One-step microwave synthesis of palladium-carbon nanotube hybrids with improved catalytic performance

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Abstract

A fast and easy one-step linker-free approach for the synthesis of palladium nanoparticle/multiwall carbon nanotube (Pd-NP/MWCNT) hybrid materials is described using microwave irradiation for the effective decomposition of Pd_2dba_3 complex in the presence of MWCNTs. High loadings of Pd nanoparticles (up to 40 wt.%) having sizes between 3 and 5 nm are deposited on the surface of MWCNTs within a time of only 2 minutes. The Pd-NP/MWCNT materials serve as efficient catalysts in C-C coupling as well as in hydrogenation reactions, all characterized by high conversion rates using a small amount of catalysts, high turnover frequency values and good recyclability.

1. Introduction

The incorporation of metallic nanoparticles on solid supports of different nature has received great interest from the scientific community during the last years, due to the promising applications and properties of these materials [1-6]. A wide range of metals, such as are gold [2], platinum [3], ruthenium [3], rhodium [4], palladium [5] or copper

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[6], reaction media (e.g. supercritical fluids [1], ionic liquids [3]) and supports (e.g. carbon nanofibers [4] and nanotubes [7]) have been used. In all cases the goal in this binomial is the achievement of a fair compromise between improved efficiency and ease of synthesis. Of particular interest are Pd-NPs deposited on carbon nanotubes (CNTs) for applications ranging from hydrogen storage to catalysis [8-15]. In this sense, we recently studied the properties of Pd-NPs anchored on single-walled carbon nanotubes, SWNTs, for its suitability as H_2 sensors [8], or materials for hydrogen storage [9,10]. However, while the expected properties of these materials are exciting, their synthesis could be somewhat complicated. Several disadvantages of most reported methods are the required pretreatment of the carbonaceous support, for instance with strong acids [11], ionic liquids [12], surfactants [13], specific solvents [14], or reagents [15], in order to functionalize the surface of the CNTs. In addition, the deposition methods of the metals imply the use of unstable metallic starting materials [16], reducing atmospheres [17], or tedious synthetic procedures [18]. In this respect, simplified methods of synthesis of hybrid NP/CNT materials with improved catalytic properties are highly desirable.

In this paper we report the easy synthesis of the Pd-NP/MWCNT hybrid materials based on microwave irradiation. This method produces the desired materials in short reaction times using commercial MWCNT and a stable Pd(0) source. We further show that the obtained materials show excellent catalytic activity in Heck and Suzuki C-C couplings, as well as in hydrogenation reactions, without the presence of any added ligand. Very high conversions in short reaction times have been attained under microwave conditions in C-C couplings, and a good recyclability of the catalyst is observed.

2. Experimental

2.1 General procedures

MWCNTs were obtained from Nanocyl Co, Belgium (Nanocyl™ NC7000, 90 % carbon purity). All reagents were purchased from Aldrich. Solvents were dried using standard procedures before use. Infrared spectra (4000-200 cm^{-1}) were recorded on a Perkin-Elmer Spectrum One spectrophotometer. ^1H and $^{13}C\{^1H\}$ NMR spectra were recorded in CD_2Cl_2, $CDCl_3$ or acetone-d_6 solutions at 25 °C on Bruker Avance-300 and Avance-400 spectrometers (δ, ppm; J, Hz), and referenced using the solvent signal as internal standard. ESI/APCI mass spectra were recorded using an Esquire 3000 ion-trap mass spectrometer (Bruker Daltonic GmbH, Bremen, Germany) equipped with a standard ESI/APCI source. Samples were introduced by direct infusion with a syringe pump. Other mass spectra (MALDI-DIT) were recorded from CH_2Cl_2 solutions on a Bruker MicroFlex spectrometer. The complex $Pd_2(dba)_3{\cdot}CHCl_3$ (dba = *trans,trans*-dibenzylideneacetone) was obtained using reported procedures [19].

