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Palladium and bimetallic palladium-nickel nanoparticles supported on multi-walled carbon nanotubes: application to carbon-carbon bond forming reactions in water
--Manuscript Draft--

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Corresponding Author:	Carmen Nájera Universitat d\'Alacant Alicante, Alicante SPAIN
Corresponding Author E-Mail:	cnajera@ua.es
Abstract:	Palladium and bimetallic Pd-Ni nanoparticles (NPs) protected by polyvinylpyrrolidone have been prepared by the reduction-by-solvent method and deposited on multi-walled carbon nanotubes (MWCNTs). The catalytic activity of these NPs to carbon-carbon bond forming reactions has been studied using 0.1 mol% Pd loading, at 120 ºC for 1 h and water as solvent under ligand-free conditions for the Suzuki-Miyaura, Hiyama, Mizoroki-Heck, and Sonogashira-Hagihara reactions. Good recyclability has been observed for the Suzuki-Miyaura reaction using Pd50Ni50/MWCNTs and for the Sonogashira-Hagihara reaction with Pd/MWCNTs.
Response to Reviewers:	Reviewer 1: This MS reports protocol for synthesis of Ni-Pd bimetallic nanoparticles and then its application for various C-C coupling reaction. The synthesis protocol is facile and material showed excellent catalytic activity. Materials were characterized thoroughly and catalytic activity was also studied for several reactions/substrates. In all, I feel it's very nice work. However, it will be interesting to compare this CNT based Pd-catalysts with known silica based Pd-catalysts for at least one C-C coupling reaction, e.g. ChemSusChem 2012, 5, 85; Chem. Soc. Rev., 2011, 40, 5181, etc. I strongly recommend this MS for publication after above minor revision. We would like to thank the referee for his/her very positive comments on our work. As suggested by the referee, we have included a comparison of our results with those from silica-supported Pd-based systems and the appropriate references have been included in the text. MANUSCRIPT AMENDED Reviewer 2: The research groups of Prof. Diego Cazorla-Amoros from the University of Alicante, Spain, report palladium and bimetallic palladium-nickel nanoparticles supported on multi-walled carbon nanotubes for application to carbon-carbon bond forming reactions in water. The Suzuki Miyaura, Hijama, Heck,and Sonogashira were conducted using 0.1 mol% Pd loading, at 120 oC for 1 h and water. The Pd and bimetallic Pd-Ni nanoparticles protected (thus liganded) by polyvinylpyrrolidone. This is an interesting and thorough study of the subject. Another important point is that the authors have clearly shown some of the weaknesses of this system, in particular in terms of metal loading and recyclability. We thank the referee for his/her positive comments on our work and his/her commendation of our research effort. The paper is certainly publishable in ChemCatChem, but a major revision is called for including consideration of the following points: - There is no comparison and discussion of the results with other methods for analogous reactions of cross C-C coupling, in particular those using considerably less Pd and much milder reaction conditions with higher yields (see Angew. Chem. 2005, 44, 7852; Acc. Chem. Res. 2014, 47, 494). There is only a short conclusion but general discussion is absent. We have included a more general discussion in order to compare our results with other catalytic systems used in different C-C coupling reactions such as the Suzuki and Heck reactions and the appropriate references have been included in the corrected version of the manuscript.

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- In connection, the cited references are ok for CNT-mediated catalysis, but not for general Pd catalysis of these reactions (see above).

Please refer to the previous point, in which we have addressed this issue.
NO ACTION NECESSARY

- There are problems with the nomenclature Pd50Ni50, etc.: the numbers of atoms in NPs are not so precise, and indeed the TEMs of the figures show size and shape disparities from one NP to another.

We apologize for the confusion in the nomenclature of our samples. The nomenclature used in our study (PdxNiy) refers to the atomic composition of the nanoparticles. This does not refer to the number of atoms in each particle but to the atomic composition.
In this sense, ICP characterization of the NPs indicated that the actual bimetallic composition is very close to the targeted one in all cases (in mol %), as indicated in new Table 8 (in the experimental section). Therefore, particle size has no influence on the composition of the particles.
We have included two comments in the "Discussion" (Table 1) and "Experimental" section and Table 8 in the Experimental section to clarify this point.
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- The influence of Ni should be analyzed and discussed, with tentative explanation of possible synergistic interactions between Ni and Pd from the mechanistic standpoint.

We thank the referee for this appropriate comment.
The main idea behind incorporating Ni in the nanoparticles composition was to decrease the cost of the active phase of the catalysts without affecting their catalytic performance. However, the presence of this metal might have an effect on the performance of Pd as active metal for the reaction.
In this sense, an increased number of Ni atoms in the nanoparticles will dilute the Pd active sites and in turn reflect in an apparent decrease of the catalytic activity, as previously related in other works of our research group (Domínguez-Domínguez et al. J. Catal. 243 (2006) 74-81).
Also, the incorporation of Ni in the nanoparticles composition brings forth the generation of an alloy between Ni and Pd. This, in turn, reflects in an electronic interaction between both metals, where Pd interacts with the Ni atoms withdrawing some electronic density from them (due to its higher electronegativity) thus generating electron deficient Ni species, as it has also been previously reported in our group (García-Aguilar et al. Carbon 66 (2014) 599-611). This partial Ni oxidation would also affect the performance of the active phase in the prepared catalysts.
Finally, being Ni more reactive than Pd, under reaction conditions it may be oxidized more easily than Pd. This may cause the metal nanoparticles to become partially dissolved in the reaction medium giving rise to some metal leaching during the different reaction cycles, as has been observed in this work in some cases.
For all these reasons, the influence of Ni on the performance of the catalysts should not be neglected and must definitely be taken into account.
These comments have been incorporated in the manuscript for clarity purposes.
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Section/Category:	
Additional Information:	
Question	Response
Submitted solely to this journal?	Yes
Has there been a previous version?	No
Dedication	No
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FULL PAPERS

Palladium and bimetallic palladium-nickel nanoparticles supported on multi-walled carbon nanotubes: application to carbon-carbon bond forming reactions in water

Atsushi Ohtaka,[a] José M. Sansano,[a] Carmen Nájera,*[a] Izaskun Miguel-García,[b] Ángel Berenguer-Murcia,[b] Diego Cazorla-Amorós,*[b]

Dedication ((optional))

Palladium and bimetallic Pd-Ni nanoparticles (NPs) protected by polyvinylpyrrolidone have been prepared by the reduction-by-solvent method and deposited on multi-walled carbon nanotubes (MWCNTs). The catalytic activity of these NPs to carbon-carbon bond forming reactions has been studied using 0.1 mol% Pd loading, at 120 °C for 1 h and water as solvent under ligand-free conditions. The Suzuki-Miyaura reaction takes place quantitatively for the cross-coupling of 4-bromoanisole with phenylboronic acid, better than potassium phenyltrifluoroborate, with $Pd_{50}Ni_{50}$/MWCNTs using K_2CO_3 as base and TBAB as additive with good recyclability during 4 cycles with some Ni leaching. The Hiyama reaction of 4-iodoanisole with trimethoxyphenyl-silane, under fluoride-free conditions using 50% aqueous NaOH solution, is performed with Pd/MWCNTs as catalyst in 83% yield with low recyclability. For the Mizoroki-Heck reaction 4-iodoanisole and styrene gave the corresponding 4-methoxystilbene quantitatively with $Pd_{50}Ni_{50}$/MWCNTs using K_2CO_3 as base and TBAB as additive although the recycle failed. In the case of the Sonogashira-Hagihara reaction Pd/MWCNTs has to be used as catalyst and pyrrolidine as base for the coupling of 4-iodoanisole with phenylacetylene under copper-free conditions. The corresponding 4-methoxytolane was quantitatively obtained allowing the recycling of the catalyst during 3 cycles.

Introduction

Carbon nanotubes (CNTs) have excellent electronic properties, good chemical stability, and large surface areas, leading therefore to promising applications as catalyst supports. The attachment of nanoparticles (NPs) on CNTs has attracted great interest, for the nanocomposites not only combine the extraordinary properties of the NPs and CNTs, but also exhibit some new properties caused by the interaction between them.[1] Several research groups have reported the synthesis of CNTs-supported metal NPs and their catalytic activity for various chemical reactions including Suzuki coupling reaction, Heck reaction and hydrogenation. However, most of the reactions were performed in organic solvents or mixed organic/aqueous solvents, and neat water is seldom used as a reaction medium.[2,3]

The enhanced catalytic activity of metal nanoparticles is well-established in the literature. Among the applications which we have tested, one of the examples that stands out in the context of the present manuscript is the deposition of diverse Pd-based nanoparticles protected by polyvinylpyrrolidone (PVP) synthesized by the reduction-by-solvent method on different carbon materials for the selective hydrogenation of phenylacetyene.[4] Recently, we reported the preparation of Pd

and bimetallic Pd-Ni nanoparticles and their deposition on single-walled carbon nanotubes (SWCNTs).[5] On the other hand, multi-walled carbon nanotubes (MWCNTs) have been found to be superior supports compared to other carbon materials such as SWCNTs. For example, MWCNTs are able to uptake the highest number of nanoparticles per unit surface area and MWCNTs-supported palladium NPs showed a slightly better reactivity.[2c,2d] We envisaged that these Pd and bimetallic Pd-Ni nanoparticles supported on MWCNTs could be useful catalysts in cross-coupling reactions having two main advantages a lower amount of palladium and to allow the recovery of these supported NPs by simple filtration from the reaction media. In addition we have chosen water as solvent not only because of its economical and ecological relevance but also because Corma has demonstrated that in water Pd clusters are easily formed from the precursor NPs, showing higher stability, faster reaction rates, and lower leaching than in organic solvents in different carbon-carbon bond

[a] Dr. A.Ohtaka, Prof. J. M. Sansano, Prof. C. Nájera
Dpto. de Química Orgánica and Centro de Innovación en Química Avanzada (ORFEO-CINQA), University of Alicante
Apdo.99, E-03080, Alicante, Spain
Fax: (+) 0034-965903549
E-mail: cnajera@ua.es

[b] Dr. I. Miguel-García, Dr. Á. Berenguer-Murcia, Prof. D. Cazorla-Amorós
Dpto. Química Inorgánica and Instituto Universitario de Materiales
University of Alicante
Fax: (+) 0034-965903454
E-mail: cazorla@ua.es
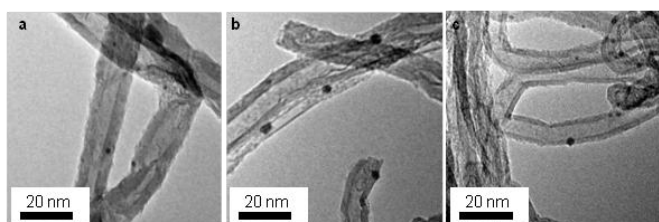Supporting information for this article is available on the WWW under http://dx.doi.org/10.1002/cctc.200xxxxxx.

forming reactions.[6] Herein we report the study about the catalytic activity of Pd and bimetallic Pd-Ni nanoparticles stabilized by PVP and supported on MWCNTs for several relevant C-C bond formation processes in water[7] such as Suzuki-Miyaura, Hiyama, Mizoroki-Heck and Sonogashira-Hagihara reactions.[8]

Results and Discussion

In order to determine the efficiency of the loading step as well as to assess the particle size and its dispersion in the prepared heterogeneous catalysts, ICP-OES and TEM studies were performed for all samples. The results of the ICP analysis for the metal contents of the prepared NPs/MWCNTs samples are summarized in Table 1. It can be observed that the initially targeted 1 wt % metal loading was not really achieved. Therefore, the rest of the metal was lost during the synthesis procedure, probably during the washing step, where Pd NPs not bound strongly enough were washed off the carbon support.

