



A simple and greener approach for the synthesis of PVC supported Pd (0): application to Heck and Sonogashira reactions in water



Basavaprabhu, M. Samarasimhareddy, Girish Prabhu, Vommina V. Sureshbabu *

#109, Peptide Research Laboratory, Department of Studies in Chemistry, Central College Campus, Dr. B.R. Ambedkar Veedhi, Bangalore University, Bangalore 560 001, India

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ABSTRACT

Preparation of PVC-supported Pd nanoparticles through the reduction of PdCl₂ by a non-toxic and eco-friendly route, employing sodium formate and NaOH in ethanol–water system has been described. The prepared PVC supported Pd nanoparticles were employed as catalyst in the cross coupling reactions, that is, Heck and Sonogashira reactions in water medium to afford the respective products in good to excellent yields.

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The use of transition metal nanoparticles of Pd, Pt, Ru, Au, Cu, and Ag as catalysts in C–C cross coupling reactions has placed nano-metal catalysis as an important frontier of study in recent years.¹ Palladium-catalyzed reactions, in particular, carbon–carbon bond forming reactions including Suzuki, Heck, Sonogashira, and Tsuji–Trost reactions either through homogeneous or heterogeneous catalysis have gained a predominant place in the arsenal of organic chemists.² The inherent problem associated with homogeneous catalysis is the separation of expensive catalyst from the product for re-use. For instance, the homogeneous Pd catalysts tend to lose their catalytic activity because of Pd metal aggregation and precipitation. Thus, heterogenization of the homogeneous Pd catalyst is an alternative feasibility to overcome such limitations by employing Pd nanoparticles on solid support.

For many technological applications the prevention of agglomeration of the nanoparticles during the use and storage is a major objective in order to provide sufficient and reliable material performance. Thus the use of polymeric carrier components could be an interesting approach. Pd nanoparticles dispersed within a polymeric matrix are receiving intense attention due to the novel and highly versatile material properties offered by these systems. Therefore, the catalytic properties of transition metal–polymer systems in general and Pd–polymer systems in particular are under systematic investigation by several groups.³ Palladium nanoparticle catalyzed coupling was pioneered by Reetz using surfactants as stabilizing agents.⁴ El-Sayed et al.⁵ reported the use of PVP

stabilized Pd nanoparticles as efficient catalysts for the Suzuki reaction in an aqueous medium (40% EtOH or CH₃CN/H₂O). Hyeon et al. reported the use of triblock copolymer in the synthesis and stabilization of Pd nanoparticles.⁶ Polymer, dendrimer, organic ligands, or surfactant stabilized Pd nanoparticles are being widely used for various cross coupling reactions.⁷ Most of them use organic or ionic liquids as solvents and high temperature or microwave irradiation conditions.

Several natural biopolymers such as chitosan, cellulose, and wool, have been used as polymer supports in Pd catalyzed transformations.⁸ Pd nanoparticles supported over polyvinyl chloride (PVC)-amino ethanol matrix and PVC-Schiff's base have been prepared and employed as efficient catalysts in Suzuki and Heck reactions.⁹ In these studies PdCl₂ could be reduced to Pd (0) in situ, without the assistance of an external reducing agent. However, the prior functionalization of the polymer requires an extra step. The application of water as a solvent in organic syntheses involving C–C cross coupling reactions and in transition-metal catalyzed reactions has been gradually developing.¹⁰ Water is cheap, non-toxic, and not flammable which could be considered as an alternative to expensive organic solvents and an attractive media for the development of environmentally harmless chemical processes. Also, separation of water-insoluble organic compounds from the aqueous phase is easy.

Recently our group demonstrated the PVC supported Pd nanoparticles for the reduction of nitro compounds and alkenes.^{11a} Suzuki cross-coupling of boronic esters with aryl halides using PVC-Pd⁰ was also documented by us.^{11b} In continuation to these studies, we wanted to explore the catalytic activity of PVC supported Pd nanoparticles to Heck and Sonogashira reactions.

