

Synthesis and Applications of Polyvinylpyridine-Grafted Silica Containing Palladium Nanoparticles as a New Heterogeneous Catalyst for Heck and Suzuki Coupling Reactions

B. Tamami* and F. Farjadian

Department of Chemistry, College of Science, Shiraz University, Shiraz 71454, Iran

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A new catalytic system based on palladium nanoparticles supported on poly(4-vinylpyridine) (P4VPy)-grafted silica is introduced. Aminopropylsilica was reacted with acryloyl chloride to form acrylamidopropylsilica. Onto this functionalized silica, 4-vinylpyridine monomer was polymerized by free radical polymerization. The P4VPy-grafted silica was characterized by FT-IR spectroscopy and the amount of (P4VPy) grafted was determined by thermogravimetric analysis (TGA). The complexation of (P4VPy)-grafted silica with Pd(Cl)₂ was carried out to obtain the heterogeneous catalytic system. Transmission electron microscopy images (TEM) showed that palladium dispersed through polymer surface in nanoparticle size. This catalytic system exhibited excellent activity in cross-coupling reactions of aryl iodides, bromides and also chlorides, with olefinic compounds in Heck-Mizoraki, and with benzylboronic acid in Suzuki-Miyaura reactions. The use of aryl chlorides in cross-coupling reactions is usually hardly successful, but excellent results were gained in the presence of terta-n-butylammonium bromide (TBAB) as an additive. The turnover number (TON) of this catalyst reaches up to 9×10^4 in these C-C bond forming reactions. High efficiency of the catalyst along with short reaction time, high yields, easy purification, recyclability, large scale synthesis and simple procedure are among the advantages of this catalytic system

Keywords: Polyvinylpyridine-grafted silica, Palladium nanoparticles, Heck reaction, Suzuki reaction, Polyvinylpyridine

INTRODUCTION

The immobilization of homogeneous catalysts on polymeric supports, offer the advantages of simple filtration, catalyst recovery, recycling, and inhibiting metal losing especially for expensive metals such as gold, platinum and palladium [1,2]. Polymer metal complexes as catalysts have been extensively studied for many years and excellent results have been achieved [3,4]. Polymeric supports containing nitrogen as donor atoms are of special interest. One of such polymers is polyvinylpyridine (PVPy) which is a functional

polymer that can coordinate with various transition metal ions. The complexes between PVPy and many kinds of transition metals have been used as catalysts for many organic transformations [5-10].

Novel heterogeneous catalysts based on silica or modified silica supports [11-15] have been reported, mainly because these material 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.

*Corresponding author. E-mail: tamami@chem.susc.ac.ir

In recent years, there has been growing interest in grafting polymer chain to the surface of silica for practical application and fundamental studies of interfacial phenomena such as support packing for liquid and gas chromatography [16], biocompatible surfaces [17], colloid stability [18] and modified inorganic membranes [19]. This technique has provided an opportunity to take the advantage of a solid linear functional polymer which can be completely compatible with solvents and substrates and of having high mechanical stability [20] and good dispersion.

Chemical bondings of polymer chains onto silica have been studied with various systems, such as: styrene [21], vinyl acetate [22], acrylic acid [19], methyl acrylat [23], vinylpyrrolidone [16,20], vinylimidazole [24] and vinylpyridine [25]. In 2008 Gao *et al.* reported grafting of poly(4-vinylpyridine)-Cu complex grafted silica and used it as a heterogeneous catalyst in oxidation reactions [25]. In 2009 Han *et al.* used poly (N-vinyl-2-pyrrolidone)-Ru complex grafted silica as a catalyst for hydrogenation of aromatics [26].