2.2 Synthesis of the Pd-NP/MWCNT hybrid materials

2.2.1 Conventional Heating

The Pd-NP/MWCNT hybrid materials were prepared by refluxing (115 °C) 100 mg of MWCNTs with different weight ratios of $[Pd_2(dba)_3{\cdot}CHCl_3]$ in dry toluene (20 mL) under argon atmosphere. After the reaction time (usually 90-120 min) the characteristic deep purple color of the Pd complex was not longer visible and a yellow color is observed on standing, due to free dba. Once cooled, the suspension was centrifuged at 4000 rpm for 10 min and the resulting solution discarded. The solid was re-suspended in toluene (20 mL) and filtered. The black solid was washed with CH_2Cl_2 (5 mL) and water (15 mL) in order to remove all residual free dba, and dried at 110 °C for a day. Several MWCNT:Pd-compound weight ratios were prepared (10:1, 1:1, 1:2, 1:3 and 1:6), and the respective materials called [Pd-**n**], (**n** = 0, 1, 2, 3, 6). Reaction was scaled up to 500 mg of MWCNTs, and reproducible yields were obtained.

2.2.2 Microwave irradiation

A similar procedure was followed for the microwave deposition by using a CEM^{TM} S-class Microwave Synthesis System. Experiments were performed at 110 °C (15-20 W) under nitrogen atmosphere. Reaction was completed after just 2 minutes of microwave heating. Materials with different MWCNT:Pd-compound weight ratios were prepared: 10:1, 1:1, 1:2, 1:3 and 1:6. The work-up of this reaction until the isolation of the hybrid materials [Pd-**0**], [Pd-**1**], [Pd-**2**], [Pd-**3**] and [Pd-**6**] was the same as the above described.

2.3 Characterization of the Pd-NP/MWCNT hybrid materials

The existence of Pd(0) throughout the samples was confirmed by XRD measurements, which were performed on a Bruker D8 Advance diffractometer using a Cu tube as X-ray source (λCuKα=1.54 Å) a tube voltage of 40 kV, and a current of 40 mA. To calculate the particle size average, the results were analyzed with the profile fitting TOPAS 2.1 in Bragg-Brentano geometry in the range 2θ = [3°-60°], with steps of 0.05° and 3s accumulation time. The metal loading in the MWCNT samples was determined by Inductive coupled plasma spectroscopy (ICPS) using a Jobin-Ybon 2000 Ultrace Analyzer. Size and distribution of Pd-NPs were studied by transmision electron microscopy (TEM), using a JEOL-2000 FXII equipment working at 200 kV. Samples were dispersed in ethanol in ultrasound bath for 10 min, and a drop of the suspension was placed onto a copper grid coated with carbon film. Raman spectra were recorded with a Horiba Jobin Yvon HR800 UV spectrometer using an excitation wavelength of 532 nm. Thermal stability was analyzed by thermogravimetric analysis (TGA) using a Setaram 92-16.18.

2.4 Catalytic Activity of the Pd-NP/MWCNT hybrid materials

2.4.1 Catalytic C-C coupling between iodobenzene and methylacrylate

A variable amount of the Pd-NP/MWCNT catalyst, corresponding to a percentage of palladium of 1, 0.1, 0.01, and 0.005 mmol% with respect to iodobenzene, was dispersed in acetonitrile (5 mL) under argon atmosphere, and methylacrylate (1.62 mmol, 144 µL), iodobenzene (1.41 mmol, 157 µL) and triethylamine (1.7 mmol, 237 µL) were added. The resulting mixture was stirred and exposed at microwave radiation (20 W) at 140 °C during 15 min (optimized conditions). After cooling to room temperature, the mixture was filtered through a 3 µm pore polycarbonate membrane filter, in order to separate the catalyst. The Pd-NP/MWCNT material was washed with CH_2Cl_2 and water and dried at 110 °C during at least 1 day. The solution containing the organic product was evaporated to dryness, and the residue dissolved in water (20 mL). The aqueous solution was extracted with CH_2Cl_2 (10 mL) three times. The combined organic extracts were evaporated to dryness, and methylcinnamate was obtained as a white solid, which was purified by crystallization from pentane (5 mL).

2.4.2 Catalytic C-C coupling between iodobenzene and phenylboronic acid

Sodium phosphate (1.23 mmol, 250.4 mg) was dissolved in 5 mL of a 4/6 ethanol/water mixture with heating. Then the corresponding amount of the Pd-NP/MWCNT catalyst was dispersed in the solution. Percentages of 1 and 3 % mmol of catalyst with respect to iodobenzene were used. Iodobenzene (1.41 mmol, 157 µL) and phenylboronic acid (2.11 mmol, 257.6 mg) were then added to the suspension and the resulting mixture was exposed at microwave radiation (20 W) during 15 min (optimized conditions). After cooling to room temperature, the mixture was filtered through a 3 µm pore polycarbonate membrane filter in order to isolate the catalyst, which was washed with

CH_2Cl_2 (10 mL) and water (10 mL), and dried at 110 °C during 1 day. The alcoholic/aqueous solution was extracted with diethylether (10 mL) three times. The organic extracts were dried with anhydrous magnesium sulfate, filtered and evaporated to dryness, allowing the isolation of pure biphenyl as the reaction product.

