Res Chem Intermed
DOI 10.1007/s11164-015-2387-5

New strategy by a two-component heterogeneous catalytic system composed of Pd–PVP–Fe and heteropoly acid as co-catalyst for Suzuki coupling reaction

Ezzat Rafiee[1,2] · **Masoud Kahrizi**[1] · **Mohammad Joshaghani**[1,2] · **Parvaneh Ghaderi-Sheikhi Abadi**[2]

Received: 18 September 2015 / Accepted: 7 December 2015

Abstract We have developed a simple and efficient catalytic protocol composed of hollow palladium-poly(*N*-vinylpyrrolidone)-nano zero valent iron and $H_5PMo_{10}V_2O_{40}$ ($Mo_{10}V_2$) supported on $Fe_2O_3@SiO_2$ core–shell nano particles, as reusable catalytic system for Suzuki coupling reaction under ligand- and base-free conditions. These reusable solid catalysts exhibited excellent activity and the methodology is applicable to diverse substrates providing good-to-excellent yields of desired products. This method has advantages of high yields, low reaction times, elimination of ligand and base, heterogeneous catalysts, and simple methodology. In order to study the role of Fe@Si–$Mo_{10}V_2$ in the Suzuki coupling reaction, electron transfer property of Fe@Si–$Mo_{10}V_2$ and Pd–PVP–Fe by means of cyclic voltammetry measurements were investigated. Moreover, this catalytic system could be recovered in a facile manner from the reaction mixture and recycled several times without any significant loss in activity. In this study, the heterogeneity of both component of our catalytic system was investigated and the content of palladium (Pd) and $Mo_{10}V_2$ into filtrates was evaluated quantitatively by inductively coupled plasma atomic emission spectroscopy (ICP-AES). According to the obtained results from the ICP-AES measurements, the small amount of Pd and $Mo_{10}V_2$ leach have been obtained.

Keywords Suzuki coupling reaction · Palladium · Heterogeneous catalyst · Heteropoly acid · Bifunctional catalytic system

---

✉ Ezzat Rafiee
ezzat_rafiee@yahoo.com; e.rafiei@razi.ac.ir

[1] Faculty of Chemistry, Razi University, Kermanshah 67149, Iran

[2] Institute of Nano Science and Nano Technology, Razi University, Kermanshah 67149, Iran

Introduction

Palladium (Pd)-catalyzed C–C bond formation reactions have drawn much attention in organic synthesis due to its industrial potential for the synthesis of chemicals and their intermediates [1–4]. Among these, the coupling of aryl halides with aryl boronic acids (Suzuki coupling) [5–8] represents the most successful method for the synthesis of biaryls.

This reaction is generally considered to be a homogeneous reaction most commonly catalyzed by soluble Pd(II) species with a variety of ligands, such as palladium-phosphine complexes [9], oxime palladacycles [10], palladium–salen complexes [11] and palladium-*N*-heterocyclic carbine complexes [12]. Homogeneous catalysts have the advantages of being dissolved in reaction medium, thus providing mild reaction conditions and higher activities compared to their heterogeneous counterparts [13]. Nevertheless, separation of the expensive catalyst from the product for reusing is often troublesome in these homogeneous systems. Moreover, aggregation and precipitation of Pd metal in the homogeneous systems always leads to lost activity of the catalysts [14].

In order to address these problems, heterogeneous Pd supported on some materials has been employed in recent years [15–22]. Among these supports, iron(0) nano particles (FeNP) have been the subject of increasing interest, mostly due to economic considerations. Because of the nano-scale size of FeNP, these particles have higher catalyst loading capacities and higher dispersion than many conventional supports, leading to the improved catalytic activity of these catalysts. Another attractive feature of FeNPs is the possibility of fast and cost-efficient separation by applying an external magnetic field, which makes them ideal candidates for practical use in catalytic process. Moreover, FeNP can reduce Pd(II) and regenerate active Pd(0) species. It should be noted that, magnetically, interactions between particles makes FeNPs susceptible to agglomeration. Thus, in order to decrease the agglomeration degree, effective coating of magnetite particles is essential. Several molecules have been used to coat the surface of metal nanoparticles. Poly(*N*-vinylpyrrolidone), PVP, is particularly useful in this regard [23, 24], since it is readily available and non-toxic. Furthermore, the twisty hydrocarbon tails of PVP may help to stabilize the Pd nanoparticles and prevent them from aggregating with each other. Also, the electron transfer between Fe(0) and Pd(II) generates Fe(II) species, which receive lone-pair electrons from PVP shell and reduce into Fe(0) [25].

In recent years, heteropoly acids (HPAs) have received a lot of attention in coupling reactions and growing studies have been done on the use of them in this field of organic transformations [26, 27].

One of the main advantages of HPAs is their electron transfer ability. The reduction potentials of HPAs containing Mo and V are high, as these ions are easily reduced [28]. These structural features make these compounds an appropriate choice for oxidation/reduction reactions. Especially in coupling reactions, HPAs can facilitate the oxidative/addition and reductive/elimination steps. Bases are one of the substantial, required components of the Suzuki coupling reaction. The use of a high amount of bases poses several problems, such as an inability to recover, contamination of environment, corrosion of equipment, and high toxicity. Hence, there is a need for an efficient, eco-friendly, and recoverable alternative for replacement of bases in the Suzuki reaction. HPAs with electron transfer ability can act as an excellent alternative for bases in the reductive elimination step in coupling reactions. Along this line, using heterogeneous HPAs, which are low in toxicity, highly stable towards humidity, recyclable, and air stable, can be useful. Supported HPAs are advantageous over conventional bases, as they can be easily recovered from the reaction mixture by simple filtration and can be reused without activation, thereby making the process economically and environmentally viable.