Palladium catalyzed C-C coupling reactions are one of the most employed organic transformations [27]. Among these transformations coupling of aryl, vinyl, benzyl or allyl halides, acetates or triflates with alkene Heck-Mizoraki reaction [28] and the reaction of organoboron compounds with organic halides or pseudohalides, Suzuki-Miyaura reaction [29], are interesting examples of carbon-carbon bond formation. These reactions are carried out in the presence of Pd catalysts involving ligands such as phosphines, amines, carbenes, dibenzylideneacetone (dba), *etc.* [27a]. The use of such homogenous systems is accompanied with the loss of expensive metal complexes and also many ligands such as phosphines are usually poisonous, air sensitive, unrecoverable and may degrade at elevated temperature. Many chemists have tried to solve these problems by designing phosphine-free heterogenous catalytic systems [27e]. Therefore, several types of ligands such as: Schiff bases, *N*-heterocyclic carbene, imidazole and pyridine supported onto silica or polymer [28d,29b] have been used in Pd catalyzed Heck or Suzuki reactions. Pyridine-functionalised supports have been successfully replaced with phosphines, since they are air stable, less expensive and non toxic. There are only a few reports in the literature on PVPy-Pd or modified PVPy-Pd complexes as heterogeneous catalyst in Heck or Suzuki

reactions [30-32]. However, as far as we know there is no report in the literature on polyvinylpyridine Pd complex grafted onto silica to be used in Heck or Suzuki reactions. In continuation of previous studies on heterogeneous Pd catalyst based on polymeric support [33] and polymer grafted silica [34] here we report the synthesis and application of poly(4-vinylpyridine)-grafted silica palladium complex and its application as heterogeneous catalyst in Heck and Suzuki reactions with various substrates.

EXPERIMENTAL

General

Substrates were purchased from Fluka AG and Merck Companies. Aminopropylsilica gel with an average particle size of 0.015-0.035 mm (>400 mesh ASTA) was supplied by Fluka. Titration of 3-aminopropylsilica (AMPS) was carried out by stirring 1.00 g of AMPS in 20 ml of 0.01 M HCl for 1 h, filtering off the solid and back titrating the filtrate with 0.01 M NaOH. Titration indicated a loading of 0.95 mmol g⁻¹ aminopropyl groups. All products were characterized by comparison of their IR and NMR spectra and physical data with those reported in the literature. Progress of reactions was followed by TLC on silica-gel Polygram SIL/UV 254 plates or by GC on Shimadzu GC 14-A with hydrogen flame ionization detector. FTIR Spectra were run on a Shimadzu FTIR-8300 spectrophotometer. ¹H and ¹³C NMR spectra were recorded on a Bruker Avance DPX instrument (250 MHz). TGA thermo grams were recorded on an instrument of Perkin Elmer with N₂ carrier gas and the rate of temperature change of 20 °C min⁻¹. TEM analyses were performed on a Philips model CM 10 instrument. Scanning electron micrographs were obtained by SEM, XL-30 FEG SEM, Philips, at 20 kV.

Metal loading test was carried out with an inductively coupled plasma (ICP) analyzer (Varian, vista-pro). UV-Vis diffuse reflectance spectroscopy (UV-Vis DRS) was performed on a Cary 5 instrument 92 by photometric mode with 300 nm min⁻¹ scan rate.

Preparation of Acrylamidopropylsilica

Acrylamidopropylsilica was prepared by the reaction between aminopropylsilica (AMPS) and acryloylchloride according to a previous procedure [35]. AMPS (10 g, 9.5

mmol amino groups) was suspended in dry THF (200 ml) and cooled to 0 °C. Triethylamine (1.51 g, 15 mmol) was added, followed by addition of acryloylchloride (1.09 g, 12 mol) over a period of 1 h. The 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 of 4 h and the modified silica was isolated by filtration and washed with THF (100 ml), water (2 × 100 ml) and THF (100 ml). The solid was then dried in an oven at 110 °C for 24 h. FT-IR (v/cm⁻¹): 2900-2985 (C-H str, weak), 1662 (amide I), 1627 (C=C, weak), 1558 (amide II).

Preparation of Poly(4-vinylpyridine) Grafted Silica

To a suspension of acrylamidopropylsilica (2 g), distilled 4-vinylpyridine (4 ml) and recrystallized benzoyl peroxide (0.05 g) were added in a 10 ml sealed tube. The mixture was heated at 100 °C in an oven for 24 h. The grafted silica polymer was soxhlet-extracted with CHCl₃, followed by washing with methanol 200 ml, water (2 × 100 ml) and dried for 12 h under vacuum at 60 °C. The amount of poly(4-vinylpyridine) grafted was determined by thermogravimetric analysis (TGA) by measuring the weight loss upon heating the silica particles in a nitrogen atmosphere at 20 °C min⁻¹ from 0 to 700 °C. It was approximately 3.4 mmol P4-VPy/g.