* Corresponding author. Tel.: +91 08022961339.

E-mail addresses: hariccb@hotmail.com, sureshbabuvommina@rediffmail.com, hariccb@gmail.com (V.V. Sureshbabu).

As a part of this study, we were interested in developing a greener approach for the preparation of PVC-Pd⁰ nanoparticles. Among the preparations of Pd nanoparticles, the chemical reduction of palladium salt in an aqueous or organic solution by suitable reducing agents such as hydrazine, hydrogen, and sodium borohydride has been widely adopted, even though these reducing agents are hazardous in nature.¹² However, an efficient and greener approach for the preparation of Pd nanoparticles is highly desirable from environmental standpoint. Thus, in the present protocol, the reduction of PdCl₂ was carried out by employing sodium formate and NaOH in the ethanol–water system¹³ at reflux condition. The present method utilizing sodium formate and NaOH serves as a better alternative for the reduction of PdCl₂ to Pd (0), as it avoids the use of hazardous H₂ and toxic hydride ion sources. Unlike the reported methods, removal of unreacted residual reagents can be achieved through simple water wash and thus handling of the present reagent system is more convenient than the earlier reported reagents.

Preparation of catalyst

A previously stirred suspension of PVC (100 mg) and PdCl₂ (4:1 wt/wt) in ethanol (8 mL) was heated to reflux and then treated with a solution of sodium formate (10%, 3 mL) and 0.1 N NaOH (2 mL) in distilled water for 4–5 min. The resulting homogeneous solution was maintained at 50–55 °C for 1.5 h. Initial brownish suspension turned colorless upon addition of sodium formate and NaOH, indicating the conversion of Pd (II) to Pd (0). Overall, the preparation of catalyst was complete in about two hours.

Thus obtained palladium nanoparticles were filtered, washed with water, and dried in vacuo. The dried sample was characterized by X-ray powder diffraction (XRD), where X-ray diffractogram confirmed Pd (0) diffraction lines at $2\theta = 40.039^\circ$, 46.581° , and 68.047° corresponding to (111), (200), and (220) lattice planes of Pd (Fig. 1). The Pd nanoparticles were further characterized by scanning electron microscopy (SEM, Fig. 2) and transmission electron microscopy (TEM, Fig. 3).

TEM analysis revealed a narrow size distribution of the palladium nanoparticles. Particle size distribution diagram, that is, histogram showed Pd nanoparticles with an average size range of 3–4 nm (Fig. 4) and ICP-AES analysis indicated 13.25% of Pd loading in the PVC matrix.

Heck reaction

Heck reaction is widely used in the C–C cross coupling reaction of alkenes in organic synthesis. It is often used to functionalize

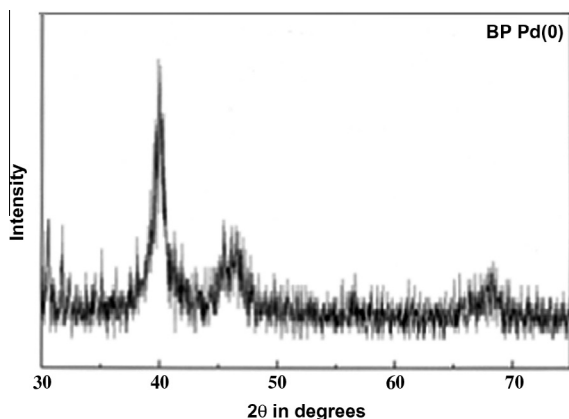


Figure 1. XRD pattern of PVC-Pd⁰ with diffraction lines at $2\theta = 40.039^\circ$, 46.581° , and 68.047° .

