(RESEARCH ARTICLE)

Magnetically recoverable Pd-SILP-Fe₃O₄@SiO₂ catalyst for the Suzuki–Miyaura cross-coupling

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Abstract

An efficient method for the synthesis of range of biaryl through Suzuki-Miyaura cross-coupling of a variety of aryl boronic acids with aryl halides employing highly water dispersible, magnetically separable, palladium tagged, magnetic nanoparticle supported, ionic liquid phase catalyst (Pd-SILP-Fe₃O₄@SiO₂) in water under aerobic conditions has been developed. This nanocatalyst exhibited high thermal stability, high catalytic efficiency, high turnover frequencies (TOF), compatibility in aqueous systems, easy magnetic recovery, and reusability up to 6th run. The major advantages of this method are mild reaction conditions, easy set-up, easy workup, low Pd loading (0.00084 mol% of Pd), higher yields, and use of water as a green solvent, which makes it both environmentally and economically appealing.

Keywords: Magnetic Nanoparticles; Supported ionic liquid; SILP; Coupling; Reusability; Water dispersible; Heterogeneous; Catalyst; Nanocatalyst

Graphical abstract

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1. Introduction

The palladium-catalyzed cross-coupling of different types of organoboron compounds with organic halides or pseudo-halides is a handy tool in organic synthesis. In 1979, Suzuki and Miyaura reported the synthesis of biaryls *via* palladium-catalyzed cross-coupling of aromatic (or vinyl) halides and boranes, boronic acids, or esters. This reaction was later known as Suzuki-Miyaura cross-coupling[1,2]. The Suzuki-Miyaura cross-coupling offers many advantages such as the use of readily available, water stable and less toxic starting materials, functional group tolerance, mild reaction conditions, high regio and stereo-selectivity, one-pot reaction with the use of a minimal amount of catalyst and high product yields. Numerous complex bioactive molecules, natural products, heterocycles, pharmaceuticals, fine chemicals, agrochemicals and modern materials were synthesized employing Suzuki-Miyaura cross-coupling[3,4]. Thus, it is now a cornerstone of modern synthetic organic chemistry and was recognized by awarding the Nobel Prize in Chemistry-2010 jointly to Richard F. Heck, Ei-ichi Negishi and Akira Suzuki "for palladium-catalyzed cross couplings in organic synthesis"[3].

A significant development in the Suzuki-Miyaura cross-coupling was mainly affected by the nature of the ligand. In 1979, the journey of the Suzuki–Miyaura cross-coupling was started with $Pd(PPh_3)_4$ tetrakis(triphenylphosphine)palladium. Recently, researchers have discovered Pd-based homogeneous catalysts like Pd(II) complexes, $Pd(OAc)_2$, Pd_2-dba_3, $PdCl_2$, $Pd(PPh_3)_2Cl_2$, $Pd(dppb)Cl_2$, and $Pd(dppf)Cl_2$[5]. In the course of development, various catalytic/solvent systems such as use of water[6-7], ionic liquids[8], deep eutectic solvents[9], PEG[10], supercritical fluids[11], hydrotropes[12], and surfactants[13] have been developed for homogeneous and heterogeneous catalysts. Considering reusability and easy separation of the catalyst variety of heterogeneous supported catalysts have been developed for which metal catalysts deposited on the surface of insoluble solid supports such as carbon, magnetic materials, silica, hydroxyapatite, zeolites, nanoparticles, metal-organic frameworks (MOF), organic polymers, clay minerals and bio-supports help minimize these disadvantages[14].

Ferrite nanoparticles (Fe_3O_4) have emerged as alternatives to conventional support materials because of their high surface area, relative non-toxicity, magnetically recoverable, comparatively low cost, and ability to act as heterogeneous catalyst supports[15]. Magnetic nanoparticle-supported ionic liquid phase catalysts (MNP-SILP) are advanced materials consisting of the properties of ILs and MNPs. Further, compared with magnetic silica core-shell nanocatalysts, MNP-supported ionic liquid phase catalysts are highly water-dispersible due to the presence of ionic liquid moiety and show higher catalytic efficiency when water is used as a solvent[16]. Numerous reports are available on Pd-SILP catalysts for Suzuki-Miyaura coupling, but only a few reports are available on MNP-supported Pd-SILP catalysts[16-17].