Preparation of the Pd Catalyst

Poly(4-vinylpyridine)-grafted silica (1.0 g) was added to a solution of PdCl₂ (0.451 g, 25.0 mmol) in DMF and stirred at 80 °C for 10 h. The solid was filtered and washed thoroughly with DMF and acetone. After that the yellowish solid was reacted with stoichiometric amount of NaBH₄ (0.6431 g, 17 mmol) in ethanol for 15 min under refluxed condition. The mixture was then filtered and washed with ethanol and acetone and the pure black solid was dried in an oven under vacuum at 60 °C for 10 h. According to the inductively coupled plasma (ICP) analysis, the Pd content in the heterogeneous catalyst was determined to be 0.25 mmol g⁻¹.

General Procedure for the Mizoroki-Heck Reaction

A suspension of aryl halide (1 mmol), K₂CO₃ (2.0 mmol), Pd complex (0.001 mmol) and DMF (5 ml) was mixed in a reaction flask and *n*-butylacrylate or styrene (1.2 mmol) was added. The reaction mixture was stirred at 120 °C. Progress of the reaction was followed by TLC on silica-gel until no traces

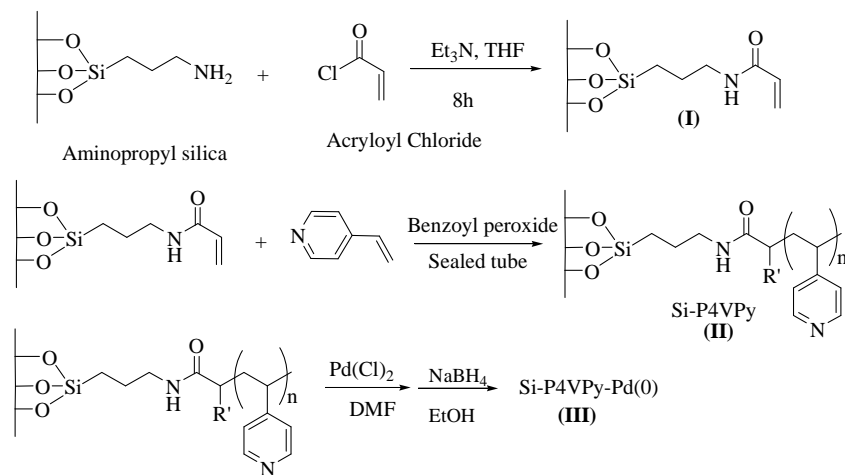
of starting aryl halide was observed. On completion of the reaction, the mixture was filtered and the filtrate poured into water (50 ml) and extracted with CH₂Cl₂ (3 × 15 ml). The combined organic phases were dried over Mg₂SO₄, filtered and the solvent evaporated under vacuum. The product was isolated by flash chromatography using petroleum ether or EtOAc or their mixture as eluents. The characterization of product was performed by comparison of its FT-IR, ¹H NMR, ¹³C NMR, and physical data with those of the authentic sample. The recycling test of the catalyst was performed in the reaction between iodobenzene and *n*-butylacrylate according to the procedure described here. After completion of the reaction the suspension was cooled down to room temperature and filtered off. The catalyst was washed with DMF, water and acetone. It was dried under vacuum and reused without any pretreatment for repeating cycles.

General Procedure for the Suzuki Reaction

In a typical procedure, a mixture of phenylboronic acid (1.5 mmol), aryl halide (1 mmol), K₂CO₃ (2.0 mmol), Pd complex (0.001 mmol) was added to 5 ml of DMF. The reaction mixture was stirred at 120 °C. After completion of the reaction, the procedure outlined above was followed. The recycling test was performed between *p*-bromo toluene and phenylboronic acid according to described procedure here and other process are according the procedure outlined above.

