Full paper

Schiff base complex of palladium immobilized on magnetic nanoparticles: an efficient and recyclable nanocatalyst for C–C coupling reactions

Somaieh Rezaei[a], Arash Ghorbani-Choghamarani[b]* and Rashid Badri[a]

A Schiff base complex of palladium anchored on Fe_3O_4 magnetic nanoparticles as an efficient and magnetically reusable nanocatalyst is reported for C–C bond formation through Heck and Suzuki reactions. The catalyst was easily recovered and reused several times without significant loss of its catalytic efficiency or palladium leaching. The magnetic nanocatalyst was characterized using Fourier transform infrared and inductively coupled plasma atomic emission spectroscopies, thermogravimetric analysis, vibrating sample magnetometry, and transmission and scanning electron microscopies. Copyright © 2016 John Wiley & Sons, Ltd.

Additional supporting information may be found in the online version of this article at the publisher's web site.

Keywords: magnetic nanoparticle; C–C coupling; Heck reaction; Suzuki reaction; Schiff base

Introduction

The immobilization of homogeneous catalysts on various support materials to facilitate catalyst separation and recycling is of great importance in catalyst science.[1,2] However, the active sites in classic heterogeneous catalysts have limited accessibility compared to homogeneous systems, and thus the activity and selectivity of classical heterogeneous catalysts are usually reduced.[3,4] Ideally, the advantages of homogeneous and heterogeneous catalysts, such as high activity and selectivity of the former and easy separation and recycling of the latter, should be combined. These goals can be achieved by nanocatalysts. Nanocatalysts bridge the gap between homogeneous and heterogeneous catalysts.[5,6] This is because when the size of the support is decreased to the nanometre scale, the surface area is substantially increased and the support can be evenly dispersed in solution, forming a homogeneous emulsion.[7] However, the nanocatalyst support can be separated from products by conventional filtration or centrifugation techniques. But, it is difficult, time consuming and expensive to separate fine particles from a reaction mixture.[8,9] Therefore, to improve the mentioned limitations, magnetic nanoparticles (MNPs) have been extensively employed as alternative catalyst supports, which can be easily removed from a reaction mixture using magnetic separation.[10] One of the most promising MNP supports is superparamagnetic iron oxide. The notable advantages of Fe_3O_4 MNPs are simple synthesis, ready availability, low cost, high surface area and low toxicity.[6,11] More importantly, magnetic separation is easier and more effective than filtration or centrifugation. Therefore, Fe_3O_4 MNPs are considered as ideal supports for the heterogenization of homogeneous catalysts.[5]

We report here the synthesis and characterization of a palladium Schiff base complex immobilized on Fe_3O_4 MNPs. This reusable catalyst was applied for the Suzuki and Heck reactions with a minimal leaching of palladium species. These cross-coupling reactions are used as a powerful method in modern synthetic organic chemistry for the preparation of advanced materials, natural products, liquid crystal materials, agrochemicals, pharmaceuticals, biologically active compounds, herbicides, UV screens, polymers and hydrocarbons.[12–16]

Experimental

Preparation of Fe_3O_4 MNPs

Free Fe_3O_4 MNPs were prepared using chemical precipitation of Fe^{3+} and Fe^{2+} ions with a molar ratio of 2:1. Typically, $FeCl_3 \cdot 6H_2O$ (5.838 g, 0.0216 mol) and $FeCl_2 \cdot 4H_2O$ (2.147 g, 0.0108 mol) were dissolved in 100 ml of deionized water at 80 °C under nitrogen atmosphere and vigorous mechanical stirring conditions. Then, 10 ml of 25% $NH_{3(aq)}$ was added to the reaction mixture. After 30 min, the reaction mixture was cooled to room temperature, and black MNPs (Fe_3O_4) were washed five times with distilled water, and each time were decanted with an external magnet and dried in vacuum.

* Correspondence to: Arash Ghorbani-Choghamarani, Department of Chemistry, Faculty of Science, Ilam University, PO Box 69315516, Ilam, Iran.
E-mail: arashghch58@yahoo.com

a Islamic Azad University, Ahwaz Branch, College of Science, Department of Chemistry, Ahwaz, Iran

b Department of Chemistry, Faculty of Science, Ilam University, PO Box 69315516, Ilam, Iran

Preparation of MNPs Bonded with Schiff Base Complex of Palladium (Schiff-base-Pd@MNPs)

