Palladium nanoparticles supported on modified crosslinked polyacrylamide containing phosphinite ligand: A novel and efficient heterogeneous catalyst for carbon–carbon cross-coupling reactions

Bahman Tamami*, Soheila Ghasemi

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

ARTICLE INFO

ABSTRACT

A novel palladium catalyst based on modified crosslinked polyacrylamide containing phosphinite ligand was synthesized and characterized. It exhibits excellent activity and stability in Mizoroki–Heck and Suzuki–Miyaura cross-coupling reactions with different aryl halides including inactive aryl chlorides. Short reaction times with good to excellent yields of the desired products express the effectiveness of this catalyst in these reactions. Transmission electron microscopy (TEM) shows that palladium particles are well-dispersed and of typical diameter of 18–30 nm. The X-ray powder diffraction (XRD) pattern of the Pd catalyst is consistent with the metallic Pd(0). The turnover number (TON) of this catalyst reaches up to 9.5×10^4 for these C–C bond forming reactions. Elemental analysis of Pd by ICP-OES and hot filtration test shows low leaching of the metal into solution from the supported catalyst which confirms the full heterogeneous character of the catalytically active species. The catalyst can be used many times in repeating cycles without considerable loss in its activity.

1. Introduction

Palladium-catalyzed C–C coupling reactions have been recognized as powerful tools and major area of interest in multiple organic transformations for academic and industrial processes [1,2]. Although it is some times since these reactions were first reported [3], their widespread applications in organic synthesis occurred only during the last decades. Coupling of aryl halides with alkenes (Mizoroki–Heck reaction) and organoboronic acids (Suzuki–Miyaura reaction) have significant importance, and are well-established methodology in modern organic synthesis. These Pd-catalyzed coupling reactions are ranked today among the most general transformations in organic synthesis, and have great industrial potential for the synthesis of chemicals, natural products, bioactive compounds, and advanced materials [4].

Many practical and economical aspects of these reactions have to be developed for their industrialization. Several important goals in this regard are; the use of aryl chlorides as substrates, the possibility of using aqueous condition, mild reaction temperature and the recovery of the catalyst [5,6]. Also, from the standpoint of environmentally benign organic synthesis, development of immo-

bilized and insoluble metal catalyst is challenging and important. The immobilizations of active catalysts on heterogonous supports have become a popular strategy to facilitate the recovery and recycling of potentially expensive ligands and complexes, and contamination of products by metallic species is prevented. However, some immobilizations suffer from limited lifetime, lack of recyclability and decrease in the catalytic activity in repeated use owing to leaching of metal from their support. In this regard, stable, reusable and active catalyst anchored to solid supports is of current interest [7–10]. Many organic and inorganic supports such as polymers, carbon, silica gel, metal oxides, zeolites, dendronized support and chitosan have been used in preparation of novel catalyst systems [11–14] (for reviews on immobilized metal catalyst, see [15]).

Phosphines and phosphinites are among the most important phosphorous-based ligands in organometallic chemistry. These ligands and their metal complexes anchored on polymeric supports or silica gel have been used in many catalytic reactions [16,17]. Recently, the phosphinite ligands are one of the most employed ones in synthetic chemistry for generation of the C–C bonds [18,19]. These ligands indebted their successful application in C–C bond formation to their influence on palladium. They can stabilize palladium and increase its reactivity. As known, a phosphine with both the characters of bulkiness and electron-richness not only accelerates the rate of oxidative addition of aryl halides to Pd(0)-phosphine complex, but also speeds up the process of reductive elimination from Pd(II) center. Although phosphinites as ligands in homogeneously catalytic processes have been widely studied, their

* Corresponding author. Tel.: +98 711 2284822; fax: +98 711 2280926.
E-mail addresses: tamami@chem.susc.ac.ir (B. Tamami),
soheila_ghasemi_chem@yahoo.com (S. Ghasemi).

application as heterogeneous system in the coupling reactions is limited.

In continuation of our studies on using polyacrylamide support [20], we herein disclose the preparation of a stable and active heterogeneous palladium catalyst containing phosphinite ligand based on polyacrylamide for use in C–C cross-coupling reactions. No reduction step is required to obtain metallic particles of Pd(0).

2. Experimental

2.1. General

Acrylamide (Fluka) was recrystallized from chloroform. Other reagents and solvents were of commercial reagent grade and obtained from Merck or Fluka and used without further purification. 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 reactions was followed by TLC on silica-gel Polygram SILG/UV 254 plates or by GLC on a Shimadzu model GC 10-A instrument with hydrogen flame ionization detector. IR spectra were run on a Shimadzu FT-IR-8300 spectrophotometer. NMR spectra were recorded on a Bruker Avance DPX instrument (250 MHz). The Pd analysis and leaching test was carried out by ICP-OES analyzer (Varian, Vista-Pro). CHN analysis was carried out on Thermo Finningan FIASHEA 1112 series instrument. X-ray diffraction data obtained with XRD, D8, Advance, Bruker, axs. 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. UV–vis diffuse reflectance spectroscopy (UV–vis DRS) was performed on Cary 5 instrument by photometric mode with 300 nm/min scan rate.