In this context, excellent performance of highly water dispersible palladium tagged ferrite nanoparticle supported ionic liquid phase catalyst, Pd-SILP-Fe_3O_4@SiO_2 (Figure 1) for Sonogashira coupling which was previously prepared by our group inspired us to explore its catalytic efficacy for the Suzuki-Miyaura coupling[18].
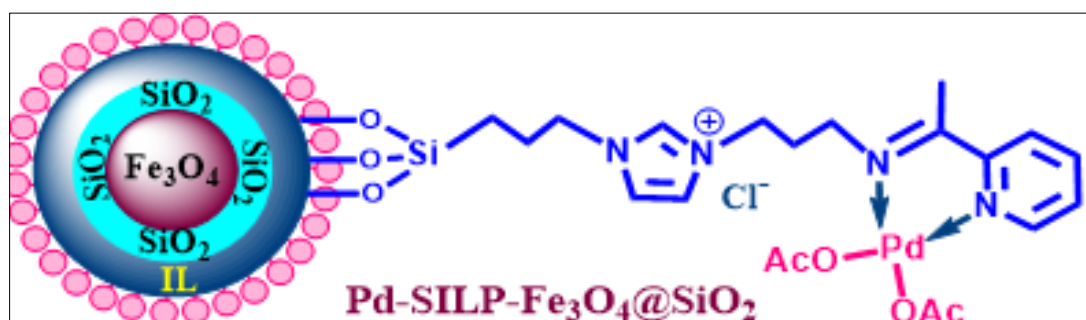

Figure 1 Pd-SILP-Fe_3O_4@SiO_2 catalyst

2. Material and method

2.1. General

Melting points were determined in an open capillary and are uncorrected. Infrared spectra were measured with a Bruker ATR infrared spectrophotometer. ^1H and ^{13}C NMR spectra were recorded on a Bruker AV 400 (400 MHz for ^1H and 100 MHz for ^{13}C NMR) spectrometer using $CDCl_3$ and DMSO-d_6 as solvent and tetramethylsilane (TMS) as an internal standard.

2.2. Materials

Aryl halides (Sigma Aldrich, Spectrochem, Alfa Aesar), phenylboronic acid (Alfa Aesar, Sigma Aldrich, Spectrochem). All other reagents and solvents were commercially obtained and used without further purification. All reactions were carried out in an air atmosphere in pre-dried glassware.

2.3. General procedure for Suzuki−Miyaura cross-coupling:

A mixture of aryl halide (1 mmol), aryl boronic acid (1.2 mmol), Pd-SILP-Fe_3O_4@SiO_2 catalyst (50 mg) and K_2CO_3 (2 mmol) in water (5 mL), stirred at 80 ℃ for an appropriate time under aerobic condition. The progress of a reaction was monitored by thin-layer chromatography (TLC) using alumina-backed silica gel 60 (F254) plates eluting with an ethyl acetate-petroleum ether solvent system. After completion of the reaction, the reaction mixture was cooled to room temperature; the catalyst was separated magnetically using a bar magnet. The product was extracted with ethyl acetate (4 × 5 mL) and the combined organic layer was washed with brine solution (5 mL) and dried over $MgSO_4$. The organic layer was then concentrated on a rotary evaporator afforded corresponding crude product. The crude product obtained was purified by column chromatography using ethyl acetate-petroleum ether (1-20%) as eluent to afford a pure coupling product.

2.4. Reusability of the catalyst

After completion of the model reaction, the catalyst was magnetically recovered using a bar magnet and washed with ethanol (2 x 5 mL) and acetone (2 x 5 mL). The recovered catalyst was dried under reduced pressure and reused for the next cycle employing similar reaction conditions. The reusability of the catalyst was investigated for up to 6 cycles for Suzuki−Miyaura cross-coupling under optimized reaction conditions.