Table 1. TEM and ICP characterization results of the heterogeneous catalysts prepared.

Catalyst	Metal loading ICP (total wt %)	d_{TEM} (nm)	D_{TEM} (%)
Pd/MWCNTs	0.75%	2.55 ± 0.57	35.3
$Pd_{90}Ni_{10}$/MWCNTs	0.62%	2.39 ± 0.42	37.6
$Pd_{70}Ni_{30}$/MWCNTs	0.58%	2.03 ± 0.57	44.3
$Pd_{50}Ni_{50}$/MWCNTs	0.70%	2.42 ± 0.51	37.2
$Pd_{30}Ni_{70}$/MWCNTs	0.69%	2.71 ± 0.54	33.2

To directly correlate the metal dispersion of NPs/MWCNTs catalysts, TEM analyses were also performed on the as-synthesized samples. Figure 1 shows TEM micrographs of (a) Pd/MWCNTs, (b) $Pd_{70}Ni_{30}$/MWCNTs, and (c) $Pd_{50}Ni_{50}$/MWCNTs. Both Pd average particle sizes (d, nm) and metal dispersion (D, %) results of the three catalysts obtained from TEM analyses are shown in the third and fourth columns of Table 1. It must be highlighted that the particle sizes of the metal nanoparticles in the catalysts are very similar to the average particle size of the metal particles of the colloid (2.4 ± 0.5 nm).[9] Thus, not only were the prepared heterogeneous catalysts of the desired atomic composition, but also they displayed a very small particle size and a narrow size distribution.

Figure 1. TEM images of catalysts (a) Pd/MWCNTs, (b) $Pd_{70}Ni_{30}$/MWCNTs and (c) $Pd_{50}Ni_{50}$/MWCNTs.

Initial studies were performed using different Pd NPs supported on MWCNTs in the Suzuki-Miyaura reaction[10] of 4-bromoanisole with phenylboronic acid using 0.1 mol% Pd loading, K_2CO_3 as base and water as solvent at 100 ºC for 1 h, reaction conditions which we stablished previously using Pd(OAc)$_2$ or an oxime-derived palladacycle[11] (Table 2). Under these reaction conditions, the best 63% yield was obtained with the bimetallic $Pd_{30}Ni_{70}$/MWCNTs (Table 2, entry 4). In all these cases, better

results were observed using the catalyst supported on MWCNTs than with Pd NPs coated with PVP (Table 2, entry 5).

Next the optimization of the reaction conditions was considered using the bimetallic $Pd_{30}Ni_{70}$/MWCNTs as precatalyst (Table 3). When KOH was used as base a lower yield was obtained with respect to K_2CO_3 (Table 3, entries 1 and 2). Working at 100 ºC with K_2CO_3 as base, the Pd loading was increased from 0.1 to 0.2 and 0.3 mol% giving slightly lower yields (Table 3, entries 2-4). When the reaction time was increased from 1 to 2 h the yield did not increase (61%) and after 3 h a slightly higher 72% was obtained (Table 3, compare entry 2 with 5 and 6). Increasing the bath temperature to 120 ºC has a positive increment in the yield from 63 to 83% (Table 3, entry 7). The addition of additives such as polyethylene glycol 300 as a 1/5 volume proportion afforded higher 92% yield (Table 3, entry 8). When the amount of phenylboronic acid was reduced from 1.5 to 1.2 equiv. and using 1 equiv. of tetra-*n*-butylammonium bromide (TBAB) which is a well-known NPs stabilizer,[12] the highest 95% yield was obtained. Under the last reaction conditions, similar yields were obtained with the rest of supported Pd NPs (Table 3, entries 10-13), although $Pd_{50}Ni_{50}$/MWCNTs seems to be the best precatalyst (entry 12).
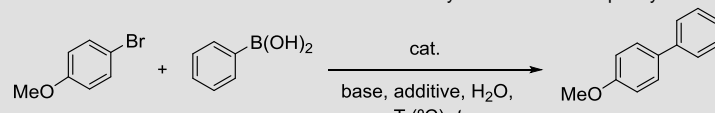
Table 2. Catalytic activity of Pd and bimetallic Pd-Ni NPs in the Suzuki-Miyaura reaction using phenylboronic acid in water.[a]

Entry	Catalyst	Yield (%)[b]
1	Pd/MWCNTs	54
2	$Pd_{70}Ni_{30}$/MWCNTs	48
3	$Pd_{50}Ni_{50}$/MWCNTs	47
4	**$Pd_{30}Ni_{70}$/MWCNTs**	**63**
5[c]	PVP-Pd	30

[a] Reaction conditions: 4-bromoanisole (0.5 mmol), phenylboronic acid (0.75 mmol), catalyst (0.1 mol% Pd), K_2CO_3 (1.5 mmol) in H_2O (0.3 mL). [b] Determined by GC analysis based on 4-bromoanisole consumption. [c] In 0.5 mL of H_2O.

Under the optimum reaction conditions involving the use of $Pd_{50}Ni_{50}$/MWCNTs (0.1 mol% of Pd), 3 equiv of K_2CO_3, and 1 equiv. of TBAB at 120 °C the recyclability of the catalyst was studied (Scheme 1). The cross-coupling reaction of 4-bromoanisole with phenylboronic acid (1.2 equiv) was performed giving 4-methoxybiphenyl in 99% yield. When the reaction was completed, the catalyst was recovered by decantation and successively subjected to second through fourth runs of the coupling reaction under the same conditions to afford 4-methoxybiphenyl in 89%, 86%, and 87% yields, respectively (Scheme 1). ICP-OES analysis revealed that a slight decrease
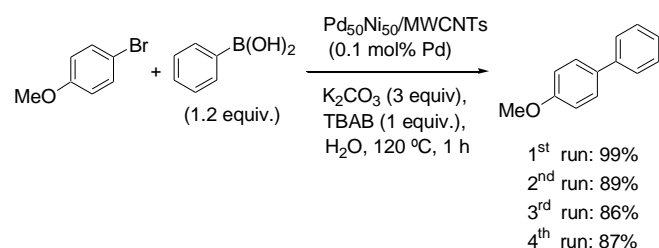
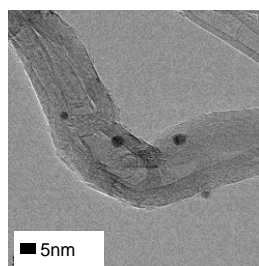**Table 3.** Reaction condition studies for the Suzuki-Miyaura reaction with phenylboronic acid in water.[a]

MeO—⟨⟩—Br + ⟨⟩—B(OH)$_2$ →[cat., base, additive, H$_2$O, T (ºC), t] MeO—⟨⟩—⟨⟩

Entry	Cat. (mol% Pd)	Base	Additive	Temp. (ºC)	Time (h)	Yield (%)[b]
1	Pd$_{30}$Ni$_{70}$/MWCNTs (0.1)	KOH	-	100	1	41
2	Pd$_{30}$Ni$_{70}$/MWCNTs (0.1)	K$_2$CO$_3$	-	100	1	63
3	Pd$_{30}$Ni$_{70}$/MWCNTs (0.2)	K$_2$CO$_3$	-	100	1	53
4	Pd$_{30}$Ni$_{70}$/MWCNTs (0.3)	K$_2$CO$_3$	-	100	1	57
5	Pd$_{30}$Ni$_{70}$/MWCNTs (0.1)	K$_2$CO$_3$	-	100	2	61
6	Pd$_{30}$Ni$_{70}$/MWCNTs (0.1)	K$_2$CO$_3$	-	100	3	72
7	Pd$_{30}$Ni$_{70}$/MWCNTs (0.1)	K$_2$CO$_3$	-	120	1	83
8	Pd$_{30}$Ni$_{70}$/MWCNTs (0.1)	K$_2$CO$_3$	PEG300[c]	120	1	92
9[d]	Pd$_{30}$Ni$_{70}$/MWCNTs (0.1)	K$_2$CO$_3$	TBAB[e]	120	1	95
10[d]	Pd/MWCNTs (0.1)	K$_2$CO$_3$	TBAB[e]	120	1	96
11[d]	Pd$_{70}$Ni$_{30}$/MWCNTs (0.1)	K$_2$CO$_3$	TBAB[e]	120	1	94
12[d]	**Pd$_{50}$Ni$_{50}$/MWCNTs (0.1)**	**K$_2$CO$_3$**	**TBAB[e]**	**120**	**1**	**>99**
13[d]	Pd$_{10}$Ni$_{90}$/MWCNTs (0.1)	K$_2$CO$_3$	TBAB[e]	120	1	95

[a] Reaction conditions: 4-bromoanisole (0.5 mmol), phenylboronic acid (0.75 mmol), catalyst (see column), base (1.5 mmol) in H$_2$O (0.3 mL). [b] Determined by GC analysis based on 4-bromoanisole consumption. [c] PEG300/H$_2$O (1/5) in 0.5 mL of volume was used as solvent. [d] 1.2 mmol of phenylboronic acid were used. [e] 0.5 mmol.

of the amount of Ni was observed (from 0.24 wt% to 0.12 wt%), and that no metal species was observed in the product. TEM image (Figure 2) of the recovered catalyst after the fourth run revealed the particle size increased slightly compared with that of the fresh catalyst (3.65 ± 0.95 nm and 2.42 ± 0.51 nm, respectively). It appears that under the conditions described in the manuscript the nanoparticles are etched and their size increases upon consecutive reaction cycles.