2.4.3 Catalytic hydrogenation of alkenes and α,β-unsaturated ketones

An amount of Pd-NP/MWCNT catalyst corresponding to 5 % mmol of palladium with respect to the reactant was placed in a 5 mL round-bottomed flask. Then 2 mL of chloroform and styrene (1 mmol, 114.5 µL) or methylacrylate (1 mmol, 86.96 µL) were added. The resulting suspension was subjected to cycles of vacuum-H_2 refilling at least 10 times. A vigorous stirring under hydrogen atmosphere is maintained during 1 hour, then the suspension was filtered through a 3 µm pore polycarbonate membrane filter. The Pd-NP/MWCNT material was washed with CH_2Cl_2 (5 mL) and water (15 mL), and dried at 110 °C during 1 day. The solution was evaporated and the crude residues were characterized as pure ethylbenzene or methylpropanoate, respectively, by ^1H NMR. Both compounds were obtained in quantitative yield.

3. RESULTS AND DISCUSSION

3.1. Synthesis of the Pd-NP/MWCNT hybrid materials

The Pd-NP/MWCNT hybrids have been prepared by refluxing $Pd_2(dba)_3{\cdot}CHCl_3$ [19] with different amounts of MWCNT in toluene. The reflux temperature is attained by conventional or by microwave heating. The microwave heating has been recently used to prepare efficiently metal-CNT hybrids [20-25]. Our method achieves higher amounts of deposited metals (up to 39%) than other previously reported [21] and avoids the use of polyols [22,25]. Both conventional and microwave heating have shown to be efficient for the preparation of the hybrids, and good deposition of palladium nanoparticles were obtained in both cases. It is worthy of note the high yield of Pd deposition achieved since most of the Pd content in the starting $Pd_2(dba)_3 \cdot CHCl_3$ complex was incorporated on the surface of the MWCNTs. Loadings of Pd higher than 30 wt.% in the case of high-loaded material [Pd-**6**] were obtained, improving our previous findings in SWNTs [8-10]. The resulting materials show homogeneous distribution of Pd-NPs (Figure 1) with sizes smaller than 7 nm (Table 1), being the microwave approach more effective in synthesis of smaller clusters (<5 nm).

Table 1- Pd loading on MWCNTs (wt. %), yield (η, %) and size^a (nm) of Pd-NPs

Sample	[Pd-**0**]	[Pd-**1**]	[Pd-**2**]	[Pd-**3**]	[Pd-**6**]
Pd^b loading (η)	-	12.4 (70)	21.8 (82)	28.7 (94)	-
Pd-NP size	-	5 nm	6 nm	6 nm	-
Pd^c loading (η)	1.9 (80)	14.1 (90)	19.8 (70)	26.1 (85)	39.0 (60)
Pd-NP size	3 nm	3 nm	3 nm	4 nm	5 nm

^{a} average size ; ^{b} 120 min of conventional heating; ^{c} 2 min of microwave heating;