2.5. Spectral Data

2.5.1. *1,1'-biphenyl* (Table 3, Entry 1)

White solid, mp 68–72 ℃ (Lit.[40] 69-70 ℃); IR (Neat): 3045, 1466, 1400, 910, 829, 739, 683 cm-1; ^{1}H NMR (400 MHz, $CDCl_3$), δ (ppm): 7.28-7.35 (m, 2H), 7.43- 7.48 (m, 4H), 7.63-7.76 (m, 4H); ^{13}C NMR (100 MHz, $CDCl_3$), δ (ppm): 127.08, 127.38, 128.82, 141.73.

2.5.2. *1-([1,1'-biphenyl]-4-yl)ethan-1-one* (Table 3, Entry 2)

White solid, mp 118-120 ℃ (Lit.[40] 119-120 ℃); IR (Neat): 2933, 1689, 1589, 1479, 1401, 1356, 1252, 1001, 951, 835, 756, 680, 588 cm-1; ^{1}H NMR (400 MHz, $CDCl_3$), δ (ppm) 2.62 (s, 3H, CH_3), 7.38–7.47 (m, 3H), 7.63 (d, 2H, J = 8 Hz), 7.69 (d, 2H, J = 8 Hz), 8.04 (d, 2H, J = 8 Hz). ^{13}C NMR (100 MHz, $CDCl_3$), δ (ppm): 26.66, 127.26, 127.30, 128.25, 128.94, 128.97, 134.95, 139.87, 149.32, 195.98.

2.5.3. *[1,1'-biphenyl]-4-carbaldehyde* (Table 3, Entry 2)

White solid, mp 58-60 ℃ (Lit.[33] 58-59 ℃); IR (Neat): 3111, 3032, 2983, 2849, 2759, 1694, 1597, 1410, 1285, 1111, 999,931, 847, 739 689 cm-1; ^{1}H NMR (400 MHz, $CDCl_3$) δ (ppm): 7.46-7.50 (m, 3H), 7.64 (d, 2H, J = 8 Hz), 7.70 (d, 2H, J = 8 Hz), 7.64 (d, 2H, J = 8 Hz), 10.06 (s, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ (ppm): 127.20, 17.35, 127.72, 128.31, 128.98, 130.75, 139.92, 146.51, 191.95.

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3. Result and discussion

Excellent performance of Pd-SILP-Fe_3O_4@SiO_2 (Figure 1) for the Sonogashira coupling which is reported by our group[18] inspired us to explore its catalytic efficiency over other carbon-carbon bond forming reactions. To accomplish this goal, a highly water dispersible palladium tagged ferrite nanoparticle supported ionic liquid phase catalyst (Pd-SILP-Fe_3O_4@SiO_2) was employed for the Suzuki-Miyaura cross-coupling.

Initially, we focused on optimizing parameters such as suitable solvent, base and amount of catalyst for Suzuki-Miyaura cross-coupling. The model reaction has been carried out using iodobenzene and phenylboronic acid as coupling partners and dimethylformamide as a solvent at room temperature in the presence of triethylamine as a base and Pd-SILP-Fe_3O_4@SiO_2 as a catalyst. No product formation was observed even after 15 h. (Entry 1; Table 1) hence reaction was carried out under reflux conditions (Figure 2). Gratifyingly, an excellent yield of 94% within 2 h was observed. (Entry 2; Table 1) Inspired by these results, we shifted our attention towards optimizing the best suitable solvent for the reaction. A model reaction has been carried out using various solvents, keeping other conditions same. It was observed that water-mediated reactions afforded a higher yield of 95% with a shorter reaction time of 1 h. (Entry 4;

Table 1). Hence, water was selected as the best suitable solvent for the Suzuki-Miyaura coupling using Pd-SILP-Fe_3O_4@SiO_2 as a catalyst under reflux conditions.

Next, considering the importance of the base, we investigated the suitable base for the reaction. A model reaction was executed using different bases such as NaOH, KOH, DABCO, Et_3N, DBU, and K_2CO_3 etc. It was observed that K_2CO_3 is the best suitable with the highest yield of 97% in 1 h. (Entry 4; Table 2).
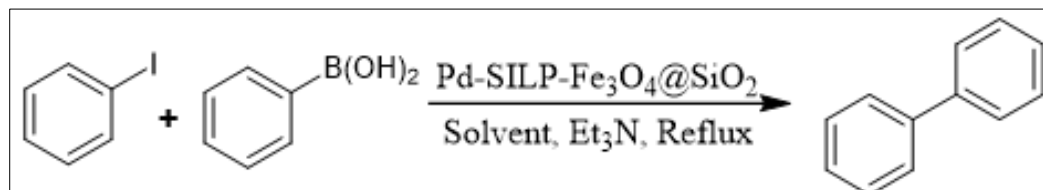

