

Catalytic activity of palladium supported on single wall carbon nanotubes compared to palladium supported on activated carbon Study of the Heck and Suzuki couplings, aerobic alcohol oxidation and selective hydrogenation

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Abstract

Nanoparticles (2–10 nm) of palladium have been deposited on single wall carbon nanotubes (SWNT) by spontaneous reduction from Pd(OAc)₂ or from oxime carbapalladacycle. These catalysts exhibit higher catalytic activity than palladium over activated carbon (Pd/C) for the Heck reaction of styrene and iodobenzene and for the Suzuki coupling of phenylboronic and iodobenzene. This fact has been attributed as reflecting the dramatic influence of the size particle on the activity of the palladium catalyst for C–C bond forming reactions as compared to other reaction types less demanding from the point of view of the particle size. Thus, in contrast to the Heck and Suzuki reactions, Pd/C is more active than palladium nanoparticles deposited on SWNT for the catalytic oxidation by molecular oxygen of cinnamyl alcohol to cinnamaldehyde and for the hydrogenation of cinnamaldehyde to 3-phenylproprionaldehyde.

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1. Introduction

Since their discovery by Iijima [1,2], there has been a considerable interest in exploring the applications of the remarkable structural, physical and chemical properties of single wall carbon nanotubes (SWNT) in all areas of physics and material chemistry. Most of the efforts have been focused on nanotechnology trying to exploit the mechanical strength [3–5] and metallic conductivity [5–10] of different kinds of SWNT as well as the possibility to functionalize covalently SWNT to obtain advanced materials [11–13].

SWNT have also been used in heterogeneous catalysis as support for noble metals [14–18]. The reports on the use of SWNT in catalysis are, however, considerably more scarce than those focused on material science and more effort is still

necessary to assess the performance of SWNT, particularly compared to widely used activated carbons. We have been involved in the use of SWNT as solid supports for catalytic reactions [19]. Our interest comes from the consideration of the importance that activated carbons have as optimum supports for many reaction types including catalytic hydrogenations and oxidations. In both cases, the known ability of SWNT to adsorb gases in even higher quantities than activated carbons might be advantageous co-operating to the success of the reaction. For instance, given that the interior of the tubes is open to the exterior, there has also been a large interest in the use of SWNT for hydrogen storage [20–27].

SWNTs are, however, structurally and chemically very different from most activated carbons. SWNT have a well-defined structure formed by thin (1.3 nm) and long (>100 nm) carbon tubes of remarkable flexibility, mechanical strength and high Young modulus that agglomerate through van der Waals forces to form bundles. Purified SWNTs free from

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catalyst particles [14] are formed by an almost perfect graphene wall terminated with carboxy groups. In contrast to this remarkable periodicity, activated carbons have ill-defined structures constituted of a wide distribution of platelets of condensed aromatic hydrocarbons of different sizes and compositions connected through methylene, oxygen, nitrogen or sulfur bridges. Also depending on the source of the activated carbons, significant percentages of heteroatoms (O, N, S) and even transition metals can be present in activated carbons forming a large variety of functional groups such as phenol, quinones and sulphonic.

In the present work, we want to report the catalytic activity of palladium metal-containing SWNTs prepared by three different procedures for a series of palladium catalyzed reactions, namely the Heck and Suzuki C–C coupling, alcohol aerobic oxidation and C=C hydrogenation. Our goal is to compare the results obtained with palladium-supported SWNT with those achieved with Pd/C to establish differences on the performance between both catalysts for a series of catalytic reaction that might exhibit different demand from the point of view of particle size. Our results show indeed that the catalytic activity of palladium on SWNT exhibits a characteristic pattern that is clearly different from that of Pd/C, the former system being specially interesting from C–C cross-coupling reactions, for which palladium particle size seems to play a crucial role compared to hydrogenations and oxidations.