As a part of our project about the use of magnetic catalysts in organic synthesis [29, 30] and emanating from our interest in Pd-catalyzed cross-coupling reactions [31–34], the present study evaluates the usefulness of a combination of palladium–PVP-nano zero valent iron (Pd–PVP–Fe) [35] and $H_5PMo_{10}V_2O_{40}$ ($Mo_{10}V_2$) [36] immobilized on $Fe_2O_3@SiO_2$ core–shell nano particles (Fe@Si–$Mo_{10}V_2$) in the Suzuki coupling reaction. In this system, low amounts of Fe@Si–$Mo_{10}V_2$ are used as an efficient base alternative, which reduces costs because of recyclability and increased efficiency in the Suzuki reaction.

Experimental

Materials and methods

All reactions were performed under an atmosphere of dry nitrogen. All chemicals used in this work were obtained from Fluka, Aldrich, or Merck companies and used without further purification. The FT-IR spectra of the samples were recorded at room temperature using a Bruker, ALPHA spectrophotometer at a spectral resolution of 4 cm^{-1} using KBr pellets. The X-ray diffraction (XRD) patterns were obtained on Inel French, EQUINOX 3000 model X-ray diffractometer using Cu-Kα radiation. The Pd and molybdenum (Mo) content was measured using inductively coupled plasma atomic emission spectroscopy (ICP-AES) on a Spectro Ciros CCD spectrometer. Thin-layer chromatography (TLC) on precoated silica gel Fluorescent 254 nm (0.2 mm) on aluminum plates were used for monitoring the reactions. The cross-coupling products were characterized by their ^1H NMR spectra. The electrochemical reduction of catalyst was studied in phosphate buffer (0.1 M), pH = 7. A glassy carbon electrode was used as the working electrode and Ag/AgCl as the reference electrode. Cyclic voltammograms (ν, 0.1 Vs^{-1}) were obtained at ambient temperature (20 ± 5 °C).

Preparation of Pd–PVP–Fe

In a typical synthesis, 0.00113 g (0.0063 mmol) $PdCl_2$ and 0.058 g (0.0014 mmol) PVP were dissolved in distilled water: *N*,*N*-dimethylformamide (DMF) (1:5 V/V) under stirring for 5 min until the solution became homogeneous. In a separate beaker, 0.015 g (0.075 mmol) of $FeCl_2{\cdot}4H_2O$ and 0.058 g (0.0014 mmol) of PVP were dissolved in similar solvent under stirring and added dropwise to $PdCl_2$ solution under an ultrasonic bath. The mixture was sonicated for 1 min under mild power to form a homogeneous solution, and then the resulting homogeneous solution was refluxed at 110 °C for 16 h. After thermal treatment, the resulting precipitate was collected, filtered, and washed with distilled water and absolute ethanol several times to remove any possible impurities, and finally dried in vacuo before reaction [35].

Preparation of $Mo_{10}V_2$

$Mo_{10}V_2$ was prepared according to the following procedure: sodium metavanadate (24.4 g) was dissolved by boiling in 100 ml of water and then mixed with 7.1 g of Na_2HPO_4 in 100 ml of water. Then this solution was cooled, 5 ml of concentrated sulfuric acid was added, and the solution developed a red color. An addition of 121.0 g of $Na_2MoO_4 \cdot 2H_2O$ dissolved in 200 ml of water was then made. While the solution was vigorously stirred, 85 ml of concentrated sulfuric acid was added slowly, and the hot solution was allowed to cool to room temperature. $Mo_{10}V_2$ was then extracted with 500 ml of diethyl ether. Evaporation of the solvent afforded a crude product which dissolved in water, concentrated to first crystal formation, and then allowed to crystallize further. The large red crystals that formed were filtered, washed with water, and air dried [36].

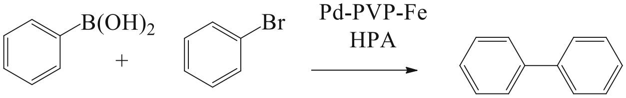
Preparation of Fe@Si–$Mo_{10}V_2$

$FeCl_2 \cdot 4H_2O$ (2.0 g) and $FeCl_3 \cdot 6H_2O$ (5.4 g) were dissolved in water (20 ml) separately, followed by the two iron salt solutions being mixed under vigorous stirring. An NH_4OH solution (0.6 M, 200 ml) was added to the stirring mixture at room temperature, immediately followed by the addition of a concentrated NH_4OH solution (25 % w/w, 30 ml). The resulting black dispersion was continuously stirred for 1 h at room temperature and then heated to reflux for 1 h to yield a brown dispersion. It was then purified by a four-times-repeated centrifugation, decantation, and redispersion cycle until a stable brown magnetic dispersion was obtained. Coating of a layer of silica on the surface of the nanoparticles was achieved by premixing a dispersion of the purified nanoparticles (8.5 % w/w, 20 ml) obtained previously with EtOH (80 ml) for 1 h at 40 °C. A concentrated ammonia solution was added and the resulting mixture stirred at 40 °C for 30 min. Subsequently, TEOS (1.0 ml) was charged to the reaction vessel and the mixture continuously stirred at 40 °C for 24 h. It was collected using a permanent magnet, followed by washing three times with EtOH, diethyl ether, and drying under vacuum for 24 h; 0.7 g of $Mo_{10}V_2$ was dissolved in 5 ml of dry MeOH. This solution was added dropwise to a suspension of 1.0 g $Fe_2O_3@SiO_2$ in MeOH (50 ml) while being dispersed by sonication. The mixture was heated at 70 °C for 72 h under vacuum while being mechanically stirred to obtain Fe@Si–$Mo_{10}V_2$. The catalyst was collected by a permanent magnet and dried under vacuum overnight [37].