Figure 2 Suzuki-Miyaura coupling of iodobenzene and phenylboronic acid using Pd-SILP-Fe_3O_4@SiO_2 catalyst and Et_3N base under reflux condition

Table 1 Optimization of solvent for the Suzuki-Miyaura coupling

Entry	Solvent	Time (h)	Yield (%)[a]
1	DMF	15	NR[b]
2	DMF	2	94
3	MeOH	2	92
4	Water	1	95
5	EtOH	2	89
6	MeCN	3	87
7	THF	3	92

Reaction conditions: Iodobenzene (1 mmol), Phenylboronic acid (1.1 mmol), Pd-SILP-Fe_3O_4@SiO_2 (100 mg), Et_3N (2 mmol), Solvent (5 mL) [a]Isolated yield, [b]Room temperature, NR- no reaction

Table 2 Optimization of base for Suzuki-Miyaura cross-coupling

Entry	Base	Time (h)	Yield (%)[a]
1	NaOH	3	86
2	KOH	3	85
3	Et_3N	2.5	88
4	K_2CO_3	1	97
5	DABCO	4	80
6	DBU	4	81

Reaction conditions: Iodobenzene (1 mmol), Phenylboronic acid (1.1 mmol), Pd-SILP-Fe_3O_4@SiO_2 (100 mg), Base (2 mmol), Water (5 mL) [a]Isolated yield.

Optimization of the catalyst loading was done by employing the different amount of catalyst for the model reaction. It was observed that only 40 mg of catalyst was sufficient to carry out the reaction efficiently (Entry 4; Table 3). Notably, there was no difference in yield and reaction time when catalyst loading was increased. However, a longer time was required to complete a reaction with an inferior yield when reduced catalyst loading. Further, no product formation

was observed when the reaction was executed without the catalyst, indicates the role of Pd-SILP-Fe$_3$O$_4$@SiO$_2$ as a catalyst.

Table 3 Optimization of catalyst loading for Suzuki-Miyaura coupling

Entry	Catalyst loading (mg)	Catalyst Loading (Mol% Pd)	Time (h)	Yield (%)[a]	TON	TOF (min^{-1})
1	80	0.0017	1	97	57058	950
2	60	0.0013	1	97	74615	1243
3	50	0.0010	1	97	97000	1616
4	40	0.00084	1	97	115476	1924
5	30	0.00063	2	85	134920	1124
6	20	0.00042	4	80	190476	793

Reaction conditions: Iodobenzene (1 mmol), Phenylboronic acid (1.1 mmol), Pd-SILP-Fe$_3$O$_4$@SiO$_2$, K$_2$CO$_3$ (2 mmol), water (5 mL) [a]Isolated yield.

Table 4 Optimization of temperature for Suzuki-Miyaura coupling reaction

Entry	Temperature (°C)	Time (h)	Yield (%)[a]
1	100	3	86
2	90	3	85
3	80	1	97
4	70	2.5	72

Reaction conditions: Iodobenzene (1 mmol), Phenylboronic acid (1.1 mmol), Pd-SILP-Fe$_3$O$_4$@SiO$_2$ (40 mg), K$_2$CO$_3$ (2 mmol), water (5 mL) [a]Isolated yield.

Finally, the optimum temperature for the model reaction has been investigated (Table 4). A model reaction has been carried out under various temperature conditions. It was observed that 80 °C is the optimum temperature for the model reaction above which yield remains constant while below yield decreases sharply (Entry 3, Table 4).

With optimized reaction conditions in hand, the generality of the method was tested by performing Suzuki-Miyaura coupling between diversely substituted aryl halides and a variety of aryl boronic acids (Figure 3). A wide range of electronically diverse aryl iodides, bromides and chlorides were coupled with various substituted aryl boronic acids in excellent yields. Various aryl halides bearing electron-withdrawing groups such as cyano, nitro, carbonyl and electron donating groups such as methyl and methoxy react smoothly with substituted aryl boronic acids to afford biaryls in excellent yields (Entries 4-8, 11-15, 18-22; Table 5). It is worth noting that highly active aryl iodide and bromide react efficiently to form coupling products in excellent yield in a short reaction time, whereas less active aryl chlorides also react smoothly to afford corresponding coupling products in moderate yields.

