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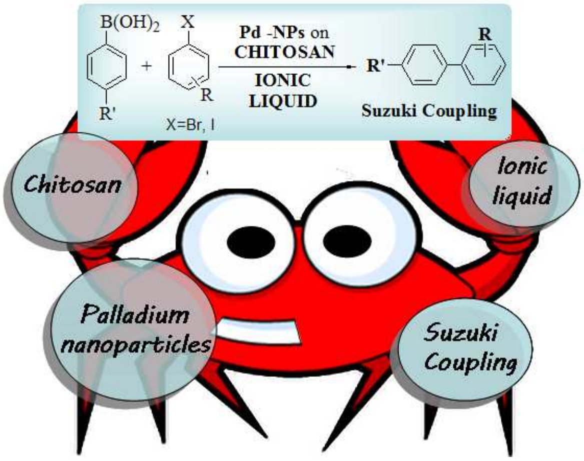
PII: S0022-328X(13)00845-0
DOI: 10.1016/j.jorganchem.2013.11.033
Reference: JOM 18378

To appear in: *Journal of Organometallic Chemistry*

Received Date: 23 September 2013
Revised Date: 4 November 2013
Accepted Date: 25 November 2013

Please cite this article as: P. Cotugno, M. Casiello, A. Nacci, P. Mastrorilli, M.M. Dell'Anna, A. Monopoli, Suzuki coupling of Iodo and Bromoarenes Catalyzed by Chitosan-Supported Pd-Nanoparticles in Ionic Liquids, *Journal of Organometallic Chemistry* (2013), doi: 10.1016/j.jorganchem.2013.11.033.



Palladium nanoparticles supported on chitosan (Pd-NPs@Chitosan) have been used in Suzuki cross coupling of bromo and iodoarenes carried out in ionic liquids. A low catalyst loading (0.1%) is used and the catalyst can be recycled without deactivation.

Highlights

- Palladium nanoparticles supported on chitosan have been used for the first time in Suzuki cross coupling of bromo and iodoarenes in ionic liquids.
- The reaction proceeded smoothly in molten tetrabutylammonium bromide affording unsymmetrical biaryls in good to excellent yields.
- A low catalyst loading (0.1%) is used and the catalyst can be recycled without deactivation.
- Hot-filtration test has been done in order to confirm a heterogeneous catalysis.

Suzuki coupling of Iodo and Bromoarenes Catalyzed by Chitosan-Supported Pd-Nanoparticles in Ionic Liquids

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Abstract. Palladium nanoparticles supported on chitosan (Pd-NPs@Chitosan) have been used for the first time in Suzuki cross coupling of bromo and iodoarenes carried out in ionic liquids. The reaction proceeded smoothly in molten tetrabutylammonium bromide (TBAB) affording unsymmetrical biaryls in good to excellent yields. A low catalyst loading (0.1%) is used and the catalyst can be recycled without deactivation.

Keywords: Suzuki coupling; heterogeneous catalyst; palladium nanoparticles; chitosan; ionic liquids

Introduction

Biaryl scaffolds are ubiquitous in nature and are widely used as structural subunit in molecules of interest in agrochemical, pharmaceutical, and material fields.[1] Since from the discovery of the Ullmann homocoupling of aryl halides promoted by stoichiometric amount of copper at high temperatures,[2] the search for more efficient syntheses of biaryl compounds has attracted many efforts by synthetic chemists for a long time. However, the Ullmann reaction is considered of narrow scope, being limited to the preparation of symmetrical biaryls, while for unsymmetrical compounds, a certain number of metal catalyzed reactions has been discovered in the last 40 years, in which palladium chemistry is used predominantly [3].