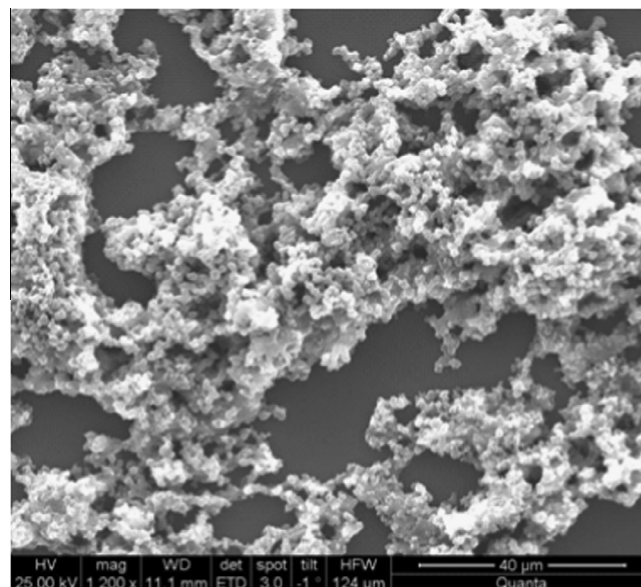


Figure 2. SEM image of PVC-Pd⁰ nanoparticles.

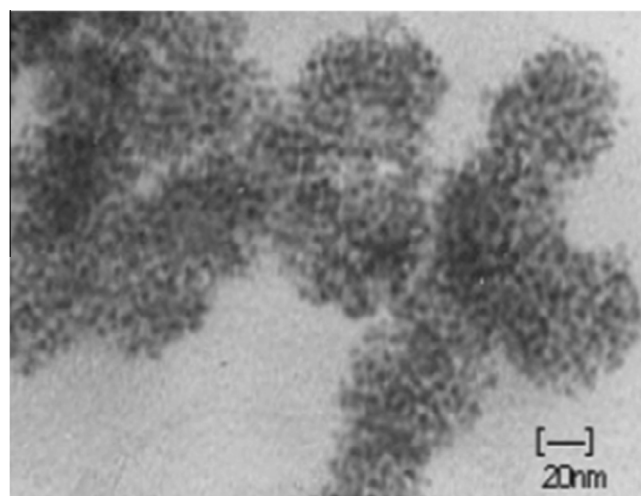


Figure 3. TEM image of PVC-Pd⁰ nanoparticles (bar length 20 nm).

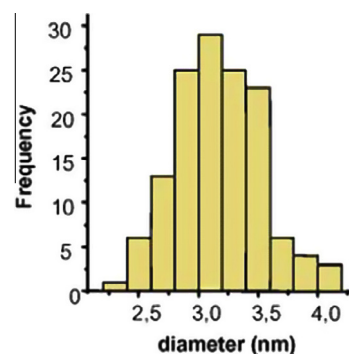


Figure 4. Particle size distribution histogram of PVC supported Pd nanoparticles (particle size 3.2 ± 0.4 nm).

aromatic rings and as an alternate to the Friedel–Crafts reaction.¹⁴ Heck reaction usually involves the interaction of an aromatic halide or anhydride with an alkene, in the presence of palladium

catalyst. Generally, the Heck reaction entails the use of elevated temperatures, hazardous organic solvents, and expensive phosphine ligands.¹⁵ Nowadays, considerable efforts have been devoted to the improvement of the efficiency and selectivity of the Pd-catalyzed Heck reactions. Key aspects for improving the Heck reaction include shortening of the reaction duration and employing recyclable catalysts that can be isolated easily from the reaction mixture.

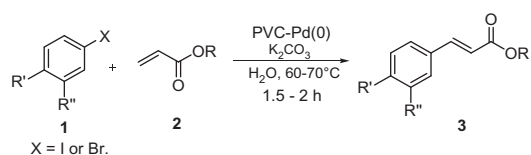
In the first part of the study, the catalytic reactivity of as-prepared Pd nanoparticles to Heck reaction involving the cross-coupling of aryl halides with methyl acrylate was studied. Palladium catalyzed Heck reactions are strongly dependent on a number of factors such as base, solvent, stabilizing ligand, temperature, and the combined effect of these. Hence, our initial interest was to optimize the reaction conditions for this protocol. For this purpose, we systematically evaluated the role of solvent, base, and catalyst loading for this synthetic protocol by subjecting iodobenzene and methyl acrylate to the cross coupling reaction (Scheme 1).