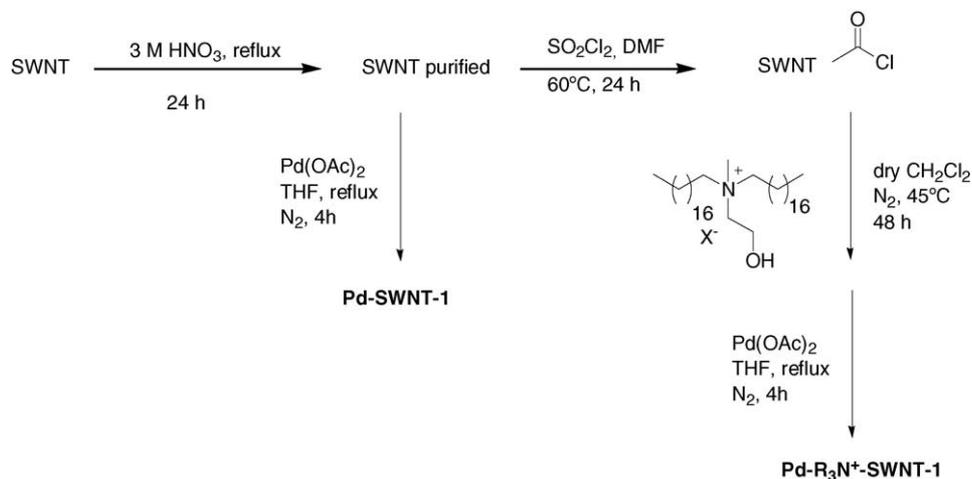
2. Results and discussion

2.1. Preparation of palladium catalysts supported on SWNT

Metal nanoparticles exhibit specific properties arising from the large surface/bulk atomic ratio. These properties are not observed in larger micrometric or submicrometric particles in where the fraction of external atoms is negligible with

respect to the number of internal atoms [28,29]. From the recent work on metal nanoparticles, it has become evident that the catalytic activity of a palladium containing catalysts depends on a large extent of the particle size, on the dispersion of the nanoparticles and on the way in which nanoparticles are stabilized against agglomeration [30–32]. Some of these properties are determined by the preparation procedure and controlled in a certain extent by the support. The preparation procedure is crucial to obtain particles of the nanometric size with adequate stability and dispersion. In the present work, we have prepared three types of SWNT supported palladium metal catalysts in where two precursors of the palladium metal have been used or in where the SWNT has been conveniently functionalized to introduce a covalently bonded quaternary ammonium stabilizer [33].

A commercial sample of HiPCO single wall carbon nanotube normally contains rest of the solid catalyst particles used for the synthesis of the SWNT from organic molecules. The typical purification procedure consists on treating the SWNT sample with concentrated aqueous solution of nitric acid at 100 °C for long times. After purification, the absence of catalyst particles can be simply assessed by thermogravimetric analysis (TGA) where the complete burning of the material should be observed and also by elemental analysis in where a high C content should be measured. In our case, TGA after purification shows no residue and at the same time the chemical analysis of ambient-equilibrated purified SWNT (still containing some humidity) show a carbon content about 80%, the remaining percentage being attributed to adsorbed water from the ambient. The simplest preparation procedure consists in contacting SWNT with a solution of palladium acetate. In the literature, it has been reported that upon contacting platinum or gold salts with SWNT a spontaneous reduction occurs forming the corresponding metal nanoparticles distributed along the carbon nanotubes [34]. A electrochemical current can be measured during the reduction. Although we have not been able to find an analogous report using palladium salts, it could be easily anticipated



Scheme 1. Synthetic route followed to obtain the SWNT-supported palladium catalyst Pd-SWNT-1 and Pd-R₃N⁺-SWNT-1.

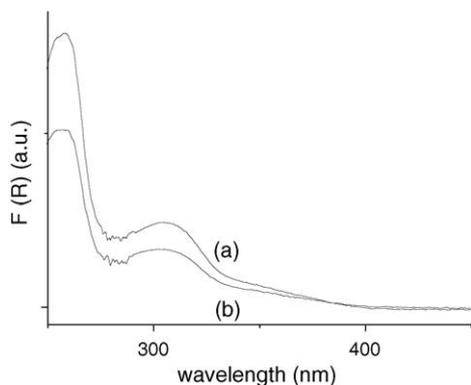


Fig. 1. Transmission UV–vis spectrum of a solution of the oxime carbapalladacycle complex (0.03 mmol) in THF (10 mL) before (a) and after treated at reflux temperature with SWNT (50 mg) for 24 h. The decrease in intensity is associated to decomposition of the complex and formation of palladium metal particles on the SWNT.

that palladium salts would exhibit a similar behaviour. In fact, we have been able to obtain palladium nanoparticles upon contacting $\text{Pd}(\text{OAc})_2$ with SWNT, this simple procedure leading to the first Pd-SWNT-1 catalyst used in this work (Scheme 1). The following pieces of evidence support that the palladium salt has been reduced upon contacting a solution of palladium complex with SWNT: (i) the reduction peak potential of Pd^{2+} in THF (versus standard hydrogen electrode (SHE)) measured by us by cyclic voltammetry was 0.466 V for $\text{Pd}(\text{OAc})_2$ and 0.509 V for carbapalladacycle oxime; (ii) the reported work function of SWNT [34] is -5.0 V in vacuum giving an energy of the Fermi level high enough to effect the reduction of Pd^{2+} and (iii) the characteristic UV-absorption band of Pd^{2+} in the oxime carbapalladacycle complex disappears gradually upon contacting a solution of this complex and SWNT (see Fig. 1). All these facts are compatible with the spontaneous reduction of Pd^{2+} to Pd(0) with formation of metallic Pd particles, as it was reported for platinum and gold.