2.2. Preparation of catalyst

2.2.1. Preparation of crosslinked polyacrylamide
N,N'-Methylene-bis-acrylamide (NNMBA) (1.13 g, 0.007 mol) and acrylamide (10 g, 0.14 mol) were dissolved in ethanol (250 ml). $K_2S_2O_8$ (62 mg, 0.23 mmol) was added to this solution and stirred at 70–75 °C for 5 h. The polymer formed was filtered off, washed several times with ethanol, THF and acetone, and then dried at 60 °C under reduced pressure.

2.2.2. Preparation of poly(N-hydroxy acrylamide)
Crosslinked polyacrylamide (5%) (1 g) was suspended in ethanol, and to this were added 5-fold excess NH_2OH/HCl (4.8 g, 70 mmol) and aqueous solution of NaOH (10 ml, 7 M) in small portions. The mixture was heated while stirring at 90–100 °C for 18 h. The resultant mixture was cooled, filtered and washed thoroughly with water, ethanol and acetone and dried under vacuum overnight to give the desired product.

2.2.3. Preparation of polymeric phosphinite ligand
To the crosslinked poly(N-hydroxy acrylamide) (1 g) in THF at an ice-cooling bath (0 °C), a solution of chlorodiphenylphosphine (2.1 ml, 11.2 mmol) in THF was added dropwise in a period of 15 min while stirring. The reaction mixture was then stirred for additional 10 h at rt, and then filtered off. The corresponding solid was washed with water, THF and ethanol and then dried under reduced pressure.

2.2.4. Preparation of palladium catalyst
The phosphinite ligand (1 g) was treated with a solution of pd(OAc)$_2$ (0.28 g) in DMF (15 ml) at 100 °C for 8 h. After complexation, the mixture was filtered and washed thoroughly with DMF, water and acetone. It was then conditioned for a total of 18 h (3 × 2 h

each refluxing in water, ethanol and acetone) and dried under vacuum. This was done in order to remove any physisorbed palladium and to make the process completely heterogeneous. To determine the Pd content of the catalyst, it was treated successively with 30 cm³ mixture of concentrated H_2SO_4, HNO_3 and HCl, and filtered. The filtrate was diluted to 50 cm³ with distilled water and subjected to ICP determination using calibration curve method. Pd content = 0.15 mmol g^{-1}.

2.3. Typical procedure for Heck cross-coupling reactions

A round-bottomed flask equipped with a condenser and stir bar was charged with aryl halide (1 mmol), n-butyl acrylate or styrene (1.2 mmol), K_2CO_3 (2.0 mmol) and Pd catalyst (13 mg, 0.2 mol%) in DMF (3 ml). The flask was placed in an oil bath, and the mixture was stirred and heated at 100 °C for the appropriate time. The reaction was monitored by TLC (or GC if necessary). After completion of the reaction, the catalyst was easily recovered by filtration and the filtrate was extracted with ethyl acetate three times. The combined organic extracts were washed with water (2× 10 ml) and brine (10 ml), and dried over anhydrous Na_2SO_4 and evaporated under reduced pressure. 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.

2.4. Typical procedure for Suzuki cross-coupling reactions

A round-bottomed flask equipped with a condenser and stir bar was charged with aryl halide (1 mmol), phenylboronic acid (1.2 mmol), K_2CO_3 (2.0 mmol) and Pd catalyst (7 mg, 0.1 mol%) in DMF (3 ml). The flask was placed in an oil bath, and the mixture was stirred and heated at 80 °C for the appropriate time. After completion of the reaction, the procedure outlined above was followed.

2.5. General procedure for recycling reactions

When the corresponding Heck or Suzuki reaction according to the procedure described in previous sections 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 reused without any pretreatment for repeating cycles.