The obtained Fe_3O_4 MNPs (1.5 g) were dispersed in 100 ml of ethanol–water (1:1 v/v) solution by sonication for 30 min, and then 2.5 ml of (3-aminopropyl)trimethoxysilane (APTES) was added to the reaction mixture. The reaction mixture was stirred using a mechanical stirring under nitrogen atmosphere at 40 °C for 8 h. Subsequently, nanoparticles were re-dispersed in ethanol via sonication five times and separated through magnetic decantation. The nanoparticle product (APTES@Fe_3O_4) was dried at room temperature. In order to prepare Schiff-base@MNPs, the APTES@Fe_3O_4 solid (1 g) was refluxed with 1 mmol of 5-bromosalicylaldehyde in ethanol for 8 h under nitrogen atmosphere. The resulting solid (Schiff-base@MNPs) was separated using magnetic decantation, washed with ethanol and dried at room temperature. Finally, for the preparation of Schiff-base-Pd@MNPs, Schiff-base@MNPs (0.5 g) was dispersed in 20 ml of dry ethanol and was mixed with 0.25 mmol of palladium. The mixture was stirred at 80 °C for 20 h. Then, $NaBH_4$ (0.3 mmol) was added to the reaction mixture and the reaction was continued for 2 h. The Schiff-base-Pd@MNPs solid product was obtained by magnetic decantation, and washed with ethanol and dried at 40 °C in air, because one of the advantages of this catalyst is that it is stable in air and moisture.

General Procedure for C–C Coupling through Suzuki Reaction

A mixture of aryl halide (1 mmol), phenylboronic acid (1 mmol), K_2CO_3 (1.5 mmol) and Schiff-base-Pd@MNPs (0.005 g, 0.81 mol%) was stirred in poly(ethylene glycol) (PEG)-400 (1 ml) at 60 °C. The progress of the reaction was monitored by TLC. After completion of the reaction, the mixture was cooled to room temperature and the catalyst was separated using an external magnet and washed with diethyl ether and the organic layer was extracted with water and diethyl ether to afford pure products. The organic layer was dried over Na_2SO_4 (1.5 g). Then the solvent was evaporated and pure biphenyl derivatives were obtained in good to excellent yields.

General Procedure for Coupling of Aryl Halides with Butyl Acrylate through Heck Reaction

A mixture of aryl halide (1 mmol), butyl acrylate (1.2 mmol), K_2CO_3 (3 mmol) and Schiff-base-Pd@MNPs (0.016 g, 2.62 mol%) was stirred in dimethylformamide (DMF) at 120 °C and the progress of the reaction was monitored by TLC. After completion of the reaction, the mixture was cooled to room temperature and the catalyst was separated using an external magnet and washed with diethyl ether and the organic layer was extracted with water and diethyl ether to afford pure products. The organic layer was dried over Na_2SO_4 (1.5 g). Then the solvent was evaporated and pure products were obtained in 88 to 97% yields.
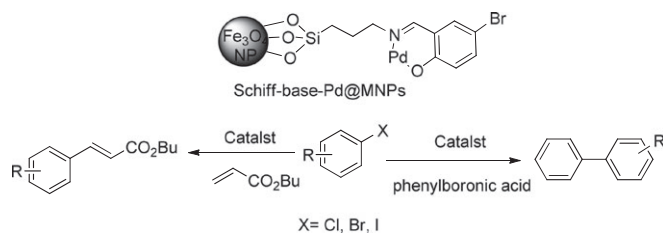
Scheme 1. Synthesis of Schiff-base-Pd@MNPs.

Results and Discussion

Catalyst Preparation

In continuation of our studies on the application of metal complexes immobilized on MNPs in organic reactions,[17] herein we report a simple and efficient method for the Suzuki and Heck carbon–carbon reactions through coupling of aryl halides with phenylboronic acid or butyl acrylate in the presence of catalytic amounts of Schiff-base-Pd@MNPs as catalyst.

The details of the preparation procedure for the supported catalyst are presented in Scheme 1. Initially, the core of Fe_3O_4 MNPs was prepared by a chemical co-precipitation technique using $FeCl_3 \cdot 6H_2O$ and $FeCl_2 \cdot 6H_2O$ in basic solution at 80 °C. Then, after coating of Fe_3O_4 MNPs with APTES, the reaction of amino groups with 5-bromosalicylaldehyde led to 5-bromosalicylaldehyde Schiff base supported on Fe_3O_4 MNPs (Schiff-base@MNPs). Finally, Schiff-base-Pd@MNPs was prepared via coordination of palladium with Schiff-base@MNPs and was characterized using transmission electron microscopy (TEM), scanning electron microscopy (SEM), thermogravimetric analysis (TGA), vibrating sample magnetometry (VSM) and inductively coupled plasma atomic emission spectroscopy (ICP-OES).