General procedure for the Suzuki coupling reaction

For Suzuki coupling reaction, a reaction tube was charged with aryl halide (4 mmol), phenylboronic acid (4 mmol), TBAB (4 mmol), Pd–PVP–Fe (0.03 g), Fe@Si–$Mo_{10}V_2$ (0.02 g), and 9 ml of EtOH/H_2O (6:3) and the resulting mixture was refluxed at 90 °C. Progress of the reaction was monitored by TLC. Upon completion of the reaction, the reaction mixture was then cooled to room temperature and both components of our catalytic system were separated by magnet, washed with diethyl ether (2 × 10 ml), water (2 × 10 ml), and then dried under vacuum for reusability. The residual mixture was extracted by CH_2Cl_2 (3 × 20 ml), the combined organic layer was dried over $MgSO_4$. The solvent was evaporated and the crude products were characterized by comparing their ^1H NMR spectra with standard data [38–50].

Table 1 Optimization of the reaction conditions[a]



Entry	Catalyst (g)		Solvent	Time (min)	Yield (%)[b]
	Pd–PVP–Fe (mol%)	HPA			
1	0.02 (3.76×10^{-4})	$Mo_{10}V_2$ (0.01)	H_2O/EtOH	30	89
2	0.02 (3.76×10^{-4})	Fe@Si-$Mo_{10}V_2$ (0.01)	H_2O/EtOH	60	89
3	002 (3.76×10^{-4})	$(NH_4)_5Mo_{10}V_2$ (0.01)	H_2O/EtOH	120	78
4	–	$Pd_{2.5}Mo_{10}V_2$ (0.01)	H_2O/EtOH	120	22
5	0.02 (3.76×10^{-4})	–	H_2O/EtOH	120	4
6	0.02 (3.76×10^{-4})	Fe@Si–$Mo_{10}V_2$ (0.02)	H_2O/DMF	60	79
7	0.02 (3.76×10^{-4})	Fe@Si–$Mo_{10}V_2$ (0.02)	H_2O	60	65
8	0.02 (3.76×10^{-4})	Fe@Si–$Mo_{10}V_2$ (0.02)	DMF	60	44
9	0.02 (3.76×10^{-4})	Fe@Si–$Mo_{10}V_2$ (0.02)	MeCN	120	23
10	0.02 (3.76×10^{-4})	Fe@Si–$Mo_{10}V_2$ (0.03)	H_2O/EtOH	40	94
11	0.02 (3.76×10^{-4})	Fe@Si–$Mo_{10}V_2$ (0.02)	H_2O/EtOH	40	91
12[c]	0.02 (3.76×10^{-4})	Fe@Si–$Mo_{10}V_2$ (0.02)	H_2O/EtOH	120	12
13	0.01 (1.88×10^{-4})	Fe@Si–$Mo_{10}V_2$ (0.02)	H_2O/EtOH	60	73
14	0.03 (5.64×10^{-4})	Fe@Si–$Mo_{10}V_2$ (0.02)	H_2O/EtOH	30	96
15	0.04 (7.52×10^{-4})	Fe@Si–$Mo_{10}V_2$ (0.02)	H_2O/EtOH	30	91

[a] Reaction conditions: Phenylboronic acid (4 mmol), bromobenzene (4 mmol), tetrabutylammonium bromide, TBAB (4 mmol), solvent (9 ml) and reflux condition

[b] Isolated yield

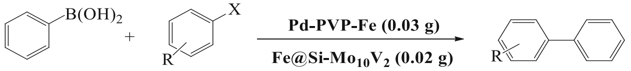
[c] Reaction proceeded in room temperature

Results and discussion

Initial investigation started with the cross-coupling reaction of phenylboronic acid and bromobenzene at reflux and under ligand- and base-free conditions as a model system. Activity of various HPAs such as $H_5PMo_{10}V_2O_{40}$ ($Mo_{10}V_2$), $Pd_{2.5}PMo_{10}V_2O_{40}$, $(NH_4)_5PMo_{10}V_2O_{40}$ and Fe@Si–$Mo_{10}V_2$ accompanied by Pd–PVP–Fe in the model reaction was investigated (Table 1, entries 1–4). $Mo_{10}V_2$ and Fe@Si–$Mo_{10}V_2$ were found to be the most effective (entries 1, 2), but there is a problem here; $Mo_{10}V_2$ in acidic form is a homogeneous catalyst in this reaction media. The major problem, limiting the utility of homogeneously catalyzed processes, is the well-known difficulty in catalyst recovery and recycling. There are two ways for heterogenization of HPAs. One is using salt of HPAs and the other way is making a supported form. Pd salt of $Mo_{10}V_2$ (entry 4) shows very low catalytic activity. Therefore, we chose Fe@Si–$Mo_{10}V_2$ as a heterogeneous recoverable catalyst. It is noteworthy that in the absence of HPA, the reaction did not proceed well (entry 5) and the starting materials remained intact after 120 min (Table 1).

