

(RESEARCH ARTICLE)



Pd-SILP-Fe₃O₄@SiO₂: An efficient supported ionic liquid phase catalyst for the Mizoroki-Heck coupling

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Abstract

An efficient method for the Mizoroki-Heck coupling of aryl halides with alkenes employing already reported palladium tagged, magnetic nanoparticle supported, ionic liquid phase catalyst (Pd-SILP-Fe₃O₄@SiO₂) in water under aerobic conditions has been developed. Various di-substituted alkenes were synthesized with excellent yields using a highly water dispersible Pd-SILP-Fe₃O₄@SiO₂ catalyst. This nanocatalyst displayed high thermal stability, compatibility in aqueous systems, high catalytic efficiency, high turnover frequencies (TOF), easy magnetic recovery, and reusability up to 6th run. The main advantages of the protocol are its robustness, mild reaction conditions, easy set-up, easy workup, low Pd loading (0.001 mol% of Pd), higher yields, and use of water as a green solvent, which makes it both environmentally and economically appealing.



Keywords: Supported ionic liquid; Magnetic Nanoparticles; Mizoroki-Heck coupling; Reusability; Water dispersible catalyst; SILP

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1. Introduction

The construction of a carbon-carbon (C–C) bond *via* cross-coupling reactions is one of the most important and powerful tools in synthetic organic chemistry; as a result, various new coupling reactions forming the C–C bond were invented and developed by the scientific community since 1855. These coupling reactions played an enormously decisive role in shaping synthetic organic chemistry, conceptualizing and building an innovative and highly significant process¹. These reactions stimulated keen interest and dedicated efforts towards broadening the scope of these reactions which led to the development of milder conditions with lower Pd loadings, use of more efficient catalytic systems involves a variety of ligands having different electronic and steric properties. Ultimately, the employment of these potent ligands resulted in the discovery of novel cross-couplings that produced additional bonds (e.g. C–N, C–O, C–P, C–S, C–B).

These coupling reactions played an important role in the synthesis of a variety of pharmaceutical drugs and their precursors, fine chemicals, functionalized structures, biologically active compounds, natural products, organic building blocks and their intermediates, etc^{2,3}. The Nobel Prize in Chemistry-2010 was awarded jointly to Richard F. Heck, Ei-ichi Negishi and Akira Suzuki for “palladium-catalyzed cross couplings in organic synthesis”¹. The Mizoroki-Heck cross-coupling is one of the powerful and simple method for the coupling of alkenes with a variety of aryl or alkyl halides to afford substituted alkenes, dienes and conjugated polymers, etc^{4,5}. Mizoroki and co-workers reported a palladium-catalyzed arylation of olefinic compounds with aryl iodides using palladium black obtained from palladium chloride as a catalyst and potassium acetate as a base in methanol at 120 °C⁶ (Figure 1).

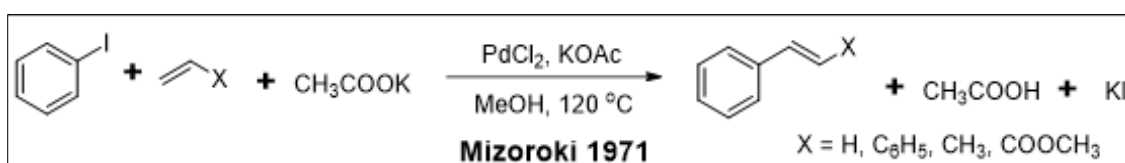


Figure 1 Palladium-catalyzed arylation of olefinic compounds reported by Mizoroki

Later on, Heck and co-workers independently reported a coupling reaction under much more convenient laboratory conditions between halides (aryl, benzyl, styryl) with terminal alkenes (styrene, 4-nitrostyrene, *cis*-1-phenyl-1-propene, methyl acrylate) using palladium acetate as catalyst and tri-*n*-butylamine as a base without the use of solvent at steam temperature⁷ (Figure 2).