RESULTS AND DISCUSSION

The immobilization of polymeric catalysts onto silica have several important advantageous such as; ease of handling and use, recyclability, chemical and thermal stability, good dispersion of catalytic sites, compatibility with the solvent and inhibiting metal loosing [11-15]. In this work poly(4-vinylpyridine) (P4VPy) grafted onto silica was synthesized. Two techniques are usually used for grafting polymer chain to the surface of a silica support, namely: graft polymerization and polymer grafting [20]. In Graft polymerization the growth of polymer chain is from the active surface sites by a step or chain polymerization reaction mechanism, in polymer grafting the live polymer chain is covalently bonded to the silica surface. We used the first method in preparation of P4VPy-grafted silica (Scheme 1).



Scheme 1. Synthesis of the poly(4-vinylpyridine)-grafted silica-pd(II) complex

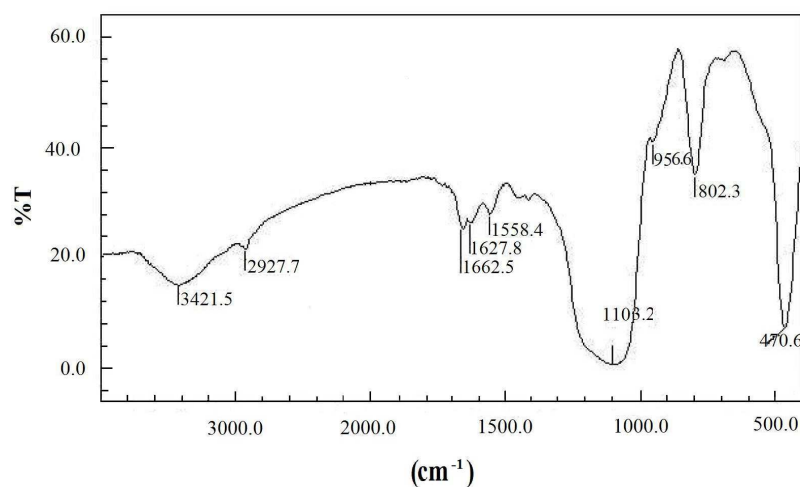


Fig. 1. FT-IR Spectrum of I.

Thus aminopropylsilica (AMPS) was reacted with acryloylchloride to form acrylamidopropylsilica (I), FT-IR spectrum showed the absorption frequencies of amide group in 1558, and in 1662 and double bond in 1627 cm^{-1} (Fig. 1).

The appearance of these bands suggests that the reaction between amine groups on the surface of the AMPS and acryloylchloride have occurred successfully. The resulting modified silica with polymerizable double bond was copolymerized with 4-vinylpyridine in the presence of benzoyl

peroxide as an initiator in a sealed tube. Figure 2 shows the FT-IR spectrum of the product II with stretching vibration absorption of C-N bond of the pyridine rings at 1596 cm^{-1} and C-C bond at 1423, 1550 and 1596 cm^{-1} .

The amount of P4VPy grafted onto silica was determined by thermogravimetric analysis (TGA) (Fig. 3), and was calculated to be about 3.4 mmol P4PVy/g.

The complexation between P4VPy grafted silica (II) and palladium chloride was carried out in DMF and the reduction

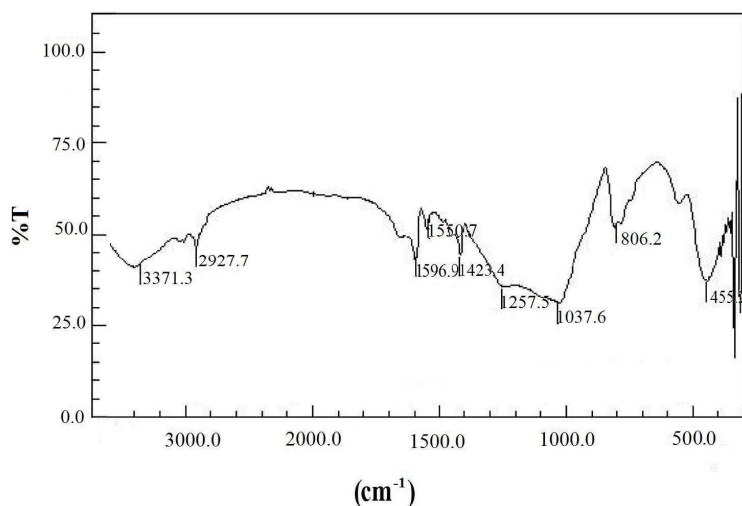


Fig. 2. FT-IR spectrum of **II**.