To establish the best reaction conditions, the effect of various solvents, such as H_2O, MeCN, DMF, and mixed solvent systems such as H_2O/EtOH and H_2O/DMF have been studied (entries 6–9, 11). H_2O/EtOH were found to be the choice in terms

Table 2 Suzuki reaction of various aryl halides with phenylboronic acid[a]



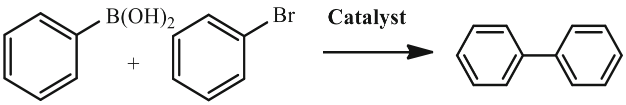
Entry	Aryl halide	Time (min)	Yield (%)[b]	TON[c]
1	Bromobenzene	30	96	175
2	4-Methoxy bromobenzene	40	94	171
3	4-Methyl bromobenzene	40	92	167
4	4-Bromo aniline	50	91	165
5	4-Bromo benzaldehyde	30	91	165
6	4-Nitro bromobenzene	30	97	177
7	1-Bromo naphthalene	40	89	162
8	Chlorobenzene	50	88	160
9	4-Methyl chlorobenzene	60	91	165
10	4-Methoxy chlorobenzene	70	86	156
11	4-Chloro aniline	80	78	142
12	4-Chloro benzaldehyde	40	93	169
13	4-Chloro bromobenzene	40	84	153
14	Fluorobenzene	24 (h)	42	76

[a] Reaction conditions: Phenylboronic acid (4 mmol), aryl halide (4 mmol), TBAB (4 mmol), H_2O/EtOH (9 ml: 2/1) and reflux conditions

[b] Isolated yield. All products were characterized by comparing their ^{1}H-NMR data with authentic samples [37–44]

[c] TON = mmol of product/mmol of Pd catalyst

Table 3 Comparison of the reaction data with other reported methods



Entry	Catalyst	Solvent	Temp. (°C)	Time (h)	Yield (%)	Ref
1	Graphene oxide/Pd	EtOH	Reflux	2.5	86	39
2	Cyclopalladated ferrocenylimine	H_2O	90	2	94	40
3	Fe@Pd/C	H_2O	80	0.5	97	41
4	Supported Pd(II) complex	H_2O/CH_3OH	R.T	8	94	42
5	Pd(salen)-HPA	H_2O/EtOH	50	5	94	43
6	Pd/NH_2–SiO_2	H_2O	60–70	1	90	44
7	Carbon-Pd catalyst	H_2O/DMF	100	3	93	45
9	Pd/Fe_3O_4@SiO_2@KCC-1	EtOH	80	6	90.8	46
10	Pd/MSN-IPr	IsoPrOH	80	2	90	47
11	Mag-IL-Pd	H_2O	60	7.5	82	48
12	Pd@SBA-15C	H_2O	80	1	98	49
13	Pd(II) bounded 2D-hexagonally ordered functionalized MCM-41	DMF	100	4	98	50
14	This work	H_2O/EtOH	Reflux	0.5	96	–

[a] The reaction is performed in the presence of Me-PhB$(OH)_2$

of yield and reaction time (entry 11). Next, the model reaction was carried out in the presence of different amounts of Fe@Si–$Mo_{10}V_2$ and Pd–PVP–Fe as catalytic system. According to the obtained results, 0.02 g of the Fe@Si–$Mo_{10}V_2$ and 0.03 g of Pd–PVP–Fe were chosen as the optimum amount of catalytic system for further reactions (entry 14).

Considering these optimized reaction conditions, various aryl halides were coupled with phenylboronic acid (Table 2). Aryl bromides gave excellent yields with shorter reaction times (entries 1–7). Aryl chlorides react efficiently with phenylboronic acid giving affordable yields of Suzuki product with longer reaction times (entries 8–13). Aryl halides containing electron-withdrawing functional groups give excellent yields with lower reaction times compared to those containing electron-donating functional groups.

To our surprise, the reaction of phenylboronic acids with fluorobenzene afforded the respective product in a moderate yield (entry 14), while previously due to high strength of C–F bond, the fluoroarenes were rarely used [38].

As shown in Table 2, the remarkable reactivity of Pd–PVP–Fe and Fe@Si–$Mo_{10}V_2$ as catalytic system in Suzuki cross-coupling reactions with various functionalized substrates also proved to exhibit an acceptable impact on the turn over number (TON) of these reactions (the Pd loading in Pd–PVP–Fe as a main catalyst was 7.8 %, which was determined using ICP-AES measurement).