It was observed that a coupling of phenylboronic acid with aryl iodide bearing electron withdrawing group afforded a higher yield of the product than that of having electron-donating groups. This may be due to the fact that the electron-withdrawing groups of aryl halide facilitate the rate-limiting oxidative addition step. It was also observed that electron-rich aryl boronic acids coupled more effectively than electron–neutral or electron-deficient aryl boronic acids (Entries 9–23; Table 5). Synthesized compounds were characterized by various spectroscopic methods.

A reaction of phenylboronic acid with 4-iodoacetophenone afforded 1-([1,1'-biphenyl]-4-yl)ethan-1-one as a coupling product with 97% yield (Entry 4, Table 5). The IR spectrum of the *1-([1,1'-biphenyl]-4-yl)ethan-1-one* displays carbonyl stretching frequency around 1689 cm^{-1} while bands at 1589 and 1479 cm^{-1} are due to C=C stretching frequency.
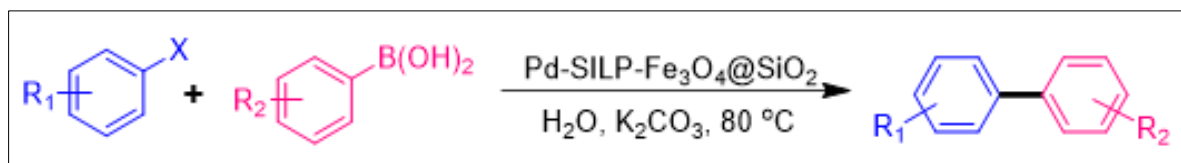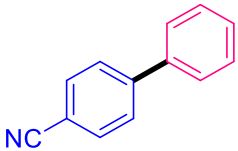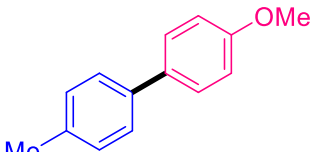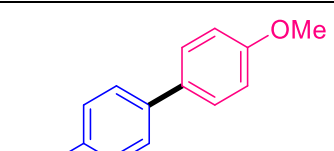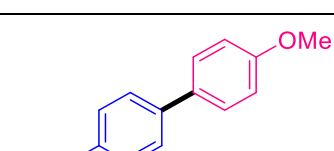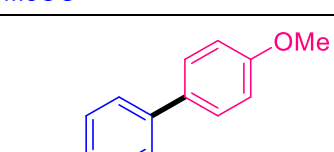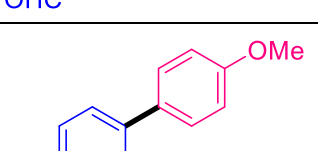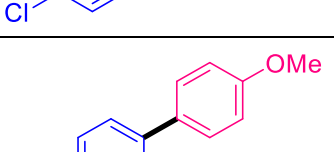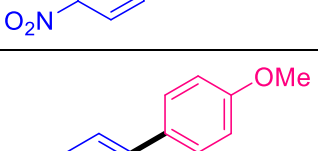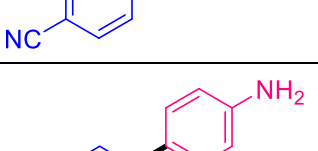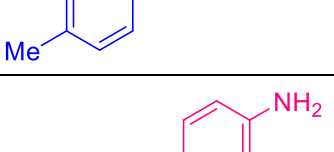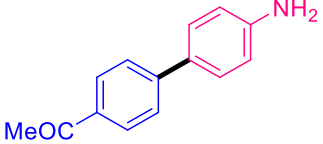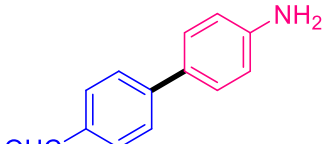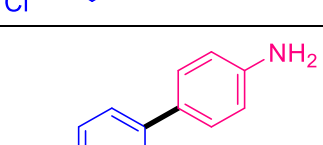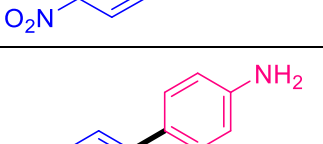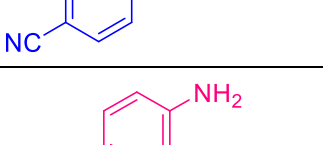
Figure 3 General reaction of Suzuki-Miyaura coupling

