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Palladium nanoparticles supported on poly (*N*-vinylpyrrolidone)-grafted silica as new recyclable catalyst for Heck cross-coupling reactions

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ABSTRACT

Novel catalytic system based on palladium nanoparticles supported on poly (*N*-vinylpyrrolidone) (PVP) grafted silica was prepared. Aminopropylsilica was reacted with acryloyl chloride to form acrylamidopropylsilica, and onto this functionalized silica vinylpyrrolidone monomer was polymerized by free-radical polymerization. The complexation of PVP-grafted silica with $PdCl_2$ was carried out to obtain the heterogeneous catalytic system. X-ray diffraction (XRD) technique and transmission electron microscopy (TEM) image showed that palladium dispersed through the support in nanometer size. This catalytic system exhibited excellent activity in cross-coupling reactions of aryl iodides, bromides and also chlorides with olefinic compounds in Heck–Mizoraki reactions in short reaction time and high yields. Elemental analysis of Pd by inductively coupled plasma (ICP) technique and hot filtration test showed low leaching of the metal into solution from the supported catalyst. The catalyst can be reused several times in repeating Heck reaction cycles without considerable loss in its activity.

1. Introduction

Palladium-catalyzed cross-coupling reactions is a versatile tool for the generation of C–C bonds [1–5]. Among different methods, the reaction of aryl halides with olefinic compounds, Heck reaction, is an excellent method in the synthesis of organic compounds [6–8]. These reactions are carried out in the presence of Pd catalysts involving ligands such as phoshines, amines, carbenes, dibenzylidineacetone (dba), etc [1]. The use of such homogenous systems is accompanied with the loss of expensive metal complexes. Many chemists have tried to solve this problem by designing heterogeneous catalytic systems [5]. The immobilization of homogenous catalysts on polymeric organic [9–13] or inorganic [14–19] supports is an expanding research area offering the advantages of easy product separation, catalyst recovery, recycling and inhibiting metal losing. In this regard, several methods include supporting Pd complexes on polymers [9–13] and anchoring of Pd complexes to various solids such as silica or modified silica [8,15] has been successfully applied. The supported catalysts on silica or modified silica are good alternatives to traditional homogenous catalysts and are environmentally friendly and display some advantageous properties, such as excellent stability (chemical and thermal), good accessibility and good dispersion of catalytic sites. The functional groups of these modified silica act as surface active sites for metal complexes with high suitable catalytic properties.

Most of the cross-coupling reactions have been carried out in the presence of phosphine ligands, but these ligands are usually poisonous, air sensitive, unrecoverable and may degrade at elevated temperature, so researchers tried to test phosphine-free catalytic systems [5]. Nitrogen chelating ligands are good candidate in replacement of phosphine ligands in Pd catalyzed cross-coupling reactions since they are air stable, less expensive and nontoxic. Several types of ligands containing nitrogen such as: Schiff bases, *N*-heterocyclic carbene, imidazole and pyridine supported onto silica have been used in Heck reactions [8]. Furthermore, in recent years, there has been growing interest in grafting polymer chains to the surface of silica for practical application and fundamental studies of interfacial phenomena [20–23]. This technique has provided an opportunity to take the advantage of a solid linear functional polymer that can be completely compatible with solvents and substrates and at the same time having high mechanical stability and good dispersion [24]. Chemical bindings of polymer chains onto silica have been studied with various monomers, such as; styrene [25], vinyl acetate [26], acrylic acid [23], methyl acrylate [27], vinylpyrrolidone [20,24], vinylimidazole [28] and vinylpyridine [29]. In 2008 Gao et al. reported the preparation of poly (4-vinylpyridine)–Cu complex grafted silica and its use as a heterogeneous catalyst in oxidation reactions [29]. In 2009 Han et al. used poly (*N*-vinylpyrrolidone)–Ru complex grafted silica as a catalyst for hydrogenation of aromatic compounds [30].