In this context, the Suzuki cross-coupling reaction is considered the most efficient way of access to biaryls. The main advantages of this process are essentially: i) mild reaction conditions (generally room temperature), ii) commercial availability of boronic acids and aromatic halides, iii) water and functional groups tolerance, iv) high stereo- and regio-selectivity. In addition, boron-containing by-products are much easier to handle and to be removed from the reaction medium, in comparison with other organometallic reagents. Finally, a very low catalyst loading are often needed and is comfortable to work under heterogeneous conditions. [4]

As far as this latter topic is concerned, many robust palladium-based catalysts for Suzuki coupling have been developed in recent years. [5-11] Among them, palladium nanoparticles (Pd-NPs) have recently gained popularity, [12] and a number of solid supports have been used for their immobilization such as double-layered hydroxide (LDH), [13] diatomite, [14] alumina-based oxides, [15] MgO, [16] and polyaniline nanofibers. [17] Moreover, many efforts have been done for searching greener reaction conditions, and a special attention have been paid to eco-friendly solvents like water [18-19] and ionic liquids. [20-21]

In this context, in the last decade we also investigated a number of organic and inorganic matrixes for anchoring metal nanocatalysts suitable to work in these environmentally benign media. [22-24] Among the several supports examined, chitosan (poly[β-(1–4)-2-amino-2-deoxy-D-glucan]) displayed better performances providing a prompt anchorage to Pd nanoparticles generated electrochemically. [24] The so formed heterogeneous catalyst was very active in the Heck olefination of haloarenes in ionic liquids, being capable of converting iodoarenes in only 15 min with an extensive recycle (about ten runs).

Chitosan is a cheap and non-toxic polymer obtained by deacetylation of chitin, that has been used in agrochemical, food and pharmaceutical fields. [25] The use in heterogeneous catalysis is encouraged by its easy and clean elimination by incineration (or dissolution in acidic water solutions) that can allow a quantitative metal recovery. [26]

Due to its strong affinity for palladium, [27] chitosan has been used as supramolecular ligand for the Suzuki coupling, [28-31] but in a sole example Pd nanoparticles have been used as the catalyst source, [32] and to the best of our knowledge no protocols of Suzuki reactions promoted by Pd-NPs on chitosan have been reported in ionic liquids media.

In this context, as a part of our program aimed at finding new eco-sustainable catalytic protocols, [33-40] we decide to extend these findings to the synthesis of biaryls. Here, we report the first application of a chemically generated Pd nanocomposite on chitosan to the Suzuki coupling carried out in ionic liquids.

Experimental Procedures

Materials. Ionic liquids [tetrabutylammonium bromide (TBAB), tetrabutylammonium acetate (TBAA), tetrabutylammonium chloride (TBAC), 1-butyl-3-methylimidazolium bromide (Bmim Br) and N-Butylpyridinium bromide (Bupy Br)], aryl halides and Pd acetate were Sigma-Aldrich reagents. Chitosan flakes (medium molecular weight of about 400,000) were purchased from Fluka and utilized as received. The structures of the biaryl compounds were determined by comparison with authentic samples, or by MS, ^{1}H-NMR and ^{13}C-NMR spectra.

Procedure for the preparation of Pd-NPs supported on chitosan (Pd-NPs@Chitosan)

The nano-composite was prepared according to a procedure previously described. The catalyst has also been deeply characterized by means of XPS, cross-sectional TEM and ETAAS analyses. [24]

Summarizing, Pd-NPs on chitosan were electro-synthesised a in a three-electrode cell by means of the sacrificial anode technique. In a typical experiment 200mg of chitosan were suspended in 5 mL of an acetonitrile/ tetrahydrofuran (1/3) mixture containing TBAB as base electrolyte (0.1M) under nitrogen atmosphere. A potential of+1.5 V (vs. reference) was applied to the working electrode during the process, that was coulometrically controlled and stopped at an electrolysis charge value of 200 C. Evaporation under vacuum of the solvent leaves a grey solid that is stored under nitrogen. The Pd concentration on chitosan was determined by Atomic Absorption Spectroscopy (ETAAS) after acid mineralization and it was found equal to 0.35% w.