Table 5 Suzuki-Miyaura coupling of aryl halides with aryl boronic acids

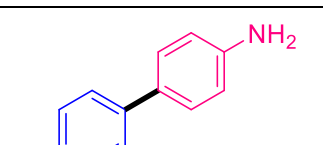| Entry	X	R₁	R₂	Product	Time [h]	Yield[a] [%]	TOF [min⁻¹]
1	I	H	H		1	97	1924
2	I	Me	H		1.5	95	1256
3	Br	OMe	H		2.5	89	706
4	I	COMe	H		1	97	1924
5	Br	CHO	H		2.5	90	714
6	I	Cl	H		1.5	96	1269
7	I	NO₂	H		1	98	1944

8	I	CN	H		1	98	1944
9	Br	Me	OMe		3	88	582
10	Cl	OMe	OMe		3.5	85	481
11	I	COMe	OMe		1	98	1944
12	I	CHO	OMe		1	98	1944
13	I	Cl	OMe		1	95	1884
14	I	NO_2	OMe		1	99	1964
15	I	CN	OMe		1	98	1944
16	I	Me	NH_2		1.5	94	1243
17	Br	OMe	NH_2		3	90	595

18	I	COMe	NH$_2$		1	97	1924
19	Cl	CHO	NH$_2$		3	90	595
20	I	Cl	NH$_2$		1.5	94	1243
21	I	NO$_2$	NH$_2$		1	99	1964
22	I	CN	NH$_2$		1	98	1944
23	Cl	H	NH$_2$		3.5	86	467

Reaction conditions: Aryl halide (1 mmol), arylboronic acid (1.1 mmol), Pd-SILP-Fe$_3$O$_4$@SiO$_2$ (0.00084 mol% Pd), K$_2$CO$_3$ (2 mmol), water (5 mL) [a]Isolated yield.

^{1}H NMR spectrum of the same compound exhibited a singlet at δ 2.62 ppm for methyl protons of the acetyl group. The remaining nine aromatic protons appeared as three doublets around δ 8.04, 7.69 and 7.63 ppm with a coupling constant J = 8 Hz for six protons and a multiplet at δ 7.38- 7.47 ppm for three protons. ^{13}C NMR spectrum of the same compound displayed two remarkable signals at δ 26.66 and 195.98 ppm for methyl carbon and carbonyl carbon, respectively. A signal appeared at δ 149.3 ppm due to aromatic carbon attached directly to the carbonyl carbon. A signal appeared at δ 127.26, 127.30, 128.25, 128.94, 128.97, 134.95 and 139.87 due to the remaining aromatic carbons present in the product. All the spectroscopic data was in agreement with the expected structure.