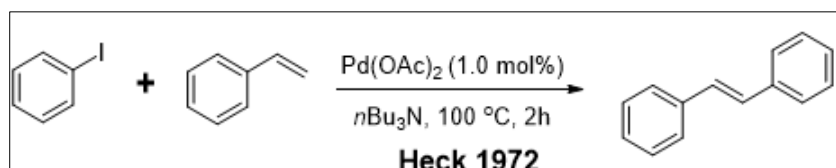


Figure 2 A coupling reaction reported by Heck

The Mizoroki-Heck coupling is broadly defined as “the palladium-catalyzed coupling of alkenyl or aryl (sp^2) halides or triflates with alkenes to yield highly substituted vinyl arenes” (Figure 3). Nowadays, the Mizoroki-Heck reaction stands as a highly robust, reliable and efficient way to generate carbon-carbon bonds, especially in creating tertiary and quaternary stereo centers and intramolecular ring formation. This reaction was highly explored in various areas because of its high efficiency, high chemo-selectivity, simple reaction conditions, and use of cost-effective and low toxic reagents⁸.

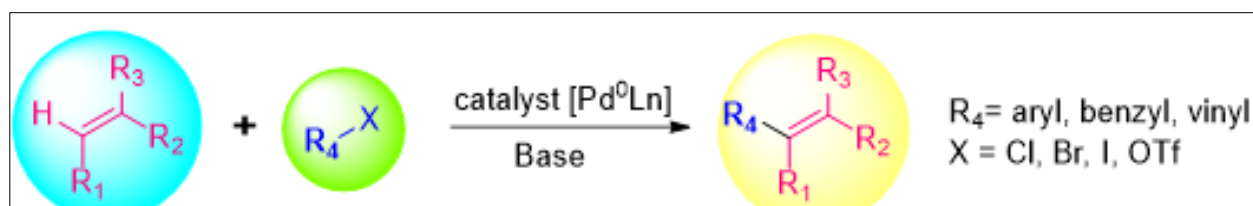


Figure 3 General reaction of Mizoroki-Heck coupling

The Mizoroki-Heck coupling can be executed using heterogeneous or homogeneous Pd (0) or Pd (II) complexes with a variety of ligands. Generally, in homogeneous catalysis, phosphines are the most commonly used ligands⁹. It is observed that a homogeneous catalyst such as a complex of palladium (0) or palladium (II) display admirable performance in the Heck coupling¹⁰. However, homogeneous catalysis has some significant downsides, including the high toxicity of the catalyst and ligands, their susceptibility to air and moisture and their expensive cost, which limits their large-scale use¹⁰. Consequently, over the past few decades, significant efforts have been made to develop phosphine-free Pd complexes that catalyze the Heck coupling using other stable ligands, such as N-heterocyclic carbenes¹¹, bispyridine¹², bispyrazole derivatives¹³, bisimidazole¹⁴, oximes¹⁵ and Schiff bases¹⁶. Despite the impressive advancements made in Mizoroki-Heck coupling, there is still a significant need for cost-effective, environmentally friendly and practical cross-coupling methods that use heterogeneous catalysts with extremely low catalyst loadings and have high turn-over numbers. Researchers have immobilized the parent homogeneous Pd-catalysts on various types of organic or inorganic supports to create heterogeneous catalysts, which would provide the benefits such as easy separation and recycling¹⁷⁻¹⁹.

A new class of ILs called supported ionic liquids (SILs) is designed by immobilizing ILs onto a porous high area support material surface either by covalent bonding or adsorption interactions, which possess advantages of ionic liquid media with solid support materials²⁰. The most common supports used to immobilize ILs are silica, polymer, cellulose, graphene oxide, iron oxides/ferrite/magnetic nanoparticles ($\text{Fe}_3\text{O}_4/\text{MNP}$), activated carbon, carbon nanotubes, chitosan, modified montmorillonite and molecular sieves²¹⁻²². This SILP catalysts are highly efficient for the Mizoroki-Heck coupling.