During a sequence of reactions carried out using different solvents such as toluene, water, acetonitrile, and ethanol, water proved to be efficient in affording good yields of the product. Consequently, water was chosen as solvent system for the present study. Among the bases screened, in the presence of K₂CO₃ the reaction proceeded well within 2 h at 70 °C compared to other bases like Cs₂CO₃, Na₂CO₃, and triethylamine. In addition, 1.69 mol % (20 mg) of the catalyst (PVC-Pd⁰) loading was found to be suitable for the reaction to go for completion. Significantly lower yields were observed when 5 and 10 mg of the catalyst were used.

To demonstrate the scope of the catalyst system, aryl halides including iodides and bromides with various substitutions were cross coupled with ethyl and methyl acrylates to give good yields of the products irrespective of the nature of substituents like nitro, methoxy, and *n*-butyl groups (Table 1). A higher temperature range of 80–85 °C was essential for the successful cross coupling of the aryl halides with electron withdrawing groups.

Sonogashira reaction

The palladium catalyzed coupling reaction between aryl or alkenyl halides or triflates and terminal alkynes has become the most important method to prepare arylalkynes and conjugated enynes, which are precursors for the assembly of natural products, pharmaceuticals, and molecular organic materials.¹⁶ Development of a copper-free procedure for the Sonogashira reaction is a particular challenge since it is traditionally a dimetallic-mediated process (palladium and copper required).^{17a–k} Nevertheless since its discovery, a great deal of work has been done to improve the original protocol so as to induce an even wider range of reactants as well as to circumvent some of major drawbacks of the protocol.¹⁸ Copper salts can induce Glaser-type homocoupling of terminal alkynes when copper–acetylide intermediates are exposed to oxidative reagents or air.¹⁹ In addition, use of two metals hinders the recovery and reutilization of the expensive Pd catalysts. Phosphines, which are frequently used in this reaction, are often air-sensitive and are not commercially available. To avoid these



Scheme 1. PVC-Pd⁰ catalyzed Heck cross coupling reaction.

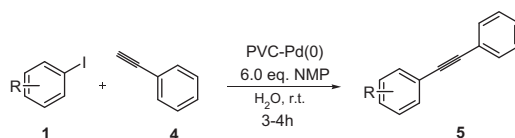
Table 1
List of cross-coupled products of Heck reaction

Entry	Reactant (1)	Product (3)	Yield (%)
1			89
2			87
3			86
4			92
5			90
6			86
7			85
8			78

drawbacks and consequently to provide access to alkylation reactions under aerobic conditions, copper- and phosphine-free procedure with the use of a polymer supported Pd catalyst has been developed.

Thus, PVC supported Pd nanoparticles were explored for the Sonogashira cross coupling reaction employing iodobenzene and phenyl acetylene as model substrates. In the quest to carry out the Sonogashira reaction in water, we screened various amine bases such as triethylamine, *N*-methylpyrrolidine (NMP), *N*-methylmorpholine (NMM), and piperidine. Among these bases, *N*-methylpyrrolidine (6.0 equiv) in the presence of nano Pd (20 mg, 6.2 mol %) afforded good yields of the product within 3 h at room temperature (Scheme 2). The protocol was further extended for the coupling of iodobenzene substituted with electron withdrawing and donating groups with phenylacetylene (Table 2). The corresponding products were isolated in good yields²⁰ and the compounds were characterized through NMR analyses.²¹

The reusability of PVC-Pd⁰ was explored in Heck as well as Sonogashira reactions. The PVC-Pd⁰ can be used in 5–6 successive



Scheme 2. PVC-Pd⁰ catalyzed Sonogashira cross-coupling reaction.