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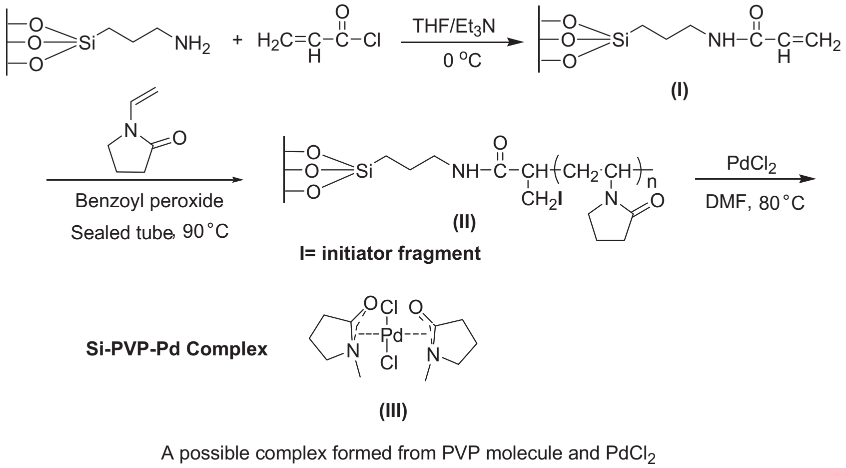


Scheme 1. Synthetic strategy for the preparation of poly (*N*-vinylpyrrolidone)-grafted silica loaded palladium catalyst.

There are few reports in the literature on the application of PVP as stabilizer of Pd [31,32] and colloidal solution of PVP-Pd [33–35] in cross-coupling reactions. However, as far as we know there is no report in the literature on poly (*N*-vinylpyrrolidone)–Pd complex grafted onto silica to be used in cross-coupling reactions. In continuation of our previous studies on heterogeneous Pd catalyst based on polymeric support [36] and polymer grafted silica [37], herein, we report the synthesis and characterization of poly (*N*-vinylpyrrolidone)-grafted silica palladium complex and its application as heterogeneous catalyst in Heck reactions with various substrates.

2. Experimental

2.1. General information

Substrates were purchased from Fluka, Merck or Aldrich Companies. Aminopropylsilica gel with an average particle size of 0.015–0.035 mm (>400 mesh ASTA) was supplied by Fluka. All products were characterized by comparison of their FT-IR and NMR spectra and physical data with those reported in the literature. All yields refer to the isolated products. Progress of the reactions was followed by TLC on silica-gel Polygram SIL/UV 254 plates or by GC on Shimadzu GC 14-A instrument with hydrogen flame ionization detector. FT-IR spectra were run on a Shimadzu FT-IR-8300 spectrophotometer. ^{1}H and ^{13}C NMR spectra were recorded on a Bruker Avance DPX instrument (250 MHz). TGA thermograms were recorded on an instrument of Perkin Elmer with N_2 carrier gas and the rate of temperature change of 20 °C/min was used. The Pd analysis and leaching test were carried out by inductively coupled plasma (ICP) analyzer (Varian, Vista-Pro). X-ray diffraction data obtained with XRD, D8, Advance, Bruker, axs. Transmission electron microscopy (TEM) analyses were performed on a Philips model CM 10 instrument. Scanning electron microscopy (SEM) were obtained by SEM, XL-30 FEG SEM, Philips, at 20 kV.

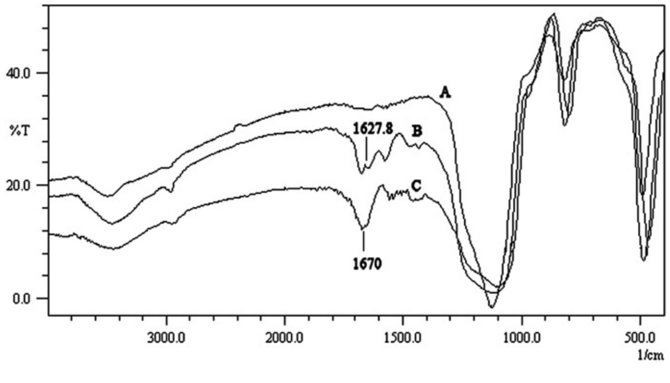


Fig. 1. FT-IR spectra of (A) aminopropylsilica (B) acrylamidopropylsilica (C) poly (*N*-vinylpyrolidone)-grafted silica.