The so-prepared nanocomposite is a cortex-type catalyst presenting Pd nanoparticles with an average core of diameter of about 3 nm, well-dispersed onto the surface of chitosan flakes. [24]

General procedure for Suzuki coupling catalyzed by Pd-NPs@Chitosan in ILs

A 5 mL screw cap vial was charged with tetrabutylammonium bromide (0.8 g, 2.5 mmol), haloarene (1 mmol), boronic acid (1.1 mmol), K_2CO_3 (1.5 mmol), H_2O (200 μL), and 30 mg of the catalyst Pd-NPs@Chitosan (loading 0.1 mol%). The resulting mixture was heated under stirring at 90 °C for 5 hrs.

Then, after cooling at room temperature, 3 mL of *n*-hexane were added to the reaction and the mixture was stirred for 1 min. Next, after centrifugation, the supernatant solution containing the biaryl product was removed with glass pipette and the operation was repeated twice. The organic phases were collected and added of *n*-decane as an external standard to evaluate conversions, yields and selectivities reported in Tables 1-2.

In case of recycle experiments, the remaining mixture was washed and centrifuged with water to remove inorganic by-products, leaving a mix containing the catalyst that was softly dried under a nitrogen steam and, upon addition of fresh reagents, repeatedly recycled under one-pot conditions. Because of the catalytic system proved to be air-stable, no care was taken to exclude oxygen during operations.

Results and Discussion

As reported in the above section, the catalyst was obtained by electro-chemical reduction of Pd acetate in the presence of flakes of chitosan and tetrabutylammonium bromide (TBAB) (see experimental section) [24].

Under these conditions, the nanoparticles metallic core is surrounded by a stabilising layer composed by tetrabutylammonium cations mixed with Br^- and $[PdBr_4]^{2-}$ anions that counterbalance the positive charges in the shell. The core-shell nanostructured catalyst is chemisorbed on the chitosan surface by means of coordination bonds with amino and hydroxyl groups of the polymer surface (Figure 1).

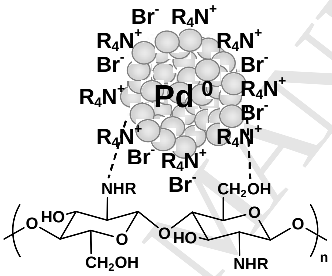


Figure 1. A representation of the core-shell structure of Pd nanoparticles chemisorbed on chitosan in tetraalkylammonium-based ionic liquids

Preliminary experiments aimed at optimizing the reaction conditions, were calibrated for processing 1 mmol of bromobenzene and *p*-tolylboronic acid as model substrates, with a catalyst loading of 0.1 mol%. A temperature of 90 °C and a reaction time of 5 hours were found as the maximum values after which no further reaction progress was observed (Table 1).

The blank experiments, carried out in the absence of catalyst or in the presence of the sole support, gave no conversion, thus showing that the catalytically active material is related to palladium nanoparticles.

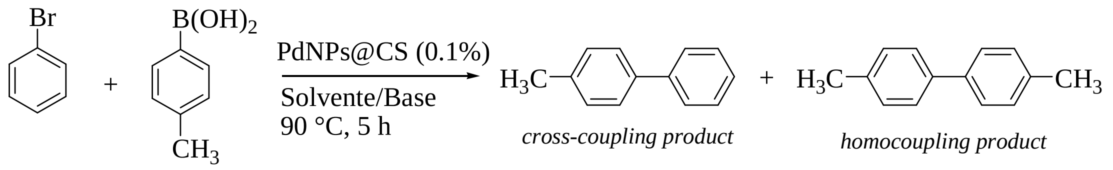
From data reported in Table 1 immediately emerged the scarce performances displayed by molecular solvents traditionally used in Suzuki coupling (toluene or DMF), even when used in the presence of water as co-solvent, which is known to have a beneficial effect on the coupling (Table 1, runs 1-4). Similarly, ionic liquids based on imidazolium and pyridinium cations like [Bmim]Br (1-Butyl-3-methylimidazolium bromide) and [BuPy]Br (1-butylpyridinium bromide) furnished disappointing results (Table 1, runs 5-7).

