

Palladium Nanoparticles Supported on Poly(*N*-vinylpyrrolidone)-Grafted Silica as an Efficient Catalyst for Copper-Free Sonogashira and Suzuki Cross-Coupling Reactions

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Palladium catalyst based on polyvinylpyrrolidone-silica hybrid support was prepared and exhibited excellent activity and stability in copper, amine and phosphine-free Sonogashira-Hagihara and Suzuki-Miyaura cross-coupling reactions. The polymeric catalyst was applied efficiently in the coupling reactions of chloro (as well as iodo) and bromoarenes. Elemental analysis of Pd by inductively coupled plasma (ICP) and hot filtration test revealed low leaching of the metal into solution from the supported system. The catalyst could be reused many times in repeated cycles without significant decline in its activity.

Keywords: organic-inorganic hybrid support, polyvinylpyrrolidone-grafted silica, palladium nanoparticles, Sonogashira reaction, Suzuki reaction

Introduction

Palladium-catalyzed cross coupling reactions are among the most employed organic transformations for the generation of C–C bonds in academic as well as industrial communities.¹⁻³ These reactions should be fully developed for their industrialization potential in all aspects such as: the use of benign solvents,⁴⁻⁶ recovery and recycling of the expensive catalysts and their complete removal from the products.⁷ Several methodologies have been developed to solve the problem of recycling of the catalysts; the simplest procedure is heterogenisation. Homogeneous catalyst could be immobilized on organic polymer⁸⁻¹¹ or inorganic supports to provide several advantages such as catalyst recovery, product separation and inhibition of metal loss.

Through inorganic supports, silica or modified silica¹² are good alternatives to conventional homogenous catalysts which are offering host of benefits like being environmentally friendly, excellent stability and good dispersion of catalytic sites. Furthermore, there has been growing interest in grafting polymer chains to the

surface of silica which provides opportunities to take the advantage of interfacial functional polymer compatible with solvents and substrates while having high mechanical stability.¹³

Various kinds of cross coupling reactions have been taken into account, among them Sonogashira-Hagihara, which consist of aryl halides coupling with terminal alkynes, as an efficient way for constructing substituted arylated alkyne compounds. Arylated alkyne compounds are important intermediates in organic synthesis including natural compounds, pharmaceutical, molecular electronics, dendrimeric, oligomeric and polymeric materials.¹⁴⁻¹⁷ Traditionally, Pd-catalyzed reactions are mostly catalyzed by homogenous Pd complexes in the presence of phosphine ligands, catalytic amount of copper salt as a cocatalyst and a large scale of amine as a solvent.¹⁸ To overcome shortcoming of traditional methods, several modified methods have been reported by different concepts including: phosphine-free reaction condition,¹⁹⁻²¹ copper and amine-free medium,²²⁻²⁴ utilization of Ni instead of Pd,^{25,26} and solid supported catalyst.^{27,28}

Another efficient method in C–C coupling reaction is Suzuki-Miyaura; the reaction of organo boron compounds with aryl halides or pseudohalides.²⁹⁻³¹ This reaction

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has gained prominence attention in the synthesis of pharmaceutical and fine chemical compounds and many modifications have been introduced in catalysts types, reaction media and reaction conditions.^{32,33}

In consequence of our recent reports on synthesis of heterogeneous Pd catalyst either based on polymeric support^{34,35} or polymer-grafted silica,^{36,37} and our successful synthesis and characterization of Pd nanoparticles supported on poly(*N*-vinylpyrrolidone)-grafted silica (Si-PVP-Pd) as a new heterogeneous catalyst in Heck cross-coupling reactions³⁸ herein, we report new application of Si-PVP-Pd catalyst for copper, amine and phosphine-free Sonogashira and Suzuki coupling reactions.

Experimental

General information

Substrates were purchased from Fluka, Merck or Aldrich Companies. Aminopropyl silica gel with mesh size of 0.015-0.035 mm was supplied by Fluka. Synthesized samples were characterized by infrared spectroscopy (IR), magnetic resonance spectroscopy (NMR) and physical data comparison with authentic samples. Yield values refer to the isolated products. Progress of reactions were followed by thin-layer chromatography (TLC) on silica-gel Polygram SIL/UV 254 plates or by gas chromatography (GC) on Shimadzu GC 10A instrument with hydrogen flame ionization detector using a 3 m length column packed with DC-200 stationary phase. Fourier transform infrared spectroscopy (FTIR) were recorded by a Shimadzu FTIR-8300 spectrophotometer. Bruker Avance DPX instrument were applied for extracting ¹H and ¹³C NMR spectra. The Pd analysis and leaching were carried out by inductively coupled plasma (ICP) analyzer (Varian, Vista-Pro).