MeO—⟨⟩—Br + ⟨⟩—B(OH)$_2$ (1.2 equiv.) →[Pd$_{50}$Ni$_{50}$/MWCNTs (0.1 mol% Pd), K$_2$CO$_3$ (3 equiv), TBAB (1 equiv.), H$_2$O, 120 ºC, 1 h] MeO—⟨⟩—⟨⟩

1st run: 99%
2nd run: 89%
3rd run: 86%
4th run: 87%

Scheme 1. Reciclability of bimetallic Pd$_{50}$Ni$_{50}$/MWCNTs for the Suzuki-Miyaura reaction with phenylboronic acid in water.
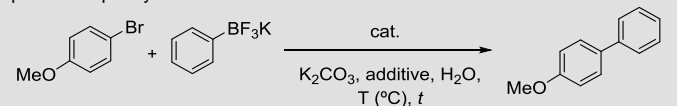

■ 5nm

Figure 2. TEM image of the Pd$_{50}$Ni$_{50}$/MWCNTs catalyst after the 4th cycle in the Suzuki-Miyaura process.

Further applications of these supported Pd NPs on MWCNTs in the same Suzuki-Miyaura reaction using 4-bromoanisole and potassium phenyltrifluoroborate were next studied (Table 4). Working at 100 ºC with 0.1 mol% Pd loading using K$_2$CO$_3$ as base in water as solvent, reaction conditions which we stablished previously by us using Pd(OAc)$_2$ or an oxime-derived palladacycle,[13] but without additives (Table 4, entries 1-5), the highest 64 and 65% yields were obtained with Pd/MWCNTs and P$_{30}$Ni$_{70}$/MWCNTs, respectively (Table 4, entries 1 and 4). Working at 120 ºC with Pd/MWCNTs either during 1 or 3 h similar (81 and 83%) yields were obtained (Table 4, entries 6 and 7). When 1 equiv. of TBAB was added a lower 76% yield was observed (Table 4, entry 8). However, a decrease of the potassium phenyltrifluoroborate from 1.5 to 1.2 equiv. increased the yield from 83 to 88% (Table 4, entries 7 and 9) and in the presence of TBAB or PEG300 to 94 and 95%, respectively (Table 4, entries 10 and 11). However, the second recycling experiment under the last reaction conditions gave 4-methoxybiphenyl in only 21% yield. We can conclude that phenylboronic acid is a better substrate than potassium phenyltrifluoroborate for the recycling of the catalyst.

Next, the Hiyama reaction[14] was first evaluated using 4-bromoanisole and trimethoxyphenylsilane as model reaction with 2.5 equiv of 50% aqueous NaOH solution in the absence of a fluoride source, reaction conditions which we stablished previously by us using Pd(OAc)$_2$ or an oxime-derived palladacycle.[15] In the presence of the different Pd NPs supported on MWCNTs (0.1 mol% of Pd) at 90 °C for 3 h to afford the desired coupling product in low yields (7-32%). Then, the coupling between 4-iodoanisole and trimethoxyphenylsilane was

performed with 2.5 equiv of 50% NaOH in the presence of Pd NPs supported in MWCNTs (0.1 mol% of Pd) at 120 °C (Table 5). In the case of using 1.5 equiv. of trimethoxyphenylsilane all the catalysts gave 4-methoxybiphenyl in 92-96% yield (Table 5, entries 1-4). However, lowering the amount of siloxane to 1.2 equiv. the best yield was obtained with Pd NPs supported in MWCNTs (Table 5, entry 5). The recycling experiments gave very low yields, 40 and 53% in the second and third cycle, respectively. It should be mentioned that after undergoing 3 reaction cycles in the Hiyama reaction, the catalyst Pd/MWCNTs showed a decrease in the yield of the desired product from 95% to 53%, indicating a strong deactivation. Post reaction ICP-OES and TEM analyses performed on the used catalyst showed a marked decrease in the metal loading (from 0.75%, see Table 1, to 0.2%) and a particle size of 5.2 ± 1.5 nm. This behaviour shows that the strongly basic reaction medium not only leaches the Pd from the catalyst into the liquid phase, but also provokes a significant increase in the Pd nanoparticle size, which ultimately results in an impoverished catalytic activity.

Table 4. Reaction conditions studies for the Suzuki-Miyaura reaction with potassium phenyltrifluoroborate in water.[a]

Entry	Cat. (mol% Pd)	Additive	Temp. (ºC)	Time (h)	Yield (%)[b]
1	Pd/MWCNTs (0.1)	-	100	1	64
2	Pd$_{70}$Ni$_{30}$/MWCNTs (0.1)	-	100	1	30
3	Pd$_{50}$Ni$_{50}$/MWCNTs (0.1)	-	100	1	44
4	Pd$_{30}$Ni$_{70}$/MWCNTs (0.1)	-	100	1	65
5	PVP-Pd	-	100	1	38
6	Pd/MWCNTs (0.1)	-	120	1	81
7	Pd/MWCNTs (0.1)	-	120	3	83
8	Pd/MWCNTs (0.1)	TBAB[c]	120	1	76
9[d]	Pd/MWCNTs (0.1)	-	120	1	88
10[d]	**Pd/MWCNTs (0.1)**	**TBAB[c]**	**120**	**1**	**94**
11[d]	**Pd/MWCNTs (0.1)**	**PEG300 [e]**	**120**	**1**	**95**

[a] Reaction conditions: 4-bromoanisole (0.5 mmol), potassium phenyltrifluoroborate (0.75 mmol), catalyst (see column), base (1.5 mmol) in H$_2$O (0.3 mL). [b] Determined by GC analysis based on 4-bromoanisole consumption. [c] 1 equiv. was added. [d] 1.2 mmol of potassium phenyltrifluoroborate were used. [e] PEG300/H$_2$O (5/1) in 0.5 mL of volume was used as solvent.
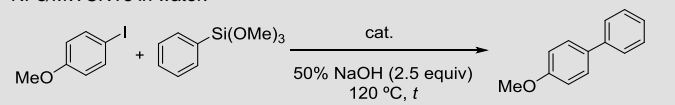
For the Mizoroki-Heck reaction[16] in water catalyzed by Pd NPs supported on MWCNTs (0.1 mol% Pd) 4-methoxyiodobenzene and styrene (1.5 equiv) were chosen as

model substrates (Table 6). The reaction conditions were studied using dicyclohexylmethylamine as base under the previous conditions developed by our group[17] with very poor results. However, better yields were obtained in the presence of KOH (3 equiv.) as base in the presence of TBAB as additive or in a mixture of PEG300 and water as solvent at 120 ºC during 1 h. In the case of Pd/MWCNTs using PEG300/H$_2$O (v/v:1/1) quantitative formation of 4-methoxystilbene was observed (Table 6, entry 1). By using TBAB (1 equiv.) as additive a 90% yield was obtained (Table 6, entry 2). Under these reaction conditions Pd$_{70}$Ni$_{30}$/MWCNTs gave the same results (Table 6, entry 3). Quantitative yields were also achieved with Pd$_{50}$Ni$_{50}$/MWCNTs and Pd$_{30}$Ni$_{70}$/MWCNTs catalysts (Table 6, entries 4 and 5). On the other hand, Pd$_{10}$Ni$_{90}$/MWCNTs gave the same yield (90%) than Pd/MWCNTss (Table 6, entry 6). When the recycling experiments were carried out with Pd$_{50}$Ni$_{50}$/MWCNTs under the best reaction conditions the reaction failed in the second run.
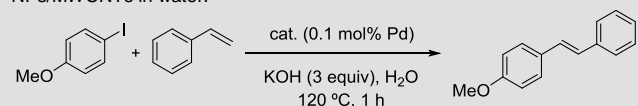
For the Sonogashira-Hagihara reaction[18] the cross-coupling between 4-iodoanisole and phenylacetylene was studied in the presence of pyrrolidine as base, at 120 ºC in water as solvent, that means reaction conditions set up by our group[19] (Table 7). In the presence of Pd/MWCNTs under copper-free conditions the reaction needed 5 h in order to get 4-methoxytolane in 74% yield. However, in the presence of PEG300/H$_2$O (1/1: v/v) as solvent a similar 73% yield was obtained (Table 7, entry 2). By increasing the amount of phenylacetylene from 1.2 to 1.5 equiv. it was possible to obtain the corresponding internal acetylene in 92% yield not only in 5 h but also in only 1 h reaction time (Table 7, entries 3-5). Quantitative yield could be obtained by using 2.0 equiv. of phenylacetylene (Table 7, entry 5). Under the last reaction conditions, the bimetallic Pd-Ni NPs gave lower yields (Table 7, entries 6-9). Therefore, the recycling experiments were carried out with Pd/MWCNTs under the reaction conditions indicated in Table 7, entry 5. The two first cycles took place in quantitative yields, but in the third one 4-methoxytolane was obtained in only 64% yield and in the fourth the reaction failed (Scheme 2).

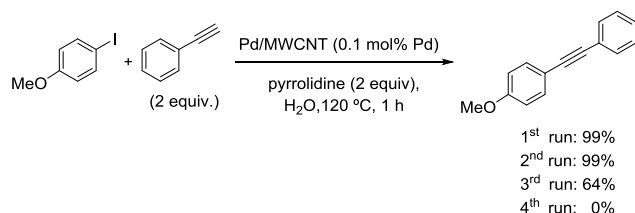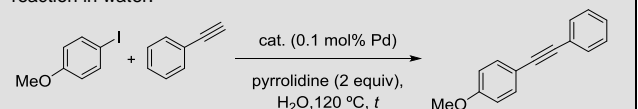**Table 5.** Reaction conditions studies for the Hiyama reaction using Pd NPs/MWCNTs in water.[a]

Entry	Cat. (mol% Pd)	PhSi(OMe)$_3$ equiv.	Time (h)	Yield (%)[b]
1	Pd/MWCNTs (0.1)	1.5	3	95
2	Pd$_{70}$Ni$_{30}$/MWCNTs (0.1)	1.5	3	96
3	Pd/MWCNTs (0.1)	1.5	1	95
4	Pd$_{70}$Ni$_{30}$/MWCNTs (0.1)	1.5	1	92
5	**Pd/MWCNTs (0.1)**	**1.2**	**1**	**85**
6	Pd$_{70}$Ni$_{30}$/MWCNTs (0.1)	1.2	1	77
7	Pd$_{50}$Ni$_{50}$/MWCNTs (0.1)	1.2	1	76
8	Pd$_{30}$Ni$_{70}$/MWCNTs (0.1)	1.2	1	82

[a] Reaction conditions: 4-iodoanisole (0.5 mmol), trimethoxyphenylsilane (see column), catalyst (0.1 mol% Pd), 50% aq. NaOH (2.5 mmol). [b] Determined by GC analysis based on 4-iodoanisole consumption.

Table 6. Reaction conditions studies for the Mizoroki-Heck reaction using Pd NPs/MWCNTs in water.[a]

Entry	Cat.	Additive	Yield (%)[b]
1	Pd/MWNT	PEG300[c]	99
2	Pd/MWNT	TBAB[d]	90
3	Pd70Ni30/MWNT	TBAB[d]	91
4	**Pd50Ni50/MWNT**	**TBAB[d]**	**99**
5	Pd30Ni70/MWNT	TBAB[d]	99
6	Pd10Ni90/MWNT	TBAB[d]	90

[a] Reaction conditions: 4-iodoanisole (0.5 mmol), styrene (0.75 mmol), catalyst (0.1 mol% Pd), KOH (1.5 mmol). [b] Determined by GC analysis based on 4-iodoanisole consumption. [c] PEG300/H2O (1/1) in 0.5 mL of volume was used as solvent. [d] TBAB (0.5 mmol).