3. Results and discussion

3.1. Synthesis and characterization of the palladium catalyst

The Pd catalyst was designed by the sequence of reactions given in Scheme 1. Crosslinked polyacrylamide **3** (5%) was prepared by free radical solution polymerization of acrylamide **1** and N,N'-methylene-bis-acrylamide **2** mixture in ethanol using $K_2S_2O_8$ as initiator. Polar nature of the crosslinking agent provides its compatibility with polymer backbone and polar solvents. We found that polymers with less than 5% NNMBA will become sticky in the next step and not physically proper for further reactions. The IR spectrum of the polymer showed the characteristic absorption of amide (N–H amide stretching) at 3193 and 3360 cm^{-1}, and carbonyl group (C=O amide stretching) at 1668 cm^{-1}. The signal at 2933 cm^{-1} was due to methylene groups. Poly(N-hydroxy acrylamide) **4** was obtained by transamidation reaction of crosslinked polyacrylamide with excess of hydroxylamine in ethanol. IR spectrum of the polymer showed a broad band at 3408 cm^{-1} due to overlapping of OH stretching and amide NH. The hydroxyl group capacity of the resin was determined by CHN analysis and was found to be 7.46 mmol/g.
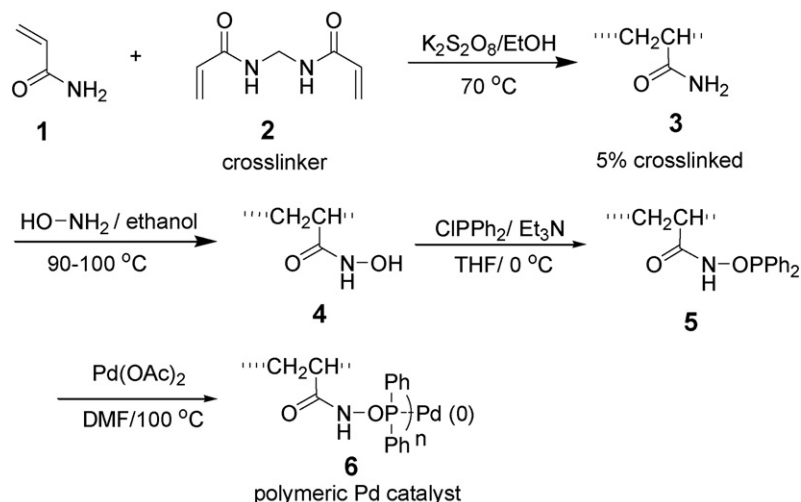
Scheme 1. Synthetic strategy for the preparation of modified polyacrylamide-supported Pd nanoparticles.
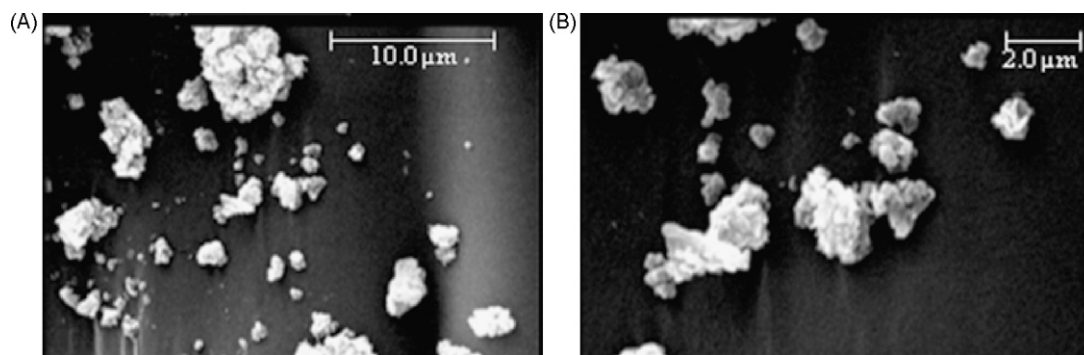
**Fig. 1.** (A) SEM image of Pd catalyst and (B) SEM close-up of image A.

The polymeric phosphinite ligand **5** was prepared by the reaction of poly(N–hydroxy acrylamide) with ClPPh$_2$ in THF. The phosphorous content of the resin was obtained by iodometric titration method and was found to be 2.8 mmol/g. Palladium complex **6** was obtained by mixing Pd(OAc)$_2$ with polymer **5** in DMF. The active Pd(0) catalyst as a black insoluble mass was formed by coordination of two P atoms to Pd(II) center, followed by the reduction to Pd(0) by another phosphinite group. This reduction pathway is generally known for Pd(II) compounds [18b–d,21]. Determination of Pd content was carried out on catalyst digestion followed by elemental analysis. ICP analysis revealed that resin **6** contained an average of 0.15 mmol/g of Pd.

To obtain a visual image of the supported catalyst, scanning electron microscopy (SEM) was carried out. By SEM images some information about the morphology of the catalyst particles was obtained as presented in Fig. 1. The SEM image shows particles with diameters in the range of nanometers to micrometers. Transmission electron microscope (TEM) image clearly shows that Pd nanoparticles were formed and well-defined spherical particles dispersed in the polymer matrix with a size in the range of 18–30 nm (Fig. 2). The X-ray powder diffraction (XRD) pattern of the Pd catalyst is consistent with the metallic Pd(0) data in the literature [22]. Fig. 3 shows the (1 1 1), (2 0 0), (2 2 0), (3 1 1) and (2 2 2) crystallographic planes of the Pd(0) nanoparticles. The Pd nanoparticle size was estimated from the XRD pattern using the Scherrer equation and was found to be 30.1 nm, close to the size observed in TEM. Further characterization of polymeric Pd complex was performed using UV–vis diffuse reflectance spectroscopy, as shown in Fig. 4. We investigated the UV–vis absorption spectra of polymeric
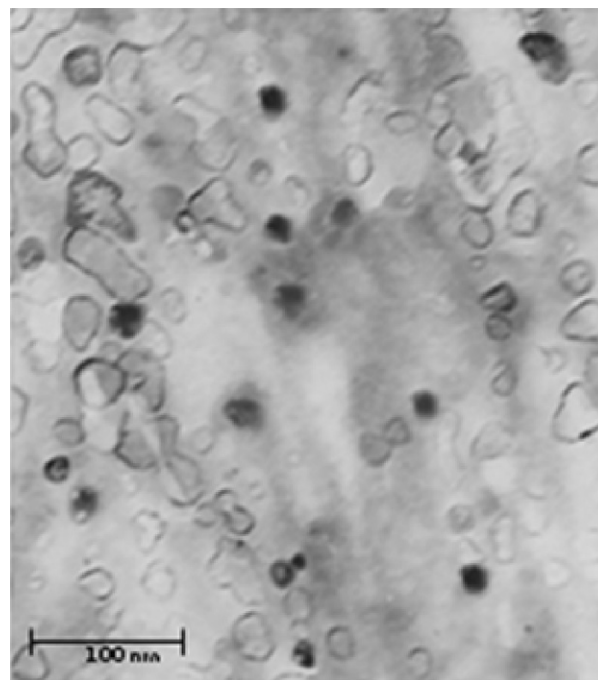
**Fig. 2.** TEM image corresponding to Pd catalyst.