In this context, highly water dispersible palladium tagged ferrite nanoparticle supported ionic liquid phase catalyst Pd-SILP- $\text{Fe}_3\text{O}_4@/\text{SiO}_2$ (Figure 4) which was previously synthesized by our group²³ was employed for the Mizoroki-Heck coupling.

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 $\text{DMSO}-d_6$ as solvent and tetramethylsilane (TMS) as an internal standard.

2.2. Materials

Aryl halides (Sigma Aldrich, Spectrochem, Alfa Aesar), methyl acrylate (Alfa Aesar), styrene (Sigma Aldrich), *tert*-Butyl acrylate (Spectrochem), acrylonitrile (Spectrochem), and triethyl amine (Spectrochem) were used as received. 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 Mizoroki-Heck coupling

A mixture of aryl halide (1.0 mmol), alkene (1.1 mmol), triethylamine (2.0 mmol), and catalyst Pd-SILP- $\text{Fe}_3\text{O}_4@/\text{SiO}_2$ (50 mg) in water (5 mL) was stirred at 90 °C 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 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 completing the model reaction, the catalyst was magnetically recovered using a bar magnet and washed with ethanol (2 × 5 mL) and acetone (2 × 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 Mizoroki-Heck coupling under optimized reaction conditions.

2.5. Spectral Data

2.5.1. (*E*)-1-(4-styrylphenyl)ethan-1-one (Table 5, Entry 3)

White solid, m.p. obs. 144–146 °C (Lit.²⁶ 144 °C); IR (Neat) : 3031, 2977, 2927, 1691, 1588, 1407, 1350, 1253, 1168, 958, 817, 754, 688, 595 cm⁻¹; ¹H NMR (CDCl₃, 400 MHz): δ (ppm): 2.61 (s, 3H), 7.13 (d, 1H, *J* = 15.9 Hz), 7.23 (d, 1H, *J* = 15.9 Hz), 7.30 (m, 2H), 7.35-7.40 (m, 4H), 7.53-7.60 (m, 1H), 7.95 (d, 2H, *J* = 8 Hz); ¹³C NMR (CDCl₃, 100 MHz) : δ 26.58, 126.52, 126.84, 127.49, 128.35, 128.81, 128.89, 131.51, 136.01, 136.74, 142.05, 197.49.

2.5.2. Methyl (*E*)-3-(4-methoxyphenyl)acrylate (Table 5, Entry 6)

White Solid, m.p. obs. 106-107 °C (Lit.²⁴ 106 °C); IR (Neat): 3034, 2944, 1710 1633, 1506, 1451, 1298, 1284, 1250, 1166, 980, 816, 761, 652 cm⁻¹; ¹H NMR (CDCl₃, 400 MHz): δ 3.79 (s, 3H), 3.84 (s, 3H), 6.31 (d, 1H, *J* = 16 Hz), 6.90 (d, 2H, *J* = 8.5 Hz), 7.47 (d, 2H, *J* = 8.5 Hz), 7.65 (d, 1H, *J* = 16 Hz); ¹³C NMR (CDCl₃, 100 MHz): δ 51.57, 55.39, 114.36, 115.33, 127.18, 129.74, 144.54, 161.43, 167.77.

2.5.3. Methyl (*E*)-3-(4-acetylphenyl)acrylate (Table 5, Entry 7)

White Solid, m.p. obs. 104-106 °C (Lit.²⁴ 103-105 °C); IR (Neat) : 2939, 2918, 1707, 1669, 1620, 1421, 1322, 1253, 1160, 999, 959, 917, 817, 666 cm⁻¹; ¹H NMR (CDCl₃, 400 MHz) δ (ppm): 2.62 (s, 3H), 3.83 (s, 3H), 6.53 (d, 1H, *J* = 16 Hz), 7.61 (d, 2H, *J* = 8 Hz), 7.71 (d, 1H, *J* = 16 Hz), 7.97 (d, 2H, *J* = 8 Hz); ¹³C NMR (CDCl₃, 100 MHz) : δ (ppm): 26.68, 51.90, 120.38, 128.16, 128.88, 138.09, 138.74, 143.32, 166.94, 197.29.