Alternatively, spontaneous Pd^{2+} reduction starting from $\text{Pd}(\text{OAc})_2$ was also accomplished on a modified SWNT in which the carboxylic acid groups present on the tips and defects of the tubes had been functionalized with long-chain quaternary alkyl ammonium ions, namely dicetyl methyl (2-hydroxyethyl) ammonium chloride ($\text{Pd-R}_3\text{N}^+$ -SWNT-1). The covalent linkage between the SWNT and the quaternary ammonium ion was accomplished through esterification of the 2-hydroxyethyl group of ammonium salt and the carboxylic groups. The actual steps of the synthesis are

also indicated in Scheme 1. The beneficial influence of long-chain alkyl quaternary ammonium in the stabilization of noble metal nanoparticles in colloidal solutions has been established [35–37]. Stabilization of nanoparticles in suspension may be probably different from stabilization of nanoparticles on solid surfaces, our aim was to test whether or not the incorporation of these quaternary ammonium units on the SWNT plays an analogous role as in solution stabilizing the Pd nanoparticles supported on the nanotube. The stabilization of the particle size could be reflected in the catalytic performance of the material. Although most of the positive influence of the presence of long-chain alkyl ammonium deals with colloids without any support, it has been observed in other cases that the presence of quaternary ammonium salts as additives play a beneficial influence on the catalysts using supported metal particle.

In the third related catalyst based on SWNT (Pd-SWNT-2), the precursor of palladium metal cluster was an organometallic oxime carbapalladacycle complex (Scheme 2). This complex is easily available by reacting in methanol Li_2PdCl_4 with 4-hydroxyacetophenone oxime [38–42]. This palladium complex has been used as a highly active pre-catalyst to generate palladium nanoparticles. The higher stability of palladium in the complex as compared to free Pd^{2+} from $\text{Pd}(\text{OAc})_2$ may have a positive influence on the palladium particle size and on the dispersion of the clusters. As expected in view of the behaviour of $\text{Pd}(\text{OAc})_2$, stirring a suspension of SWNT and the oxime carbapalladacycle leads to a gradual palladium reduction with formation of black palladium as indicated by the progressive decrease in the solution of the absorption band at 340 nm responsible for the yellow colour of the oxime carbapalladacycle (Fig. 1).

The series of three palladium catalysts supported on SWNT were studied by TEM. The corresponding TEM images show that the SWNT catalysts consist on bundles of thin single-walled tubes in where palladium nanoparticles are dispersed. Selected images are shown in Fig. 2. The particle size distribution was determined by a statistical analysis of a set of the images with a surface area of $500 \text{ nm} \times 500 \text{ nm}$. In the cases of Pd-SWNT-1 and Pd- R_3N^+ -SWNT-1 TEM images show that the dispersion of the palladium particles is relatively high and that there is a broad particle size distribution. Nevertheless, what is relevant for our study is the presence of nanoparticles in the range 1–10 nm. Fig. 2 also presents the particle size distribution analysis for Pd-SWNT-1 and Pd-SWNT-2. As expected, this study shows that the particle size distribution depends on a certain extent on the actual prepa-



Scheme 2. Synthetic route followed for the preparation of the SWNT-supported palladium catalyst Pd-SWNT-2.