The reaction data, along with some literature data for comparison, are given in Table 3. These catalysts showed good reactivity. However, the use of base, ligand,

Table 4 $Mo_{10}V_2$ leaching measured by ICP-AES

Run number	1	2	3	4
Leach (wt%)	9.75	6.1	4.87	3.67

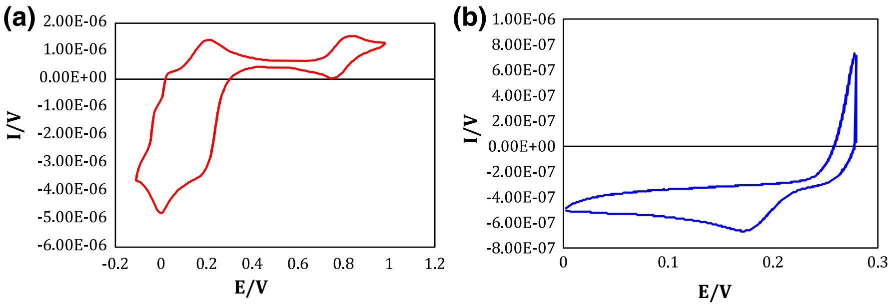


Fig. 1 Cyclic voltammogram of **a** Fe@Si–$Mo_{10}V_2$ and **b** Pd–PVP–Fe-modified glassy carbon electrode in a phosphate buffer solution of pH = 7, 100 mV/s

and non-recyclable catalysts in these reported systems is not beneficial to industrial and synthetic applications.

In order to study on the role of Fe@Si–$Mo_{10}V_2$ on the Suzuki coupling reaction, we decided to investigate the electron transfer property of Fe@Si–$Mo_{10}V_2$ and Pd–PVP–Fe by means of CV measurements. The CV responses of Fe@Si–$Mo_{10}V_2$ and Pd–PVP–Fe modified glassy carbon electrode in a phosphate buffer solution of pH = 7 is shown in Fig. 1. In the potential range between $E = -0.1$ V and $E = 1.00$ V, three pairs of redox peaks were observed for Fe@Si–$Mo_{10}V_2$ modified electrode. It can be attributed to electron-transfer reaction of Mo(V)/Mo(IV), Mo(IV)/Mo(III), and V(V)/V(IV) couples. Also, the characteristic symmetrical reduction wave of palladium is identified with its reduction peak located at $E = +0.17$ V. Comparing with the CV of Fe@Si–$Mo_{10}V_2$, we can deduce that the presence of HPA species can facilitate the oxidation and reduction of palladium in catalytic cycles of Suzuki coupling reaction.

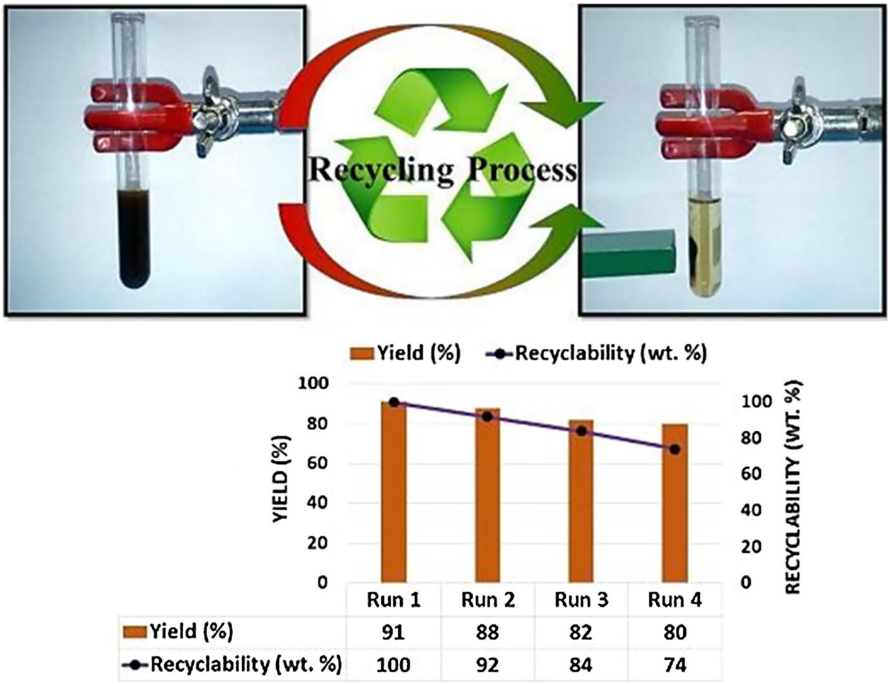
The reusability of the catalysts is a very important theme, especially for commercial applications. The advantage of our catalytic system lied in not only the high catalytic activity attributed to the formation of C–C bond but also in the easy separation and recyclability. Recycling experiments were carried out for the cross-coupling of bromobenzene and phenylboronic acid under the optimum conditions in Table 1. At the fourth reaction runs, 74 wt% of the catalyst (compared with the amount of fresh one used in the first run) was recovered and yield of the product decreased from 91 to 80 % after fourth runs (Fig. 2). This decrease in the product yield may be due to the leaching of the active site.

To check whether this catalyst is completely heterogeneous, the content of Pd and $Mo_{10}V_2$ into filtrates was evaluated quantitatively by inductively coupled plasma atomic emission spectroscopy (ICP-AES). According to the obtained results from the ICP-AES measurements, the Pd leach is negligible and a small amount of $Mo_{10}V_2$ leach was obtained (Table 4).

Another test was performed to check if this active catalytic system is indeed heterogeneous (Fig. 3). First, hot filtration of the catalysts after obtaining a conversion of about 50 % was done. Thereafter, the reaction was continued with the residual solution. No further conversion was observed in the reaction as a proof that no homogeneous catalyst was present in the reaction mixture.