Table 2
List of cross coupling products of Sonogashira reaction


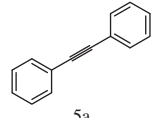
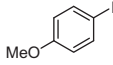
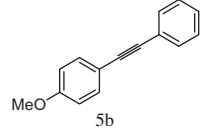

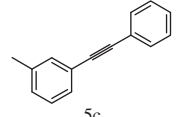
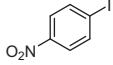
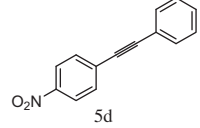

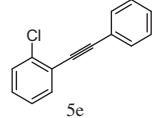

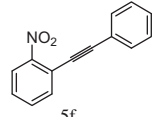
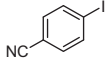
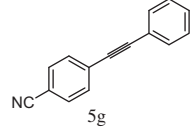
Entry	Reactant (1)	Product (5)	Yield (%)
1		 5a	93
2		 5b	90
3		 5c	89
4		 5d	78
5		 5e	81
6		 5f	69
7		 5g	87

Table 3
Catalyst recycling experiment

	1st cycle	2nd cycle	3rd cycle	4th cycle	5th cycle
Heck (yield): reaction time—1.5 h	89	89	87	86	84
Sonogashira (yield): reaction time—3.0 h	93	92	92	90	88

runs with no loss in its activity in both Heck and Sonogashira reactions. Recycling experiment was carried out employing phenylacetylene-iodobenzene and methylacrylate-iodobenzene as model substrates for Sonogashira and Heck reactions, respectively. The yields obtained in each recycling process are listed below (Table 3).

Further to demonstrate the activity of the catalyst, continuity experiment was carried out, that is, the catalyst was removed at half conversion of the reaction and the reaction was continued. However, further conversion was not noticed after the removal of the catalyst (as monitored through TLC). This experiment revealed that there was no significant leaching of the Pd nanoparticles in solution under the present experimental conditions. In addition, the recycling experimental results confirm the stability of Pd-PVC composite. The slight decrease observed in the yield during the recycling experiment can be accounted to agglomeration of metal

nanoparticles within the PVC matrix during the course of the reaction or accumulation of some organic species on the composite that hinders the interaction between catalyst and reactant molecules.

Herein we describe the preparation of PVC-supported Pd nanoparticles through the reduction of PdCl₂ by a non-toxic and eco-friendly route, employing sodium formate and NaOH in the ethanol–water system. The prepared PVC supported Pd nanoparticles were employed as catalyst in the cross coupling reactions, that is, Heck and Sonogashira reactions to afford the respective products in good to excellent yields. Under the present conditions, Sonogashira reaction can be carried out at room temperature without the use of CuI or phosphine ligands. The generation and stabilization of catalytically active nanoparticles in water have several important advantages over both traditional homogeneous and supported transition-metal catalysts in terms of lower cost, and avoiding the usage of organic solvents. This approach also provides two additional advantages: it could facilitate the recovery and reuse of palladium and could also reduce the palladium contamination of the isolated product, a significant problem for the pharmaceutical industry.