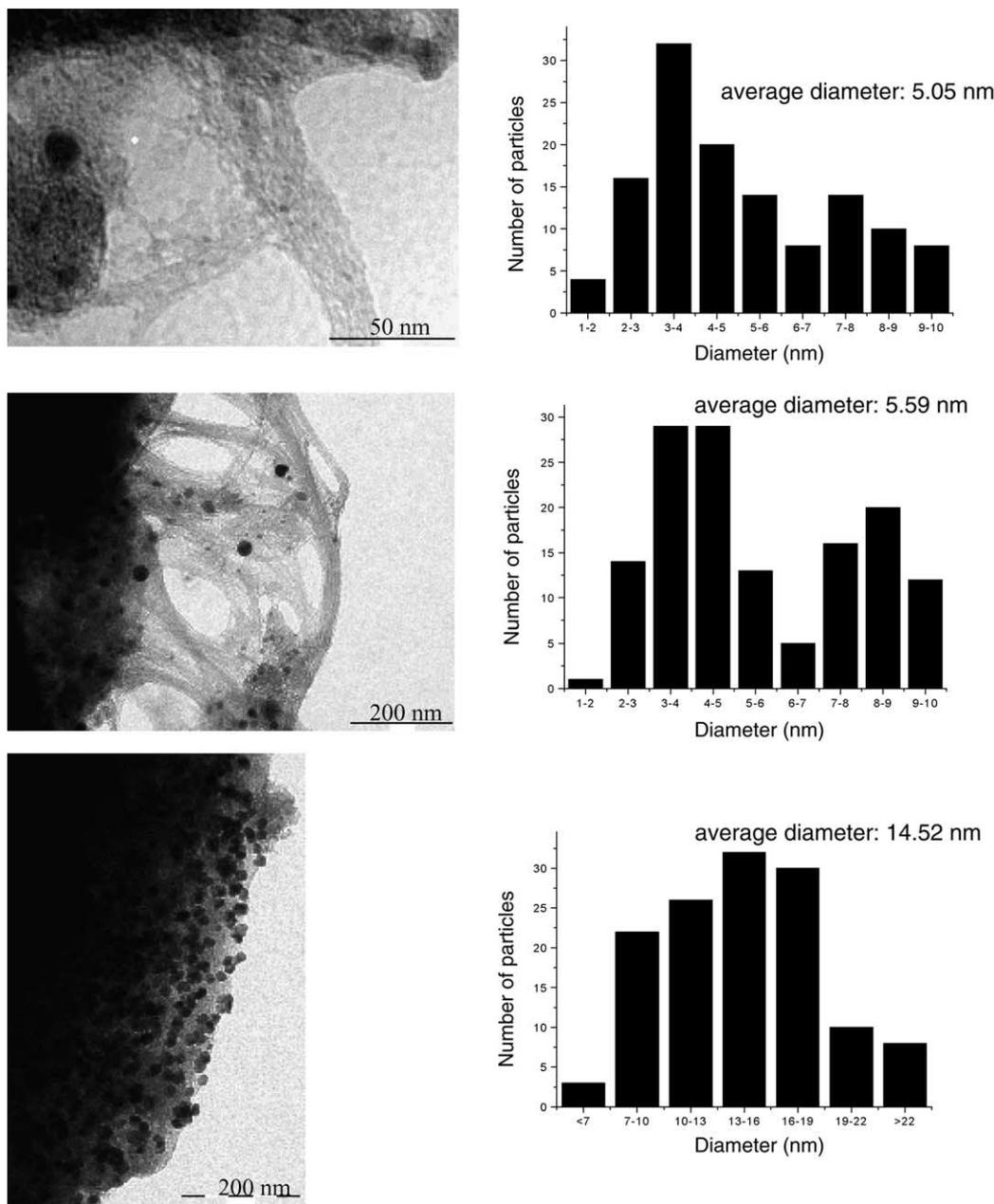


Fig. 2. Transmission electron microscopy images for Pd-SWNT-1 (top), Pd-R₃N⁺-SWNT-1 (center) and commercial Pd/C (Aldrich, 1% w/w, bottom) together with diameter size distribution of palladium nanoparticles for at least five different TEM images of Pd-SWNT-1, Pd-SWNT-2 and Pd/C. The palladium nanoparticles (<2–3 nm) appear as little dark dots together with some palladium cluster (>10 nm).

ration procedure (see Fig. 2). This TEM study agrees with the previous report on the spontaneous reduction of noble metals on SWNT and overall confirms the nanometric size of palladium metal particles formed on SWNTs. It is expected that this different particle size distribution could be reflected in differences in the catalytic activity for some reactions.

For the sake of comparison, we have carried out an analogous TEM study of commercial Pd/C (Fig. 2). TEM analyses showed that the particle size distribution for Pd/C is significantly broader with a considerable number of Pd particles larger than in Pd-SWNTs. Although a more deep understand-

ing of the reduction process on SWNT is still needed, a likely rationalisation of the smaller particle size using SWNT as support can be put forward based on the presence of carboxylic acid groups. Carboxylate groups would establish a Coulombic interaction with Pd²⁺ analogous to other known metal ion–carboxylate complexes, followed by a subsequent controlled reduction by the electrons of the SWNT walls. In the case of activated carbons, the presence of a variety of different functional groups that interact differently with metal ions would lead to a less homogeneous initial distribution of Pd²⁺ with formation of larger agglomerates.

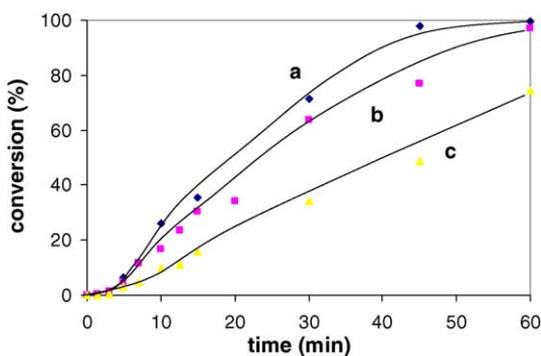
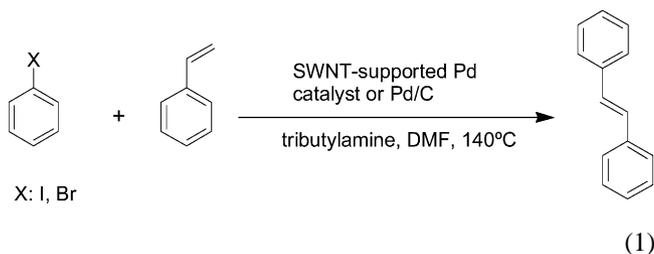


Fig. 3. Time conversion plot for the Heck reaction of iodobenzene (1 eq.), styrene (1.5 eq.) and tributylamine (2 eq.) in DMF (5 mL) at 140 °C in the presence of Pd-SWNT (a), Pd-R₃N⁺-SWNT-1 (b) and Pd/C (c) (3 mg, 0.01 Pd mol%).