Table 1
Optimization of base and solvent for Heck reaction of iodobenzene with *n*-butyl acrylate[a].
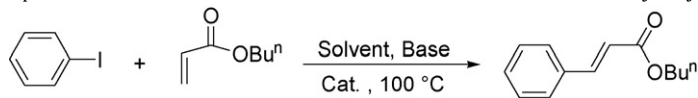
| Entry	Base	Solvent	Pd (mol%)	Time	Conversion (%)[b]
1	K_2CO_3	THF	0.2	3 h	N.R
2	K_2CO_3	CH_3CN	0.2	3 h	60
3	K_2CO_3	EtOH	0.2	3 h	10
4	K_2CO_3	H_2O	0.2	3 h	55
5	K_2CO_3	DMF	0.2	1 h	100
6	Et_3N	DMF	0.2	3 h	90
7	NaOAc	DMF	0.2	3 h	50
8	KF	DMF	0.2	3 h	40
9	$K_3PO_4 \cdot 12H_2O$	DMF	0.2	3 h	55
10	–	DMF	0.2	3 h	20
11	K_2CO_3	DMF	0.1	3 h	100
12	K_2CO_3	DMF	0.01	14 h	100
13	K_2CO_3	DMF	0.001	18 h	100

[a] Reaction conditions: iodobenzene (1 mmol), *n*-butyl acrylate (1.2 mmol), base (2 mmol), pd catalyst (0.2–0.001 mol%), and 3 ml of solvent at 100 °C.
[b] Conversions based on iodobenzene.
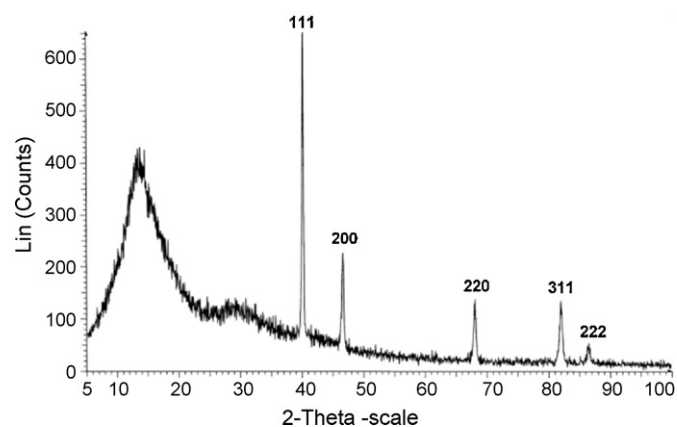
Fig. 3. Powder XRD patterns of Pd catalyst.

ligand before and after complexation in the range of 200–750 nm. The polymeric phosphinite ligand shows an absorbance shoulder at 308 nm due to the $\pi \rightarrow \pi^*$ transition and another wide band in the range of 410–470 nm due to the $n \rightarrow \pi^*$ transition. The $\pi \rightarrow \pi^*$
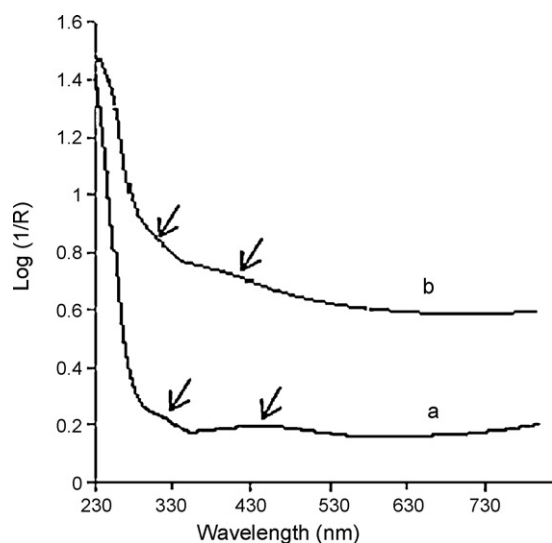

Fig. 4. UV–vis diffuse reflectance spectra for the polymeric phosphinite ligand (a) and its corresponding palladium catalyst (b).