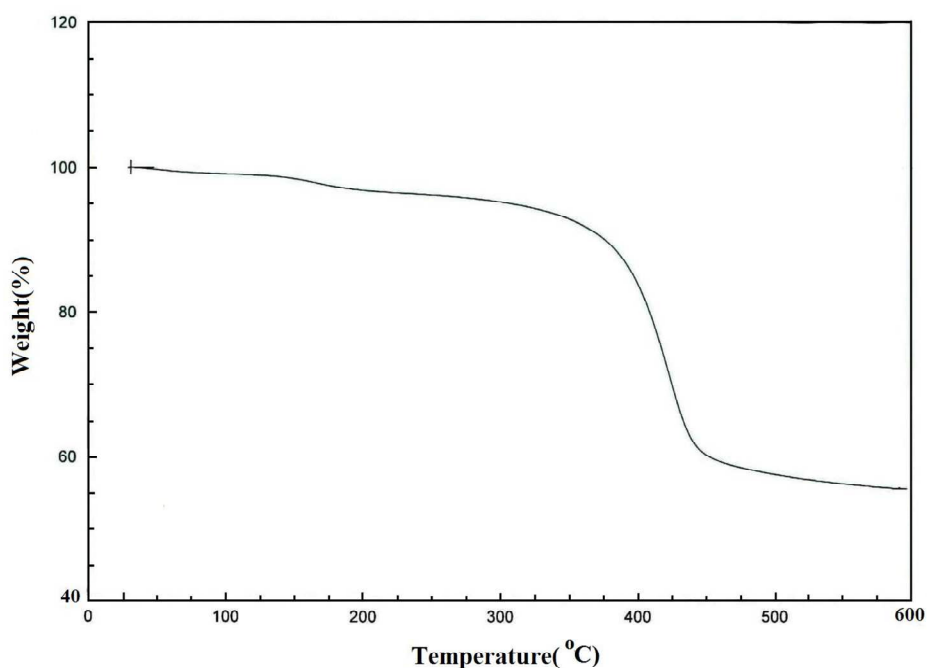


Fig. 3. TGA curve of **II**.

process in ethanol in presence of NaBH₄ to obtain polymeric Pd(0) complex III. Determination of Pd content of III was performed by digestion of the catalyst followed by Inductively Coupled Plasma (ICP) analyzer which revealed the presence

of 0.26 mmol Pd/g for this heterogeneous catalyst.

Scanning Electron Microscopy (SEM) and Transmission Electron Microscopy (TEM) images of the catalyst are shown in Fig. 4. The SEM image shows shiny Pd particles on the

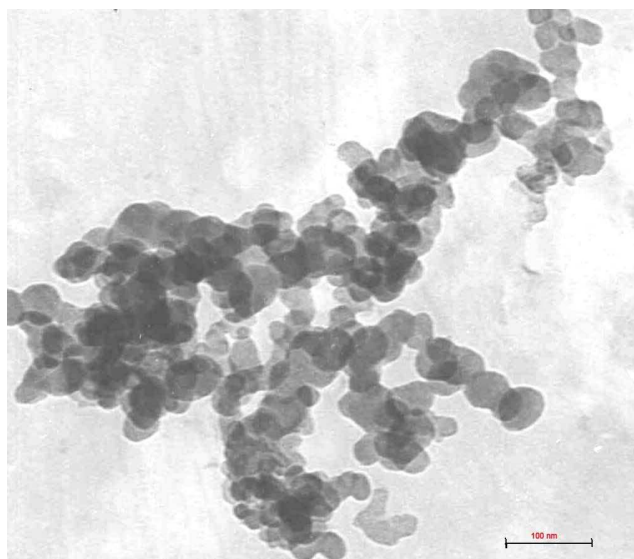


Fig. 4. SEM (top) and TEM (bottom) images of III.

smooth surface of the cubic like grafted P4VPy. According to the TEM image palladium particles are well dispersed through the catalyst surface in nanoparticle size between 30-50 nm.