Preparation of the supported palladium catalyst

The palladium catalyst supported on polyvinylpyrrolidone-silica hybrid support was prepared as described in our previous paper.³⁸ Poly(*N*-vinylpyrrolidone) (PVP) grafted silica was obtained by reaction between acryloylchloride and aminopropylsilica (AMPS) and its subsequent copolymerization with 1-vinyl-2-pyrrolidone monomer in the presence of benzoyl peroxide as initiator in a 10 mL sealed tube at 90 °C. The product was Soxhlet-extracted with CHCl₃ to remove homopolymer and complexed with PdCl₂ in dimethylformamide (DMF) at 80 °C. ICP analysis revealed that the catalyst contained an average of 0.25 mmol g⁻¹ of Pd.

General procedure for Sonogashira-Hagihara reaction

A suspension of K₂CO₃ (2.0 mmol), aryl halide (1.0 mmol) and Pd complex (0.5 mol%) were mixed in DMF (5 mL) on a round-bottomed flask and phenylacetylene (1.2 mmol) was added afterward. The reaction mixture was stirred at 100 °C. After completion of the reaction, the mixture was filtered and the filtrate poured into water (50 mL) and extracted with EtOAc (3 × 15 mL). The combined organic phases were dried over Na₂SO₄, filtered and evaporated in vacuum. Products were isolated by flash chromatography using petroleum ether, EtOAc or their mixture as eluents.

General procedure for Suzuki-Miyaura reaction

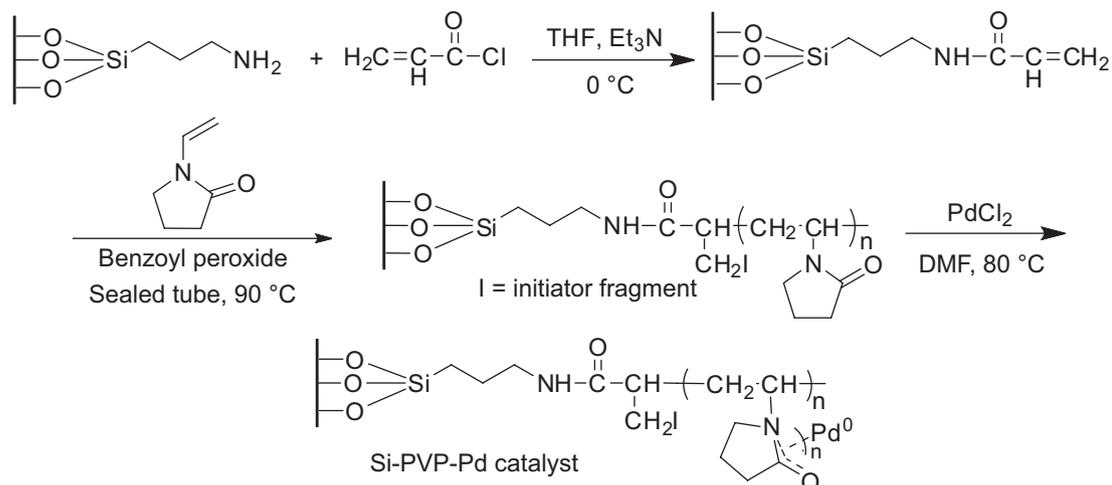
Mixture of aryl halide (1.0 mmol), K₂CO₃ (2.0 mmol), Pd complex (0.3 mol%), DMF (5 mL) and phenylboronic acid (1.2 mmol) were mixed and stirred in a round-bottomed flask at 100 °C. After completion of the reaction, the product extraction was followed according to the outlined previous procedure.

Recycling of the catalyst

When the Suzuki or Sonogashira reactions were completed, the mixture was cooled down to room temperature and filtered off. Consequently, the solid was washed with DMF, water and acetone and dried under vacuum condition. This resultant was then utilized in the next reaction cycle without any pre-treatment with a new portion of reagents.