band was not significantly affected by chelation and just changed from 308 to 300 nm on complexation with palladium. Because all of the phosphinite groups of the polymeric ligand do not participate on complexation with Pd, the complex shows a wide but weak absorbance band due to $n \rightarrow \pi^*$ on the range of 380–450 nm. No $d \rightarrow d$ transition was observed for this complex. The formation of deep black colored complexes and the absence of this transition were attributed to $t_{2g}^6 e_g^4$ configuration or metallic Pd(0) complex.
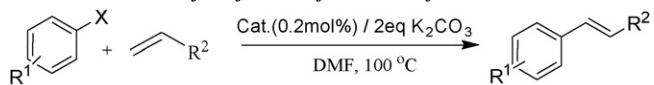
3.2. Catalytic activity of the catalyst in C–C coupling reactions

To check the potency of modified polyacrylamide-supported Pd catalyst, it was first used in Heck coupling reactions, which is a versatile and most studied method for generation of C–C bond in organic synthesis. The coupling of iodobenzene with *n*-butyl acrylate was initially studied as a model reaction. The reaction conditions were optimized, and the results are presented in Table 1. It was found that the best system for this reaction was DMF in combination with K_2CO_3, which yielded a 100% conversion of iodobenzene within 1 h using 0.2 mol% of Pd catalyst (entry 5). Also, we examined the effect of catalyst loading on the coupling reaction of iodobenzene with *n*-butyl acrylate. The loading of the catalyst can be reduced down up to 0.001 mol% of Pd (TON = 9.5×10^4) by prolonging the reaction time in order to get full conversion. This is the indication of an effective catalytic system.

To survey the generality of the catalytic protocol, we investigated the reaction using a variety of aryl iodides and bromides with *n*-butyl acrylate or styrene under the optimized condition (Scheme 2). The results are shown in Table 2. The electron-neutral, electron-rich and electron-poor aryl iodides and bromides reacted with olefins very well. The catalytic performance was excellent for the substrate with electron-withdrawing groups (entries 4–7, 12, 14, and 21–24). Nevertheless the efficiencies were only slightly lower for the substrates with electron-donating groups (entries 2, 8, 15, 19 and 25). This cross-coupling reaction was also tolerant
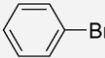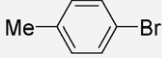

X= Cl, Br, I
R^1= H, OMe, NO_2, CN, COMe, Cl, Me, CHO
R^2= CO_2Bu^n, Ph
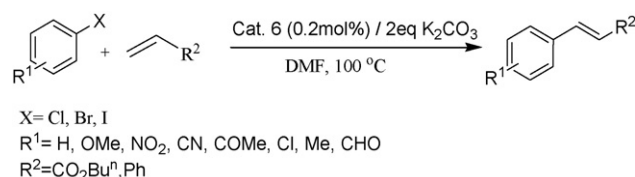
Scheme 2. Mizoroki–Heck cross-coupling reactions.

Table 2
Heck reaction of *n*-butyl acrylate or styrene with aryl halides[a].

Entry	Aryl halides	R^2	Time	Yield[b] (%)
1	(phenyl)–I	CO_2Bu^n	1 h	92
2	MeO–(phenyl)–I	CO_2Bu^n	1.5 h	95
3	(phenyl)–Br	CO_2Bu^n	2 h	89
4	O_2N–(phenyl)–Br	CO_2Bu^n	40 min	93
5	NC–(phenyl)–Br	CO_2Bu^n	40 min	90
6	MeOC–(phenyl)–Br	CO_2Bu^n	5 h	85
7	Cl–(phenyl)–Br	CO_2Bu^n	5 h	80
8	Me–(phenyl)–Br	CO_2Bu^n	6 h	83
9	(phenyl, 2-Me)–Br	CO_2Bu^n	8.5 h	87
10	(phenyl, 3-Me)–Br	CO_2Bu^n	14 h	75
11	(phenyl)–Cl	CO_2Bu^n	15 h	70[c]
12	O_2N–(phenyl)–Cl	CO_2Bu^n	2 h	92[c]
13	(phenyl, 2-NO_2)–Cl	CO_2Bu^n	24	65[c]
14	MeOC–(phenyl)–Cl	CO_2Bu^n	5 h	82[c]
15	Me–(phenyl)–Cl	CO_2Bu^n	9 h	82[c]
16	(phenyl, 2-CHO)–Cl	CO_2Bu^n	24	60[c]
17	(phenyl, NC)–Cl	CO_2Bu^n	10	65[c]
18	(phenyl)–I	Ph	3.5 h	92
19	MeO–(phenyl)–I	Ph	4 h	93

Table 2 (*Continued*)

Entry	Aryl halides	R^2	Time	Yield[b] (%)
20	⬡—Br	Ph	5 h	80
21	O_2N—⬡—Br	Ph	3 h	90
22	NC—⬡—Br	Ph	3 h	90
23	MeOC—⬡—Br	Ph	10 h	80
24	Cl—⬡—Br	Ph	10 h	84
25	Me—⬡—Br	Ph	15 h	81

[a] Molar ratio of the reagents ArX:n-butyl acrylate or styrene:K_2CO_3:palladium catalyst = 1.0:1.2:2.0:0.002. Reaction conditions: DMF, 100 °C.
[b] Isolated yields.
[c] With additional tetrabutylammonium bromide (0.05 mmol).

for substrate with ortho substitution, which is sterically hindered, and meta substitution and led to good yields (entries 9, 10, 13, 16 and 17). In general, the reaction with less reactive styrene proceeds slower compared to n-butyl acrylate.