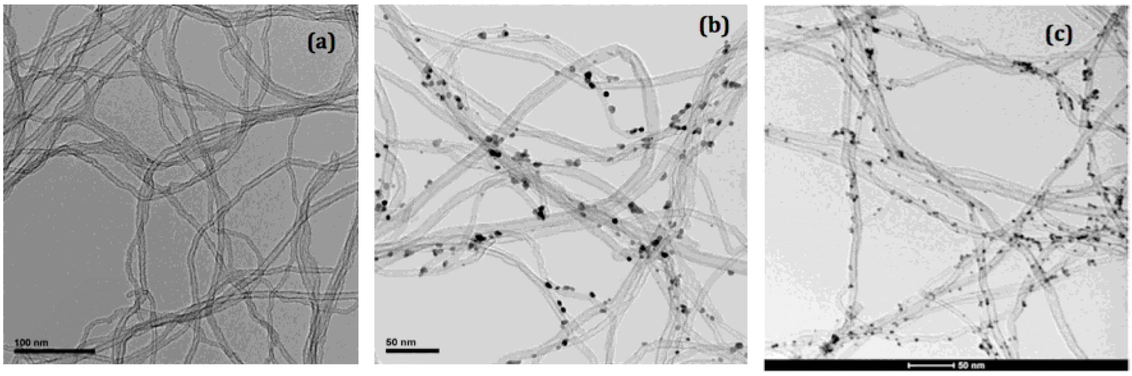

Fig. 1- TEM micrographs of pristine MWCNTs (a); [Pd-2] sample prepared in conventional heating (b) and under microwave irradiation (c). Micrographs show homogeneous distribution of Pd-NPs, with most of the particles in the range of 4-6 nm for conventional heating and in the range of 2-5 nm for microwave heating

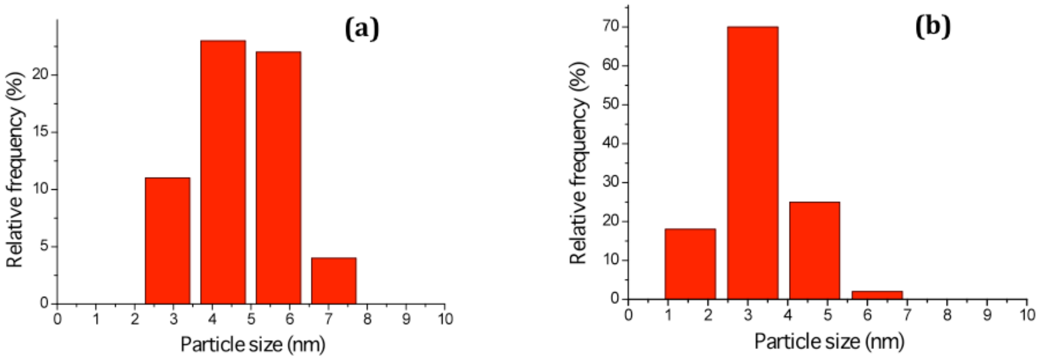

Fig. 2- Histogram showing the size distribution of Pd-NPs, for the [Pd-1] sample, prepared with (a) conventional heating (4-6 nm) and (b) microwave heating (2-5 nm)

This fact is clearly seen when the histograms of size distribution of the NPs are examined (Figure 2). Both histograms show that the diameters of most of the particles fall in a very narrow range, especially in the case of microwave heating, and that the average values for the conventional heating method are slightly larger than for the microwave heating method (Table 1).

Also important to highlight is the significant time reduction for Pd-NP deposition on MWCNT surface achieved by microwave heating, which required just 2 minutes versus 2 hours under conventional heating at the same temperature (115 °C). The Figure 3 shows the profile of the Pd-loading *vs* reaction time for the synthesis of [Pd-**2**]. The reaction has an induction period, since no deposition is observed during the first 15s of heating, being this fact probably related with the decoordination of the dba ligand. After this period a very fast reaction occurs, and increasing amounts of Pd are deposited as reaction time increases. The asymptotic form of the curve shows that the optimum reaction times are between 90 and 120 s, and longer heating times do not provide an improvement of the yield. Interestingly, an experiment carried out without CNTs only gave rise to the formation of a continuous Pd film deposited on the reaction flask and abundant, heavily sintered, black Pd. Moreover, this experiment needed longer reaction times (up to 10 min), showing very different decomposition profiles. Thus it seems that CNTs play a dual role in the preparation of the hybrids. On the one hand, due to their high thermal conductivity microwave heat is effectively distributed along their surface, and thus CNTs promote a fast decomposition of the complex on their surface, being "hotter" compared to the surrounding solution. On the other hand, once the complex is decomposed, CNTs act as effective nucleation surface of the formed nanoclusters [21]. In the absence of the CNTs the energy is dispersed, the heating is not so efficient and, definitely, the formation of Pd-NPs is not observed.

