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Palladium and Bimetallic Palladium–Nickel Nanoparticles Supported on Multiwalled Carbon Nanotubes: Application to Carbon–Carbon Bond-Forming Reactions in Water

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Palladium and bimetallic Pd–Ni nanoparticles (NPs) protected by polyvinylpyrrolidone were prepared by the reduction-by-solvent method and deposited on multiwalled carbon nanotubes (MWCNTs). The catalytic activity of these NPs to carbon–carbon bond-forming reactions was studied by using 0.1 mol% Pd loading, at 120 °C for 1 h and water as a solvent under ligand-free conditions. The Suzuki–Miyaura reaction took place quantitatively for the cross-coupling of 4-bromoanisole with phenylboronic acid, better than those obtained with potassium phenyltrifluoroborate, with $Pd_{50}Ni_{50}$/MWCNTs as a catalyst and K_2CO_3 as a base and TBAB as an additive, with good recyclability during 4 cycles with some Ni leaching. The Hiyama reaction of 4-iodoanisole with trimethoxyphenylsilane, under fluoride-free conditions using 50% aqueous NaOH solution, was performed with Pd/MWCNTs as a 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 a base and TBAB as an additive although the recycle failed. In the case of the Sonogashira-Hagihara reaction, Pd/MWCNTs had to be used as a catalyst and pyrrolidine as a 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 NPs 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 phenylacetylene.[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, multiwalled 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 NPs per unit surface area and MWCNTs-supported palladium NPs showed a slightly better reactivity.[2c,d] We envisaged that these Pd and bimetallic Pd–Ni NPs 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 et al. have 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 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]

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Results and Discussion

To determine the efficiency of the loading step as well as to assess the particle size and its dispersion in the prepared heterogeneous catalysts, inductively coupled plasma optical emission spectroscopy (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. In Figure 1 TEM micrographs of Pd/MWCNTs, $Pd_{70}Ni_{30}$/MWCNTs, and $Pd_{50}Ni_{50}$/MWCNTs are shown. Both Pd average particle sizes (*d*, nm) and metal dispersion (*D*, %) results of the three catalysts obtained from TEM analyses are given in Table 1. Remarkably, 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.

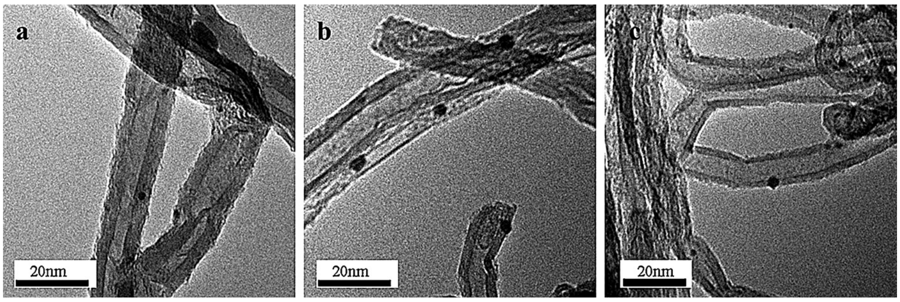
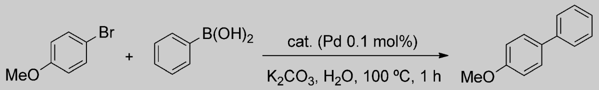


Figure 1. TEM images of catalysts a) Pd/MWCNTs, b) $Pd_{70}Ni_{30}$/MWCNTs, and c) $Pd_{50}Ni_{50}$/MWCNTs.

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

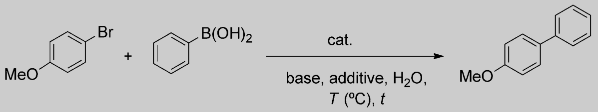
[a] Reaction conditions: 4-bromoanisole (0.5 mmol), phenylboronic acid (0.75 mmol), catalyst (0.1 mol% Pd), K_2CO_3 (1.5 mmol) in H_2O (0.3 mL). [b] Determined by GC analysis based on 4-bromoanisole consumption. [c] In 0.5 mL of H_2O.

Initial studies were performed by 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 a base, and water as a solvent at 100 °C for 1 h, reaction conditions which we established 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 by using the catalyst supported on MWCNTs than with Pd NPs coated with PVP (entry 5).