These findings are in line with our previous ones on the Heck coupling, [24] in which ionic liquids bearing planar aromatic cations, like $[\text{Bmim}]^+$ and $[\text{BuPy}]^+$, proved to be less efficient than the ones possessing tetrahedral cations, such as the tetraalkylammonium salts, probably due to the superior ability of these latter in stabilizing the nanoparticles core.

Among the quaternary ammnonium salts, tetrabutylammonium bromide (TBAB) displayed the best performances if compared with the analogous molten salts bearing acetate and chloride anions (Table 1, runs 8-12).

Table 1

Optimization of reaction conditions in the Suzuki coupling of bromobenzene and p-tolylboronic acid catalysed by Pd-NPs@Chitosan[a)]



Run	**Solvent**	**Base/Additive**	**Conv$^{b)}$. (%)**	**Sel.$^{c)}$ (%)**
1	DMF	NaOH	22	89
2	DMF	K_2CO_3	35	45
3	DMF	K_2CO_3/H_2O	35	93
4	Toluene	K_2CO_3	40	97
5	[Bmim]Br	K_2CO_3	8	95
6	[Bmim]Br	K_2CO_3/H_2O	10	96
7	[BuPy]Br	K_2CO_3	14	97
8	TBAA	TBAA	51	97
9	TBAA	K_2CO_3	35	97
10	TBAC	K_2CO_3	25	96
11	TBAB	TBAA	58	97
12	TBAB	K_2CO_3	88	98
13	TBAA	$K_2CO_3/H_2O^{d)}$	48	97
14	**TBAB**	**$K_2CO_3/H_2O^{d)}$**	**98**	**96**
15	**TBAB**	**$Cs_2CO_3/H_2O^{d)}$**	**98**	**98**

[a)] Reaction conditions: *p*-tolyl boronic acid (1.1 mmol), bromobenzene (1 mmol), base (1.5 mmol), catalyst Pd-NPs@Chitosan (0.1 mol%), solvent (1 mL or 0.8 g of molten salt TBAA or TBAB), heated under stirring for 5 hours. [b)] As determined by GLC using *n*-decane as external standard. [c)] Percentage of the coupling respect to the homocoupled product. [d)] Reaction carried out with addition of 200 μL of water.

The nature of the base, as already reported by us, [22,35] strongly affected the coupling, and in these cases better results were obtained by using inorganic bases such as K_2CO_3 or Cs_2CO_3 (Table 1, runs 12, 14-15).

As expected, the addition of small amounts of water had a beneficial effect on conversion, probably due to two main reasons: i) the increase of the solubility of inorganic bases into the reaction mixture and ii) the formation *in situ* of the good nucleophile OH^- which would activate boronic acid by forming boronate species (Table 1, runs 13-15).

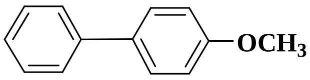
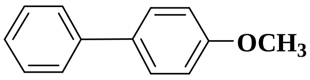
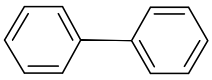
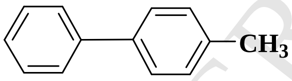
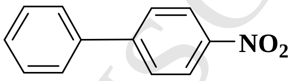
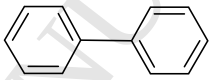
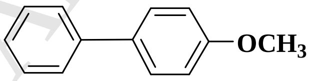
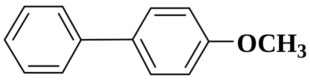
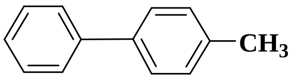
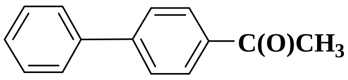
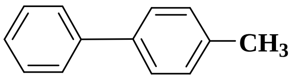
On the basis of this preliminary screening, the optimal reaction conditions for Suzuki coupling promoted by Pd-NPs on chitosan could be established as follows: molten TBAB as the solvent, Pd catalyst (0.1 mol%), K_2CO_3 (1.5 eq), H_2O as an additive (200 µL), 90 °C as the temperature. Potassium carbonate was preferred to cesium carbonate due to the toxicity of the latter one.