Results and Discussion

The palladium catalyst was prepared by the sequential of reactions given in Scheme 1. Firstly, acrylamidopropylsilica was synthesized according to a previous procedure.³⁹ Free-radical graft polymerization of vinylpyrrolidone onto silica particles was performed by mixing acrylamidopropylsilica, distilled vinylpyrrolidone monomer and recrystallized benzoyl peroxide as initiator in a sealed tube. The quantity of grafted PVP onto silica was measured by thermogravimetric analysis (TGA) and determined to be 1.9 mmol g⁻¹. Subsequently, PdCl₂ was complexed with PVP grafted silica and the Pd content was determined by ICP upon catalyst digestion. ICP data revealed the presence of an average of 0.25 mmol g⁻¹ of Pd on catalyst structure. Pd nanoparticle formation during complexation is inevitable, since PVP is an electron rich center which can reduce Pd complexes. Besides, Pd nanoparticle formation



Scheme 1. Preparation of Pd supported on poly(*N*-vinylpyrrolidone)-grafted silica.

can also occur due to presence of DMF which is known as reducing agent.^{40,41} Scanning electron microscopy (SEM) and transmission electron microscopy (TEM) images of the catalyst showed well-dispersed Pd nanoparticle through surface. TEM image showed that Pd nanoparticles size are in the range of 20–25 nm. SEM and TEM images of the catalyst are presented in Figure 1.

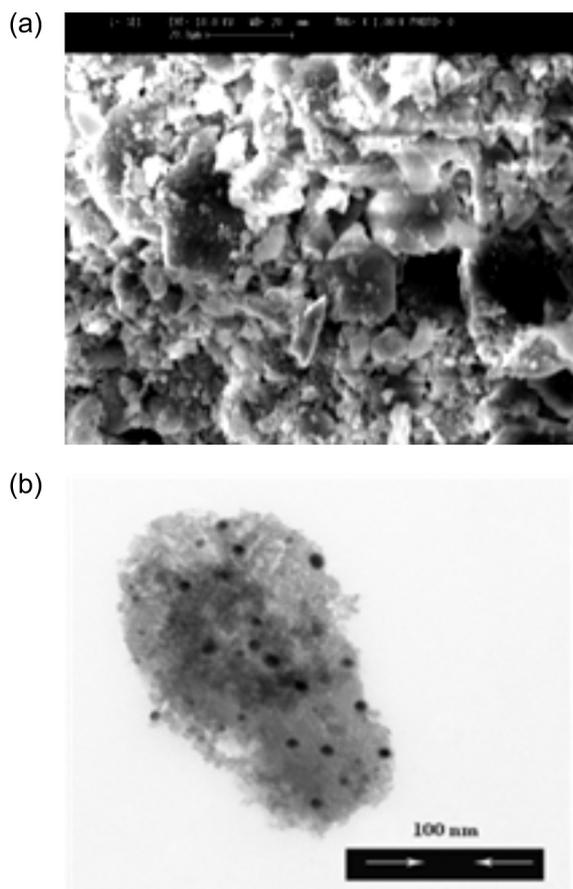


Figure 1. (a) SEM image and (b) TEM image of palladium supported on poly(*N*-vinylpyrrolidone)-grafted silica.³⁸

Sonogashira-Hagihara cross-coupling reaction has become one of the most important method to prepare arylalkynes and conjugated enynes. Traditionally, the reaction is performed in the presence of copper iodide as a cocatalyst and excess amount of amine as solvent or cosolvent. We decided to apply Si-PVP-Pd for Sonogashira reaction of aryl iodides, bromides and chlorides with phenylacetylene under copper and amine-free condition.

Initially, in a model reaction, the coupling of bromobenzene and phenylacetylene was investigated. The effect of different solvents on reaction's condition was examined and Table 1 represents the extracted results. On the other hand, the base has a crucial role in Sonogashira reaction.^{42,43} Consequently, the influence of different bases was also investigated for the model reaction. The best choice as solvent was determined to be DMF. The coupling reaction did not occur in the absence of a base (Table 1, entry 6) and among different salts which were tested, K₂CO₃ showed the best conversion (Table 2, entry 5). It

Table 1. Effect of different solvents and bases on the reaction of bromobenzene and phenylacetylene^a

entry	Solvent	Base	time / h	Conversion ^b / %
1	H ₂ O	K ₂ CO ₃	24	60
2	MeOH	K ₂ CO ₃	24	50
3	CH ₃ CN	K ₂ CO ₃	24	60
4	THF	K ₂ CO ₃	24	40
5	DMF	K ₂ CO ₃	5	100
6	DMF	none	24	trace
7	DMF	NaOAc	10	70
8	DMF	Et ₃ N	10	50
9	DMF	KF	10	45

^aReaction condition: bromobenzene (1.0 mmol), phenylacetylene (1.2 mmol), base (2 mmol), Pd cat. (0.5 mol%) in solvent (5–10 mL) at 100 °C; ^bconversion based on bromobenzene.

gave quantitative conversion of bromobenzene without considerable formation of homo-coupling product. Finally, the optimum reaction condition was considered to be: 0.5 mol% of Si-PVP-Pd catalyst, 2 eq. K_2CO_3 in DMF at 100 °C.