Next the optimization of the reaction conditions was considered by using the bimetallic $Pd_{30}Ni_{70}$/MWCNTs as a precatalyst (Table 3). If KOH was used as base, a lower yield than with K_2CO_3 was obtained (Table 3, entries 1 and 2). If working at 100 °C with K_2CO_3 as a base, the Pd loading was then increased from 0.1 to 0.2 and 0.3 mol%, but the latter two loadings gave slightly lower yields (entries 2–4). If the reaction time was increased from 1 to 2 h the yield did not increase (61%) and after 3 h a slightly higher yield of 72% was obtained (entries 2, 5 and 6). Increasing the bath temperature to 120 °C had a positive increment in the yield from 63 to 83% (entry 7). The addition of additives such as poly(ethylene glycol) 300 (PEG 300) as a 1/5 volume proportion afforded higher 92% yield (entry 8). If the amount of phenylboronic acid was reduced from 1.5 to 1.2 equivalents and 1 equivalent of tetra-*n*-butylammonium bromide (TBAB) was added, which is a well-known NPs stabilizer,[12] the highest 95% yield was obtained. Under the last reaction conditions, similar yields were obtained with all remaining supported Pd NPs (entries 10–13), although $Pd_{50}Ni_{50}$/MWCNTs seemed to be the best precatalyst (entry 12).

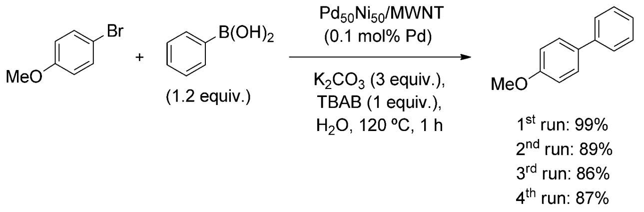
Under the optimum reaction conditions involving the use of $Pd_{50}Ni_{50}$/MWCNTs (0.1 mol% of Pd), 3 equivalents of K_2CO_3, and 1 equivalent of TBAB at 120 °C, the recyclability of the catalyst was studied (Scheme 1). The cross-coupling reaction of 4-bromoanisole with phenylboronic acid (1.2 equiv.) was performed giving 4-methoxybiphenyl in 99% yield. If the reaction was

Table 3. Reaction condition studies for the Suzuki–Miyaura reaction with phenylboronic acid in water.[a]



Entry	Cat. [(mol% Pd)]	Base	Additive	T [°C]	t [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, base (1.5 mmol) in H_2O (0.3 mL). [b] Determined by GC analysis based on 4-bromoanisole consumption. [c] PEG 300/H_2O (1:5) in 0.5 mL volume was used as a solvent. [d] 1.2 equiv. of phenylboronic acid were used. [e] TBAB (0.5 mmol).



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

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 a slight decrease of the amount of Ni (from 0.24 wt% to 0.12 wt%), and that no metal species was observed in the product. TEM images (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 the NPs are etched and their size increases upon consecutive reaction cycles.

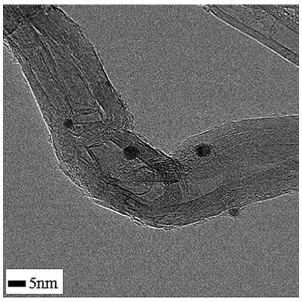
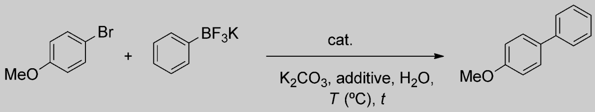


Figure 2. TEM image of the $Pd_{50}Ni_{50}$/MWCNTs catalyst after the 4th cycle in the Suzuki–Miyaura process.