2.2. Preparation of the catalyst

2.2.1. Preparation of acrylamidopropylsilica

Acrylamidopropylsilica was prepared by the reaction between aminopropylsilica (AMPS) and acryloyl chloride according to a previous procedure [38]. The capacity of AMPS was first determined by reverse acid-base titration method, and was found to be 0.95 mmol of amino group per gram of AMPS. The aminopropylsilica (10 g, 9.5 mmol amino groups) was suspended in dry THF (200 mL) and the suspension cooled down to 0 °C. Triethylamine (1.51 g, 0.015 mol) was added, followed by addition of acryloyl chloride (1.09 g, 0.012 mol) over a period of 1 h. Temperature of the reaction reached 5 °C at the end of the addition. The thick slurry was then stirred at 0 °C for a further 4 h and the modified silica was isolated by filtration and washing with THF (100 mL), water (2 × 100 mL) and acetone (100 mL). The solid obtained was then dried in an oven at 110 °C for 24 h.

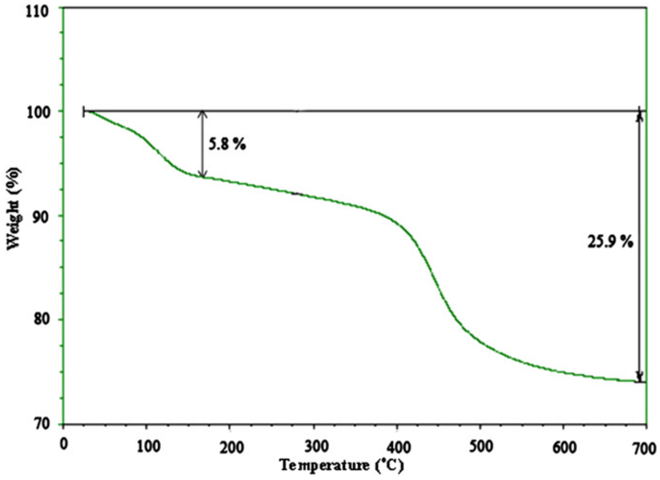


Fig. 2. Thermogravimetric analysis (TGA) of poly (*N*-vinylpyrrolidone)-grafted silica.

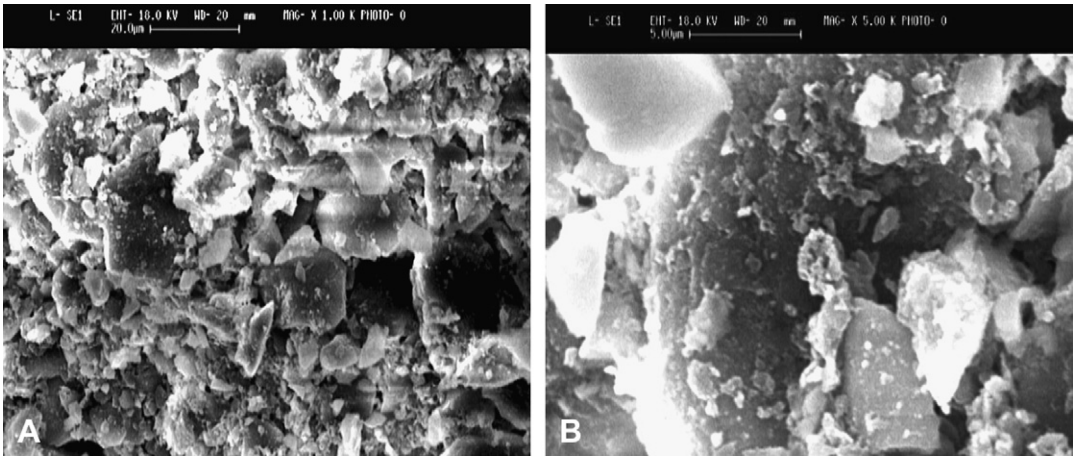


Fig. 3. (A) Scanning electron microscopy (SEM) image of palladium supported on poly (*N*-vinylpyrrolidone)-grafted silica (B) SEM close-up of image A.