Further characterization of the polymeric silica Pd(0) complex was performed using UV-Vis absorption spectra of P4VPy-grafted silica and its Pd complex Fig. 5. Since pyridine is a heterocyclic compound it is expected to have several electronic transition belonging to $\pi-\pi^*$ and $n-\pi^*$ in the range of 200-300 nm. In Fig. 5 for II we have two absorbances in 230

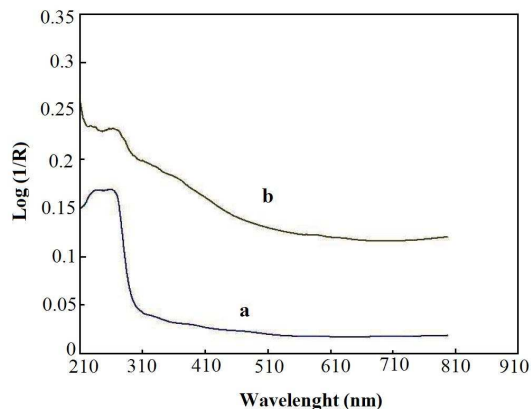


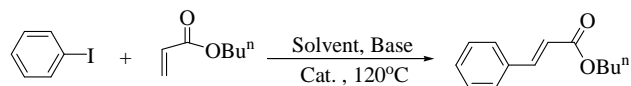
Fig. 5. UV-Vis diffuse reflectance spectra (a) poly(4-vinylpyridine)-grafted silica (II) (b) complexation with Pd(0) (III).

and 250 nm and for III these two absorbances shifted to lower areas and became weaker. This is due to the complexation of pyridine ligands with Pd and as if all active sites do not participate in complexation we still have both shoulders. No $d \rightarrow d$ transition was observed for this complex in (b), the absence of this transition is attributed to $t_{2g}^6 e_g^4$ configuration or metallic Pd(0) complex.

The activity of the supported catalyst was first examined in Heck coupling reaction of aryl halides with styrene and *n*-butylacrylate. In a model reaction, the coupling of iodobenzene with *n*-butylacrylate was studied in the presence of a base and the catalyst in a solvent under reflux condition. The reaction conditions were optimized, and the results are presented in Table 1.

It was found that the best system was DMF as solvent and K_2CO_3 as a base using 0.1 mmol% of catalyst at 120 °C. The amount of the catalyst can be even reduced down to 0.001 mol% of Pd by prolonging the reaction time to 4 h. The turn over number (TON = mol of product/mole of catalyst) is calculated for the least amount of catalyst to be 9×10^5 as a factor to show the high efficiency of the catalyst. Generality of this reaction system was shown when other coupling reactions were carried out using *n*-butylacrylate or styrene as olefinic substrate, with aryl halides (Table 2).

The electron-neutral, electron-rich and electron-poor aryl halides reacted with *n*-butylacrylate very well to generate the

Table 1. Optimization of Base, Solvent and Catalyst for Heck Reaction of Iodobenzene with *n*-Butyl Acrylate^a

Entry	Base	Solvent	Pd (mol %)	Time	Conversion (%) ^b
1	K ₂ CO ₃	THF	0.5	4 h	N.R
2	K ₂ CO ₃	EtOH	0.5	4 h	20
3	K ₂ CO ₃	DMSO	0.5	2 h	90
4	K ₂ CO ₃	H ₂ O	0.5	3 h	90
5	K ₂ CO ₃	DMF	0.5	2 h	100
6	Et ₃ N	DMF	0.5	2.5 h	90
7	Cs ₂ CO ₃	DMF	0.5	2 h	95
10	No catalyst	DMF	0.5	24 h	10
11	K ₂ CO ₃	DMF	0.2	2 h	100
12	K ₂ CO ₃	DMF	0.1	2 h	100
13	K ₂ CO ₃	DMF	0.05	2 h	90
14	K ₂ CO ₃	DMF	0.001	4 h	90

^aReaction conditions: iodobenzene (1 mmol), *n*-butyl acrylate (1.2 mmol), base (2 mmol), Pd catalyst (0.5-0.001 mol%), and 3 ml of solvent at 120 °C. ^bConversions based on iodobenzene.