Catalyst Characterization

The size of the catalyst was evaluated using SEM and TEM. The SEM and TEM images of Schiff-base-Pd@MNPs show that the catalyst is formed of nanometre-sized particles. As shown in Figs 1 and 2, most of the particles are quite homogeneous and quasi-spherical with an average diameter of about 10 nm.

The functionalization of Fe_3O_4 MNPs with organic layers and Schiff base complex of palladium is inferred using TGA. Figure 3
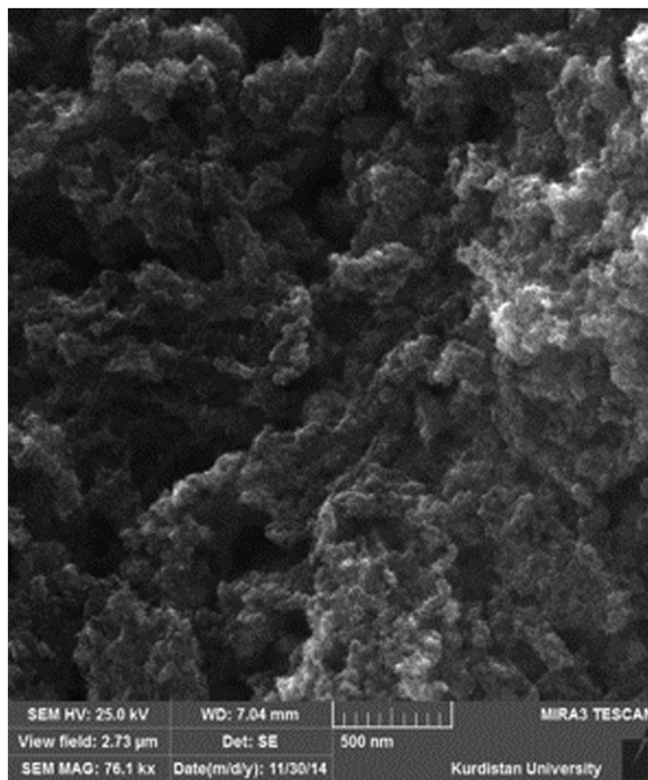
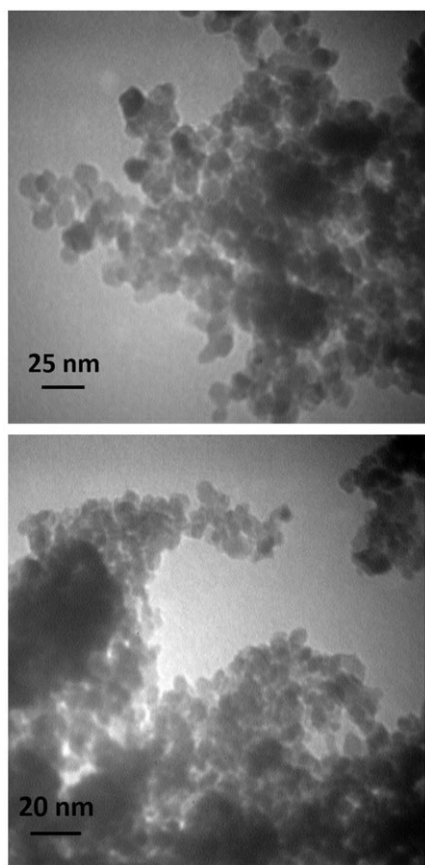**Figure 1.** SEM image of Schiff-base-Pd@MNPs.

Figure 2. TEM images of Schiff-base-Pd@MNPs.

