbon nanotubes-based support which strongly modify the residence time of the reactants and products and their desorption behavior; (iii) the difference on the surface acidity, i.e. oxygenate groups, compared to those present on the other supports surface. Toebes et al. [34] have recently reported that the hydrocinnamaldehyde formation can be highly enhanced by removing the oxygenated groups present on the carbon nanofibers surface-based catalyst.

Fig. 5 reports the evolution of the hydrogenation products selectivity as a function of the total conversion on the tested catalysts. According to these results the C=C bond hydrogenation selectivity was extremely high, i.e. >80%, on the Pd supported on aligned multi-walled carbon nanotubes array, regardless of the level of conversion. It seemed that the first hydrogenation product, i.e. hydrocinnamaldehyde, was rapidly desorbed from the active site and no further transformation occurred, leading to a high selectivity. It is noteworthy that the hydrocinnamaldehyde selectivity observed here is among the highest value reported up to now in the literature [23,24,26]. The formation of a relatively high amount of the total hydrogenated product, 3-phenyl-1-propanol (PP), was observed at low conversion and could be attributed to the peculiar adsorption mode of the cinnamaldehyde on a certain face of the palladium particle. Palladium has a cubic face-centered (fcc) structure with two main orientations of (200) and (111). According to the theoretical calculation of Delbecq and Sautet [35] the (111) face of palladium favors the simultaneous adsorption of the C=C and C=O bonds of the

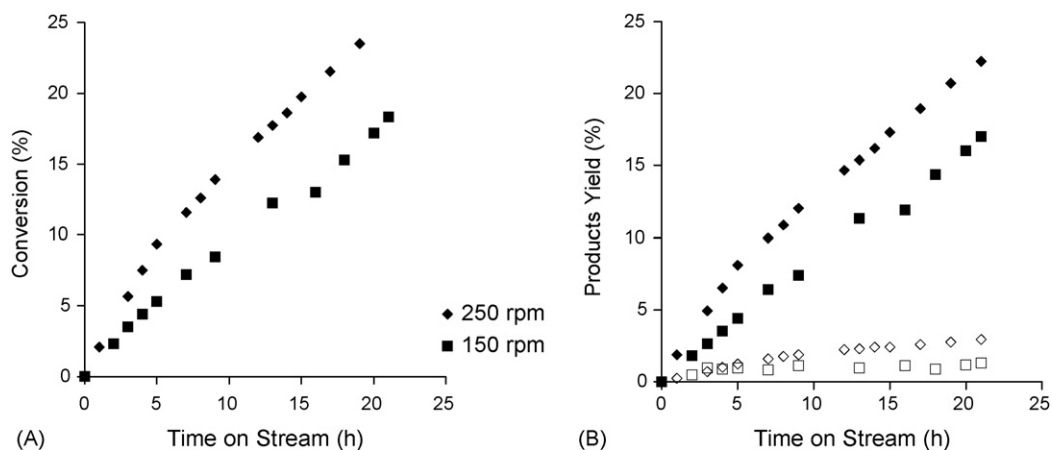


Fig. 4. (A) The hydrogenation activity and (B) selectivity expressed in terms of conversion, and the products yield in the liquid-phase hydrogenation of cinnamaldehyde on the Pd/carbon nanotubes catalyst. Reaction temperature, 80 °C, hydrogen flow rate: 50 ml min⁻¹, stirring speed: 150 and 250 rpm. Hydrocinnamaldehyde (■ and ◆) and 3-phenyl-1-propanol (◇ and □).

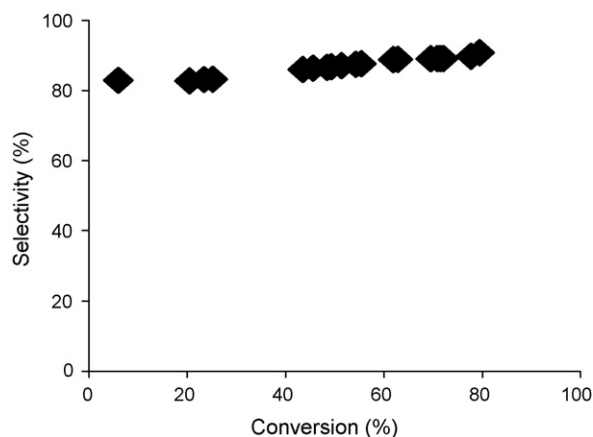


Fig. 5. Selectivity vs. conversion for the palladium supported on the carbon nanotubes with aligned pattern anchored on the silica wall reactor. The conversion was obtained by varying either the amount of catalyst or the concentration of the cinnamaldehyde in the reactor. The reaction was carried out at 80 °C with a stirring rate of 250 rpm and a flow rate of hydrogen of 50 ml min⁻¹.

reactant which led to the formation of the total hydrogenated product instead of hydrocinnamaldehyde. However, it has also been reported by the authors that due to kinetic reason only the C=C bond hydrogenation occurred, instead of simultaneous hydrogenation.

Finally, it is interesting to note that the hydrogenation activity remains extremely stable as a function of the running cycles indicating that no deactivation, either by palladium loss or support breakage, was occurred during the different catalytic cycles. This observation pointed out the superior properties of the aligned carbon nanotubes on macroscopic substrate for their use as catalyst support, especially in liquid-phase reactions.

4. Conclusion

In conclusion, it has been shown that silica supported aligned carbon nanotubes can be efficiently employed as a macroscopic catalytic structured reactor for liquid-phase reactions with nanoscopic properties. The nanoscopic support confers to the catalyst a high external surface area and allows the rapid diffusion of the reactants towards the active sites. The carbon nanotubes were strongly attached on the surface of the silica reactor according to the sonication treatment in an acidic medium. The CNTs/SiO₂ tube was directly used as mechanical stirrer for the reaction and the strong anchorage of the tubes prevent any fine formation during the catalytic test, which could be detrimental for the recovery of the products. The macroscopic shaping allows the easy separation of the catalyst and products at the end of the test without any need for filtration, as is usually encountered with a traditional powder catalyst.

The relatively high catalytic activity observed was attributed to the high external surface area and the absence of the ink-bottled pores inside the support which strongly reduced the diffusional problems. The existence of a strong interaction between the deposited palladium particles and the carbon nanotube surface led to the even dispersion of the palladium particles on the nanotube surface. The selectivity towards the hydrocinn-

amaldehyde, i.e. C=C bond hydrogenation, remained high and constant regardless of the level of conversion, i.e. selectivity of 90% at a conversion of about 80%. The observed results highlighted the peculiar properties of carbon nanotubes as a catalyst support compared to those usually encountered with traditional supports such as alumina, silica or activated charcoal. The possibility to prepare these carbon nanotubes in a macroscopic shape with high anisotropy also opens a new route for their use in the catalysis field and reduce as much as possible the problems linked with their manipulation. Work is on going to check these properties for other types of reaction where the selectivity needs to be improved. The influence of the heating mode, i.e. microwaves instead of heat conduction, will also be evaluated on these 1D materials.

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