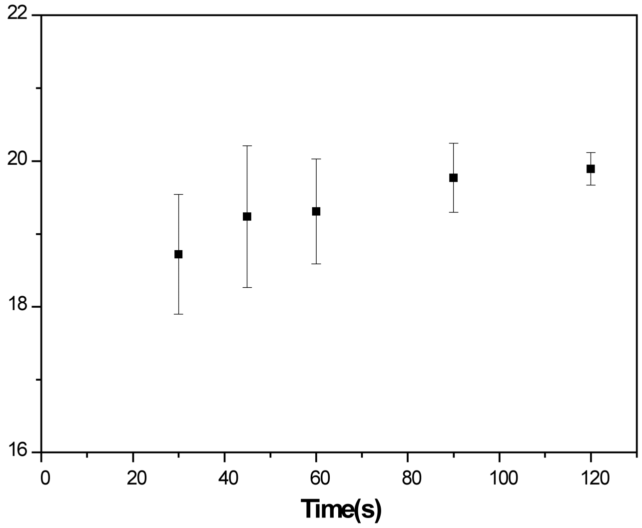

Fig. 3- Pd-loading (wt.%) ***vs*** **reaction time profile for sample [Pd-2]**

Comparison of the Raman spectra of pristine and modified MWCNT evidences that no significant modification of the carbonaceous skeleton has taken place (Figure 4). Therefore, we suggest that only the interaction of the metallic centers with the delocalized π-electron density on the MWCNT surface could be the responsible for the stabilization of the Pd-NPs [20]. Furthermore, this interaction must be strong since these materials exhibit good catalytic activity, and even more important, good recyclability, as we will show later on. This strong interaction could explain the nanometric size of the Pd-NPs reached.

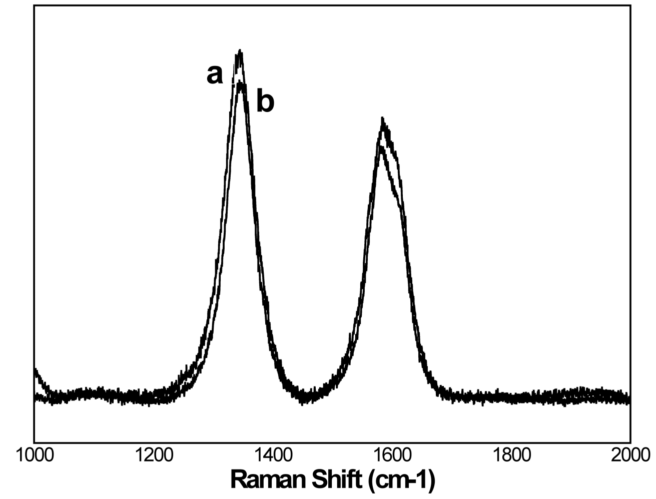

Fig. 4 (a) Raman spectrum of pristine MWCNT; (b) Raman spectrum of Pd-NP/MWCNT hybrid materials obtained by microwave heating.

Summarizing, deposition of palladium by microwave heating leads to materials with good Pd-NPs loadings homogeneously distributed, with smaller sizes, and in considerably shorter times than those obtained under conventional heating. Altogether underlines the higher efficiency of the microwave method over the conventional heating in the preparation of Pd-NP/MWCNT hybrid materials

3.2. Catalytic Activity

Catalytic activity of these materials has been examined for Heck, Suzuki and hydrogenation reactions in order to check for a wide prospect of applications. One of the global concerns on heterogeneous catalysis is an adequate interaction between the active form of the metal and the support, which allows a proper activity and recyclability. The modification of the CNTs is designed usually to achieve a strong interaction between the NP and the CNT. In our system there are no linkers between the MWCNTs and the NPs, since only the aforementioned π-interaction seems to be operating [20]. Furthermore, this interaction seems to be strong since the prepared materials show high catalytic activity, comparable with the best results reported up to now on the literature [26], and good recyclability. This fact could also explain the nanometric size of the Pd-NPs reached by this method. For the Mizoroki-Heck reaction, the activity of the catalysts was analyzed for the coupling between methylacrylate ($H_2C{=}CHCO_2Me$) and iodobenzene (PhI) (Fig. 5) to give *trans*-methylcinnamate. No other coupling products (*cis*- or *gem*-isomers) were observed.

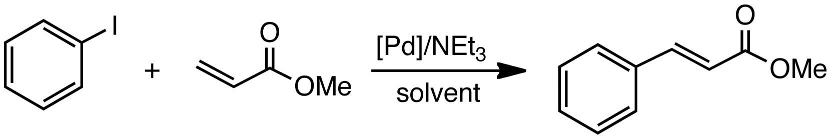

Fig 5.- Heck reaction between iodobenzene and methylacrylate.