shows the TGA curves for Fe_3O_4 MNPs, APTES@MNPs, Schiff-base@-MNPs and Schiff-base-Pd@MNPs. The TGA curve of Schiff-base-Pd@MNPs shows the mass loss of the organic functional groups as it decomposes upon heating. The weight loss at temperatures below 200 °C is due to the removal of physically adsorbed solvent and surface hydroxyl groups. In the TGA curve of Schiff-base-Pd@-MNPs, decomposition of organic groups is evident with a weight
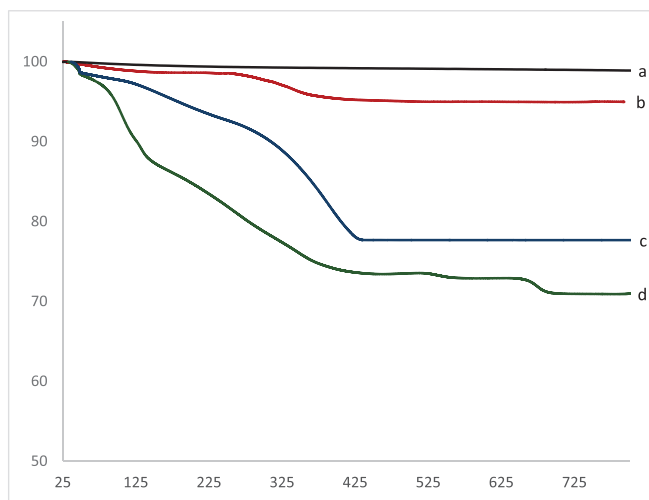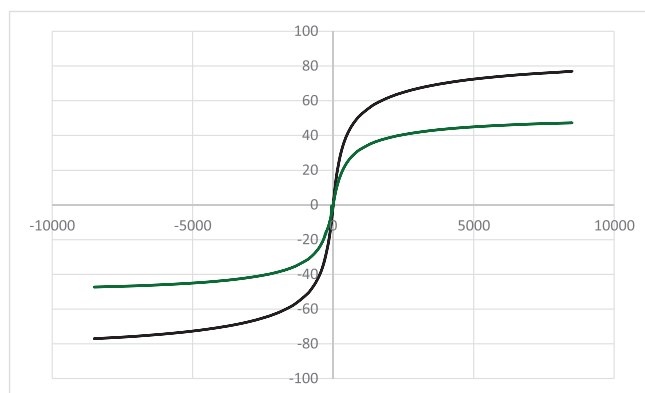

Figure 4. Magnetization curves for (black) Fe_3O_4 MNPs and (green) Schiff-base-Pd@MNPs.

loss of about 29%. Meanwhile, weight losses of about 2, 5 and 22% occur for Fe_3O_4 MNPs, APTES@MNPs and Schiff-base@MNPs, respectively. On the basis of these results, the grafting of Schiff base complex of palladium on the Fe_3O_4 surface is verified.

In order to determine the exact amount of palladium in Schiff-base-Pd@MNPs, the ICP-OES technique was used. Based on ICP-OES analysis, the amount of palladium in the catalyst is 1.63×10^{-3} mol g^{-1} based on ICP-OES.

The magnetic property of Fe_3O_4 MNPs was compared with that of Schiff-base-Pd@MNPs using VSM at room temperature. The
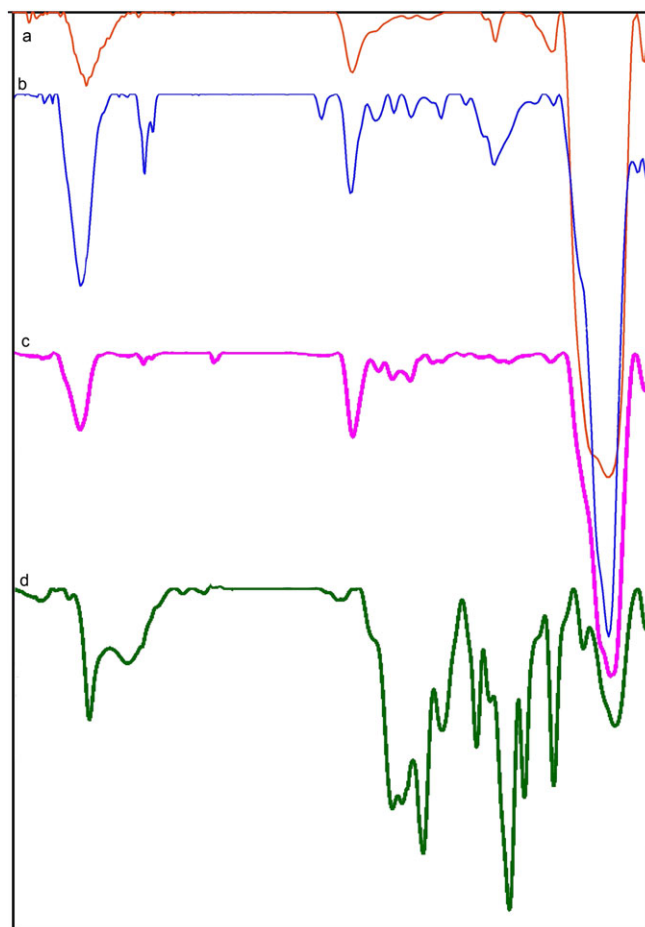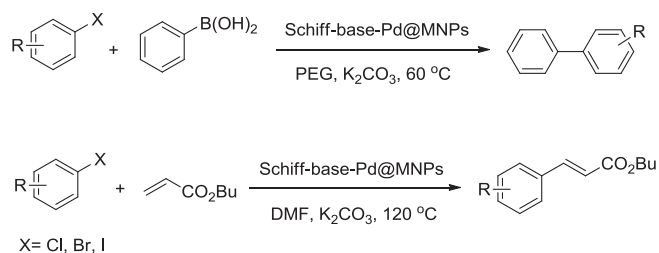

Figure 3. TGA curves of (a) Fe_3O_4 MNPs, (b) APTES@MNPs, (c) Schiff-base@MNPs and (d) Schiff-base-Pd@MNPs.