2.2. Catalytic activity

The palladium supported Pd-SWNT-1 and Pd-SWNT-2 catalysts showed high activity for the Heck reaction of iodobenzene with styrene in DMF at 150 °C using NaAcO as base. Since the percentage of palladium metal varies in each sample of SWNT catalyst, for the sake of having a valid comparison all the reactions were carried out keeping the substrate-to-palladium molar ratio constant at 0.01 mol%. In all cases, *t*-stilbene was the only product detected (Eq. (1)). The Pd-SWNT-1 catalysts prepared from Pd(AcO)₂ exhibits the highest activity in the series and no benefits were observed when the catalysts was prepared starting from the oxime carbapalladacycle complex (Pd-SWNT-2) or by introducing covalently on the SWNT dicetylmethylammonium (Pd-R₃N⁺-SWNT-1). Fig. 3 showed the time conversion plot for this Heck reaction in the presence of SWNT-supported palladium catalysts. Importantly, the activity of Pd/C is considerably lower than those catalysts obtained using SWNT as support. This low activity of Pd/C as Heck catalyst is in agreement with previous reports in the literature [43–45] and exemplifies the influence of the support on the catalytic activity. Most likely, these results reflect the high demand of the Heck reaction for small particle size palladium particles [46–49].



When performing a reaction using a solid catalyst two important issues that need to be addressed are to determine whether or not the reaction is truly heterogeneous and the reusability of the solid catalyst. In the case of Pd-SWNT-1 and Pd-SWNT-2 catalysts, leaching of the palladium from the SWNT support to hot DMF was demonstrated by per-

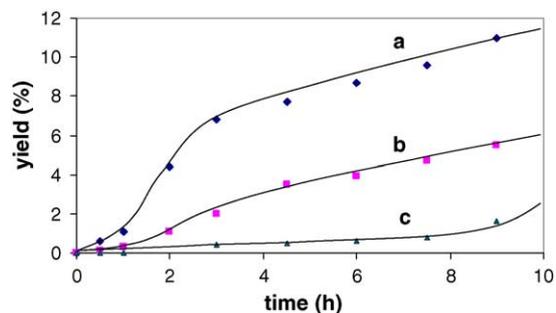


Fig. 4. Time conversion plot for the oxidation of cinnamyl alcohol (1 eq.) in ethanol (5 mL) under oxygen bubbling (flow: 25–30 mL min⁻¹) at 80 °C in the presence of Pd/C (a), Pd-SWNT-1 (b) and Pd-R₃N⁺-SWNT-1 (c) (4 mg, 0.2 Pd mol%).

forming a reaction under the typical conditions, and filtering the solid at 50% conversion while the mixture was still hot. The clear solutions were allowed to react further in the absence of the solid, whereby the same temporal profile as in the presence of the Pd-SWNT solids were observed. If the activity would have been exclusively due to the presence of the Pd-SWNT solid catalysts, the reaction would have stopped. These experiments demonstrate that under the reaction conditions in DMF, palladium nanoparticles become desorbed from the support and suspended in the liquid phase.

The extent of leaching was significantly lower when the Heck reaction is carried out in *o*-xylene using tributylamine as base instead of DMF (20% in toluene as compared to 100% in DMF). Obviously, the nature of the solvent is known to play a crucial role in the occurrence and extent of leaching from a solid to the liquid phase since the migration depends on the partition coefficient between the two phases. In previous studies on the extent of leaching on palladium complexes supported on porous silicates, it has been established that migration of palladium to the solvent is lower in toluene than in DMF [50–52].

Obviously, leaching can be a major problem when dealing with solid catalyst due to the eventual depletion of the metal content with the consequent loss in activity. However, in spite of the occurrence of the palladium leaching during the reaction, no significant decrease in the catalytic activity of the solids was observed. Maintenance of the catalytic activity can be explained by the re-deposition of most of the palladium nanoparticles on the SWNT as the reaction ends and the system cools down. This behavior is also generally observed in Pd/C systems and has been described as the “boomerang effect” [53,54].

Palladium supported on single wall carbon nanotubes were also tested as catalysts for the aerobic oxidation of cinnamyl alcohol in ethanol (Eq. (2)) and the selective C=C hydrogenation of cinnamaldehyde to 3-phenylpropionaldehyde in ethanol (Eq. (3)). The aim of this study was to determine whether or not the reported superior ability of SWNT to adsorb hydrogen and other gases with respect to active carbon could play a positive role in heterogeneous catalysis using gas reactants. Figs. 4 and 5 show selected time-conversion