In order to show the effect of reuse on the structural features of the catalysts, the FT-IR spectra and XRD pattern of the fresh Pd–PVP–Fe and Fe@Si–$Mo_{10}V_2$ and reused ones are presented in Fig. 4. It is notable that, in this catalytic system, Pd–PVP–Fe and Fe@Si–$Mo_{10}V_2$, both components separated at the same time.

For Pd–PVP–Fe, the band at 750 cm^{-1} corresponds to the C–C stretching vibration, and 1100 cm^{-1} is related to the C–N stretching vibration (pyridine ring). The peaks at about 1300 and 1550 cm^{-1} are related to C–H stretching vibrations and stretching vibration of C=O, but in the case of Fe@Si–$Mo_{10}V_2$, the bands for the Keggin structure of neat $Mo_{10}V_2$ occurred at about 1086, 1024, 927, and 835 cm^{-1}. The presence of two bands at about 400–1000 cm^{-1} indicates the presence of Fe_3O_4 in the structure of Fe@Si–$Mo_{10}V_2$. The FT-IR spectrum of the recovered catalysts shows all of the characteristic peaks of the fresh catalysts, which confirms that the structure of both components of the catalytic system during the reuse and recovery processes remains unchanged.



	Run 1	Run 2	Run 3	Run 4
▬ Yield (%)	91	88	82	80
-●- Recyclability (wt. %)	100	92	84	74

Fig. 2 Reusability of FeSi–$Mo_{10}V_2$ and Pd–PVP–Fe in the model reaction and catalysts recovery

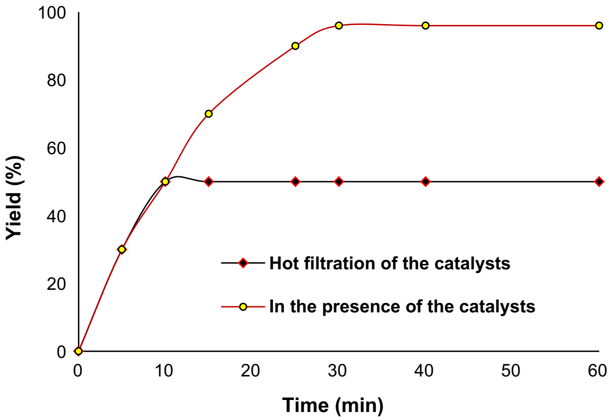


Fig. 3 Reaction progress before and after filtration of the catalysts

Also, the XRD patterns of the fresh and recovered catalysts are shown in Fig. 4. As presented, in XRD patterns of recovered Pd–PVP–Fe and Fe@Si–$Mo_{10}V_2$, the Pd^0 have a crystalline structure with peaks appearing at around $2\theta = 40.12°$, 46.36°, 68.12°, 82.10°, and 86.62°, while the diffraction peaks observed at 45.90°, 53.30°, and 77.75° correspond to the presence of nano zero valent irons in the Pd–PVP–Fe structure. As can be seen, in the overall XRD pattern of recovered catalyst and co-catalyst, the characteristic peaks of both Pd–PVP–Fe and Fe@Si–$Mo_{10}V_2$ were observed clearly. From the standpoint of this, we can conclude that during the recovery and reusing processes, all of the fresh and reused catalysts have similar catalytic behaviors and structural properties.

We believe that HPA play a significant role in the transmetalation step in Suzuki coupling reactions. As is shown in Scheme 1, the mechanism begins with oxidative addition of the arylhalides to the Pd(0) to form a Pd(II) complex. At this point, the Pd–X bond activation is done by Fe@Si–$Mo_{10}V_2$ acidic hydrogens. H–X is a very good leaving group, and, produced intermediately, is a very active component for alkylation. A produced polyoxoanion then adds to the organoborane to form a borate reagent making its Ar′ group more nucleophilic. Transmetalation with the borate then follows, where its Ar′ group replaces the H–X on the palladium complex. Reductive elimination then gives the final coupled product, regenerates the palladium catalyst, and then the catalytic cycle can begin again. Also, further research is under investigation in our laboratory.

Conclusions

In conclusion, we have applied a green protocol based on the simultaneous use of Pd–PVP–Fe and Fe@Si–$Mo_{10}V_2$. This catalytic system demonstrated excellent catalytic activity for the carbon–carbon cross-coupling Suzuki reaction. The presence of Fe@Si–$Mo_{10}V_2$ is essential for obtaining high performances of the