With this protocol in hand, we extended the coupling to various aryl halides and boronic acids. Results reported in Table 2 show a good catalytic activity of the system Pd-NPs@Chitosan, which can promote the coupling of haloarenes bearing both electron-donating and electron-withdrawing groups with good to excellent yields. Only a slight decrement of yield was observed in the case of the less reactive *p*-bromotoulene and *p*-bromoanisole (Table 2, runs 8-9).

In case of iodides, the temperature was lowered to 70° C in order to limit the undesirable side-reaction of homocoupling of boronic acid (Table 2, runs 1-2). Unfortunately, chlorobenzene proved to be unreactive under our conditions (Table 2, run 11).

Table 2

Suzuki cross-coupling reaction catalyzed by Pd-NPs@Chitosan in TBAB[a)]

Run	X	R^1	R^2	T	Product	Yield (%)[b)]
1	I	H	OCH_3	70		96
2	I	H	OCH_3	90		77[c)]
3	I	H	H	70		98
4	I	CH_3	H	70		95
5	I	NO_2	H	70		98
6	Br	H	H	90		97
7	Br	H	OCH_3	90		92
8	Br	OCH_3	H	90		88
9	Br	H	CH_3	90		91
10	Br	C(O)CH_3	H	90		95
11	Cl	H	CH_3	90		<1

[a)] Reaction conditions: boronic acid (1.1 mmol), halobenzene (1 mmol), K_2CO_3 (1.5 mmol), catalyst PdNPs@Chitosan (0.1 mol%), solvent (0.8 g of molten TBAB), heated under stirring for 5 hours. [b)] As determined by GLC using *n*-decane as external standard. [c)] A 20% of biphenyl was detected.

To evaluate the catalyst robustness we carried out appropriate recycling experiments. After each run, the supported nanocatalyst was washed by centrifugation, firstly with hexane

(3x3mL) and then with water to remove both organic and inorganic residues. Then, the solid was used in the next run without isolation and further manipulations.

Results in figure 2 show that Pd-NPs@CS nanocomposite underwent a loss of activity after the third cycle, probably due to the leaching of Pd during the reaction or the loss of material during the recycling procedure.