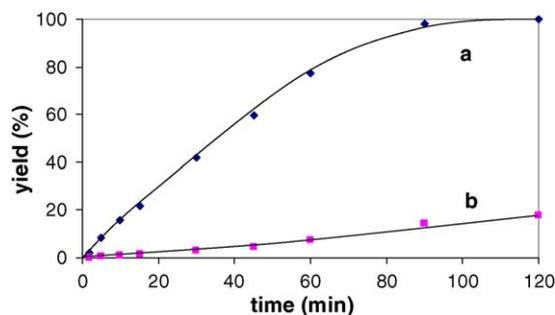
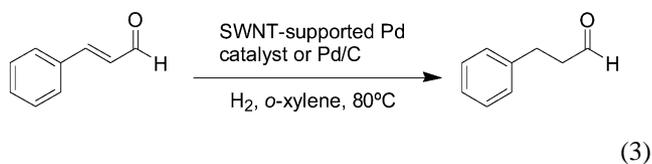
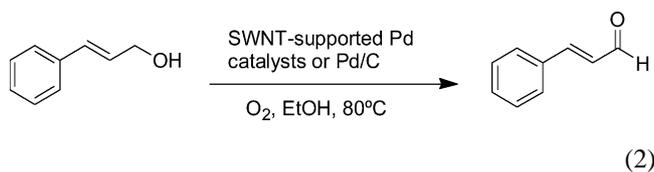


Fig. 5. Time conversion plot for the selective hydrogenation of cinnamaldehyde (1 eq.) in *o*-xylene (5 mL) under hydrogen bubbling (flow: 20 mL min^{-1}) at 80°C in the presence of Pd/C (a) Pd-R₃N⁺-SWNT-1 (b) (4 mg, 0.2 Pd mol%).

plots for these two reactions under some of the conditions studied, showing that this turns out not to be the case.



In contrast to the results observed for the C–C cross-coupling, Pd/C becomes far more active than the series of palladium supported on SWNT for both reactions, the aerobic oxidation of cinnamyl alcohol and for the C=C hydrogenation of cinnamaldehyde. Thus, although the Pd-SWNT was also able to affect the aerobic oxidation or hydrogenation, the initial reaction rate at the same substrate-to-palladium ratio is considerably lower for the Pd-SWNT catalysts than for Pd/C. In the case of hydrogenation, the difference in the reaction mechanism and the occurrence of the known hydrogen spill-over effect renders the reaction less sensitive to the particle size distribution in the length scale of the Pd-SWNT and Pd/C tested in this work [55–58]. A trend worth noting is, however, that the same relative activity in the series of Pd-SWNT was maintained and no beneficial influence of quaternary ammonium ion functionalization or of the use of an organometallic complex as precursor of the palladium metal clusters was observed.

In summary, it is well known that the activity of palladium-supported catalysts depends dramatically on the metal dispersion and the particle size. However, there are some reactions that should be more demanding than others with respect to the particle size. In particular, C–C bond coupling reactions are very demanding from the point of view of palladium particle size [46–49]. Probably for this reason, the activity of palladium nanoparticles supported

on single wall carbon nanotubes is higher than that of palladium supported on activated carbon. On the other hand, Pd/C is more effective when the reaction involves gases, presumably because these reactions are less demanding from the point of view of palladium particle size. The preparation procedure and covalent functionalization of the SWNT modifies the activity of the resulting palladium catalyst, but no improvement has been achieved with respect to the simplest procedure based on the spontaneous reduction of Pd(OAc)₂ upon contacting with the carbon nanotubes. These catalytic results can be rationalised considering the specific demands for C–C bond forming reactions in terms of small particle size as compared to hydrogenations and oxidations.

3. Experimental section

The reagents and solvents were obtained from commercial sources and were used without further purification. Gas chromatographic analyses were performed on a HP 5890 instrument equipped with a 25 m capillary column of 5% phenylmethylsilicone. GC/MS analyses were performed on a Agilent 5973N spectrometer equipped with the same column and in the same conditions as GC. ¹H and ¹³C NMR were recorded in a 300 MHz Bruker Avance instrument using CD₃OD or DMSO-d₆ as solvents and TMS as internal standard. IR spectra were recorded on a Jasco 460 plus spectrophotometer using sealed greaseless quartz cells provided with CaF₂ windows. Self-supported wafers (10 mg) were obtained by mixing the solid with KBr and pressing the mixture at 10 Ton cm^{-1} for 5 min. UV–vis spectra were recorded on a Shimadzu scanning spectrophotometer using THF as solvent. Elemental analysis of the solids was determined by chemical combustion using a Perkin-Elmer CHNSO analyzer. The Pd content of the SWNTs was determined by dispersing the solid in a mixture 1:1:1 of HF:HCl:HNO₃ concentration (2.5 mg in ca. 3 mL), diluting the solution in water and measuring by quantitative atomic absorption spectroscopy.