Under optimized catalytic conditions using conventional heating, the Heck coupling afforded moderate yields for the methylcinnamate (45-54 %) in reaction times as long as 8-12 h. Moreover the highest Pd retention achieved was in the range 78-97 wt.%. We have seen before how microwave irradiation allows an efficient synthesis of the starting materials [Pd-**n**] (n = 0, 1, 2, 3 or 6) decreasing substantially the reaction times (from hours to minutes) without detriment of the properties of the obtained materials. We subsequently reasoned that microwaves could shorten even more the reaction times of the Heck processes, improving both the retention of the Pd on the MWCNTs and the reaction yield.

First experiments under microwave irradiation (Table 2) showed that using the material with 1 mmol % of Pd (catalyst [Pd-**1**]) the reaction time could be as short as 15 min (entry 3), providing high conversions, and, more importantly, very high retentions of the Pd (leaching is only 4% in entry 3).

Table 2- Heck catalytic activity of [Pd-n] under microwave heating

	[Pd]	t (min)	yield(%)[c]	%Pd ret	TON[d]	TOF[e]
(1)	1% [Pd-**1**][a]	7	55	93	55	471
(2)	1% [Pd-**1**][a]	10	65	90	65	390
(3)	1% [Pd-**1**][a]	15	93	>96	93	372
(4)	0.1% [Pd-**0**][a]	15	27	100	270	1080
(5)	0.1% [Pd-**0**][a]	60	82	100	820	820
(6)	0.1% [Pd-**0**][b]	15	100	100	1000	4000
(7)	0.01%[Pd-**0**][b]	15	100	100	10000	40000
(8)	0.005%[Pd-**0**][b]	15	100	100	20000	80000

experimental conditions: NCMe, [a]100 °C, [b]140 °C, [c]yield =[(isolated product)/(theoretical product)]×100, [d]TON (turnover number) = [(mmol product)/(mmol catalyst)], [e]TOF (turnover frequency) = [(mmol product)/(mmol catalyst×hour)].

Under these conditions we have attempted to decrease the amount of catalyst to 0.1 mmol % (entry 4), using the material with the lowest Pd-content [Pd-**0**]. However, the yield drops to 27% and, although no leaching was observed, further improvement was necessary. Two possibilities were then tested. The increase of the reaction time (60 min) at the same temperature gave good yields (entry 5), but the increase of the temperature at 140 °C keeping the reaction time at 15 min (entry 6) was the best option, since it provided a quantitative yield of isolate product. Further decrease of the amount of Pd to 0.01% and 0.005 mmol% (entries 7 and 8) gives quantitative yields of methylcinnamate in only 15 min, affording TON (turnover numbers) and TOF (turnover frequency) values even better than the best results up to now reported [26], being the leaching for these individual runs is in all cases below the detection limits**.**

We have performed additional cross-check experiments to examine the eventual leaching effects in these catalytic reactions. Therefore, a Heck reaction has been carried out using 1% catalyst [Pd-**1**] (NCMe, 15 min, 100 °C, entry 3). After the reaction time the solution was filtered to remove the catalyst. To the clear solution a new batch of reagents was added, and microwave heating was applied for additional 15 min. Further work-up of this mixture affords the expected *trans*-methylcinnamate in a global yield of 56%. Assuming that the yield in the first run corresponds to 93% (Table 2, entry 3), the obtained global yield implies a small increase (19%) during the second run, compared with the first one. This means that the amount of Pd in solution should be very small since homeopathic amounts of Pd are able to achieve large conversions, and, moreover, that this Pd in solution seems to be less active that the Pd deposited in the MWNT.

Once the high activity and stability of the catalysts is confirmed, an additional relevant feature is their recyclability. To check this aspect four consecutive batches of reagents were added to the same catalyst [Pd-**0**] under optimized conditions (NCMe, 140 °C, 15 min). After each run, the catalyst was isolated and washed before a new addition of reagents, in order to ensure that the activity is solely due to the Pd remaining on the CNTs, and not to the presence of Pd in solution. The yields obtained on each run are collected on Table 3, as well as the retained Pd on the final catalyst.

Table 3.- Test of recyclability[a] of [Pd-0] catalyst

	Yield	% Pd retained
15 min (yield) (run 1)	100%	100%
15 min (yield) (run 2)	100%	-
15 min (yield) (run 3)	100%	-
15 min (yield) (run 4)	100%	72%

[a] conditions: 0.1% Pd, NCMe, 140 °C, microwave irradiation

As it can be seen, quantitative yields are obtained on each case, meaning that there is no loss of activity throughout successive runs. More interestingly, the amount of Pd retained at the end of the four runs is still 72%, showing a good, yet improvable, recyclability.