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 - (a) *PVC-Pd⁰ catalyzed Heck reaction of iodobenzene with methyl acrylate*: In a typical procedure, iodobenzene (0.30 g, 1.47 mmol), methyl acrylate (0.14 g, 1.67 mmol), and PVC-Pd (20 mg, 1.69 mol %) were taken in a round-bottomed flask containing 10 ml of water. To this solution was added 2.0 mmol of K₂CO₃. The reaction mixture was stirred for 1.5–2 h at 60–70 °C. The progress of the reaction was monitored by TLC. After completion of the reaction, the reaction mixture was filtered and the filtrate was extracted with EtOAc (10 ml × 2). The combined organic layer was dried over anhydrous Na₂SO₄ and evaporated under reduced pressure. The crude material was purified by column chromatography (hexane–EtOAc, 100:1) to afford the corresponding product in high purity.
(b) *PVC-Pd⁰ catalyzed Sonogashira reaction of iodobenzene with phenylacetylene*: Typical procedure: To a mixture of the PVC-Pd catalyst (20 mg, 6.2 mol %) and iodobenzene (81.6 mg, 0.40 mmol) in H₂O (3.0 mL) were added phenylacetylene (81.7 mg, 0.80 mmol) and NMP (6.0 mmol). The reaction mixture was stirred at room temperature for 3–4 h and filtered. The filtrate was extracted twice with EtOAc (6 mL). The combined EtOAc extracts were washed with water (4 mL) and brine (2 mL), dried over anhydrous Na₂SO₄, and concentrated in vacuo. The resulting residue was chromatographed on silica gel (hexane–EtOAc, 100:1) to give quantitative yield of diphenylacetylene.
 - Characterization data for selected compounds:
Methyl 3-phenyl acrylate (3a): Colorless liquid; ¹H NMR (400 MHz, CDCl₃) δ 3.80 (s, 3H), 6.42 (d, J = 16.2 Hz, 1H), 7.36–7.39 (m, 3H), 7.50–7.54 (m, 2H), 7.70 (d, J = 16.2 Hz, 1H) ppm; ¹³C NMR (75 MHz, CDCl₃) δ 51.6, 117.8, 128.0, 128.6, 130.2, 134.4, 144.8, 167.5 ppm.
Ethyl 3-p-tolyl acrylate (3b): White solid; ¹H NMR (400 MHz, CDCl₃) δ 1.35 (t, J = 7.2 Hz, 3H), 2.38 (s, 3H), 4.27 (q, 7.1 Hz, 2H), 6.38 (d, J = 16.2 Hz, 1H), 7.19 (d, J = 18.2 Hz, 2H), 7.40 (d, J = 8.2 Hz) ppm; ¹³C NMR (100 MHz, 75 CDCl₃) δ 14.6, 21.8, 60.8, 116.8, 128.2, 129.6, 131.8, 140.7, 144.6, 167.8 ppm.
Methyl 3(4-methoxyphenyl)acrylate (3e): White solid; ¹H NMR (400 MHz, CDCl₃) δ 3.78 (s, 3H), 3.84 (s, 3H), 6.30 (d, J = 15.8 Hz, 1H), 6.90 (d, J = 8.7 Hz, 2H), 7.46 (d, J = 8.7 Hz, 2H), 7.66 (d, J = 15.8 Hz, 1H) ppm; ¹³C NMR (75 MHz, CDCl₃) δ 51.5, 55.3, 114.4, 115.2, 127.1, 129.8, 144.5, 161.2, 167.6 ppm.
1,2-Diphenylethyne (5a): White solid; ¹H NMR (400 MHz, CDCl₃) δ 7.31–7.38 (m, 6H), 7.51–7.56 (m, 4H) ppm; ¹³C NMR (75 MHz, CDCl₃) δ 89.4, 123.3, 128.2, 128.3, 131.8 ppm.
3-Methoxy-4-(2-phenylethynyl)benzene (5b): White solid; ¹H NMR (400 MHz, CDCl₃) δ 3.82 (s, 3H), 6.86 (d, J = 6.8 Hz, 2.1 Hz, 2H), 7.28–7.39 (m, 3H), 7.41–7.56 (m, 4H) ppm; ¹³C NMR (75 MHz, CDCl₃) δ 55.3, 88.2, 89.1, 114.2, 115.4, 123.5, 127.8, 128.3, 131.4, 131.7, 140.2 ppm.
1-(2-(4-Nitrophenyl)ethynyl)benzene (5d): Yellow solid; ¹H NMR (400 MHz, CDCl₃) δ 7.34–7.38 (m, 3H), 7.52–7.56 (m, 2H), 7.63 (d, J = 8.6 Hz, 2H), 8.18 (d, J = 8.6 Hz, 2H) ppm; ¹³C NMR (75 MHz, CDCl₃) δ 87.8, 94.6, 122.2, 123.6, 128.4, 129.1, 130.2, 131.8, 132.3, 146.8 ppm.