3.1. Procedure for the synthesis of 4-hydroxyacetophenone oxime (2)

4-Hydroxy-acetophenone (**1**) (3 g, 0.022 mol) was added to a solution of hydroxylamine hydrochloride (5.13 g, 0.074 mol) and sodium acetate (10.26 g, 0.125 mol) in water (26 mL). The solution was stirred at reflux temperature for 1 h. After that time, diethyl ether was added several times for extraction. The organic phases were dried and the solvent evaporated under vacuum. To the obtained residue, hexane was added and 1-(4-hydroxyphenyl)ethanone oxime (**2**) started to precipitate as a white solid (3.25 g, 0.0215 mol, 98%). Mp: $146\text{--}147^\circ\text{C}$; IR (KBr, cm^{-1}): 3324, 1642, 1603, 1514, 1444, 1316, 1240, 1176, 940, 825, 589. ¹H NMR δ_{H} (ppm, 300 MHz, CD₃OD): 7.49 (2H, d, $J = 5 \text{ Hz}$),

6.77 (2H, d, $J=5$ Hz), 2.18 (3H, s). ^{13}C NMR δ_{C} (ppm, 300 MHz, CD_3OD): 159.9, 156.7, 130.2, 128.9, 116.5, 12.55. MS (FAB): m/z 151. Anal. Calcd for $\text{C}_8\text{H}_9\text{NO}_2$ (151.15): C, 63.5; H, 5.95; N, 9.26. Found: C, 63.19; H, 6.22; N, 9.35.

3.2. Procedure for the synthesis of the oxime carbapalladacycle

To a solution of Li_2PdCl_4 (524.1 mg, 2 mmol) in methanol (4 mL), a methanolic solution (2 mL) of (**2**) (302 mg, 2 mmol) and sodium acetate (0.164 g, 2 mmol) was added. The mixture was stirred at room temperature for 72 h. The mixture was filtered and after adding water (5 mL), the cyclopalladated complex (**3**) starts to precipitate as a yellow solid (75%). $\text{Mp} > 250^\circ\text{C}$; IR (KBr, cm^{-1}): 3429, 1627, 1584, 1472, 1430, 1375, 1326, 1260, 1211, 1037, 873, 799, 608. ^1H NMR δ_{H} (ppm, 300 MHz, DMSO-d_6): 10.38(1H, s), 9.88(1H, s), 9.77(1H, s), 9.63(1H, s), 7.3 (2H, s), 7.15 (2H, d, $J=8$ Hz), 6.5 (2H, d, $J=8$ Hz), 2.23 (6H, s). ^{13}C NMR δ_{C} (ppm, 300 MHz, DMSO-d_6): 167.5, 157.3, 154.7, 133.1, 128.3, 122.1, 111.8, 11.6. MS (FAB): m/z 584. Anal. Calcd for $\text{C}_{16}\text{H}_{16}\text{N}_2\text{O}_4\text{Pd}_2\text{Cl}_2$ (584.04): C, 32.87; H, 2.74; N, 4.79. Found: C, 32.12; H, 2.87; N, 4.59.

3.3. Purification of the SWNT

HiPCO nanotube from Carbolex Co. (100 mg) was magnetically stirred in HNO_3 (3 M, 10 mL) at 100°C for 24 h. Then, the dispersion was centrifuged and the obtained nanotube was washed with bidistilled water (two times) and THF (two times) by centrifugation until the solution was completely transparent. Raman spectrum of purified SWNT showed the characteristic peaks at 1596, 1345 and 167 cm^{-1} , the latter corresponding to the breathing mode being specific of single walled nanotube. The thermogravimetric analysis of purified SWNT measured under air flow shows a loss of weight of 98%, indicating that no inorganic catalyst is present in the sample.

3.4. Procedure for anchoring the dicetylmethylammonium groups on SWNT

Purified SWNT (100 mg) were dispersed in thionyl chloride (25 mL) and DMF (1 mL). The mixture was placed in a pre-heated oil bath and magnetically stirred at 65°C for 24 h. Then, the chlorinated SWNT was isolated by filtration through a PTFE membrane filter (pore diameter: 0.2 nm) under vacuum, washed with dry CH_2Cl_2 (50 mL) and quickly placed in a previously dry round-bottomed flask that contains a solution of dicetyl-2-hydroxyethylmethylammonium chloride (1 g, 2 mmol) in dry CH_2Cl_2 (5 mL) under argon atmosphere at room temperature. Then, pyridine (0.5 mL, 6.45 mmol) was added and the dispersion was heated at 45°C for 48 h under nitrogen atmosphere. The functional-

ized SWNT was filtered through a PTFE membrane filter (pore diameter: 0.2 nm) under vacuum and Soxhlet-extracted with CH_2Cl_2 for 6 h. Raman peaks as purified SWNT. Loss of weight by TGA: 88%. Elemental analysis of ambient-equilibrated SWNT: C 79.62% H 3.21% N 1.39%. Ammonium groups loading: 0.5 mmol g^{-1} .