Figure 5. FT-IR spectra of (a) Fe_3O_4 MNPs, (b) APTES@MNPs, (c) Schiff-base@MNPs and (d) Schiff-base-Pd@MNPs (d).

Scheme 2. Schiff-base-Pd@MNPs catalyses C–C coupling through Suzuki and Heck reactions.

room temperature magnetization curves of Fe_3O_4 MNPs and Schiff-base-Pd@MNPs are shown in Fig. 4. The M_s value decreases from 77 emu g^{-1} for Fe_3O_4 MNPs to 47.29 emu g^{-1} for Schiff-base-Pd@-MNPs.[18] On the basis of these results, the good grafting of organic layers including palladium complex on the Fe_3O_4 is verified.

Successful functionalization of the Fe_3O_4 MNPs can be inferred from the Fourier transform infrared (FT-IR) technique. Figure 5 shows FT-IR spectra for Fe_3O_4 MNPs, APTES@MNPs, Schiff-base@MNPs and Schiff-base-Pd@MNPs. Two strong absorption bands of the Fe–O stretching vibration at 560 and 440 cm^{-1}, symmetric and asymmetric modes of the O–H bond stretching vibration near 3120 and 3390 cm^{-1} and O–H deformation vibration near 1620 cm^{-1} are observed in the FT-IR spectrum of bare Fe_3O_4 MNPs. Modification of Fe_3O_4 MNPs using APTES is proved with C–H stretching vibrations that appear at 2920 and 2856 cm^{-1} and also N–H stretching mode appearing as a broad band at 3440 cm^{-1}. Schiff-base@MNPs exhibits a ν(C=N) stretch at 1620 cm^{-1} while in the Schiff-base-Pd@MNPs this peak appears at lower frequency.[2]

Catalytic Study

After characterization of the catalyst, its catalytic activity was studied in Suzuki and Heck reactions. These C–C coupling reactions catalysed by Schiff-base-Pd@MNPs are outlined in Scheme 2.

In order to optimize Suzuki reaction conditions, we examined the coupling of iodobenzene with phenylboronic acid as a model reaction in various solvents, with different bases and in the presence of various amounts of catalyst at 25–80 °C (Table 1). As expected, no product is obtained in the absence of catalyst or base, even after 24 h (Table 1, entries 1 and 2). As evident from Table 1, the best results are observed in PEG-400 at 60 °C in the presence of 5 mg (0.81 mol%) of Schiff-base-Pd@MNPs using 1.5 mmol of K_2CO_3 (Table 1, entry 12).

After optimization of the reaction conditions, the coupling of a variety of aryl halides with phenylboronic acid was investigated to confirm the generality of this method. All products are obtained in good to high yields. The results of this study are summarized in Table 2. A variety of aryl halides, aryl iodides, aryl bromides and aryl chlorides, were successfully employed to prepare the corresponding biphenyl derivatives in excellent yields.

In the second part of our study of the application of the catalytic activity of Schiff-base-Pd@MNPs in C–C coupling reactions, we investigated the applicability of this catalyst to the Heck reaction using coupling of aryl halides with butyl acrylate. In order to optimize the reaction conditions, we examined the coupling of iodobenzene with butyl acrylate as a model reaction (Table 3). In order to choose the reaction media, various solvents (water, DMF, 1,4-dioxane, dimethylsulfoxide (DMSO) and PEG) and amounts of Schiff-base-Pd@MNPs were examined. The best results are observed in DMF using 0.016 g (2.62 mol%) of catalyst (Table 3, entry 2). Also, the model reaction was tested using various bases (KOH, K_2CO_3, Na_2CO_3 and Et_3N): the best results are observed using 3 mmol of K_2CO_3. Also, the effect of temperature was studied and the best result is obtained at 120 °C.

After the optimization of the reaction conditions, various aryl halides containing several functional groups were reacted under optimum condition and the corresponding products are obtained in good to excellent yields (Table 4). The experimental procedure is very simple and convenient, and has the ability to tolerate a variety of other functional groups.