1st run: 99%
2nd run: 99%
3rd run: 64%
4th run: 0%

Scheme 2. Reciclability of Pd NPs/MWCNTs catalyst for the Sonogashira-Hagihara reaction in water.

Table 7. Reaction conditions studies for the Sonogashira-Hagihara reaction in water.[a]

Entry	Cat.	Additive	Time (h)	Yield (%)[b]
1	Pd/MWCNTs	-	5	74
2	Pd/MWCNTs	PEG300[c]	5	73
3[d]	Pd/MWCNTs	-	5	92
4[d]	Pd/MWCNTs	-	1	92
5[e]	**Pd/MWCNTs**	**-**	**1**	**99**
6[e]	Pd70Ni30/MWCNTs	-	1	74
7[e]	Pd50Ni50/MWCNTs	-	1	69
8[e]	Pd30Ni70/MWCNTs	-	1	68
9[e]	Pd10Ni90/MWCNTs	-	1	60

[a] Reaction conditions: 4-iodoanisole (0.5 mmol), phenylacetylene (0.75 mmol), catalyst (0.1 mol% Pd), pyrrolidine (1 mmol). [b] Determined by GC analysis based on 4-iodoanisole consumption. [c] PEG300/H2O (1/1) in 0.5 mL of volume was used as solvent. [d] 1.5 equiv. of phenylacetylene was used. [e] 2 equiv. of phenylacetylene was used.

Conclusion

In this work, the catalytic activity of palladium and bimetallic Pd-Ni nanoparticles (NPs) protected by polyvinylpyrrolidone, prepared by the reduction-by-solvent method and deposition on multi-walled carbon nanotubes (MWCNTs), in different carbon-carbon bond forming reactions has been evaluated. Bimetallic Pd50Ni50/MWCNTs using K2CO3 as base and TBAB as additive is the best catalyst for the Suzuki-Miyaura reaction of 4-bromoanisole with phenylboronic acid and for the Mizoroki-Heck reaction of 4-iodoanisole with styrene. An effective recycling could be performed only in the former case. On the other hand, Pd/MWCNTs was the catalyst of choice for Hiyama reaction of 4-iodoanisole with trimethoxyphenylsilane under fluoride-free conditions with 50% aqueous NaOH as base and for the Sonogashira-Hagihara reaction of 4-iodoanisole with phenylacetylene under copper-free conditions with pyrrolidine as base. The recyclability was moderate only for the latter reaction. All these processes have been carried out under ligand-free conditions at 120 ºC (bath temperature) during 1 h with relative low 0.1 mol% Pd loading in water as solvent.

Experimental Section

Typical procedure for the synthesis of Pd-based catalysts

Colloidal Pd-based nanoparticles were synthesized following the procedure described in our previous work,[20] using ethylene glycol as reducing agent in the so-called reduction-by-solvent method. The syntheses were performed under an Argon atmosphere in a Schlenk system. In a typical synthesis, the palladium precursor solution was prepared, in a two-necked, round-bottom flask, by adding 0.2245 g of palladium (II) acetate (Sigma-Aldrich, Ref. 205869, 98% pure) and 50 mL of 1,4-dioxane (Sigma-Aldrich, Ref. 533971, 99% pure) under vigorous stirring for 1 h, resulting in a dark-orange solution. In another two-necked, round-bottom flask, a solution containing 1.1114 g of poly(n-vinylpyrrolidone) (Sigma-Aldrich, Ref. 234257, Mw _ 40 000) and 120 mL of anhydrous ethylene glycol (Sigma-Aldrich, no. 293237, 99% pure) was prepared. Different amounts of NiSO4·6H2O (depending on the final colloid composition) were added to the mixture, and the system was stirred for 3 h at 80 ºC. The solution was light green in color. This solution was cooled to 0 ºC by means of an ice bath. Both solutions were mixed under stirring to ensure homogenization. Immediately, the pH of the resulting mixture was adjusted to 9-10 by dropwise addition of a 1 M NaOH solution. The final solution was then heated at 100 ºC under vigorous stirring. After a few minutes, the dark brown colloidal solution was formed. The heating was continued for 2 h, after which the colloidal suspension was cooled to room temperature.

The prepared colloids were purified as reported in the literature.[20] An aliquot containing the desired amount of nanoparticles was added to a large excess of acetone. This treatment produced the extraction of the protecting polymer to the acetone phase, provoking flocculation of the metallic particles. This made purification possible by either decantation or centrifugation, depending on the metallic composition of the nanoparticles. After removal of the acetone phase, the purified colloids were redispersed in a known amount of MeOH by very gentle

stirring to obtain colloidal suspensions of perfectly known concentration.

Typical procedure for the preparation of heterogeneous catalysts

Multiwall Carbon Nanotubes (MWCNTs, NanoBlack) were obtained from the Columbian Chemicals Co. and used as received. The different colloidal nanoparticles were supported on the MWCNTs using the impregnation method. First, the appropriate volume of the nanoparticles in methanol dispersion was mixed with the carbon material. All catalysts were prepared so as to have a final metal loading of 1wt %. The suspension was then gently stirred at room temperature for 2 days. After this, the suspension was transferred to an oven at 60 ºC until the methanol was evaporated. The collected solid was washed with a mixture of ethanol and water (50/50%, v/v) several times. Finally, the carbon support containing the deposited nanoparticles was dried at 110 ºC overnight.

Catalysts characterization

The metal composition in the as-prepared nanoparticles was determined using inductively coupled plasma-optical emission spectroscopy (ICP-OES), in a Perkin-Elmer Optima 4300 ICP-OES spectrometer. Before analysis, the samples were treated in a HCl:HNO$_3$ mixture for 48 h to dissolve the metallic nanoparticles. The metal loadings were obtained from the emission intensities by means of the appropriate calibration curves for Pd and Ni. An average of three analyses was done to calculate the metal content present in the samples. The loading of the heterogeneous catalysts was also performed in the same way both before and after catalytic tests in order to determine the leaching of the nanoparticles catalysts into the reaction medium.

The as-prepared metallic colloids and the corresponding heterogeneous catalysts were characterized by transmission electron microscopy (TEM) both before and after undergoing catalytic tests using a JEOL JEM-2010 high-tilt instrument operating at 200 kV with a structural partial resolution of 0.5 nm. The composition of the nanoparticles was measured by EDS coupled to the TEM equipment (OXFORD instruments model INCA Energy TEM100). The spatial resolution of the analytical TEM used (15 nm) allowed measurement of the composition of groups of about 5 particles, with a sufficient signal-to-noise ratio. The catalysts particle size distribution and Pd dispersion were calculated as reported elsewhere.[4]

Typical procedure for the Suzuki-Miyaura cross-coupling reaction with phenylboronic acid

To a screw-capped vial with a stirring bar were added 4-bromoanisole (93.5 mg, 0.5 mmol), phenylboronic acid (73 mg, 0.6 mmol), Pd$_{50}$Ni$_{50}$/MWCNTs (0.1 mol% of Pd), TBAB (161 mg, 0.5 mmol), K$_2$CO$_3$ (207 mg, 1.5 mmol), and water (0.3 mL). After stirring at 120 °C for 1 h, the reaction mixture was cooled to room temperature. After separating the catalyst and the aqueous phase by centrifugation, the aqueous phase was decanted. Recovered catalyst was washed with H$_2$O (5 × 1.0 mL) and ethyl acetate (5 × 1.0 mL), which were then added to the aqueous phase. The aqueous phase was extracted eight times with ethyl acetate. The combined organic extracts were dried over MgSO$_4$ and concentrated under reduced pressure. The product

was obtained in 99% yield and analyzed by GC and ^{1}H NMR. The recovered catalyst was dried *in vacuo* and reused.

Typical procedure for the Suzuki-Miyaura cross-coupling reaction with potassium phenyltrifluoroborate

To a screw-capped vial with a stirring bar were added 4-bromoanisole (93.5 mg, 0.5 mmol), potassium phenyltrifluoroborate (110 mg, 0.6 mmol), Pd/MWCNTs (0.1 mol% of Pd), K$_2$CO$_3$ (207 mg, 1.5 mmol), and PEG300/water (1/1: v/v) (0.3 mL). After stirring at 120 °C for 1 h, the reaction mixture was cooled to room temperature. After the same work-up described above the product was obtained in 83% yield and analyzed by GC and ^{1}H NMR. The recovered catalyst was dried *in vacuo* and reused.

Typical procedure for the Hiyama cross-coupling reaction

To a screw-capped vial with a stirring bar were added 4-iodoanisole (117 mg, 0.5 mmol), trimethoxyphenylsilane (149 mg, 0.75 mmol), Pd/MWCNTs (0.1 mol% of Pd), and 50% NaOH aqueous solution (0.1 g, 2.5 equiv). After stirring at 120 °C for 1 h, the reaction mixture was cooled to room temperature. After separating the catalyst and the aqueous phase by centrifugation, the aqueous phase was decanted. Recovered catalyst was washed with H$_2$O (5 × 1.0 mL) and ethyl acetate (5 × 1.0 mL), which were then added to the aqueous phase. The aqueous phase was extracted eight times with ethyl acetate. The combined organic extracts were dried over MgSO$_4$ and concentrated under reduced pressure. The product was analyzed by GC and ^{1}H NMR. The recovered catalyst was dried *in vacuo* and reused.

Typical procedures for the Mizoroki-Heck reaction

To a screw-capped vial with a stirring bar were added 4-iodoanisole (117 mg, 0.5 mmol), styrene (78.1 mg, 0.75 mmol), Pd$_{50}$Ni$_{50}$/MWCNTs (0.1 mol% of Pd), TBAB (161 mg, 0.5 mmol), and 3.0 mol·L^{-1} aqueous KOH solution (0.5 mL). After stirring at 120 °C for 1 h, the reaction mixture was cooled to room temperature. After separating the catalyst and the aqueous phase by centrifugation, the aqueous phase was decanted. Recovered catalyst was washed with H$_2$O (5 × 1.0 mL) and ethyl acetate (5 × 1.0 mL), which were then added to the aqueous phase. The aqueous phase was extracted eight times with ethyl acetate. The combined organic extracts were dried over MgSO$_4$ and concentrated under reduced pressure. The product was analyzed by GC. The recovered catalyst was dried *in vacuo* and reused.