The system efficiency was further explored for coupling of various aryl halides under optimized condition (Table 2). Different aryl halides including aryl chlorides were generated excellent to moderate yield of the coupling products. It was observed that the method has tolerance to the presence of both electron-donating and electron-

withdrawing groups on aryl halides. The reaction of less active chloroarenes had to be run in the presence of tetra(butyl)ammonium bromide (TBAB) (Jeffery catalyst) as an additive (Table 2, entry 7-11).^{44,45} The catalytic cycle for the coupling reaction involves a series of transformations around the palladium catalyst. First step is an oxidative addition in which active Pd^0 catalyst inserts into the aryl halide bond. The last step in all coupling reactions is the regeneration of Pd^0 species by reductive elimination of the Pd^{II} compound in the presence of a base. TBAB has promoting influence in this step by assistance in

Table 2. Sonogashira reaction of phenylacetylene with different aryl halides in the presence of Si-PVP-Pd catalyst^a

entry	Ar-X	Product	time / h	Yield ^b / %
1		1a	1	95
2		1b	4	90
3		1a	5	80
4		1c	5	80
5		1d	3	95
6		1e	1	90
7 ^c		1a	6	60
8 ^c		1b	15	35
9 ^c		1c	5	75
10 ^c		1d	3.5	86
11 ^c		1e	2.5	90

^aReaction condition: aryl halide (1.0 mmol), phenylacetylene (1.2 mmol), K_2CO_3 (2 mmol), Pd cat. (0.5 mol%) in DMF (5 mL) at 100 °C; ^bisolated yield of products; ^cTBAB (5 mol%).

the regeneration of zerovalent Pd catalyst. Several possible mechanisms proposed by Jeffery^{46,47} in this matter are: an extraction mechanism, an interfacial mechanism and two nucleophilic catalysis mechanism.

After reaction completion, isolation of the supported catalyst was easily performed by filtration process. The resulting isolated catalyst was re-used for the coupling reaction between iodobenzene and phenylacetylene (Table 3). The catalyst was recycled successfully after seven run to record a turnover number (TON) of 1400 in total. In order to reveal Pd leaching during the reaction, the amount of Pd of the filtrate were measured by ICP technique. Analysis of the crude reaction mixture indicated a total Pd leaching of about 3% from the supported system which occurred after third and sixth run. There is no change in the size and morphology of the Pd nanoparticles of

Table 3. Recycling of the catalyst for the reaction of iodobenzene with phenylacetylene^a

Run	time / h	Conversion ^b / %
1	1	> 99
2	1	> 99
3	1.5	> 99
4	1.5	> 99
5	1.5	> 99
6	2	> 99
7	2	> 99

^aReaction condition: iodobenzene (1.0 mmol), phenylacetylene (1.2 mmol), K₂CO₃ (2 mmol), recycled Pd cat. (0.5 mol%) in DMF (5 mL) at 100 °C; ^bconversion based on iodobenzene.

the recycled catalyst, as evident from X-ray diffraction (XRD) analysis. The XRD patterns for the catalyst after a successful Sonogashira reaction showed the expected crystallinity of Pd⁰ nanoparticles at (111), (200), (220) and (311) crystallographic planes (Figure 2).

The scope of this methodology is further extended for Suzuki coupling reaction which is one of the versatile methods for the generation of biaryls. Using K₂CO₃ as a base and DMF as a solvent, phenylboronic acid was found to couple smoothly with different aryl halides providing the corresponding biaryls (Table 4). *Ortho* and *meta* substituted aryl halide was also applied and produce only 30 and 40% of the corresponding products after 24 h. Similar to the Sonogashira reaction, aryl chlorides give the coupling products in the presence of TBAB (Table 4, entry 10-13).⁴⁴⁻⁴⁷

The recycling experiment for the reaction of phenylboronic acid with iodobenzene was performed during 6 runs with no considerable leaching, so prolonging the reaction time was necessary.