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 °C with 0.1 mol% Pd loading using K_2CO_3 as a base in water as the solvent, reaction conditions that we established previously 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 (entries 1 and 4). By working at 120 °C with Pd/MWCNTs either during 1 or 3 h, similar (81 and 83%) yields were obtained (entries 6 and 7). If 1 equivalent 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 equivalents increased the yield from 83 to 88% (entries 7 and 9), and in the presence of TBAB or PEG 300 to 94 and 95%, respectively (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 a model reaction with 2.5 equivalents of 50% aqueous NaOH solution in the absence of a fluoride source, reaction conditions that we established 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 afforded the desired coupling product in low yields (7–32%). Then, the coupling between 4-iodoanisole and trimethoxyphenylsilane was performed with 2.5 equivalents 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 equivalents of trimethoxyphenylsilane, all the catalysts gave 4-methoxybiphenyl in 92–96% yield (Table 5, entries 1–4). However, if lowering the amount of siloxane to 1.2 equivalents, the best yield was obtained with Pd NPs supported in MWCNTs (entry 5). The recycling experiments gave very low yields, 40 and 53% in the second and third cycle, respectively. Notably, after undergoing 3 reaction cycles in the Hiyama reaction, the catalyst Pd/MWCNTs displayed a decrease in the yield of the desired prod-

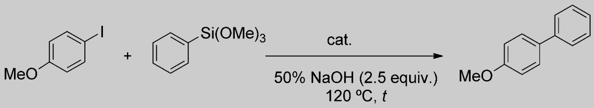
Table 4. Reaction conditions studies for the Suzuki–Miyaura reaction with potassium phenyltrifluoroborate in water.[a]



Entry	Cat. [(mol % Pd)]	Additive	T [°C]	t [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, base (1.5 mmol) in H_2O (0.3 mL). [b] Determined by GC analysis based on 4-bromoanisole consumption. [c] 1 equiv. was added. [d] 1.2 equiv. of potassium phenyltrifluoroborate was used. [e] PEG 300/H_2O (5:1) in 0.5 mL volume was used as a solvent.

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



Entry	Cat. [(mol % Pd)]	PhSi(OMe)$_3$ [equiv.]	t [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

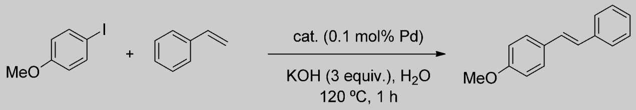
[a] Reaction conditions: 4-iodoanisole (0.5 mmol), trimethoxyphenylsilane, catalyst (0.1 mol % Pd), 50 % aqueous NaOH (2.5 mmol). [b] Determined by GC analysis based on 4-iodoanisole consumption.

uct from 95 % to 53 %, indicating a strong deactivation. Post-reaction ICP–OES and TEM analyses performed on the used catalyst revealed 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 behavior demonstrates 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[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 by using dicyclohexylmethylamine as a 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 a base in the presence of TBAB as an additive or in a mixture of PEG 300 and water as a solvent at 120 °C during 1 h reaction time. In the case of Pd/MWCNTs by using PEG 300/H_2O (1:1 volume/volume ratio), quantitative formation of 4-methoxystilbene was observed (Table 6, entry 1). By using TBAB (1 equiv.) as an additive, a 90 % yield was obtained (entry 2). Under these reaction conditions, $Pd_{70}Ni_{30}$/MWCNTs gave the same results (entry 3). Quantitative yields were also achieved with $Pd_{50}Ni_{50}$/MWCNTs and $Pd_{30}Ni_{70}$/MWCNTs catalysts (entries 4 and 5). On the other hand, $Pd_{10}Ni_{90}$/MWCNTs gave the same yield (90 %) as Pd/MWCNTs (entries 2 and 6). If the recycling experiments were performed 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 °C in water as a solvent, which means the reaction conditions set up by our group,[19] and the results are presented in Table 7. In the presence of Pd/MWCNTs under copper-free conditions, the reaction needed 5 h to obtain 4-methoxytolane in 74 % yield. However, in the presence of PEG 300/H_2O (1:1, volume/volume ratio) as a solvent, a similar 73 % yield was obtained (Table 7, entry 2). By increasing the amount of phenylacetylene from 1.2 to 1.5 equivalents 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 (entries 3–5) . Quantitative yield could be obtained by using 2.0 equivalents of phenylacetylene (entry 5). Under the last reaction conditions, the bimetallic Pd–Ni NPs gave lower yields (entries 6–9). Therefore, the recycling experiments were performed with Pd/MWCNTs under the reaction conditions indicated in 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).