Table 1. Optimization of Suzuki reaction conditions for coupling of iodobenzene with PhB(OH)$_2$ in the presence of Schiff-base-Pd@MNPs

Entry	Catalyst (mg)	Solvent	Base	Amount of base (mmol)	Temperature (°C)	Time (min)	Yield (%)[a]
1	—	PEG	K_2CO_3	1.5	80	24	Trace
2	5	PEG	—	1.5	80	24	Trace
3	8	PEG	K_2CO_3	1.5	80	40	96
4	5	PEG	K_2CO_3	1.5	80	50	98
5	3	PEG	K_2CO_3	1.5	80	100	91
6	5	DMF	K_2CO_3	1.5	80	60	93
7	5	DMSO	K_2CO_3	1.5	80	85	92
8	5	1,4-Dioxane	K_2CO_3	1.5	80	70	94
9	5	PEG	Na_2CO_3	1.5	80	90	86
10	5	PEG	Et_3N	1.5	80	55	93
11	5	PEG	KOH	1.5	80	120	75
12	5	PEG	K_2CO_3	1.5	60	70	96
13	5	PEG	K_2CO_3	1.5	40	150	82
14	5	PEG	K_2CO_3	1.5	r.t.	240	Trace

[a]Isolated yield.

Table 2. Catalytic C–C coupling reaction of aryl halides using phenylboronic acid in the presence of catalytic amount of Schiff-base-Pd@MNPs (5 mg, 0.81 mol%) in PEG-400 at 60 ℃
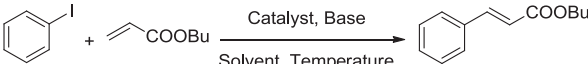
Entry	Aryl halide	Time (min)	Yield (%)[a]	Melting point (℃)
1	Iodobenzene	70	96	66–68[19]
2	4-Iodoanisole	75	95	80–82[19]
3	4-Iodotoluene	80	94	41–44[20]
4	4–Bromonitrobenzene	390	94	111–113[17]
5	4–Bromobenzonitrile	240	97	85–86[20]
6	4-Bromotoluene	265	96	42–44[17]
7	Bromobenzene	40	96	69[19]
8	4–Bromochlorobenzene	80	92	52–54[20]
9	Chlorobenzene	225	93	67–68[17]
10	4-Chloronitrobenzene	70	97	110–113[17]

[a]Isolated yield.

Table 4. Coupling of aryl halides with butyl acrylate in the presence of catalytic amounts of Schiff-base-Pd@MNPs (16 mg, 2.62 mol%)

Entry	Aryl halide	Time (h)	Yield (%)[a]
1	Iodobenzene	6	97
2		7	96
3	4-Bromotoluene	10.5	91
4	2-Iodotoluene	3.5	95
5		6	94
6	Bromobenzene	5.5	88
7		5.5	91
8	4-Bromophenol	4	89
9	1-Bromo-3-(trifluoromethyl)benzene	4.5	90
10		8	90

[a]Isolated yield.

Reusability of Catalyst

Schiff-base-Pd@MNPs as a magnetically reusable nanocatalyst can be easily recycled for repeated use in the formation of C
C bonds. To investigate this issue, the recyclability of the catalyst was examined for the coupling of iodobenzene with phenylboronic acid as a model reaction. We find that this catalyst demonstrates markedly excellent reusability; after the completion of the reaction, the catalyst was easily and rapidly separated from the products using an external magnet, followed by washing with diethyl ether to remove residual product and decantation of the reaction mixture (Fig. 6). Then, the reaction vessel was charged with fresh reactants and subjected to the next run. As shown in Fig. 6, the catalyst was used over six runs without any significant loss of activity or palladium leaching. The average isolated yield for six runs is 93.5%, which clearly demonstrates the practical recyclability of this catalyst.

In order to show the amount of leaching of the catalyst, the amount of palladium in the catalyst was obtained using ICP-OES after six re-uses. The amount of palladium in the catalyst is found to be 1.61×10^{-3} mol g^{-1} after six cycles based on ICP-OES measurements. Therefore the catalyst can be recovered and recycled without any significant leaching of palladium. Based on ICP-OES analysis, the amount of palladium in Schiff-base-Pd@MNPs after six runs is comparable to that of fresh catalyst (1.63×10^{-3} mol g^{-1} for fresh Schiff-base-Pd@MNPs).

In order to investigate the leaching of palladium during reaction and heterogeneity of this catalyst, we conducted a hot filtration test for the coupling of 4-iodotoluene with phenylboronic acid (Table 2, entry 3). In this experiment, the yield of product was obtained as 76% after half the reaction time (40 min). Then the reaction was repeated and catalyst was separated after half the reaction time, and filtrated solution was allowed to continue reacting until 80 min. The yield of the reaction in this stage was 79%, confirming that the leaching of palladium in the reaction mixture is negligible.