Typical procedures for the Sonogashira-Hagihara reaction

To a screw-capped vial with a stirring bar were added 4-iodoanisole (117 mg, 0.5 mmol), phenylacetylene (102 mg, 1.0 mmol), Pd/MWCNTs (0.1 mol% of Pd), pyrrolidine (71 mg, 1.0 mmol), and water (0.5 mL). After stirring at 120 °C for 1 h, the reaction mixture was cooled to room temperature. After separating the catalyst and the aqueous phase by centrifugation, the aqueous phase was decanted. Recovered catalyst was washed with H$_2$O (5 × 1.0 mL) and ethyl acetate (5 × 1.0 mL), which were then added to the aqueous phase. The aqueous phase was extracted eight times with ethyl acetate. The

combined organic extracts were dried over MgSO$_4$ and concentrated under reduced pressure. The product was analyzed by GC. The recovered catalyst was dried *in vacuo* and reused.

All the products obtained are described in the literature and the analytical data perfectly fits with the reported values.

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Entry for the Table of Contents (Please choose one layout only)

Layout 1:

FULL PAPER

From black to green: The catalytic activity of palladium and bimetallic Pd-Ni nanoparticles (NPs) deposited on multi-walled carbon nanotubes (MWCNTs) as catalyst for cross-coupling reactions in water at 120 ºC during 1 h with 0.1 mol% Pd loading under ligand-less conditions is disclosed. These reaction conditions represent an environmentally friendly alternative to those previously reported reactions in organic solvents.

Atsushi Ohtaka, José M. Sansano, Carmen Nájera*, Izaskun Miguel-García, Ángel Berenguer-Murcia, Diego Cazorla-Amorós*

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Palladium and bimetallic palladium-nickel nanoparticles supported on multi-walled carbon nanotubes: application to carbon-carbon bond forming reactions in water

FULL PAPERS

Palladium and bimetallic palladium-nickel nanoparticles supported on multi-walled carbon nanotubes: application to carbon-carbon bond forming reactions in water

Atsushi Ohtaka,[a] José M. Sansano,[a] Carmen Nájera,*[a] Izaskun Miguel-García,[b] Ángel Berenguer-Murcia,[b] Diego Cazorla-Amorós,*[b]

Dedication ((optional))

Palladium and bimetallic Pd-Ni nanoparticles (NPs) protected by polyvinylpyrrolidone have been prepared by the reduction-by-solvent method and deposited on multi-walled carbon nanotubes (MWCNTs). The catalytic activity of these NPs to carbon-carbon bond forming reactions has been studied using 0.1 mol% Pd loading, at 120 ºC for 1 h and water as solvent under ligand-free conditions. The Suzuki-Miyaura reaction takes place quantitatively for the cross-coupling of 4-bromoanisole with phenylboronic acid, better than potassium phenyltrifluoroborate, with $Pd_{50}Ni_{50}$/MWCNTs using K_2CO_3 as base and TBAB as additive with good recyclability during 4 cycles with some Ni leaching. The Hiyama reaction of 4-iodoanisole with trimethoxyphenyl-silane, under fluoride-free conditions using 50% aqueous NaOH solution, is performed with Pd/MWCNTs as catalyst in 83% yield with low recyclability. For the Mizoroki-Heck reaction 4-iodoanisole and styrene gave the corresponding 4-methoxystilbene quantitatively with $Pd_{50}Ni_{50}$/MWCNTs using K_2CO_3 as base and TBAB as additive although the recycle failed. In the case of the Sonogashira-Hagihara reaction Pd/MWCNTs has to be used as catalyst and pyrrolidine as base for the coupling of 4-iodoanisole with phenylacetylene under copper-free conditions. The corresponding 4-methoxytolane was quantitatively obtained allowing the recycling of the catalyst during 3 cycles.

Introduction

Carbon nanotubes (CNTs) have excellent electronic properties, good chemical stability, and large surface areas, leading therefore to promising applications as catalyst supports. The attachment of nanoparticles (NPs) on CNTs has attracted great interest, for the nanocomposites not only combine the extraordinary properties of the NPs and CNTs, but also exhibit some new properties caused by the interaction between them.[1] Several research groups have reported the synthesis of CNTs-supported metal NPs and their catalytic activity for various chemical reactions including Suzuki coupling reaction, Heck reaction and hydrogenation. However, most of the reactions were performed in organic solvents or mixed organic/aqueous solvents, and neat water is seldom used as a reaction medium.[2,3]

The enhanced catalytic activity of metal nanoparticles is well-established in the literature. Among the applications which we have tested, one of the examples that stands out in the context of the present manuscript is the deposition of diverse Pd-based nanoparticles protected by polyvinylpyrrolidone (PVP) synthesized by the reduction-by-solvent method on different carbon materials for the selective hydrogenation of phenylacetyene.[4] Recently, we reported the preparation of Pd and bimetallic Pd-Ni nanoparticles and their deposition on single-walled carbon nanotubes (SWCNTs).[5] On the other hand, multi-walled carbon nanotubes (MWCNTs) have been found to be superior supports compared to other carbon materials such as SWCNTs. For example, MWCNTs are able to uptake the highest number of nanoparticles per unit surface area and MWCNTs-supported palladium NPs showed a slightly better reactivity.[2c,2d] We envisaged that these Pd and bimetallic Pd-Ni nanoparticles supported on MWCNTs could be useful catalysts in cross-coupling reactions having two main advantages a lower amount of palladium and to allow the recovery of these supported NPs by simple filtration from the reaction media. In addition we have chosen water as solvent not only because of its economical and ecological relevance but also because Corma has demonstrated that in water Pd clusters are easily formed from the precursor NPs, showing higher stability, faster reaction rates, and lower leaching than in organic solvents in different carbon-carbon bond

[a]   Dr. A. Ohtaka, Prof. J. M. Sansano, Prof. C. Nájera
      Dpto. de Química Orgánica and Centro de Innovación en Química Avanzada (ORFEO-CINQA), University of Alicante
      Apdo.99, E-03080, Alicante, Spain
      Fax: (+) 0034-965903549
      E-mail: cnajera@ua.es
[b]   Dr. I. Miguel-García, Dr. Á. Berenguer-Murcia, Prof. D. Cazorla-Amorós
      Dpto. Química Inorgánica and Instituto Universitario de Materiales
      University of Alicante
      Fax: (+) 0034-965903454
      E-mail: cazorla@ua.es
      Supporting information for this article is available on the WWW under http://dx.doi.org/10.1002/cctc.200xxxxxx.

forming reactions.[6] Herein we report the study about the catalytic activity of Pd and bimetallic Pd-Ni nanoparticles stabilized by PVP and supported on MWCNTs for several relevant C-C bond formation processes in water[7] such as Suzuki-Miyaura, Hiyama, Mizoroki-Heck and Sonogashira-Hagihara reactions.[8]
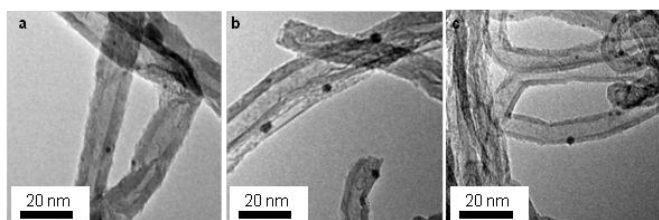
Results and Discussion

In order to determine the efficiency of the loading step as well as to assess the particle size and its dispersion in the prepared heterogeneous catalysts, ICP-OES and TEM studies were performed for all samples. The results of the ICP analysis for the metal contents of the prepared NPs/MWCNTs samples are summarized in Table 1. It can be observed that the initially targeted 1 wt % metal loading was not really achieved. Therefore, the rest of the metal was lost during the synthesis procedure, probably during the washing step, where Pd NPs not bound strongly enough were washed off the carbon support.

Table 1. TEM and ICP characterization results of the heterogeneous catalysts prepared.

Catalyst	Metal loading ICP (total wt %)	d_{TEM} (nm)	D_{TEM} (%)
Pd/MWCNTs	0.75%	2.55 ± 0.57	35.3
$Pd_{90}Ni_{10}$/MWCNTs[a]	0.62%	2.39 ± 0.42	37.6
$Pd_{70}Ni_{30}$/MWCNTs[a]	0.58%	2.03 ± 0.57	44.3
$Pd_{50}Ni_{50}$/MWCNTs[a]	0.70%	2.42 ± 0.51	37.2
$Pd_{30}Ni_{70}$/MWCNTs[a]	0.69%	2.71 ± 0.54	33.2

[a] The nomenclature Pd_xNi_y denotes the atomic composition of the metal nanoparticles employed during their synthesis, irrespective of their particle size (see Experimental section).

To directly correlate the metal dispersion of NPs/MWCNTs catalysts, TEM analyses were also performed on the as-synthesized samples. Figure 1 shows TEM micrographs of (a) Pd/MWCNTs, (b) $Pd_{70}Ni_{30}$/MWCNTs, and (c) $Pd_{50}Ni_{50}$/MWCNTs. Both Pd average particle sizes (d, nm) and metal dispersion (D, %) results of the three catalysts obtained from TEM analyses are shown in the third and fourth columns of Table 1. It must be highlighted that the particle sizes of the metal nanoparticles in the catalysts are very similar to the average particle size of the metal particles of the colloid (2.4 ± 0.5 nm).[9] Thus, not only were the prepared heterogeneous catalysts of the desired atomic composition, but also they displayed a very small particle size and a narrow size distribution.

Figure 1. TEM images of catalysts (a) Pd/MWCNTs, (b) $Pd_{70}Ni_{30}$/MWCNTs and (c) $Pd_{50}Ni_{50}$/MWCNTs.

Initial studies were performed using different Pd NPs supported on MWCNTs in the Suzuki-Miyaura reaction[10] of 4-bromoanisole with phenylboronic acid using 0.1 mol% Pd loading, K_2CO_3 as base and water as solvent at 100 ºC for 1 h, reaction conditions which we stablished previously using Pd(OAc)$_2$ or an oxime-

derived palladacycle[11] (Table 2). Under these reaction conditions, the best 63% yield was obtained with the bimetallic $Pd_{30}Ni_{70}$/MWCNTs (Table 2, entry 4). In all these cases, better results were observed using the catalyst supported on MWCNTs than with Pd NPs coated with PVP (Table 2, entry 5).