3.5. Deposition of palladium nanoparticles on purified or functionalized SWNTs using $\text{Pd}(\text{OAc})_2$ as palladium source

Following the procedure reported by Reetz and co-workers, $\text{Pd}(\text{OAc})_2$ (5.6 mg, 0.025 mmol) was dissolved in anhydrous THF (9 mL) and 3 mL of this yellow solution were filtered using a glass syringe coupled with a swinney 13 mm filter (Millipore) through a PTFE membrane filter (pore diameter: 0.2 nm) to remove any insoluble palladium species, and magnetically stirred in a pre-heated oil bath at reflux temperature for 4 h under nitrogen atmosphere in the presence of 50 mg of purified SWNT (Pd-SWNT-1) or functionalized SWNT (Pd:ammonium salt molar ratio 1:3, Pd- R_3N^+ -SWNT-1). After this time the stirring was stopped and a clear supernatant was observed. The Pd/SWNTs were filtered through a PTFE membrane filter (pore diameter: 0.2 nm), washed with anhydrous THF (100 mL) and dried. Raman peaks as purified SWNT. Loss of weight by TGA: 88% (Pd-SWNT-1). Palladium analysis: 0.149 mmol g^{-1} (Pd-SWNT-1) and 0.136 mmol g^{-1} (Pd- R_3N^+ -SWNT-1).

3.6. Deposition of palladium nanoparticles on purified SWNT using the carbapalladacycle oxime complex as palladium source

A dark yellow solution of the carbapalladacycle complex (8.7 mg, 0.03 mmol) anhydrous THF (10 mL) was magnetically stirred in a pre-heated oil bath at reflux temperature under nitrogen atmosphere in the presence of 50 mg of purified SWNT (Pd-SWNT-2). The course of the reaction was periodically followed by stopping the stirring and taken aliquots (100 μL) that were diluted in THF (c.a. 3 mL) and monitored by UV spectroscopy. After 48 h, the Pd/SWNT was filtered through a PTFE membrane filter (pore diameter: 0.2 nm), washed with anhydrous THF (100 mL) and dried. Raman peaks as purified SWNT. Loss of weight by TGA: 82%. Palladium analysis: 0.537 mmol g^{-1} (Pd-SWNT-2)

3.7. Procedure for the measurement of the reduction potential peaks for palladium compounds

A solution of $\text{Pd}(\text{OAc})_2$ (6.7 mg, 0.03 mmol) or carbapalladacycle complex (8.7 mg, 0.03 mmol) in dry THF (50 mL) was magnetically stirred under N_2 atmosphere in the presence of the corresponding platinum working electrodes, using a KCl saturated calomel electrode (SCE) as reference ($E^0(\text{V})$)

versus SHE = 0.2412) and a computer controlled potentiostat. The voltammetry was performed at a rate of 50 mV min⁻¹.

3.8. Typical procedure for C–C coupling reactions

Pd-SWNT-1 (3 mg) was placed in a double-necked round-bottomed flask and iodobenzene (496.8 μL, 4.44 mmol), styrene (765.1 μL, 6.69 mmol), tributylamine (2.014 mL, 8.92 mmol) and DMF (5 mL) were added (0.01 Pd mol%). For other catalysts, the amount of solid was maintained (3 mg) while the amount of reagents and solvent was varied to keep the substrate-to-palladium molar ratio constant. The resulting suspension was placed in a preheated oil bath at 140 °C with magnetic stirring. After stopping the stirring, 50 μL samples of the supernatant were periodically taken and analysed by GC. At 1 h, the reaction was cooled for 15 min and CH₂Cl₂ (10 mL) was added. The mixture was stirred for 5 min, filtered through a PTFE membrane filter (pore diameter: 0.2 nm) and the solid washed (100 mL of CH₂Cl₂) and dried. All the products were characterized by comparison with pure samples and GC–MS.

3.9. Typical procedure for oxidation of cinnamyl alcohol

A solution of cinnamyl alcohol (32.5 mg, 0.242 mmol) in ethanol (5 mL) was magnetically stirred in a pre-heated oil bath at 80 °C in the presence of 4 mg of purified SWNT (Pd-SWNT-1, 0.2 Pd mol%). Then, oxygen (flow: 25–30 mL min⁻¹) was bubbled into the solution. The course of the reaction was periodically followed by stopping the stirring and taken aliquots (50 μL) that were quickly cooled and analyzed by GC. All the products were characterized by comparison with pure samples and by GC–MS.

3.10. Typical procedure for hydrogenation of cinnamaldehyde

A solution of cinnamaldehyde (35.9 mg, 0.272 mmol) in *o*-xylene (5 mL) was magnetically stirred (400 rpm.) in a pre-heated oil bath at 80 °C in the presence of 4 mg of functionalized SWNT (Pd-R₃N⁺-SWNT-1, 0.2 Pd mol%). Then, hydrogen (flow: 20 mL min⁻¹) was bubbled into the solution. The course of the reaction was periodically followed by stopping the stirring and taken aliquots (50 μL) that were quickly cooled and analyzed by GC. All the products were characterized by comparison with pure samples and by GC–MS.

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