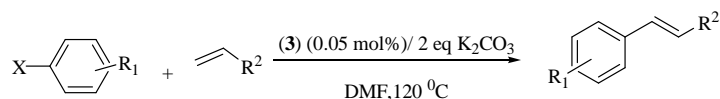
corresponding cross-coupling products in good to excellent yields. Heck reactions under these conditions could be done by this catalyst using *n*-butylacrylate and aryl chlorides in the presence of catalytic amount of tetra-*n*-butylammonium bromide (TBAB) (entries 11-14). It is worth mentioning that aryl chlorides are not reactive and have been employed less in palladium-catalyzed coupling reactions, because the oxidative addition of C-Cl bond to Pd(0) species is usually difficult [36]. The reaction of aryl chlorides with styrene were sluggish and did not give the desired products in acceptable time. In comparison with other few pyridine or PVPy supported Pd systems [30-31] our catalytic system showed improvement in reaction time and yield.

We, also, examined our catalyst in Suzuki-Miyaura cross-coupling reaction which is one of the most powerful and versatile methods for the generation of biaryls [29]. We optimized the condition in terms of catalyst, base, solvent and

temperature in the reaction between phenylboronic acid and *p*-bromotoluene as a model (Table 3).

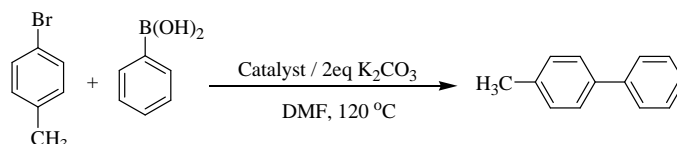
Similar to Heck reaction, the best results were obtained with 0.1 mol% of catalyst in the presence of K₂CO₃ as a base and DMF as a solvent at 120 °C. It is important to mention that catalyst kept its efficiency when reduced down to 0.001 mol%, the TON = 9 × 10⁵. The reactions completed much faster in comparison with the Heck reactions. Under the optimized condition several aryl halides were reacted with phenylboronic acid (Table 4). Aryl chlorides reacted without addition of TBAB (entries 13-15), however the yields were much higher when TBAB was added (entries 16-19) that showed improvement in reaction time and yield.

In order to check the recyclability of the catalyst, the cross-coupling of iodobenzene with *n*-butylacrylate in Heck reaction and Suzuki reaction of *P*-bromo toluene with phenylboronic acid was examined. The recovered catalyst was successfully

Table 2. Heck Reaction of *n*-Butylacrylate or Styrene with Aryl Halides^a


Entry	Aryl halide	R ²	Time (h)	Yield (%) ^b
1		CO ₂ Bu ⁿ	2	88
2		CO ₂ Bu ⁿ	2.30	85
3		CO ₂ Bu ⁿ	2	87
4		CO ₂ Bu ⁿ	1.30	93
5		CO ₂ Bu ⁿ	1	94
6		CO ₂ Bu ⁿ	4	80
7		CO ₂ Bu ⁿ	6	90
8		CO ₂ Bu ⁿ	8	83
9		CO ₂ Bu ⁿ	12	55
10		CO ₂ Bu ⁿ	12	70
11		CO ₂ Bu ⁿ	3.30	70 ^c
12		CO ₂ Bu ⁿ	3	85 ^c
13		CO ₂ Bu ⁿ	5	82 ^c
13		CO ₂ Bu ⁿ	7	80 ^c
14		Ph	3.5	75
16		Ph	5	70
17		Ph	8	82
18		Ph	8	75
19		Ph	10	70

^aMolar ratios of ArX: *n*-butylacrylate or styrene: K₂CO₃:palladium catalyst = 1.0:1.2:2.0:0.001. Reaction condition: DMF, 120 °C. ^cWith additional tetra-*n*-butylammonium bromide (0.01 mmol). The characterization of product was performed by comparison of its FT-IR, ¹H NMR, ¹³C NMR and physical data with those of the authentic sample.