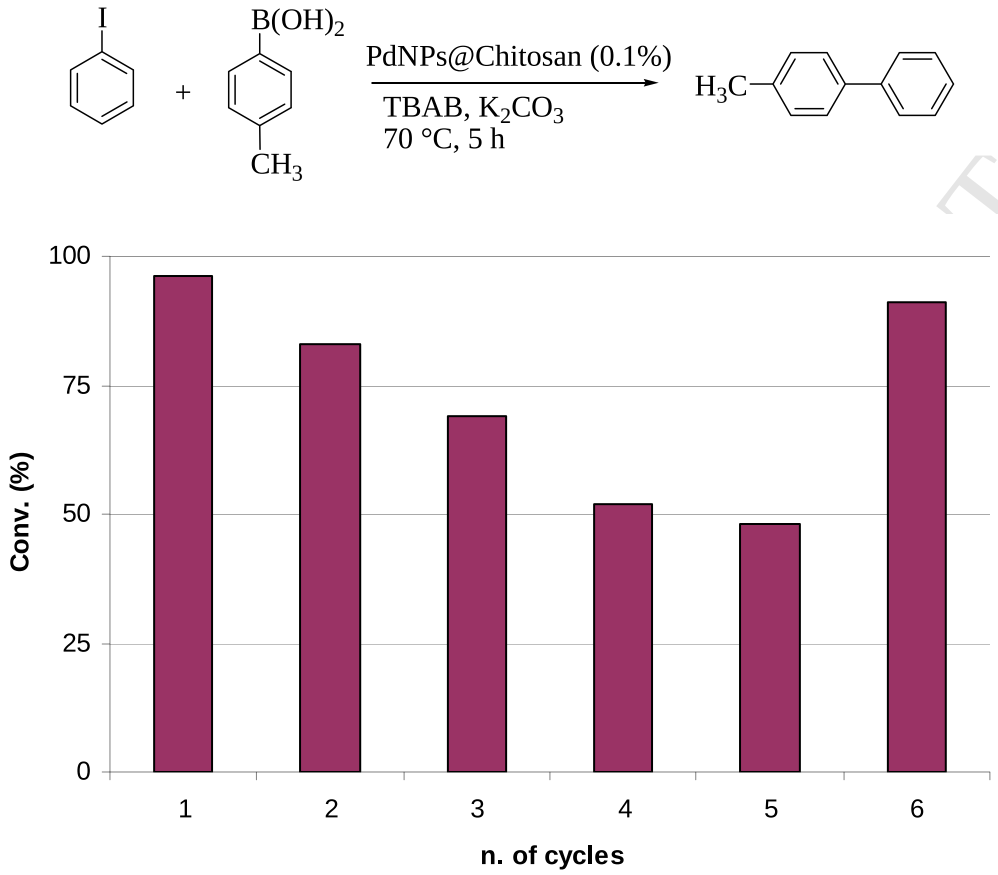


Figure 2. Recycling experiments in the Suzuki coupling catalyzed by PdNPs@Chitosan in TBAB. Reaction conditions: Iodotoluene (1.0 mmol), phenylboronic acid (1.1 mmol), K_2CO_3 (1.5 mmol), H_2O 200 µL, catalyst PdNPs@Chitosan (0.1 mol%), TBAB (0.8 g) at 70 °C. Recycle number 6 was obtained by weighing the recovered catalyst coming from the fifth recycle, then adding fresh reagents in a proper amount to realize a Pd loading of 0.1 mol% (see ref. [41]). Reaction conditions: PhI (0.5 mmol), phenylboronic acid (0.55 mmol), K_2CO_3 (0.75 mmol), H_2O 100 µL, catalyst PdNPs@Chitosan (16 mg, 0.1 mol%), TBAB (0.4 g) at 70 °C

However, being the catalyst loading very low (0.1 mol%) and the yield averaged on three runs of 80% ca., an overall TON of 2400 can be estimated. In order to ascertain if the loss of activity was due to the leaching of palladium during the reaction, a hot filtration test was performed.

Data in figure 3 clearly show that catalytic activity dropped down when the Pd-

NPs@Chitosan nanocomposite was removed from the reaction mixture (see dashed line in Figure 3), thus confirming that catalysis is heterogeneous in nature and that the metal leaching can be neglected. Consequently, the decrement of catalytic activity can be attributed to a progressive loss or inactivation of palladium nanoparticles during the recycling manipulations. In order to ascertain which of the two explanations actually occurs, at the end of the fifth cycle, the catalyst was removed, washed, dried under vacuum and weighted, giving 18 mg of nanocomposite and clearly evidencing a loss of catalytic material. As a further confirmation, the addition of fresh reagents calibrated on the remaining 18 mg of PdNPs@Chitosan [41], after 5 hours gave the desired biphenyl in 91% of conversion (Fig. 2, run 6), still showing a good activity of the catalyst and excluding its deactivation. Experiments are in progress to improve the recycling procedure and minimize the loss of active material.