Comparison of Catalysts

In order to show the efficiency of the described catalytic system, the results obtained for the coupling of iodobenzene with
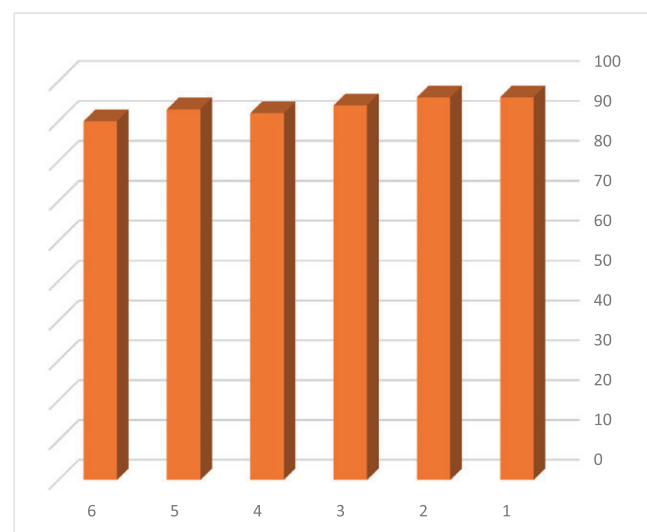
Table 3. Optimization of reaction conditions for cross coupling reaction of iodobenzene with butyl acrylate

Entry	Catalyst (mg)	Solvent	Base	Temperature (℃)	Time (h)	Yield (%)[a]
1	12	DMF	K$_2$CO$_3$	120	12	77
2	14	DMF	K$_2$CO$_3$	120	8.6	91
3	16	DMF	K$_2$CO$_3$	120	6	97
4	18	DMF	K$_2$CO$_3$	120	5.7	97
5	16	H$_2$O	K$_2$CO$_3$	120	10	43
6	16	DMSO	K$_2$CO$_3$	120	7.2	94
7	16	1,4-Dioxane	K$_2$CO$_3$	120	10	38
8	16	PEG	K$_2$CO$_3$	120	9.8	86
9	16	DMF	Et$_3$N	120	10	36
10	16	DMF	KOH	120	10	55
11	16	DMF	Na$_2$CO$_3$	120	7.3	96
12	16	DMF	K$_2$CO$_3$	100	10	74

[a]Isolated yield.

Figure 6. Recycling experiment of Schiff-base-Pd@MNPs in coupling of iodobenzene with phenylboronic acid.

Table 5. Comparison of results for Schiff-base-Pd@MNPs with other catalysts for the coupling of iodobenzene with phenylboronic acid

Entry	Catalyst (mol% of Pd)	Conditions	Time (min)	Yield (%)[a]	Ref.
1	NHC–Pd(II) complex (1.0 mol%)	Tetrahydrofuran, Cs_2CO_3, 80 °C	720	88	[21]
2	Pd NPs (1.0 mol%)	H_2O, KOH, 100 °C	720	95	[22]
3	CA/Pd(0) (0.5–2.0 mol%)	H_2O, K_2CO_3, 100 °C	120	94	[23]
4	Pd/Au NPs (4.0 mol%)	EtOH–H_2O, K_2CO_3, 80 °C	1440	88	[24]
5	Pd(II)–NHC complex (1 mol%)	DMF, Cs_2CO_3, 100 °C	1440	99	[25]
6	N,N′-bis(2-pyridinecarboxamide)-1,2-benzene palladium complex (1 mol%)	H_2O, K_2CO_3, 100 °C	180	97	[26]
7	LDH–Pd(0) (0.3 g)	K_2CO_3, 1,4-dioxane–H_2O (5:1), 80 °C	600	96	[27]
8	PANI–Pd (2.2 mol%)	K_2CO_3, 1,4-dioxane–H_2O (1:1), 95 °C	240	91	[28]
9	Schiff-base-Pd@MNPs (0.81 mol%)	PEG, K_2CO_3, 60 °C	70	96	This work

[a]Isolated yield

phenylboronic acid are compared with previously reported procedures. Comparison of the results shows a better catalytic activity and shorter reaction time for Schiff-base-Pd@MNPs in the Suzuki reaction (Table 5).