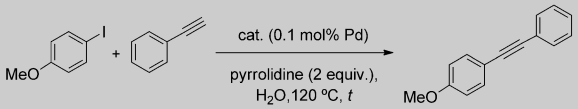
Table 6. Reaction conditions studies for the Mizoroki–Heck reaction using Pd NPs/MWCNTs in water.[a]



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

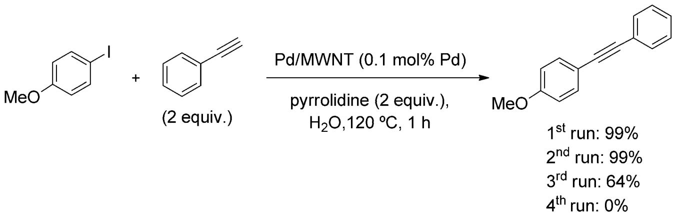
[a] Reaction conditions: 4-iodoanisole (0.5 mmol), styrene (0.75 mmol), catalyst (0.1 mol% Pd), KOH (1.5 mmol). [b] Determined by GC analysis based on 4-iodoanisole consumption. [c] PEG 300/H_2O (1:1) in 0.5 mL volume was used as a solvent. [d] TBAB (0.5 mmol).

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



Entry	Cat.	Additive	t [h]	Yield [%][b]
1	Pd/MWCNTs	–	5	74
2	Pd/MWCNTs	PEG 300[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 (0.6 mmol), catalyst (0.1 mol% Pd), pyrrolidine (1 mmol). [b] Determined by GC analysis based on 4-iodoanisole consumption. [c] PEG 300/H_2O (1:1) in 0.5 mL volume was used as a solvent. [d] 1.5 equiv. of phenylacetylene were used. [e] 2 equiv. of phenylacetylene were used.



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

Conclusions

The catalytic activity of palladium and bimetallic Pd–Ni nanoparticles (NPs) protected by polyvinylpyrrolidone, prepared by the reduction-by-solvent method and deposited on multiwalled carbon nanotubes (MWCNTs), in different carbon–carbon-bond-forming reactions has been evaluated. Bimetallic $Pd_{50}Ni_{50}$/MWCNTs using K_2CO_3 as a base and TBAB as an 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 a 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 were performed under ligand-free conditions at 120 °C (bath temperature) during 1 h reaction time with relative low 0.1 mol% Pd loading in water as a solvent.

Experimental Section

Synthesis of Pd-based catalysts

Colloidal Pd-based nanoparticles were synthesized by 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 palladium(II) acetate (0.2245 g, Sigma–Aldrich, Ref. 205869, 98% pure) and 1,4-dioxane (50 mL, 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 poly(*n*-vinylpyrrolidone) (1.1114 g, Sigma–Aldrich, Ref. 234257, *Mw* 40000) and anhydrous ethylene glycol (120 mL, Sigma–Aldrich, no. 293237, 99% pure) was prepared. Different amounts of $NiSO_4{\cdot}6\,H_2O$ (depending on the final colloid composition) were added to the mixture, and the system was stirred for 3 h at 80 °C. The solution was light green in color. This solution was cooled to 0 °C 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 °C 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 RT.

The prepared colloids were purified as reported in the literature.[20] An aliquot containing the desired amount of NPs 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.

Preparation of heterogeneous catalysts

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

Catalysts characterization

The metal composition in the as-prepared nanoparticles was determined by ICP–OES, in a PerkinElmer 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 NPs catalysts into the reaction medium.

The as-prepared metallic colloids and the corresponding heterogeneous catalysts were characterized by TEM both before and after undergoing catalytic tests by 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 approximately 5 particles, with a sufficient signal-to-noise ratio. The catalysts particle-size distribution and Pd dispersion were calculated as reported elsewhere.[4]

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 RT. 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 spectroscopy. The recovered catalyst was dried in vacuo and reused.

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 vol/vol, 0.3 mL). After stirring at 120 °C for 1 h, the reaction mixture was cooled to RT. After the same work-up described above the product was obtained in 83% yield and analyzed by GC and ^1H NMR spectroscopy. The recovered catalyst was dried in vacuo and reused.

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, 12.5 mmol). After stirring at 120 °C for 1 h, the reaction mixture was cooled to RT. 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 spectroscopy. The recovered catalyst was dried in vacuo and reused.

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 RT. 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.

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 RT. 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 fitted with the reported values.

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