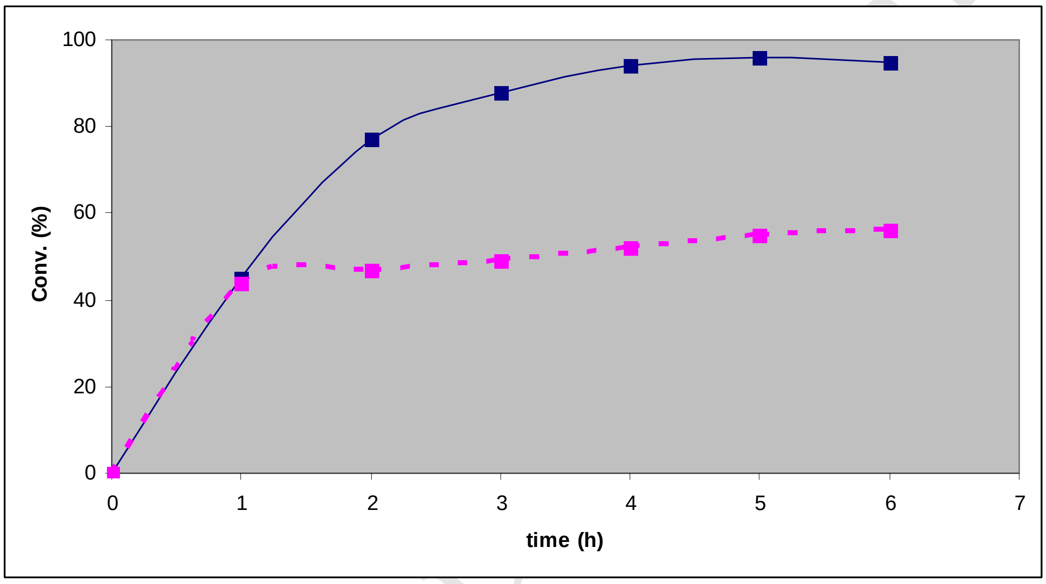


Figure 3. Hot-Filtration test. Reaction conditions: Iodotoluene (1.0 mmol), phenylboronic acid (1.1 mmol), K_2CO_3 (1.5 mmol), H_2O (200 μL), catalyst Pd-NPs@Chitosan (0.1 mol%), TBAB (0.8 g) at 70 °C. Continue line: reaction performed as in table 2, run 2. Dashed line: reaction results after catalyst removal at about 50% of conversion.

The role of Pd colloids in the catalytic cycle and their behaviour at the presence of tetraalkylammonium salts has been the subject of many pioneering studies [42], and results of our hot filtration test, which account for a heterogeneous catalysis, may appear in contrast with some of them. Indeed, Reetz et al. [42d] demonstrated the easy solubilisation of Pd clusters stabilized by $Oct_4N^+(HCO^{2-})$ as a consequence of the oxidative insertion into the C-I bond of iodobenzene, with formation of soluble aryl-palladium species. This means that in our reactions the leaching of the metal into the ionic medium would be expected and consequently a homogeneous catalysis would occur.

It should be noted that the question homogeneous vs heterogeneous nature of catalysis in the case of metal nanoparticles has been long debated, and we do not have an exhaustive explanation for the present case. We can speculate, as also reported by others [43], that catalysis should occur on the nanoparticles surface, but if Pd-aryl species are released into the reaction medium as an effect of the oxidative addition, then the Pd atoms may re-deposit on colloid due to molecular collisions after the closure of cycle. In this case, catalysis would be homogeneous in nature and clusters should act only as a catalyst reservoir.

Conclusions

In this work we have reported for the first time the use of a Pd nanoparticle-based catalyst supported on chitosan to the Suzuki coupling carried out in ionic liquids. Excellent yields and selectivities have been achieved in relatively short reaction times (5 hrs) on a wide array of iodo- and bromo-arenes bearing both electron-donating and electron-withdrawing groups.

Satisfactory activity and good TONs (2400 ca.) were achieved in a one-pot manner and the catalyst may be reused provided that careful manipulations are carried out to prevent accidental loss of active material. The gradation of the aryl bromide conversion slightly depended on the electronic effect of substituent in para-position to the bromine. The studies also revealed that the palladium leaching into the solution during the reaction is negligible and therefore the catalysis is heterogeneous in nature.

Remarkably advantageous conditions like the low catalyst loading (0.1%), the use of cheap and eco-friendly support (chitosan) and of a green solvent (TBAB, an ionic liquid) provide to the method great benefits in terms of safety, economy and sustainability. In addition, the use of water as an additive proved to be particularly advantageous for its ability to dissolve boron side-products coating the catalyst surface.

Therefore, we believe that it can compete with the most efficient known protocols, and due to its simple operating procedure we can anticipate that it will find wide applicability.

Acknowledgments

Partial financial support of this work by the Ministry of University and Scientific Research of Italy (MIUR) and by University of Bari is gratefully acknowledged.

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