Conclusions

In summary, Schiff-base-Pd@MNPs was used as a green, efficient, highly reusable and air- and moisture-stable nanocatalyst for carbon–carbon bond formation through Suzuki and Heck reactions. The advantages of these protocols are the use of a commercially available, eco-friendly, cheap and chemically stabile material. Product separation and catalyst recycling are easy with the assistance of an external magnet. This catalyst was characterized using the VSM, TEM, TGA, SEM and ICP-OES techniques. Also, the catalyst can be reused for up to six runs without any significant loss of its activity or palladium leaching.

References

[1] F. Havasi, A. Ghorbani-Choghamarani, F. Nikpour, *New J. Chem.* **2015**, *39*, 6504.
[2] A. Ghorbani-Choghamarani, B. Tahmasbi, F. Arghand, S. Faryadi, *RSC Adv.* **2015**, *5*, 92174.
[3] Y. Zhu, L. P. Stubbs, F. Ho, R. Liu, C. P. Ship, J. A. Maguire, N. S. Hosmane, *Chem CatChem* **2010**, *2*, 365.
[4] A. Ghorbani-Choghamarani, B. Tahmasbi, *New J. Chem.* **2016**, *40*, 1205.
[5] M. Hajjami, B. Tahmasbi, *RSC Adv.* **2015**, *5*, 59194.
[6] S. Shylesh, V. Schunemann, W. R. Thiel, *Angew. Chem. Int. Ed.* **2010**, *49*, 3428.
[7] M. Hajjami, A. Ghorbani-Choghamarani, R. Ghafouri-Nejad, B. Tahmasbi, *New J. Chem.* **2016**; *40*, 3066.
[8] C. W. Lim, I. S. Lee, *Nano Today* **2010**, *412*, 5.
[9] A. Rostami, B. Tahmasbi, A. Yari, *Bull. Kor. Chem. Soc.* **2013**, *34*, 1521.
[10] B. Atashkar, A. Rostami, H. Gholami, B. Tahmasbi, *Res. Chem. Intermed.* **2015**, *41*, 3675.
[11] V. Polshettiwar, R. Luque, A. Fihri, H. Zhu, M. Bouhrara, J. M. Basset, *Chem. Rev.* **2011**, *111*, 3036.
[12] S. M. Islam, A. S. Roy, P. Mondal, N. Salam, *Appl. Organometal. Chem.* **2012**, *26*, 625.
[13] S. Pasa, Y. S. Ocak, H. Temel, T. Kilicoglu, *Inorg. Chim. Acta* **2013**, *405*, 493.
[14] A. Ghorbani-Choghamarani, H. Rabiei, *Tetrahedron Lett.* **2016**, *57*, 159.
[15] S. Nadri, M. Joshaghani, E. Rafiee, *Appl. Catal. A* **2009**, *362*, 163.
[16] A. R. Hajipour, F. Rafiee, *J. Iran. Chem. Soc.* **2015**, *12*, 1177.
[17] A. Ghorbani-Choghamarani, B. Tahmasbi, P. Moradi, *Appl. Organometal. Chem.* **2016**, *30*, 422.
[18] B. Atashkar, A. Rostami, B. Tahmasbi, *Catal. Sci. Lett.* **2013**, *3*, 2140.
[19] A. Ghorbani-Choghamarani, F. Nikpour, F. Ghorbani, F. Havasi, *RSC Adv.* **2015**, *5*, 33212.
[20] Y. Y. Peng, J. Liu, X. Lei, Z. Yin, *Green Chem.* **2010**, *12*, 1072.
[21] T. Chen, J. Gao, M. Shi, *Tetrahedron* **2006**, *62*, 6289.
[22] M. Nasrollahzadeh, S. M. Sajadi, M. Maham, *J. Mol. Catal. A* **2015**, *396*, 297.
[23] V. W. Faria, D. G. M. Oliveira, M. H. S. Kurz, F. F. Goncalves, C. W. Scheeren, G. R. Rosa, *RSC Adv.* **2014**, *4*, 13446.
[24] M. Nasrollahzadeh, A. Azarian, M. Maham, A. Ehsani, *J. Ind. Eng. Chem.* **2015**, *21*, 746.
[25] Q. Xu, W. L. Duan, Z. Y. Lei, Z. B. Zhu, M. Shi, *Tetrahedron* **2005**, *61*, 11225.
[26] Q. Du, W. Zhang, H. Ma, J. Zheng, B. Zhou, Y. Li, *Tetrahedron* **2012**, *68*, 3577.
[27] S. Singha, M. Sahoo, K. M. Parida, *Dalton Trans.* **2011**, *40*, 7130.
[28] H. A. Patel, A. L. Patel, A. V. Bedekar, *Appl. Organometal. Chem.* **2015**, *29*, 1.

Supporting information

Additional supporting information may be found in the online version of this article at the publisher's web site.