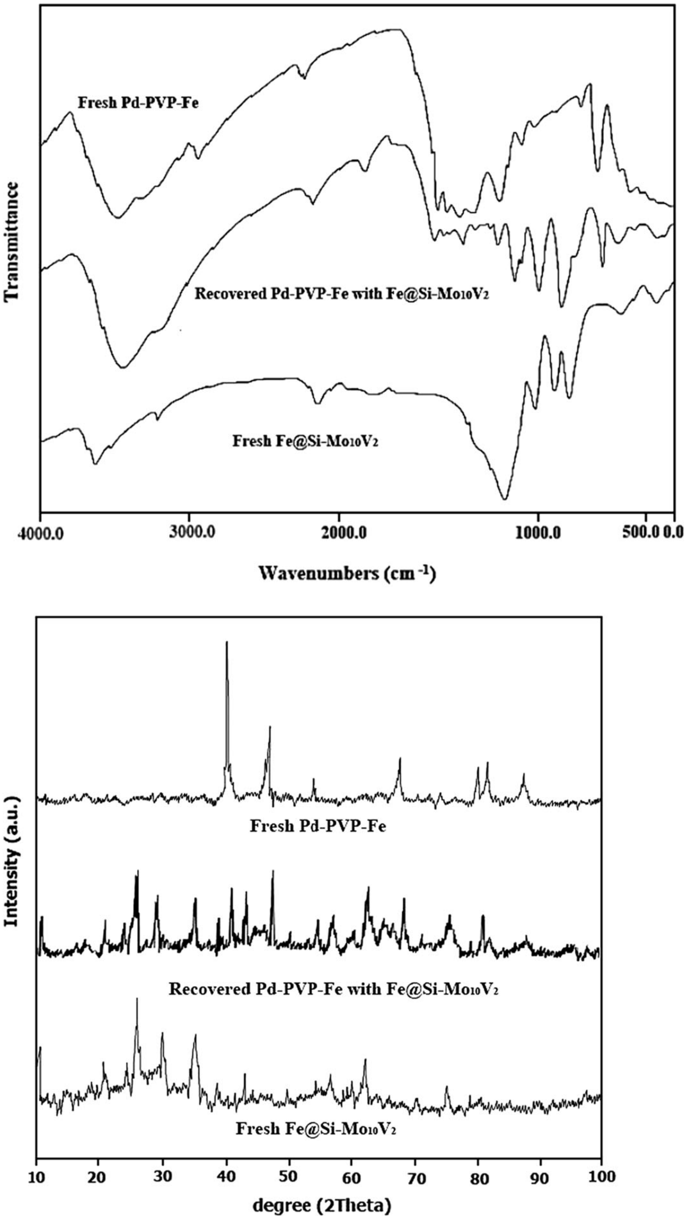
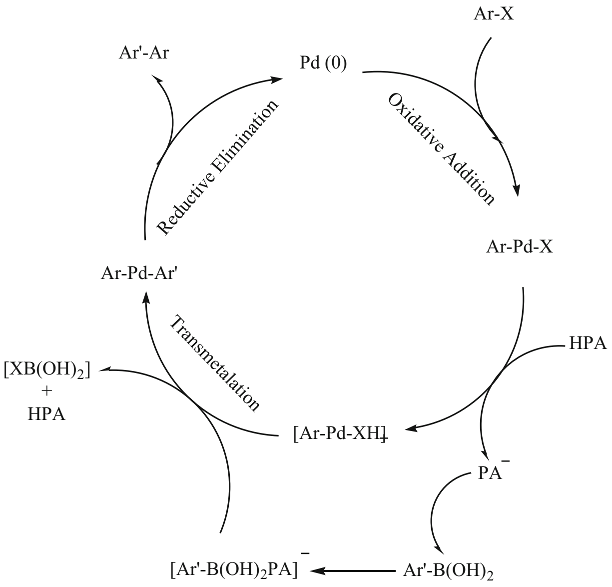


Fig. 4 FT-IR spectra and XRD pattern of fresh Pd–PVP–Fe, Fe@Si–$Mo_{10}V_2$, and recovered ones in the presence of Fe@Si–$Mo_{10}V_2$

catalytic system; most probably it can activate precursors and regenerate the Fe(II) and Pd(II) to active catalytic species. High stability, easy removal from the reaction mixture, and reusability of the catalyst up to four consecutive cycles with minimal



Scheme 1 Proposed mechanism

loss of activity are the major advantages of this catalytic system. According to the obtained results from the ICP-AES measurements, a small amount of Pd and $Mo_{10}V_2$ leach have been obtained. Further work is in progress to broaden the scope of these types of catalytic systems for various organic transformations.

Acknowledgments The authors thank the Razi University Research Council for support of this work.

References

1. M. Pérez-Lorenzo, J. Phys. Chem. Lett. **3**, 167 (2011)
2. A. Balanta, C. Godard, C. Claver, Chem. Soc. Rev. **40**, 4973 (2011)
3. S.K. Beaumont, J. Chem. Technol. Biotechnol. **87**, 595 (2012)
4. A. Modak, J. Mondal, V.K. Aswal, A. Bhaumik, J. Mater. Chem. **20**, 8099 (2010)
5. D. Ganapathy, G. Sekar, Catal. Commun. **39**, 50 (2013)
6. A. Molnar, Chem. Rev. **111**, 2251 (2011)
7. N. Nakagawa, T. Hatakeyama, M. Nakamura, Chem. Lett. **44**, 486 (2015)
8. L. Yin, J. Liebscher, Chem. Rev. **107**, 133 (2007)
9. R. Martin, S.L. Buchwald, Acc. Chem. Res. **41**, 1461 (2008)
10. J.F. Civicos, D.A. Alonso, C. Najera, Eur. J. Org. Chem. **19**, 3670 (2012)
11. P. Liu, X.-J. Feng, R. He, Tetrahedron **66**, 631 (2010)
12. Z.Y. Wang, G.Q. Chen, L.X. Shao, J. Org. Chem. **77**, 6608 (2012)
13. C. Coperet, M. Chabanas, R.P. Saint-Arroman, J.M. Basset, Angew. Chem. Int. Ed. **42**, 156 (2003)
14. V. Polshettiwar, R. Luque, A. Fihri, H. Zhu, M. Bouhrara, J.M. Basset, Chem. Rev. **111**, 3036 (2011)
15. L. Djakovitch, K. Koehler, J. Am. Chem. Soc. **123**, 5990 (2001)
16. R.B. Bedford, U.G. Singh, R.I. Walton, R.T. Williams, S.A. Davis, Chem. Mater. **17**, 701 (2005)
17. M.J. Jin, A. Taher, H.J. Kang, M. Choi, R. Ryoo, Green Chem. **11**, 309 (2009)
18. R.K. Ramchandani, B.S. Uphade, M.P. Vinod, R.D. Wakharkar, V.R. Choudhary, A. Sudalai, Chem. Commun. **21**, 2071 (1997)