Table 3. Optimization of Base, Solvent and Catalyst for Suzuki Reaction of Bromotoluene with Benzeneboronic acid

Entry	Base	Solvent	Pd (mol%)	Time	Conversion (%) ^b
1	K ₂ CO ₃	THF	0.5	4 h	N.R
2	K ₂ CO ₃	EtOH	0.5	4 h	50
3	K ₂ CO ₃	Acetone	0.5	2 h	90
4	K ₂ CO ₃	H ₂ O	0.5	2 h	90
5	K ₂ CO ₃	DMF	0.5	0.45 min	100
6	Et ₃ N	DMF	0.5	4.5 h	60
7	Cs ₂ CO ₃	DMF	0.5	0.45 h	95
10	NaOH	DMF	0.5	1 h	95
11	KF	DMF	0.5	2 h	30
12	KOH	DMF	0.5	2 h	20
13	K ₂ CO ₃	DMF	0.5	0.45 min	100
14	K ₂ CO ₃	DMF	0.2	0.45 min	100
15	K ₂ CO ₃	DMF	0.1	0.45 min	100
16	K ₂ CO ₃	DMF	0.05	0.45 min	90
17	K ₂ CO ₃	DMF	0.001	1.5 h	90

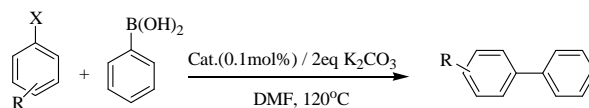
^aReaction conditions: *p*-bromotoluene (1 mmol), phenylboronic acid (1.5 mmol), base (2 mmol), Pd catalyst (0.5-0.001 mol%), and 3 ml of solvent at 120 °C. ^bConversions based on *p*-bromotoluene.

used in 5 subsequent reactions without appreciable change in its efficiency.

CONCLUSIONS

Polyvinylpyridine-grafted (P4VPy) silica was synthesized. The amount of P4VPy grafted onto silica was determined by TGA. It was complexed with PdCl₂ and palladium reduced to Pd(0). TEM images of the P4VPy-grafted silica Pd complex

shows that palladium dispersed through polymer surface in nanoparticle size. High efficiency and stability of this catalyst system was shown in the Heck and Suzuki reaction with a number of aryl halides. The electron-neutral, electron-rich and electron-poor aryl halides showed good reactivity to generate the corresponding cross-coupling products in good to excellent yields with high TON. The use of aryl chlorides in cross-coupling reactions is usually hardly successful, but excellent results were gained in the presence of tetra-*n*-butylammonium

Table 4. Suzuki Reaction of Benzenboronic Acid with Aryl Halides^a


Entry	Aryl halide	Time (h)	Yield (%) ^b
1		20 min	88
2		40 min	70
3		40 min	85
5		30 min	80
5		20 min	83
6		2.5 h	70
7		0.45 min	75
8		1.5	80
9		18	85
10		24	80
11		24	85
12		1.5	85
13		7 h	40
12		6 h	50
13		7.5 h	45
13		1 h	75 ^c
15		15 min	80 ^c
16		0.45 min	70 ^c
17		1.5 h	70 ^c

^aMolar ratio of the reagents ArX: phenylboronic acid: K₂CO₃:palladium catalyst 1.0:1.2:2.0:0.001. Reaction conditions: DMF, 120 °C. ^bIsolated yields. ^cWith additional tetra-*n*-butylammonium bromide (0.01 mmol). The characterization of product was performed by comparison of its FT-IR, ¹H NMR, ¹³C NMR, and physical data with those of the authentic sample.

bromide (TBAB) as an additive. Simple filtration reusability of the catalyst, excellent dispersity, short reaction time, high yields and large scale synthesis, are among the advantages with respect to many other reported Pd catalysts.

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