2.2.2. *Preparation of poly (N-vinylpyrrolidone)-grafted silica*

To a suspension of acrylamidopropylsilica (2.0 g) in fresh 1-vinyl-2-pyrrolidone (4 mL), recrystallized benzoyl peroxide (0.05 g) was added in a 10 mL sealed tube. The mixture was heated at 90 °C in an oven for 15 h. The product was soxhlet-extracted with $CHC1_3$ (200 mL) for 24 h, followed by washing with methanol (2 × 200 mL) and water (2 × 100 mL) and dried for 12 h under vacuum.

2.2.3. *Preparation of palladium catalyst*

Poly (*N*-vinylpyrrolidone)-grafted silica (1.0 g) was added to a solution of $PdCl_2$ (0.177 g, 1.0 mmol) in DMF (30 mL) and stirred at 80 °C for 5 h under nitrogen atmosphere. The solid catalyst was filtered, washed thoroughly with DMF and water and dried under reduced pressure. To determine the Pd content of the catalyst, it was treated with 30 mL mixture of concentrated H_2SO_4 and HCl (1/1), and filtered. The filtrate was diluted to 50 mL with distilled water and subjected to ICP determination using calibration curve method.

2.3. *General procedure for the Mizoraki–Heck reaction*

To a suspension of aryl halide (1 mmol), K_2CO_3 (2.0 mmol) and Pd complex (0.5 mol%) in DMF (30 mL) was added *n*-butyl acrylate or styrene (1.2 mmol). The reaction mixture was stirred at 120 °C. The reaction was monitored by TLC (or GC if necessary). On completion of the reaction, the mixture was filtered and the filtrate poured into water (50 mL) and extracted with CH_2Cl_2 (3 × 15 mL). The combined organic phases were dried over Na_2SO_4, filtered and evaporated in vacuum. The mixture was then purified by column chromatography over silica-gel or recrystallization to afford a product with high purity. Characterization of the products was performed by comparison of their FT-IR, ^{1}H NMR, ^{13}C NMR and physical data with those of the authentic samples.

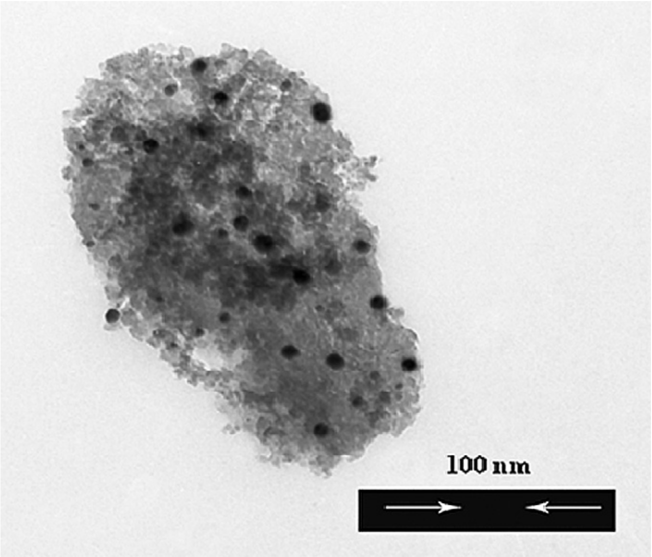


Fig. 4. Transmission electron microscopy (TEM) image of palladium supported on poly (*N*-vinylpyrrolidone)-grafted silica.

2.4. *General procedure for recycling reactions*

When the Heck reaction according to the above procedure was finished, the suspension was cooled down to room temperature and filtered off. The polymer was washed with DMF, water and acetone. It was dried under vacuum and then used in the next reaction cycle with a new portion of reagents without any pretreatment.