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 found to convert activated aryl chlorides at high temperature [23]. It is clear that aryl chlorides are best activated by Pd complex containing electron-rich bulky phosphine [24]. The electron-releasing properties of these phosphine ligands not only favor the difficult oxidative addition of aryl-chloro bond, but also the bulk of the ligand favors the final reductive elimination step in the catalytic cycle. In our catalytic system, the reaction with chlorides had to be run in the presence of tetrabutylammonium bromide (TBAB) (Jeffery Catalyst) as an additive [25] (entries 11–17). The reaction of aryl chlorides with styrene is sluggish and do not give the desired products in acceptable times.

The polyacrylamide-supported Pd catalyst can also be applied in the Suzuki reaction which is one of the most powerful and versatile method for the generation of new biaryls (Scheme 3). As shown in Table 3 different aryl halides react with phenylboronic acid to give the corresponding biaryls. Compared to Heck reaction described in the previous paragraph, Suzuki reaction was performed under milder reaction condition (80 °C) and less palladium catalyst (0.1 mol%). Moreover, similar to Heck reaction aryl chlorides can also give the coupling products in the presence of TBAB.

3.3. Heterogeneity test and catalyst reuse

The reusability of supported catalysts is very important theme and makes them useful for commercial applications. Thus, the
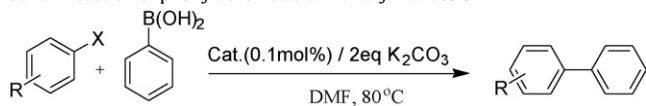

X= Cl, Br, I
R=H, OMe, NO₂, CN, COMe, Me, Ph, Cl, CHO
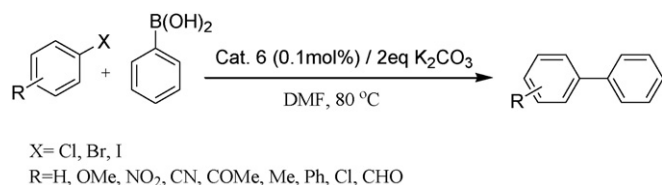
Scheme 3. Suzuki–Miyaura cross-coupling reactions.

recovery and reusability of the supported catalyst have been investigated using iodobenzene with n-butyl acrylate as model substrates. The catalyst is highly reusable. It was used for 10 cycles and retained its catalytic activity in these repeating cycles. The Pd catalyst exhibited only a slight loss in its activity and required a bit longer time to achieve full conversion even after 10 cycles. The results are tabulated in Table 4.

In view of multiple recycling and continuous processing, fixation of Pd particles on solid supports should provide catalysts prepared at low cost and allow easy separation by filtration, however, a major drawback of this technique reported in the publications is leaching [26]. Therefore, the 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 iodobenzene and n-butyl acrylate was analyzed by ICP in 10 repeating cycles. Low palladium contamination was observed during this experiment. Analysis of the crude reaction mixture for the first reaction indicates a leaching of 0.48% of the palladium. Residual palladium levels present in product in different catalytic runs was analyzed. This catalytic system shows 6.1% palladium leaching after 10 runs. We did not observe the palladium black formation in the reaction even after the 10th cycle. For further investigation, the organic phase of the first run of reaction between bromobenzene and n-butyl acrylate was separated from the solid and then new portions of reactants (bromobenzene, n-butyl acrylate and K_2CO_3) were added to the clear filtrate. The composition of the reaction mixture was determined by GLC. Then after 24 h reaction time, the composition was determined again. The reaction had not progressed and 94% bromobenzene was remained in the reaction mixture. This observation confirmed negligible palladium leaching from the supported system.

In order to ascertain whether the catalyst was behaving in a truly heterogeneous manner, or whether it is merely a reservoir for more active soluble form of Pd, hot filtration test was performed. In a typical experiment, Pd complex (0.2 mol%), bromobenzene (1 mmol), n-butyl acrylate (1.2 mmol), K_2CO_3 (2.0 mmol) and DMF (3 ml) were taken in a round-bottomed flask and stirred at 100 °C for 30 min. 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.

Table 3
Suzuki reaction of phenylboronic acid with aryl halides[a].

Entry	Aryl halides	Time	Yield[b] (%)
1		40 min	96
2	MeO— —I	1 h	92
3	—Br	1 h	85
4	O₂N— —Br	40 min	95
5	NC— —Br	40 min	95
6	MeOC— —Br	1.5 h	85
7	Me— —Br	2 h	80
8	(Me, Br)	3.5 h	80
9	(Me, Br)	3.5 h	70
10	—Br	4 h	81
11	Cl— —Br	40 min	90
12	—Cl	7 h	75[c]
13	O₂N— —Cl	1.5 h	90[c]
14	(NO₂, Cl)	7 h	75[c]
15	MeOC— —Cl	2 h	88[c]
16	OHC— —Cl	2 h	91[c]
17	(CHO, Cl)	7 h	70[c]
18	Me— —Cl	5 h	75[c]
19	MeO— —Cl	16 h	85[c]

Table 4
Recycling of Pd catalyst for the Heck reaction of iodobenzene with *n*-butyl acrylate[a].