Next the optimization of the reaction conditions was considered using the bimetallic $Pd_{30}Ni_{70}$/MWCNTs as precatalyst (Table 3). When KOH was used as base a lower yield was obtained with respect to K_2CO_3 (Table 3, entries 1 and 2). Working at 100 ºC with K_2CO_3 as base, the Pd loading was increased from 0.1 to 0.2 and 0.3 mol% giving slightly lower yields (Table 3, entries 2-4). When the reaction time was increased from 1 to 2 h the yield did not increase (61%) and after 3 h a slightly higher 72% was obtained (Table 3, compare entry 2 with 5 and 6). Increasing the bath temperature to 120 ºC has a positive increment in the yield from 63 to 83% (Table 3, entry 7). The addition of additives such as polyethylene glycol 300 as a 1/5 volume proportion afforded higher 92% yield (Table 3, entry 8). When the amount of phenylboronic acid was reduced from 1.5 to 1.2 equiv. and using 1 equiv. of tetra-n-butylammonium bromide (TBAB) which is a well-known NPs stabilizer,[12] the highest 95% yield was obtained. Under the last reaction conditions, similar yields were obtained with the rest of supported Pd NPs (Table 3, entries 10-13), although $Pd_{50}Ni_{50}$/MWCNTs seems to be the best precatalyst (entry 12).
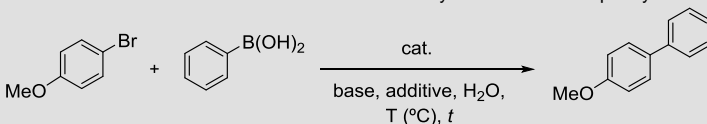
Table 2. Catalytic activity of Pd and bimetallic Pd-Ni NPs in the Suzuki-Miyaura reaction using phenylboronic acid in water.[a]

Entry	Catalyst	Yield (%)[b]
1	Pd/MWCNTs	54
2	$Pd_{70}Ni_{30}$/MWCNTs	48
3	$Pd_{50}Ni_{50}$/MWCNTs	47
4	**$Pd_{30}Ni_{70}$/MWCNTs**	**63**
5[c]	PVP-Pd	30

[a] Reaction conditions: 4-bromoanisole (0.5 mmol), phenylboronic acid (0.75 mmol), catalyst (0.1 mol% Pd), K_2CO_3 (1.5 mmol) in H_2O (0.3 mL). [b] Determined by GC analysis based on 4-bromoanisole consumption. [c] In 0.5 mL of H_2O.

Under the optimum reaction conditions involving the use of $Pd_{50}Ni_{50}$/MWCNTs (0.1 mol% of Pd), 3 equiv of K_2CO_3, and 1 equiv. of TBAB at 120 °C the recyclability of the catalyst was studied (Scheme 1). The cross-coupling reaction of 4-bromoanisole with phenylboronic acid (1.2 equiv) was performed giving 4-methoxybiphenyl in 99% yield. When the reaction was completed, the catalyst was recovered by decantation and successively subjected to second through fourth runs of the coupling reaction under the same conditions to afford 4-methoxybiphenyl in 89%, 86%, and 87% yields, respectively (Scheme 1). ICP-OES analysis revealed that a slight decrease
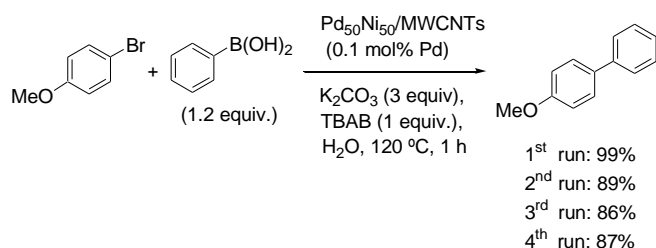
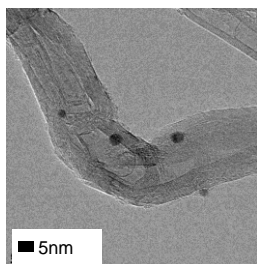**Table 3.** Reaction condition studies for the Suzuki-Miyaura reaction with phenylboronic acid in water.[a]

Entry	Cat. (mol% Pd)	Base	Additive	Temp. (ºC)	Time (h)	Yield (%)[b]
1	$Pd_{30}Ni_{70}$/MWCNTs (0.1)	KOH	-	100	1	41
2	$Pd_{30}Ni_{70}$/MWCNTs (0.1)	K_2CO_3	-	100	1	63
3	$Pd_{30}Ni_{70}$/MWCNTs (0.2)	K_2CO_3	-	100	1	53
4	$Pd_{30}Ni_{70}$/MWCNTs (0.3)	K_2CO_3	-	100	1	57
5	$Pd_{30}Ni_{70}$/MWCNTs (0.1)	K_2CO_3	-	100	2	61
6	$Pd_{30}Ni_{70}$/MWCNTs (0.1)	K_2CO_3	-	100	3	72
7	$Pd_{30}Ni_{70}$/MWCNTs (0.1)	K_2CO_3	-	120	1	83
8	$Pd_{30}Ni_{70}$/MWCNTs (0.1)	K_2CO_3	PEG300[c]	120	1	92
9[d]	$Pd_{30}Ni_{70}$/MWCNTs (0.1)	K_2CO_3	TBAB[e]	120	1	95
10[d]	Pd/MWCNTs (0.1)	K_2CO_3	TBAB[e]	120	1	96
11[d]	$Pd_{70}Ni_{30}$/MWCNTs (0.1)	K_2CO_3	TBAB[e]	120	1	94
12[d]	**$Pd_{50}Ni_{50}$/MWCNTs (0.1)**	**K_2CO_3**	**TBAB[e]**	**120**	**1**	**>99**
13[d]	$Pd_{10}Ni_{90}$/MWCNTs (0.1)	K_2CO_3	TBAB[e]	120	1	95

[a] Reaction conditions: 4-bromoanisole (0.5 mmol), phenylboronic acid (0.75 mmol), catalyst (see column), base (1.5 mmol) in H_2O (0.3 mL). [b] Determined by GC analysis based on 4-bromoanisole consumption. [c] PEG300/H_2O (1/5) in 0.5 mL of volume was used as solvent. [d] 1.2 mmol of phenylboronic acid were used. [e] 0.5 mmol.

of the amount of Ni was observed (from 0.24 wt% to 0.12 wt%), and that no metal species was observed in the product. TEM image (Figure 2) of the recovered catalyst after the fourth run revealed the particle size increased slightly compared with that of the fresh catalyst (3.65 ± 0.95 nm and 2.42 ± 0.51 nm, respectively). It appears that under the conditions described in the manuscript the nanoparticles are etched and their size increases upon consecutive reaction cycles.
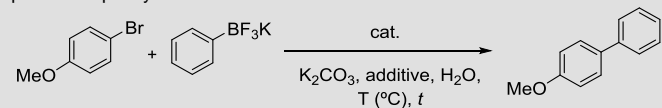

Scheme 1. Reciclability of bimetallic $Pd_{50}Ni_{50}$/MWCNTs for the Suzuki-Miyaura reaction with phenylboronic acid in water.

Figure 2. TEM image of the $Pd_{50}Ni_{50}$/MWCNTs catalyst after the 4th cycle in the Suzuki-Miyaura process.

Further applications of these supported Pd NPs on MWCNTs in the same Suzuki-Miyaura reaction using 4-bromoanisole and potassium phenyltrifluoroborate were next studied (Table 4). Working at 100 ºC with 0.1 mol% Pd loading using K_2CO_3 as base in water as solvent, reaction conditions which we stablished previously by us using Pd(OAc)$_2$ or an oxime-derived palladacycle,[13] but without additives (Table 4, entries 1-5), the highest 64 and 65% yields were obtained with Pd/MWCNTs and P$_{30}$Ni$_{70}$/MWCNTs, respectively (Table 4, entries 1 and 4). Working at 120 ºC with Pd/MWCNTs either during 1 or 3 h similar (81 and 83%) yields were obtained (Table 4, entries 6 and 7). When 1 equiv. of TBAB was added a lower 76% yield was observed (Table 4, entry 8). However, a decrease of the potassium phenyltrifluoroborate from 1.5 to 1.2 equiv. increased the yield from 83 to 88% (Table 4, entries 7 and 9) and in the presence of TBAB or PEG300 to 94 and 95%, respectively (Table 4, entries 10 and 11). However, the second recycling experiment under the last reaction conditions gave 4-methoxybiphenyl in only 21% yield. We can conclude that phenylboronic acid is a better substrate than potassium phenyltrifluoroborate for the recycling of the catalyst.

Other results found in the literature for the Suzuki-Miyaura reaction performed in heterogeneous media include Pd-based systems supported on different inorganic oxides, such as fibrous silica[143a] or mesoporous materials [153b, 13c]. The systems reported performed similarly to those obtained in our study in the absence of TBAB, with the main differences being that our study is focused in using water as the only solvent and our support should

Table 4. Reaction conditions studies for the Suzuki-Miyaura reaction with potassium phenyltrifluoroborate in water.[a]

Entry	Cat. (mol% Pd)	Additive	Temp. (ºC)	Time (h)	Yield (%)[b]
1	Pd/MWCNTs (0.1)	-	100	1	64
2	Pd$_{70}$Ni$_{30}$/MWCNTs (0.1)	-	100	1	30
3	Pd$_{50}$Ni$_{50}$/MWCNTs (0.1)	-	100	1	44
4	Pd$_{30}$Ni$_{70}$/MWCNTs (0.1)	-	100	1	65
5	PVP-Pd	-	100	1	38
6	Pd/MWCNTs (0.1)	-	120	1	81
7	Pd/MWCNTs (0.1)	-	120	3	83
8	Pd/MWCNTs (0.1)	TBAB[c]	120	1	76
9[d]	Pd/MWCNTs (0.1)	-	120	1	88
10[d]	**Pd/MWCNTs (0.1)**	**TBAB[c]**	**120**	**1**	**94**
11[d]	**Pd/MWCNTs (0.1)**	**PEG300 [e]**	**120**	**1**	**95**

[a] Reaction conditions: 4-bromoanisole (0.5 mmol), potassium phenyltrifluoroborate (0.75 mmol), catalyst (see column), base (1.5 mmol) in H$_2$O (0.3 mL). [b] Determined by GC analysis based on 4-bromoanisole consumption. [c] 1 equiv. was added. [d] 1.2 mmol of potassium phenyltrifluoroborate were used. [e] PEG300/H$_2$O (5/1) in 0.5 mL of volume was used as solvent.
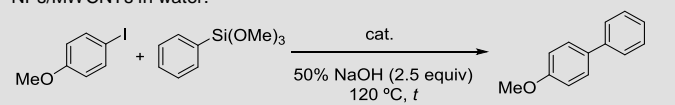
possess an enhanced hydrothermal stability as compared to amorphous silica-based supports. In this sense, it must be noted that even though the catalytic performance of our systems is poorer than the well-known homogeneous systems used for this type of C-C coupling reactions[16,13d] (their outstanding performance deriving from a very low catalytic loading and excellent catalytic activity and selectivity), the easy recovery and reusability of the catalysts makes for a very convenient advantage from an applied point of view.