3. Results and discussion

3.1. *Synthesis and characterization of supported catalyst*

The palladium catalyst was designed by the sequence of reactions given in Scheme 1. Acrylamidopropylsilica (**I**) was prepared by reaction between aminopropylsilica (AMPS) and acryloyl chloride according to a previous procedure [38]. The FT-IR spectrum of AMPS showed a broad band at 1050–1200 cm^{-1} due to Si–O and at 3250 cm^{-1} corresponding to NH_2 (Fig. 1). In FT-IR spectrum of acrylamidopropylsilica absorption frequencies of amide group appeared at 1558, and 1662 cm^{-1} and double bond at 1627 cm^{-1} (Fig. 1). The appearance of these bands suggests that the reaction between amine groups on the surface of the AMPS and acryloyl chloride have occurred successfully. Poly (*N*-vinylpyrrolidone)-grafted silica (**II**) was obtained by free-radical copolymerization between acrylamidopropylsilica (**I**) and vinylpyrrolidone monomer in the

Scheme 2. Mizoraki–Heck cross-coupling reactions.

Table 1
Effect of different bases on the reaction of bromobenzene and *n*-butyl acrylate.[a]

Entry	Base	Time (h)	Yield (%)[b]
1	none	24	trace
2	K_2CO_3	4	80
3	NaOAc	10	70
4	Et_3N	10	50
5	$K_3PO_4.12H_2O$	10	65

[a] Reaction conditions: bromobenzene (1 mmol), *n*-butyl acrylate (1.2 mmol), base (2 mmol), Pd catalyst (0.5 mol%) in DMF (3 mL) at 120 °C.
[b] Isolated yield.

presence of benzoyl peroxide as an initiator. FT-IR spectrum of (**II**) shows the characteristic band of N—C=O at 1670 cm^{-1} (Fig. 1). The amount of grafted poly (*N*-vinylpyrro1idone) onto silica was calculated by thermogravimetric analysis (TGA) upon heating the grafted silica in nitrogen atmosphere at the rate of 20 °C/min from 0 to 700 °C. It was found to be 1.9 mmol/g (5.8% water and 20.1% PVP) (Fig. 2). Palladium complex (**III**) was obtained by mixing poly (*N*-vinylpyrro1idone)-grafted silica with $PdCl_2$ in DMF at 80 °C. Determination of Pd content was carried out on catalyst digestion followed by ICP analysis. The Pd content of the catalyst was 0.25 mmol/g.

To obtain the morphology and particle size of the catalyst, scanning electron microscopy (SEM) and transmission electron microscopy (TEM) images of the catalyst were carried out. The SEM image shows shiny Pd particles on the crushed ice like of the grafted PVP which dispersed with a well degree of homogeneity (Fig. 3). According to TEM image, the palladium particles are well dispersed through the catalyst surface in nanometer size between 20–25 nm (Fig. 4).

3.2. Catalytic activity of the catalyst in Heck cross-coupling reactions

The activity of the supported catalyst was first examined in the Heck coupling reaction of different aryl halides with styrene and *n*-butyl acrylate (Scheme 2). In a model reaction, the coupling of bromobenzene with *n*-butyl acrylate was initially studied. In the process of coupling reaction the choice of solvent and base is crucial, so these parameters were optimized and the results are summarized in Tables 1 and 2. It was found that the best system was DMF as solvent and K_2CO_3 as base using 0.5 mmol% of catalyst at 120 °C. The generality of this reaction system was shown with other coupling reactions using *n*-butyl acrylate and styrene as olefinic substrates with different aryl halides including iodo, bromo and even chloroarens. The results are presented in Table 3.

The electron-neutral, electron-rich and electron-poor aryl halides reacted with *n*-butyl acrylate and styrene efficiently to produce the corresponding cross-coupling products in good to excellent yields.