Aiming to enlarge the scope of use of these catalysts and this methodology we have studied other catalytic reactions, and good results have been obtained in the Suzuki-Miyaura coupling between phenylboronic ($PhB(OH)_2$) and iodobenzene (IPh) (Fig. 6). Under optimized conditions ($EtOH/H_2O$, K_3PO_4, microwaves, 80 °C, 15 min) [27], we have achieved 100% yield of isolated biphenyl using amounts of catalyst as low as 0.1 mmol % of [Pd-**0**]. Very interestingly, the ICP analysis of this material after catalysis shows that the amount of Pd retained is 100 wt% and that no detectable leaching has been produced.

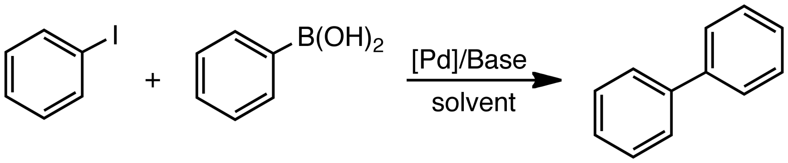

Fig. 6- Suzuki reaction between iodobenzene and phenylboronic acid

In the same way, the hybrid [Pd-**2**] catalyzed efficiently the hydrogenation of styrene and methyl acrylate, in $CHCl_3$ or methanol, under very mild reaction conditions (1 atm H_2, 25 °C, Fig. 7).

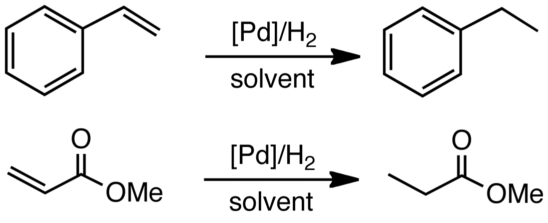

Fig. 7- Hydrogenations performed with Pd-NP/MWCNT hybrid materials

In both cases we have observed a complete conversion of the starting substrate, and yields of 100% of isolated ethylbenzene and methylpropanoate could be obtained. No other hydrogenation products have been detected. The determination of Pd on the catalytic material after reaction yields in a 100% retention of Pd in the hydrogenation of styrene, while values up to 90 wt% retention are obtained in the case of methylcinnamate. There results show that this is a very promising area, offering high yields and complete retention of the metal on the support in some cases.

4.- Conclusions

We have developed a very simple and fast method of synthesis of Pd-NP/MWCNT hybrid materials under microwave irradiation, using non-functionalized MWCNTs and an accesible Pd source, achieving amounts of Pd deposited in the range 1-40 wt%. These materials behave as very efficient catalysts under microwave irradiation in CC couplings and also in hydrogenations in mild conditions, providing very high conversions and good recyclability. Further studies using these materials on a broad scope of substrates and catalytic reactions are currently in progress.

Acknowledgements

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Table Captions

Table 1- Pd loading on MWCNTs (wt. %), yield (η, %) and size[a] (nm) of Pd-NPs

Table 2- Heck catalytic activity of [Pd-n] under microwave heating

Table 3- Test of recyclability[a] of [Pd-0] catalyst

Figure Captions

Fig. 1 - TEM micrographs of pristine MWCNTs (a); [Pd-2] sample prepared in conventional heating (b) and under microwave irradiation (c). Micrographs show homogeneous distribution of Pd-NPs, with most of the particles in the range of 4-6 nm for conventional heating and in the range of 2-5 nm for microwave heating.

Fig. 2- Histogram showing the size distribution of Pd-NPs, for the [Pd-1] sample, prepared with (a) conventional heating (4-6 nm) and (b) microwave heating (2-5 nm).

Fig. 3 - Pd-loading (wt.%) vs reaction time profile for sample [Pd-2]

Fig. 4 - (a) Raman spectrum of pristine MWCNTs; (b) Raman spectrum of Pd-NP/MWCNT hybrid materials obtained by microwave heating.

Fig. 5 - Heck reaction between iodobenzene and methylacrylate.

Fig. 6 - Suzuki reaction between iodobenzene and phenylboronic acid

Fig. 7 - Hydrogenations performed with Pd-NP/MWCNT hybrid materials