Next, the Hiyama reaction[174] was first evaluated using 4-bromoanisole and trimethoxyphenylsilane as model reaction with 2.5 equiv of 50% aqueous NaOH solution in the absence of a fluoride source, reaction conditions which we stablished previously by us using Pd(OAc)$_2$ or an oxime-derived palladacycle.[185] In the presence of the different Pd NPs supported on MWCNTs (0.1 mol% of Pd) at 90 °C for 3 h to afford the desired coupling product in low yields (7-32%). Then, the coupling between 4-iodoanisole and trimethoxyphenylsilane was performed with 2.5 equiv of 50% NaOH in the presence of Pd NPs supported in MWCNTs (0.1 mol% of Pd) at 120 °C (Table 5). In the case of using 1.5 equiv. of trimethoxyphenylsilane all the catalysts gave 4-methoxybiphenyl in 92-96% yield (Table 5, entries 1-4). However, lowering the amount of siloxane to 1.2 equiv. the best yield was obtained with Pd NPs supported in MWCNTs (Table 5, entry 5). The recycling experiments gave very low yields, 40 and 53% in the second and third cycle, respectively. It should be mentioned that after undergoing 3 reaction cycles in the Hiyama reaction, the catalyst Pd/MWCNTs showed a decrease in the yield of the desired product from 95% to 53%, indicating a strong deactivation. Post reaction ICP-OES and TEM analyses performed on the used catalyst showed a marked

decrease in the metal loading (from 0.75%, see Table 1, to 0.2%) and a particle size of 5.2 ± 1.5 nm. This behaviour shows that the strongly basic reaction medium not only leaches the Pd from the catalyst into the liquid phase, but also provokes a significant increase in the Pd nanoparticle size, which ultimately results in an impoverished catalytic activity.

For the Mizoroki-Heck reaction[196] in water catalyzed by Pd NPs supported on MWCNTs (0.1 mol% Pd) 4-methoxyiodobenzene and styrene (1.5 equiv) were chosen as model substrates (Table 6). The reaction conditions were studied using dicyclohexylmethylamine as base under the previous conditions developed by our group[20,17] with very poor results. However, better yields were obtained in the presence of KOH (3 equiv.) as base in the presence of TBAB as additive or in a
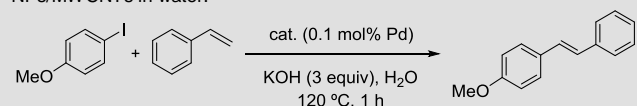
mixture of PEG300 and water as solvent at 120 ºC during 1 h. In the case of Pd/MWCNTs using PEG300/H$_2$O (v/v:1/1) quantitative formation of 4-methoxystilbene was observed (Table 6, entry 1). By using TBAB (1 equiv.) as additive a 90% yield was obtained (Table 6, entry 2). Under these reaction conditions Pd$_{70}$Ni$_{30}$/MWCNTs gave the same results (Table 6, entry 3). Quantitative yields were also achieved with Pd$_{50}$Ni$_{50}$/MWCNTs and Pd$_{30}$Ni$_{70}$/MWCNTs catalysts (Table 6, entries 4 and 5). On the other hand, Pd$_{10}$Ni$_{90}$/MWCNTs gave the same yield (90%)

Table 5. Reaction conditions studies for the Hiyama reaction using Pd NPs/MWCNTs in water.[a]

Entry	Cat. (mol% Pd)	PhSi(OMe)$_3$ equiv.	Time (h)	Yield (%)[b]
1	Pd/MWCNTs (0.1)	1.5	3	95
2	Pd$_{70}$Ni$_{30}$/MWCNTs (0.1)	1.5	3	96
3	Pd/MWCNTs (0.1)	1.5	1	95
4	Pd$_{70}$Ni$_{30}$/MWCNTs (0.1)	1.5	1	92
5	**Pd/MWCNTs (0.1)**	**1.2**	**1**	**85**
6	Pd$_{70}$Ni$_{30}$/MWCNTs (0.1)	1.2	1	77
7	Pd$_{50}$Ni$_{50}$/MWCNTs (0.1)	1.2	1	76
8	Pd$_{30}$Ni$_{70}$/MWCNTs (0.1)	1.2	1	82

[a] Reaction conditions: 4-iodoanisole (0.5 mmol), trimethoxyphenylsilane (see column), catalyst (0.1 mol% Pd), 50% aq. NaOH (2.5 mmol). [b] Determined by GC analysis based on 4-iodoanisole consumption.
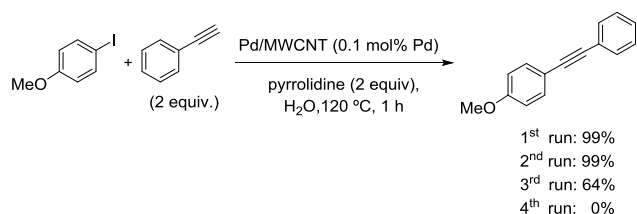
than Pd/MWCNTss (Table 6, entry 6). When the recycling experiments were carried out with Pd$_{50}$Ni$_{50}$/MWCNTs under the best reaction conditions the reaction failed in the second run. As stated above in the case of the Suzuki-Miyaura reaction, our catalysts show a poorer performance than homogeneous systems based on noble metal nanoparticles protected by relatively complex protecting agents such as dendrimers, which in certain cases may act as supports[16,13d]. Other examples of such systems employed in the Mizoroki-Heck reaction include the formation of nanoparticles in microemulsion systems, which may be immobilized in polymers with intrinsic microporosity to give rise to heterogenous catalysts[21,17a].

4

Table 6. Reaction conditions studies for the Mizoroki-Heck reaction using Pd NPs/MWCNTs in water.[a]

Entry	Cat.	Additive	Yield (%)[b]
1	Pd/MWNT	PEG300[c]	99
2	Pd/MWNT	TBAB[d]	90
3	Pd$_{70}$Ni$_{30}$/MWNT	TBAB[d]	91
4	**Pd$_{50}$Ni$_{50}$/MWNT**	**TBAB[d]**	**99**
5	Pd$_{30}$Ni$_{70}$/MWNT	TBAB[d]	99
6	Pd$_{10}$Ni$_{90}$/MWNT	TBAB[d]	90

[a] Reaction conditions: 4-iodoanisole (0.5 mmol), styrene (0.75 mmol), catalyst (0.1 mol% Pd), KOH (1.5 mmol). [b] Determined by GC analysis based on 4-iodoanisole consumption. [c] PEG300/H$_2$O (1/1) in 0.5 mL of volume was used as solvent. [d] TBAB (0.5 mmol).

Table 7. Reaction conditions studies for the Sonogashira-Hagihara reaction in water.[a]

Entry	Cat.	Additive	Time (h)	Yield (%)[b]
1	Pd/MWCNTs	-	5	74
2	Pd/MWCNTs	PEG300[c]	5	73
3[d]	Pd/MWCNTs	-	5	92
4[d]	Pd/MWCNTs	-	1	92
5[e]	**Pd/MWCNTs**	**-**	**1**	**99**
6[e]	Pd$_{70}$Ni$_{30}$/MWCNTs	-	1	74
7[e]	Pd$_{50}$Ni$_{50}$/MWCNTs	-	1	69
8[e]	Pd$_{30}$Ni$_{70}$/MWCNTs	-	1	68
9[e]	Pd$_{10}$Ni$_{90}$/MWCNTs	-	1	60

[a] Reaction conditions: 4-iodoanisole (0.5 mmol), phenylacetylene (0.75 mmol), catalyst (0.1 mol% Pd), pyrrolidine (1 mmol). [b] Determined by GC analysis based on 4-iodoanisole consumption. [c] PEG300/H$_2$O (1/1) in 0.5 mL of volume was used as solvent. [d] 1.5 equiv. of phenylacetylene was used. [e] 2 equiv. of phenylacetylene was used.

For the Sonogashira-Hagihara reaction[22,8] the cross-coupling between 4-iodoanisole and phenylacetylene was studied in the presence of pyrrolidine as base, at 120 ºC in water as solvent, that means reaction conditions set up by our group[23,9] (Table 7). In the presence of Pd/MWCNTs under copper-free conditions the reaction needed 5 h in order to get 4-methoxytolane in 74% yield. However, in the presence of PEG300/H$_2$O (1/1: v/v) as solvent a similar 73% yield was obtained (Table 7, entry 2). By increasing the amount of phenylacetylene from 1.2 to 1.5 equiv. it was possible to obtain the corresponding internal acetylene in 92% yield not only in 5 h but also in only 1 h reaction time (Table 7, entries 3-5). Quantitative yield could be obtained by using 2.0 equiv. of phenylacetylene (Table 7, entry 5). Under the last reaction conditions, the bimetallic Pd-Ni NPs gave lower yields (Table 7, entries 6-9). Therefore, the recycling experiments were carried out with Pd/MWCNTs under the reaction conditions indicated in Table 7, entry 5. The two first cycles took place in quantitative yields, but in the third one 4-methoxytolane was obtained in only 64% yield and in the fourth the reaction failed (Scheme 2).

1st run: 99%
2nd run: 99%
3rd run: 64%
4th run: 0%

Scheme 2. Reciclability of Pd NPs/MWCNTs catalyst for the Sonogashira-Hagihara reaction in water.

Considering our catalytic systems as a whole, it becomes important to establish (or at least draw some hypothesis) on the role of the Ni present in the metal nanoparticles. From an applied standpoint, one of the main ideas behind the incorporation of Ni in the nanoparticles was to decrease the cost of the active phase of the catalysts without affecting their catalytic performance. However, the presence of this metal might have an effect on the performance of Pd as active metal for the reaction. In this sense, an increased number of Ni atoms in the nanoparticles will dilute the Pd active sites and in turn reflect in an apparent decrease of the catalytic activity, as previously related in other works of our research group.[9,21] Furthermore, the incorporation of Ni in the nanoparticles composition brings forth the generation of an alloy between Ni and Pd, which reflects in an electronic interaction between both metals, where Pd withdraws some electronic density from them (due to its higher electronegativity) thus generating electron deficient Ni species, as it has also been previously reported in our group.[5,22] This partial Ni oxidation may also affect the performance of the active phase in the prepared catalysts, although the exact extent of this phenomenon lies beyond the scope of the present paper. Finally, being Ni more reactive than Pd, under reaction conditions it may be oxidized more easily than Pd. This may cause the metal nanoparticles to become partially dissolved in the reaction medium giving rise to some metal leaching during the different reaction cycles, as has been observed in this work in some cases.

Conclusion

In this work, the catalytic activity of palladium and bimetallic Pd-Ni nanoparticles (NPs) protected by polyvinylpyrrolidone, prepared by the reduction-by-solvent method and deposition on

multi-walled carbon nanotubes (MWCNTs), in different carbon-carbon bond forming reactions has been evaluated. Bimetallic $Pd_{50}Ni_{50}$/MWCNTs using K_2CO_3 as base and TBAB as additive is the best catalyst for the Suzuki-Miyaura reaction of 4-bromoanisole with phenylboronic acid and for the Mizoroki-Heck reaction of 4-iodoanisole with styrene. An effective recycling could be performed only in the former case. On the other hand, Pd/MWCNTs was the catalyst of choice for Hiyama reaction of 4-iodoanisole with trimethoxyphenylsilane under fluoride-free conditions with 50% aqueous NaOH as base and for the Sonogashira-Hagihara reaction of 4-iodoanisole with phenylacetylene under copper-free conditions with pyrrolidine as base. The recyclability was moderate only for the latter reaction. All these processes have been carried out under ligand-free conditions at 120 ºC (bath temperature) during 1 h with relative low 0.1 mol% Pd loading in water as solvent.