Finally, a comparison was made to evaluate the efficiency of reported system with our previous reports on heterogeneous Pd catalysts (Table 5).³⁴⁻³⁷ Present catalyst yielded the coupling product in the conditions such as solvent, base, amounts of catalyst, temperature and recyclability that is comparable with other reported systems.³⁴⁻³⁷

Conclusions

In summary, we have presented Pd nanoparticles supported on poly(*N*-vinylpyrrolidone)-silica hybrid material

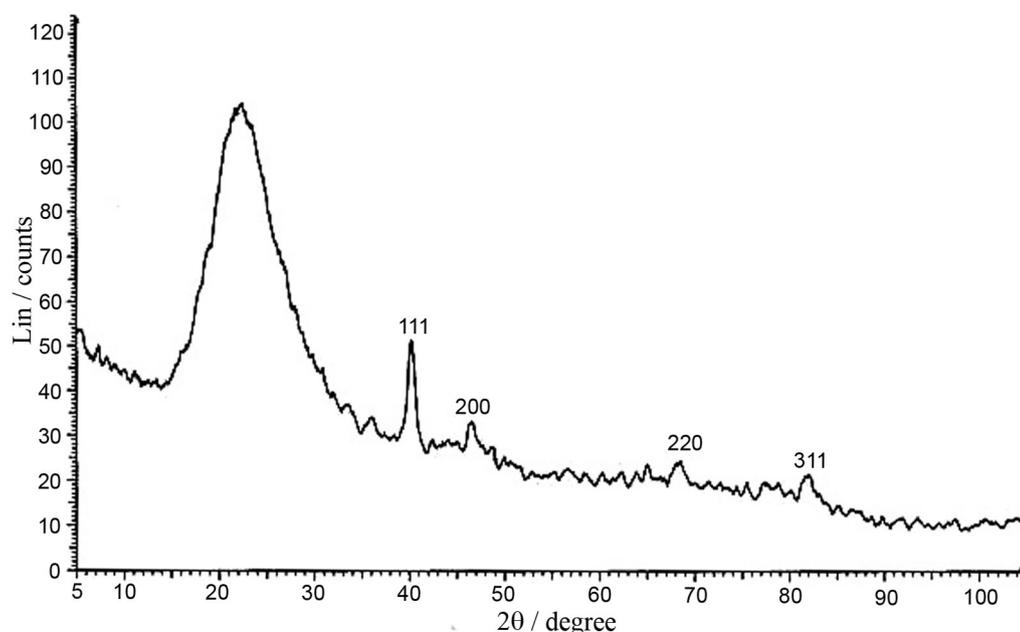
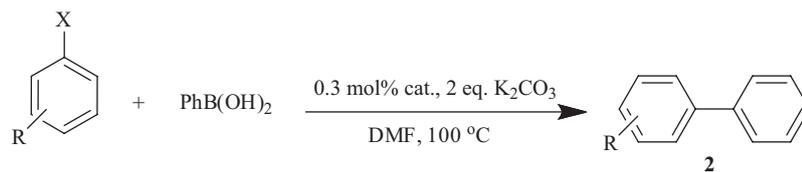


Figure 2. XRD pattern of palladium supported on poly(*N*-vinylpyrrolidone)-grafted silica after a Sonogashira reaction.

Table 4. Suzuki reaction of phenylboronic acid with different aryl halides in the presence of Si-PVP-Pd catalyst^a