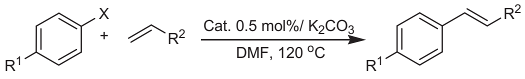
The more easily accessible and cheaper aryl chlorides have not been employed much, in palladium-catalyzed coupling reactions, primarily because the oxidative addition of C—Cl bond to Pd (0) species is usually difficult. Few heterogeneous Pd catalysts were

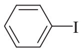
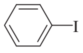
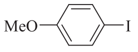
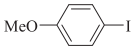
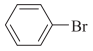
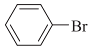
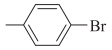
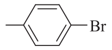
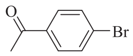
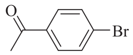
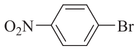
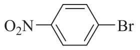
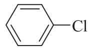
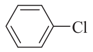
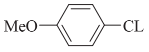
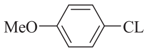
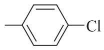
Table 2
Effect of different solvents on the reaction of bromobenzene and *n*-butyl acrylate.[a]

Entry	Base	Time (h)	Yield (%)[b]
1[c]	H_2O	24	55
2	DMF	4	80
3[c]	CH_3CN	24	60
4[c]	THF	24	20
5[c]	MeOH	4	40

[a] Reaction conditions: bromobenzene (1 mmol), *n*-butyl acrylate (1.2 mmol), K_2CO_3 (2 mmol), Pd catalyst (0.5 mol%), and 3 mL of solvent at 120 °C.
[b] Isolated yield.
[c] reflux temperature of solvents.

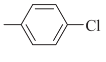
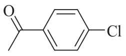
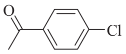
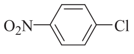
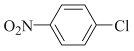
Table 3
Heck reaction of styrene and *n*-butyl acrylate with different aryl halides.[a]



Entry	Ar-X	R^2	Time (h)	Yield (%)[b]
1		CO_2Bu^n	0.5	95
2		Ph	1	93
3		CO_2Bu^n	1	95
4		Ph	2.5	95
5		CO_2Bu^n	4	80
6		Ph	6.5	80
7		CO_2Bu^n	4	85
8		Ph	7	90
9		CO_2Bu^n	2	95
10		Ph	3.5	92
11		CO_2Bu^n	1	93
12		Ph	2	95
13[c]		CO_2Bu^n	15	60
14[c]		Ph	18	60
15[c]		CO_2Bu^n	24	40
16[c]		Ph	24	50
17[c]		CO_2Bu^n	8	80

(*continued on next page*)

Table 3 (*continued*)

Entry	Ar-X	R^2	Time (h)	Yield (%)[b]
18[c]		Ph	10	70
19[c]		CO_2Bu^n	4	85
20[c]		Ph	6	85
21[c]		CO_2Bu^n	1	90
22[c]		Ph	2	85

[a] Molar ratio of the reagents ArX:*n*-butyl acrylate or styrene:K_2CO_3:palladium catalyst = 1.0:1.2:2.0:0.005. Reaction conditions: DMF, 120 °C.

[b] Isolated yields.

[c] With additional tetrabutylammonium bromide (0.05 mmol).

found to convert activated aryl chlorides at high temperature [39–42]. In our catalytic system, reactions of chloroarens required to increase the temperature up to 140 °C in long reaction times, but the addition of tetrabutylammonium bromide (TBAB) (Jeffery Catalyst) as an additive [43,44] permitted us to decrease the temperature to 120 °C and reactions performed in acceptable time (entries 13–22).

The powder X-ray diffraction (XRD) patterns for the catalyst after a successful Heck reaction showed the expected crystallinity of Pd (0) nanoparticles and amorphous silica (Fig. 5). The diffraction rings can be ascribed to the (111), (200), (220), (311), crystallographic planes of the Pd (0) nanoparticles. The Pd nanoparticle size was estimated by Scherrer equation from XRD pattern data, to be 19.6 nm [45]. The calculated size matches approximately to the size observed from TEM image. The same result was also obtained for the XRD pattern of the catalyst after its use in the Heck reaction for several cycles. This reveals the excellent stability and recovery of the catalyst.