Experimental Section

Typical procedure for the synthesis of Pd-based catalysts

Colloidal Pd-based nanoparticles were synthesized following the procedure described in our previous work,[2420] using ethylene glycol as reducing agent in the so-called reduction-by-solvent method. The syntheses were performed under an Argon atmosphere in a Schlenk system. In a typical synthesis, the palladium precursor solution was prepared, in a two-necked, round-bottom flask, by adding 0.2245 g of palladium (II) acetate (Sigma-Aldrich, Ref. 205869, 98% pure) and 50 mL of 1,4-dioxane (Sigma-Aldrich, Ref. 533971, 99% pure) under vigorous stirring for 1 h, resulting in a dark-orange solution. In another two-necked, round-bottom flask, a solution containing 1.1114 g of poly(n-vinylpyrrolidone) (Sigma-Aldrich, Ref. 234257, Mw _ 40 000) and 120 mL of anhydrous ethylene glycol (Sigma-Aldrich, no. 293237, 99% pure) was prepared. Different amounts of $NiSO_4 \cdot 6H_2O$ (depending on the final colloid composition, which is noted as Pd_xNi_y where x and y indicates the atomic percentage of Pd and Ni, respectively) were added to the mixture, and the system was stirred for 3 h at 80 ºC. The solution was light green in color. This solution was cooled to 0 ºC by means of an ice bath. Both solutions were mixed under stirring to ensure homogenization. Immediately, the pH of the resulting mixture was adjusted to 9-10 by dropwise addition of a 1 M NaOH solution. The final solution was then heated at 100 ºC under vigorous stirring. After a few minutes, the dark brown colloidal solution was formed. The heating was continued for 2 h, after which the colloidal suspension was cooled to room temperature.

The prepared colloids were purified as reported in the literature.[2420] An aliquot containing the desired amount of nanoparticles was added to a large excess of acetone. This treatment produced the extraction of the protecting polymer to the acetone phase, provoking flocculation of the metallic particles. This made purification possible by either decantation or centrifugation, depending on the metallic composition of the nanoparticles. After removal of the acetone phase, the purified colloids were redispersed in a known amount of MeOH by very gentle stirring to obtain colloidal suspensions of perfectly known concentration.

Typical procedure for the preparation of heterogeneous catalysts

Multiwall Carbon Nanotubes (MWCNTs, NanoBlack) were obtained from the Columbian Chemicals Co. and used as received. The different colloidal nanoparticles were supported on the MWCNTs using the impregnation method. First, the appropriate volume of the nanoparticles in methanol dispersion was mixed with the carbon material. All catalysts were prepared so as to have a final metal loading of 1wt %. The suspension was then gently stirred at room temperature for 2 days. After this, the suspension was transferred to an oven at 60 ºC until the methanol was evaporated. The collected solid was washed with a mixture of ethanol and water (50/50%, v/v) several times. Finally, the carbon support containing the deposited nanoparticles was dried at 110 ºC overnight.

Catalysts characterization

The metal composition in the as-prepared nanoparticles was determined using inductively coupled plasma-optical emission spectroscopy (ICP-OES), in a Perkin-Elmer Optima 4300 ICP-OES spectrometer. Before analysis, the samples were treated in a $HCl:HNO_3$ mixture for 48 h to dissolve the metallic nanoparticles. The metal loadings were obtained from the emission intensities by means of the appropriate calibration curves for Pd and Ni. An average of three analyses was done to calculate the metal content present in the samples. The loading of the heterogeneous catalysts was also performed in the same way both before and after catalytic tests in order to determine the leaching of the nanoparticles catalysts into the reaction medium.

Characterization results of the NPs composition indicated that the nanoparticles prepared by this procedure present a bimetallic composition that is very close to the nominal metal content within a margin of ±4 mol%. The targeted and actual metal composition of the NPs in each case are detailed in Table 8. Particle size has no effect on the metal composition obtained in each case.

Table 8. ICP characterization of the NPs composition	
Nominal composition	Actual metal composition of the NPs (mol %, ICP)
NiPd (90:10)	14% Pd
	86% Ni
NiPd (70:30)	27% Pd
	73% Ni
NiPd (50:50)	52% Pd
	48% Ni
NiPd (30:70)	69% Pd
	31% Ni
Pd (100)	100% Pd

The as-prepared metallic colloids and the corresponding heterogeneous catalysts were characterized by transmission electron microscopy (TEM) both before and after undergoing catalytic tests using a JEOL JEM-2010 high-tilt instrument operating at 200 kV with a structural partial resolution of 0.5 nm. The composition of the nanoparticles was measured by EDS coupled to the TEM equipment (OXFORD instruments model INCA Energy TEM100). The spatial resolution of the analytical TEM used (15 nm) allowed measurement of the composition of groups of about 5 particles, with a sufficient

signal-to-noise ratio. The catalysts particle size distribution and Pd dispersion were calculated as reported elsewhere.[4]

Typical procedure for the Suzuki-Miyaura cross-coupling reaction with phenylboronic acid

To a screw-capped vial with a stirring bar were added 4-bromoanisole (93.5 mg, 0.5 mmol), phenylboronic acid (73 mg, 0.6 mmol), $Pd_{50}Ni_{50}$/MWCNTs (0.1 mol% of Pd), TBAB (161 mg, 0.5 mmol), K_2CO_3 (207 mg, 1.5 mmol), and water (0.3 mL). After stirring at 120 °C for 1 h, the reaction mixture was cooled to room temperature. After separating the catalyst and the aqueous phase by centrifugation, the aqueous phase was decanted. Recovered catalyst was washed with H_2O (5 × 1.0 mL) and ethyl acetate (5 × 1.0 mL), which were then added to the aqueous phase. The aqueous phase was extracted eight times with ethyl acetate. The combined organic extracts were dried over $MgSO_4$ and concentrated under reduced pressure. The product was obtained in 99% yield and analyzed by GC and ^1H NMR. The recovered catalyst was dried *in vacuo* and reused.

Typical procedure for the Suzuki-Miyaura cross-coupling reaction with potassium phenyltrifluoroborate

To a screw-capped vial with a stirring bar were added 4-bromoanisole (93.5 mg, 0.5 mmol), potassium phenyltrifluoroborate (110 mg, 0.6 mmol), Pd/MWCNTs (0.1 mol% of Pd), K_2CO_3 (207 mg, 1.5 mmol), and PEG300/water (1/1: v/v) (0.3 mL). After stirring at 120 °C for 1 h, the reaction mixture was cooled to room temperature. After the same work-up described above the product was obtained in 83% yield and analyzed by GC and ^1H NMR. The recovered catalyst was dried *in vacuo* and reused.

Typical procedure for the Hiyama cross-coupling reaction

To a screw-capped vial with a stirring bar were added 4-iodoanisole (117 mg, 0.5 mmol), trimethoxyphenylsilane (149 mg, 0.75 mmol), Pd/MWCNTs (0.1 mol% of Pd), and 50% NaOH aqueous solution (0.1 g, 2.5 equiv). After stirring at 120 °C for 1 h, the reaction mixture was cooled to room temperature. After separating the catalyst and the aqueous phase by centrifugation, the aqueous phase was decanted. Recovered catalyst was washed with H_2O (5 × 1.0 mL) and ethyl acetate (5 × 1.0 mL), which were then added to the aqueous phase. The aqueous phase was extracted eight times with ethyl acetate. The combined organic extracts were dried over $MgSO_4$ and concentrated under reduced pressure. The product was analyzed by GC and ^1H NMR. The recovered catalyst was dried *in vacuo* and reused.

Typical procedures for the Mizoroki-Heck reaction

To a screw-capped vial with a stirring bar were added 4-iodoanisole (117 mg, 0.5 mmol), styrene (78.1 mg, 0.75 mmol), $Pd_{50}Ni_{50}$/MWCNTs (0.1 mol% of Pd), TBAB (161 mg, 0.5 mmol), and 3.0 mol·L^{-1} aqueous KOH solution (0.5 mL). After stirring at 120 °C for 1 h, the reaction mixture was cooled to room temperature. After separating the catalyst and the aqueous phase by centrifugation, the aqueous phase was decanted. Recovered catalyst was washed with H_2O (5 × 1.0 mL) and ethyl acetate (5 × 1.0 mL), which were then added to the aqueous phase. The aqueous phase was extracted eight times with ethyl acetate. The combined organic extracts were dried over $MgSO_4$ and concentrated under reduced pressure. The product was analyzed by GC. The recovered catalyst was dried *in vacuo* and reused.

Typical procedures for the Sonogashira-Hagihara reaction

To a screw-capped vial with a stirring bar were added 4-iodoanisole (117 mg, 0.5 mmol), phenylacetylene (102 mg, 1.0 mmol), Pd/MWCNTs (0.1 mol% of Pd), pyrrolidine (71 mg, 1.0 mmol), and water (0.5 mL). After stirring at 120 °C for 1 h, the reaction mixture was cooled to room temperature. After separating the catalyst and the aqueous phase by centrifugation, the aqueous phase was decanted. Recovered catalyst was washed with H_2O (5 × 1.0 mL) and ethyl acetate (5 × 1.0 mL), which were then added to the aqueous phase. The aqueous phase was extracted eight times with ethyl acetate. The combined organic extracts were dried over $MgSO_4$ and concentrated under reduced pressure. The product was analyzed by GC. The recovered catalyst was dried *in vacuo* and reused.

All the products obtained are described in the literature and the analytical data perfectly fits with the reported values.

Keywords: Cross-coupling reactions•Palladium catalysis•Carbon nanotubes•Water•Nanoparticles

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Entry for the Table of Contents (Please choose one layout only)

Layout 1:

FULL PAPER

From black to green: The catalytic activity of palladium and bimetallic Pd-Ni nanoparticles (NPs) deposited on multi-walled carbon nanotubes (MWCNTs) as catalyst for cross-coupling reactions in water at 120 ºC during 1 h with 0.1 mol% Pd loading under ligand-less conditions is disclosed. These reaction conditions represent an environmentally friendly alternative to those previously reported reactions in organic solvents.

Atsushi Ohtaka, José M. Sansano, Carmen Nájera*, Izaskun Miguel-García, Ángel Berenguer-Murcia, Diego Cazorla-Amorós*

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Palladium and bimetallic palladium-nickel nanoparticles supported on multi-walled carbon nanotubes: application to carbon-carbon bond forming reactions in water