Finally, the reusability of the Pd-SILP-Fe$_3$O$_4$@SiO$_2$ catalyst was investigated for the reaction between iodobenzene and phenylboronic acid under optimized reaction conditions. After completion of the reaction, the catalyst Pd-SILP-Fe$_3$O$_4$@SiO$_2$ was separated employing a bar magnet, washed thoroughly with ethanol, dried at 50 °C for 6 h and reused for the next run. The product was extracted from the reaction mixture using ethyl acetate. The recovered catalyst was reused for at least six cycles without significant loss in the catalytic activity. (Fig. 4)
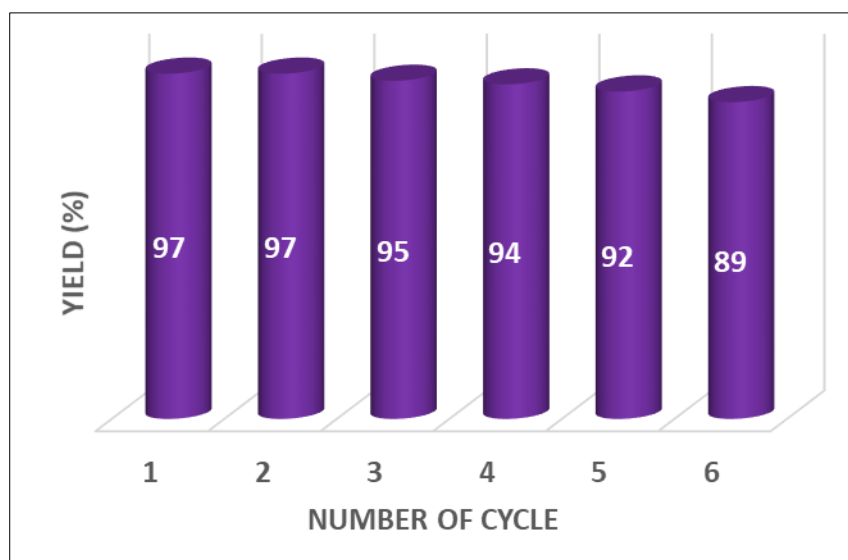
Figure 4 Reusability of the catalyst

Table 6 Comparison of the catalytic activity of the Pd-SILP-Fe_3O_4@SiO_2 catalyst with other supported and Pd-SILP catalysts

Entry	Catalyst[ref]	Reaction conditions	Time (min)	Yield (%)[a]	TOF (min^{-1})
1	Mag-IL-Pd[19]	K_2CO_3, H_2O, 60 °C, 0.025 mol% Pd	360	95	633
2	SBA-15-Pd-2[15]	K_2CO_3, EtOH/H_2O, 50 °C, 0.1 mol% Pd	60	95	15.83
3	Pd@SILP-PS[20]	K_2CO_3, EtOH, RT, 0.20 mol% Pd	20	96	4.8
4	FemSILP-NHC-Pd complex[21]	K_3PO_4, EtOH, Reflux, 0.05 mol% Pd	20	80	80
5	SiO_2-BisILsR[PdEDTA][16]	Na_2CO_3, H_2O, 100 °C, 0.1 mol% Pd	360	99	0.33
6	Pd-M-T-S[17]	K_2CO_3, EtOH/H_2O, RT, 0.1 mol% Pd	30	99	30
7	SG-MNP-PEI-Pd[22]	Cs_2CO_3, dioxane, 90 °C,	960	88	-
8	HNT-IL-2[23]	K_2CO_3, 120 °C, H_2O/EtOH, MW, 0.1 mol% Pd	10	99	99
9	Pd-SILP-Fe_3O_4@SiO_2	K_2CO_3, H_2O, 80 °C, 0.00084 mol% Pd (present work)	60	97	1924

The catalytic efficiency of the Pd-SILP-Fe_3O_4@SiO_2 was compared with numerous heterogeneous, Pd-SILP catalysts reported previously for the Suzuki-Miyaura cross-coupling of iodobenzene and phenylboronic acid. From these results, it was observed that the catalyst, Pd-SILP-Fe_3O_4@SiO_2 was equally efficient in terms of yield and reaction time but superior in terms of metal loading and turnover frequency to most of the Pd-SILP catalytic systems (Entry 9, Table 6).

4. Conclusion

In summary, we have explored Pd-SILP-Fe_3O_4@SiO_2 as a highly water dispersible, magnetically separable and robust heterogeneous catalyst for the synthesis of biaryl through Suzuki-Miyaura cross-coupling of a variety of aryl boronic acids with aryl halides. The Suzuki-Miyaura cross-coupling of aryl iodides, bromides and even less reactive chlorides

with aryl boronic acids produced corresponding coupling products in good to excellent yield. The reaction was carried out using water as a green solvent with a very low loading of the catalyst (0.00084 mol%). Easy recovery and reusability of catalyst at least six consecutive reaction cycles without significant loss in the catalytic activity makes the protocol highly efficient, economical and ecological.

Supplementary Information

Supplementary information associated with this article is available at https://rb.gy/pd10vo

Compliance with ethical standards

Acknowledgement

Disclosure of conflict of interest

The author declares no conflict of interest.

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