Entry	Cycle	Time	Isolated yield (%)	TON[b]	TOF (h^{-1})[c]
1	1st	1 h	95	475	475
2	2nd	1 h	96	480	480
3	3rd	1.5 h	93	465	310
4	4th	1.5 h	95	475	316.7
5	5th	1.5 h	92	460	306.7
6	6th	1.5 h	96	480	320
7	7th	2	92	460	230
8	8th	2	95	475	237.5
9	9th	3	93	465	155
10	10th	3	95	475	158.3
TON for 10 runs		4795	Av. TOF (h^{-1})		298.92

[a] Reaction conditions: molar ratio of iodobenzene:*n*-butyl acrylate:K$_2$CO$_3$:Pd catalyst = 1.0:1.2:2.0:0.002 in DMF at 100 °C. All reactions were carried out with 100% conversion of iodobenzene.

[b] TON = mmol of products/mmol of catalyst.

[c] TOF = TON/time.

4. Conclusion

In conclusion, a new palladium catalyst based on modified crosslinked polyacrylamide was designed and applied in Mizoroki–Heck and Suzuki–Miyaura cross-coupling reactions. Through TEM and XRD we can observe high metal dispersion and small particle sizes in nanoscale. Short reaction times, high yields, easy purification, recyclability and low Pd leaching are main characteristic of the process. This supported catalyst is air-stable and all reactions can be conducted in air.

Acknowledgments

References

[1] M. Larhed, A. Hallberg, in: E. Negishi (Ed.), Handbook of Organopalladium Chemistry for Organic Synthesis, Wiley–Interscience, New York, 2002.
[2] I.P. Beletskaya, A.V. Cheprakov, Chem. Rev. 100 (2000) 3009–3066.
[3] (a) T. Mizoroki, K. Mori, A. Ozaki, Bull. Chem. Soc. 44 (1971) 581–1581;
(b) R.F. Heck, J.P. Nolley Ir, J. Org. Chem. 37 (1972) 2320–2322.
[4] L. Brandsma, S.F. Vasilersky, H.D. Verkruijsse, Applications of Transition Metal Catalysts in Organic Synthesis, Springer, Berlin, 1988;
(b) K.C. Nicolaou, E.J. Sorensen, Classics in Total Synthesis, VCH, New York, 1996 (Chapter 31).
[5] B.M. Choudary, S. Madhi, N.S. Chowdari, M.L. Kantam, B. Sreedhar, J. Am. Chem. Soc. 124 (2002) 14127–14136.
[6] (a) B.H. Lipshutz, B.R. Taft, Org. Lett. 10 (2008) 1329–1332;
(b) B.H. Lipshutz, T.B. Petersen, A.R. Abela, Org. Lett. 10 (2008) 1333–1336;
(c) B.H. Lipshutz, A.R. Abela, Org. Lett. 10 (2008) 5329–5332.
[7] (a) Y.M.A. Yamada, K. Takeda, H. Takahashi, S. Ikegami, Tetrahedron 60 (2004) 4097–4105;
(b) B. Baruwati, D. Guin, S.V. Manorama, Org. Lett. 9 (2007) 5377–5380.
[8] (a) R.B. Bedford, U.G. Singh, R.I. Walton, R.T. Williams, S.A. Davis, Chem. Mater. 17 (2005) 701–707;
(b) Z. Zhang, Z. Wang, J. Org. Chem. 71 (2006) 7485–7487.
[9] H. Hagiwara, Y. Sugawara, K. Isobe, T. Hoshi, T. Suzuki, Org. Lett. 6 (2004) 2325–2328.
[10] (a) B. Karimi, A. Zamani, J.H. Clark, Organometallics 24 (2005) 4695–4698;
(b) B. Karimi, D. Enders, Org. Lett. 8 (2006) 1237–1240;
(c) B. Karimi, P. Fadavi Akhavan, Chem. Commun. 25 (2009) 3750–3752.
[11] (a) K. Kaneda, M. Higuchi, T. Imanaka, J. Mol. Catal. 63 (1990) L33–L36;
(b) P. Mehnert, D.W. Weaver, J.Y. Ying, J. Am. Chem. Soc. 120 (1998) 12289–12296;
(c) M. Dams, L. Drijkoningen, B. Pauwels, G. Van Tendeloo, D.E. De Vos, P.A. Jacobs, J. Catal. 209 (2002) 225–236;
(d) K. Lin, M. Song, D. Cai, Tetrahedron Lett. 44 (2003) 3955–3957.