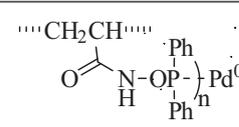
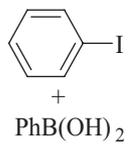
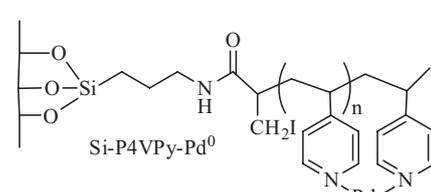
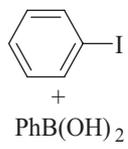
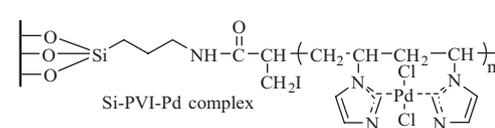
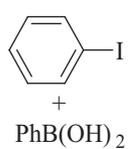
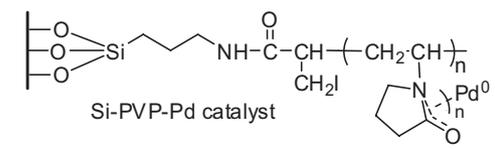
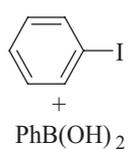
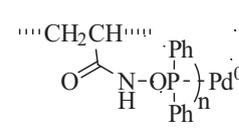
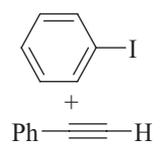
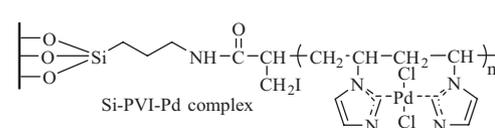
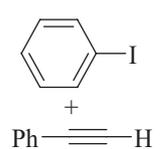
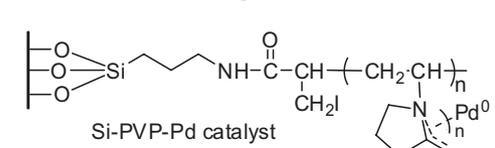
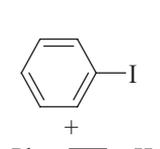
entry	Ar-X	Product	time / h	Yield ^b / %
1		2a	0.5	92
2		2b	1	80
3		2a	2	85
4		2c	12	75
5		2d	24	30
6		2e	24	40
7		2f	1	85
8		2g	0.5	90
9		2h	1	80
10 ^c		2a	15	65
11 ^c		2c	12	75
12 ^c		2i	10	85
13 ^c		2f	3	85

^aReaction condition: aryl halide (1.0 mmol), phenylboronic acid (1.2 mmol), K₂CO₃ (2 mmol), Pd cat. (0.3 mol%) in DMF (5 mL) at 100 °C; ^bisolated yield of products; ^cTBAB (5 mol%).

as an efficient and practical catalyst for the Suzuki and copper-free Sonogashira reactions. Different aryl halides

including chloroarenes showed good reactivity to generate the corresponding products in good to excellent yields.

Table 5. A comparison of the Si-PVP-Pd catalyst with some previous heterogeneous Pd catalysts used in Suzuki or Sonogashira coupling reactions

No.	Catalyst	Reactant	Conditions	Ref.
1	 <p>Pd⁰ nanoparticles supported on modified crosslinked polyacrylamide</p>		40 min; 96% 2 eq. K ₂ CO ₃ ; 0.1 mol% cat. DMF; 80 °C	34
2	 <p>Polyvinylpyridine-grafted silica containing palladium nanoparticles</p>		20 min; 88% 2 eq. K ₂ CO ₃ ; 0.1 mol% cat. DMF; 120 °C	36
3	 <p>Poly(<i>N</i>-vinylimidazole) grafted silica containing palladium nanoparticles</p>		0.5 h; 96% 2 eq. K ₂ CO ₃ ; 0.3 mol% cat. NMP; 100 °C	37
4	 <p>Poly(vinylpyrrolidone) grafted silica containing palladium nanoparticles</p>		0.5 h; 92% 2 eq. K ₂ CO ₃ ; 0.3 mol% cat. DMF; 100 °C	this work
5	 <p>Pd⁰ nanoparticles supported on modified crosslinked polyacrylamide</p>		4 h; 90% 2 eq. K ₂ CO ₃ ; 0.5 mol% cat. NMP; 100 °C; 5 mol% TBAB	35
6	 <p>Poly(<i>N</i>-vinylimidazole) grafted silica containing palladium nanoparticles</p>		1 h; 91% 2 eq. K ₂ CO ₃ ; 0.5 mol% cat. DMF; 100 °C	37
7	 <p>Poly(vinylpyrrolidone) grafted silica containing palladium nanoparticles</p>		1 h; 95% 2 eq. K ₂ CO ₃ ; 0.5 mol% cat. DMF; 100 °C	this work

NMP: *N*-Methylpyrrolidone.

Our catalytic results are comparable with those similar heterogeneous systems reported in the literature. This

catalyst can be recovered and reused several times with only negligible leaching of palladium from the supported system.

Supplementary Information

Supplementary data (¹H and ¹³C NMR spectra of coupling products) are available free of charge at <http://jbcs.sbq.org.br> as PDF file.

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