3.3. *Heterogeneity tests (experimental evidence for leaching and redeposition of palladium) and catalyst reuse*

The possibility of recycling the catalyst is very important theme and makes them useful for commercial applications. Thus, we investigated the recovery and reusability of the supported catalyst using iodobenzene with *n*-butyl acrylate as model substrates. Seven consecutive cycles of the reaction showed that the catalyst did not lose its activity and could be completely recycled (Table 4). There is no change in the size and morphology of the palladium nanoparticles of the used catalyst. The estimated turn over number (TON = mole of product/mole of catalyst) is calculated to be 1400 for the whole recycling processes.

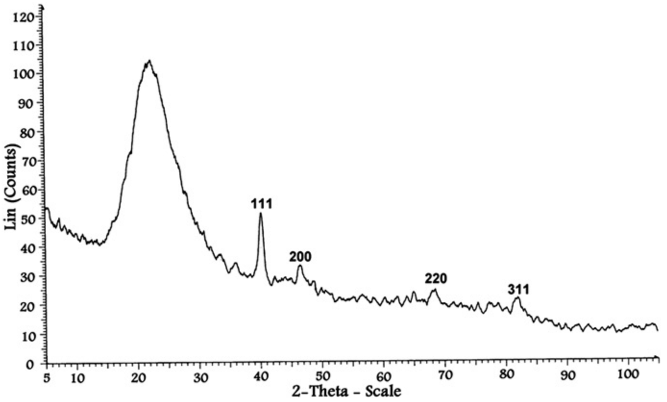


Fig. 5. X-ray diffraction (XRD) pattern of palladium supported on poly (*N*-vinylpyrrolidone)-grafted silica.

Table 4
Coupling of iodobenzene with *n*-butyl acrylate using recycled catalysts.[a]

Cycle	Conversion (%)[b]	Time (min)
1	100	30
2	100	30
3	100	45
4	100	45
5	100	45
6	100	60
7	100	60

[a] Reaction conditions: iodobenzene (1 mmol), *n*-butyl acrylate (1.2 mmol), K_2CO_3 (2 mmol), Pd catalyst (0.5 mol%) and DMF (3 mL) at 120 °C.

[b] conversion based on iodobenzene by GC.

Low contamination of residual metal in the isolated products is an important characteristic for supported metal catalyst. To probe the issue of palladium leaching in our system, the filtrate of the reaction between bromobenzene and *n*-butyl acrylate was analyzed by ICP. Analysis of the crude reaction mixture indicated a low Pd leaching of 0.62%. In addition, by adding new portions of reactants (bromobenzene, *n*-butyl acrylate and K_2CO_3) to the clear filtrate, the reaction did not progress and bromobenzene remained almost intact in the reaction mixture.

Hitherto, our catalytic system may be a reservoir for more active soluble form of Pd that redeposit to the support after reaction, or behaving in a truly heterogeneous manner. In order to investigate this issue about working mechanism, hot filtration test was performed. In a typical experiment, Pd compelx (0.5 mol %), bromobenzene (1 mmol), styrene (1.2 mmol), K_2CO_3 (2.0 mmol), and DMF (5 mL) were taken in a round-bottomed flask and stirred at 120 °C for 75 min under a nitrogen atmosphere. At this stage (25% conversion), the catalyst was filtered off and the experiment was continued with the filtrate for another 24 h. There was no detectable increase in the product concentration, as is evident from the GC analysis. It is confirmed the heterogeneous character of the catalytically active species in this reaction.

4. Conclusion

In conclusion, a novel catalytic system based on palladium nanoparticles supported on poly (*N*-vinylpyrrolidone)-grafted silica was designed and applied in Mizoraki–Heck cross-coupling reactions with a variety aryl halides. Different aryl halides including chloroarens showed good reactivity to generate the corresponding products in good to excellent yields. Through TEM and XRD we can observe high Pd dispersion and small particle sizes in nano scale. Short reaction times, high yields, easy purification, recyclability and very low Pd leaching are main characteristic of the process.

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