[12] (a) R.S. Varma, K.P. Naicker, P.J. Liesen, Tetrahedron Lett. 40 (1999) 2075–2078;
(b) V. Polshettiwar, R.S. Varma, Tetrahedron 64 (2008) 4637–4643.
[13] (a) C.A. McNamara, M.J. Dixon, M. Bradley, Chem. Rev. 102 (2002) 3275–3300;
(b) I.P. Beletskaya, A.R. Khokhlov, E.A. Tarasenko, V.S. Tyurin, J. Organomet. Chem. 692 (2007) 4402–4406;
(c) V. Polshettiwar, A. Molnar, Tetrahedron 63 (2007) 6949–6976.
[14] H. Zhou, G.L. Zhuo, X.Z. Jiang, J. Mol. Catal. A: Chem. 248 (2006) 26–31.
[15] (a) P.T. Anastas, J.C. Warner, Green Chemistry: Theory and Practice, Oxford University Press, Oxford, 1998;
(b) P.T. Anastas, L.G. Heine, T.C. Williamson (Eds.), Green Chemical Synthesis and Processes: Recent Advances in Chemical Processing, The American Chemical Society, Washington, DC, 2001;
(c) N.E. Leadbeater, M. Marco, Chem. Rev. 102 (2002) 3217–3274;
(d) F. Alonso, I.P. Beletskayab, M. Yusa, Tetrahedron 61 (2005) 11771–11835.
[16] (a) A. Mansour, M. Portnoy, J. Mol. Catal. A: Chem. 250 (2006) 40–43;
(b) G. Singh, S. Bali, A.K. Singh, Polyhedron 26 (2007) 897–903.
[17] (a) D.E. Bergbreiter, A.M. Kippenberger, G. Tao, Chem. Commun. (2002) 2158–2159;
(b) M. Guino, K.K. Hiib, Tetrahedron Lett. 46 (2005) 6911–6913.
[18] (a) B. Punji, C. Ganesamoorthy, M.S. Balakrishna, J. Mol. Catal. A: Chem. 259 (2006) 78–83;
(b) N. Iranpoor, H. Firouzabadi, R. Azadi, Eur. J. Org. Chem. 13 (2007) 2197–2201;
(c) N. Iranpoor, H. Firouzabadi, R. Azadi, J. Organomet. Chem. 693 (2008) 2469–2472;
(d) H. Firouzabadi, N. Iranpoor, M. Gholinejad, Tetrahedron 65 (2009) 7079–7084.
[19] (a) I.D. Kostas, B.R. Steele, A. Terzis, S.V. Amosova, Tetrahedron 59 (2003) 3467–3473;
(b) A. Naghipour, S.J. Sabounchei, D. Morales-Morales, D. Canseco-Gonzalez, C.M. Jensen, Polyhedron 26 (2007) 1445–1448;
(c) Y.-H. Cheng, C.-M. Weng, F.-E. Hong, Tetrahedron 63 (2007) 12277–12285;
(d) B.-S. Zhang, C. Wang, J.-F. Gong, M.-P. Song, J. Organomet. Chem. 694 (2009) 2555–2561.
[20] (a) B. Tamami, H. Mahdavi, React. Funct. Polym. 51 (2002) 7–13;
(b) B. Tamami, M. Kolahdoozan, Tetrahedron Lett. 45 (2004) 1535–1537;
(c) B. Tamami, A. Fadavi, M. Tamami, Iran. Polym. J. 15 (2006) 799–807;
(d) B. Tamami, S. Ghasemi, J. Iran. Chem. Soc. 5 (2008) S26–S32.
[21] D.E. Bergbreiter, P.L. Osburn, A. Wilson, E.M. Sink, J. Am. Chem. Soc. 122 (2000) 9058–9064.
[22] S. Martinez, A. Vallribera, C.L. Cotet, M. Popovici, L. Martin, A. Roig, M. Moreno-Manas, E. Molins, New J. Chem. 29 (2005) 1342–1345.
[23] (a) S. Prockl, W. Kleist, M.A. Gruber, K. Kohler, Angew. Chem., Int. Ed. 43 (2004) 1881–1882;
(b) K. Kohler, W. Kleist, S.S. Prockl, Inorg. Chem. 46 (2007) 1876–1883.
[24] (a) A.F. Littke, G.C. Fu, J. Org. Chem. 64 (1999) 10–11;
(b) S. Urgaonkar, M. Nagarajan, J.G. Verkade, Org. Lett. 5 (2003) 815–818;
(c) L. Ackermann, R. Vicente, N. Hofmann, Org. Lett. 11 (2009) 4274–4276.
[25] (a) T. Jeffery, Tetrahedron Lett. 26 (1985) 2667–2670;
(b) T. Jeffery, Tetrahedron 52 (1996) 10113–10130.
[26] (a) C. Venkatesan, A.P. Singh, J. Catal. 227 (2004) 148–163;
(b) J. Horniakova, T. Raja, Y. Kubota, Y. Sugi, J. Mol. Catal. A: Chem. 217 (2004) 73–80;
(c) N.T.S. Phan, M. Van der Sluys, C. Jones, J. Adv. Synth. Catal. 348 (2006) 609–679.