19. A.S. Singh, U.B. Patil, J.M. Nagarkar, Catal. Commun. **35**, 11 (2013)
20. X.C. Chen, Y.Q. Hou, H. Wang, Y. Gao, J.H. He, J. Phys. Chem. C **112**, 8172 (2008)
21. A.R. Siamaki, A.E.R.S. Khder, V. Abdelsayed, M.S. El-Shall, B.F. Gupton, J. Catal. **279**, 1 (2011)
22. J. Hu, Y. Wang, M. Han, Y. Zhou, X. Jiang, P. Sun, Catal. Sci. Technol. **2**, 2332 (2012)
23. H.L. Liu, P. Houa, W.X. Zhang, J.H. Wu, Colloids Surf. A **356**, 21 (2010)
24. S. Li, W. Zhang, M.H. So, ChM Che, R. Wang, R. Chen, J. Mol. Catal. A Chem. **359**, 81 (2012)
25. M. Jukić, I. Sviben, Z. Zorić, S. Milardović, Croat. Chem. Acta **85**, 269 (2012)
26. S. Pathan, A. Patel, RSC Adv. **2**, 116 (2012)
27. P. Zhao, Y. Leng, M. Zhang, J. Wang, Y. Wua, J. Huang, Chem. Commun. **48**, 5721 (2012)
28. I.V. Kozhevnikov, K.I. Matveev, Appl. Catal. **5**, 135 (1983)
29. E. Rafiee, S. Eavani, Green Chem. **13**, 2116 (2011)
30. E. Rafiee, S. Eavani, B. Malaekeh-Nikouei, Chem. Lett. **41**, 438 (2012)
31. M. Joshaghani, E. Faramarzi, E. Rafiee, M. Daryanavard, J. Xiao, C. Baillie, J. Mol. Catal. A Chem. **259**, 35 (2006)
32. M. Joshaghani, M. Daryanavard, E. Rafiee, J. Xiao, C. Baillie, Tetrahedron Lett. **48**, 2025 (2007)
33. S. Nadri, M. Joshaghani, E. Rafiee, Tetrahedron Lett. **50**, 5470 (2009)
34. S. Nadri, M. Joshaghani, E. Rafiee, Organometallics **28**, 6281 (2009)
35. P. Ghaderi-Sheikhi Abadi, E. Rafiee, S. Nadri, G. Hajian, M. Joshaghani, Appl. Catal. A Gen. **487**, 139 (2014)
36. G.A. Tsigdinos, C. Hallada, J. Inorg. Chem. **7**, 437 (1968)
37. E. Rafiee, S. Rezaei J. Taiwan Inst. Chem. Eng. (2015). doi:10.1016/j.jtice.2015.11.027
38. J.R. Ruiz, C. Jimenez-Sanchidrian, M. Mora, J. Fluor. Chem. **127**, 443 (2006)
39. S.S. Shendage, A.S. Singh, J.M. Nagarkar, Tetrahedron Lett. **55**, 857 (2014)
40. J. Wang, B. Mu, Zh Fu, L. Wang, T. Li, Y. Wu, Chin. J. Catal. **35**, 1059 (2014)
41. W. Tang, J. Li, X. Jin, J. Sun, J. Huang, R. Li, Catal. Commun. **43**, 75 (2014)
42. S. Keesara, M.R. Mandapati, S. Parvathaneni, Appl. Catal. A Gen. **496**, 58 (2015)
43. J. Tong, H. Wang, X. Cai, Q. Zhang, H. Ma, Z. Lei, Appl. Organometal. Chem. **28**, 95 (2014)
44. P. Veerakumar, M. Velayudham, K.-L. Lu, S. Rajagopal, Appl. Catal. A Gen. **455**, 247 (2013)
45. M. Shokouhimehr, T. Kim, S.W. Jun, K. Shin, Y. Jang, B.H. Kim, J. Kim, T. Hyeon, Appl. Catal. A Gen. **476**, 133 (2014)
46. X.D. Le, Z.P. Dong, Y.S. Liu, Z.C. Jin, T.D. Huy, M. Le, J. Ma, J. Mater. Chem. A. **2**, 19696 (2014)
47. H.Q. Yang, Y.W. Wang, Y. Qin, Y.Z. Chong, Q.Z. Yang, G. Li, L. Zhang, W. Li, Green Chem. **13**, 1352 (2011)
48. B. Karimi, F. Mansouri, H. Vali, Green Chem. **16**, 2587 (2014)
49. J. Zhi, D. Song, Z. Li, X. Lei, A. Hu, Chem. Commun. **47**, 10707 (2011)
50. K. Dhara, K. Sarkar, D. Srimani, S.K. Saha, P. Chattopadhyay, A. Bhaumik, Dalton Trans. **39**, 6395 (2010)