2.5.4. (*E*)-1-methoxy-4-styrylbenzene (Table 5, Entry 2)

White Solid, m. p. obs. 134-136 °C (Lit.²⁵ 135.1 - 137 °C); IR (Neat): 2935, 1593, 1300, 1241, 1171, 1025, 963, 817, 750, 685 cm⁻¹; ¹H NMR (CDCl₃, 400 MHz) δ (ppm): 3.83 (s, 3H), 6.90 (d, 2H, *J* = 8 Hz), 6.97 (d, 1H, *J* = 16 Hz), 7.07 (d, 1H, *J* = 16 Hz), 7.21-7.25 (m, 2H), 7.32-7.36 (m, 2H), 7.43-7.50 (m, 4H); ¹³C NMR (CDCl₃, 100 MHz): δ (ppm): 55.03, 114.2, 126.3, 126.6, 127.2, 127.7, 128.2, 128.6, 130.1, 137.7, 159.3.

3. Result and discussion

The excellent performance of Pd-SILP-Fe₃O₄@SiO₂ for the Sonogashira coupling inspired us to explore its catalytic efficiency for other coupling reactions. To accomplish this goal, a highly water dispersible palladium tagged ferrite nanoparticle supported ionic liquid phase catalyst (Pd-SILP-Fe₃O₄@SiO₂) was employed for the Mizoroki-Heck coupling.

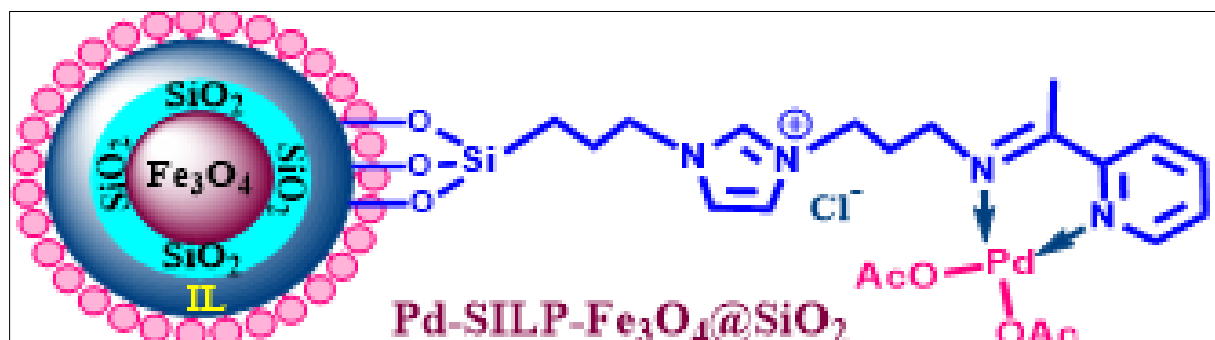
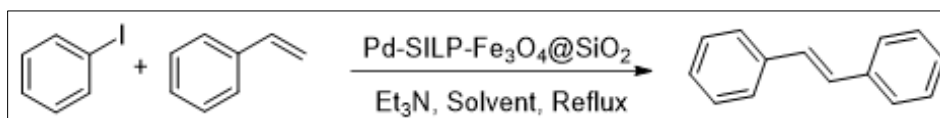


Figure 4 Pd-SILP-Fe₃O₄@SiO₂ catalyst

An efficient Pd-SILP catalyst in hand, initially, we focused on optimization of parameters such as suitable solvent, base and amount of catalyst for the Mizoroki-Heck coupling. The model reaction has been carried out using iodobenzene and styrene as coupling partners and dimethylformamide as a solvent at room temperature in the presence of triethylamine as a base and Pd-SILP-Fe₃O₄@SiO₂ as a catalyst. No product formation was observed even after 12 hours (Entry 1, Table 1); hence reaction was carried out under reflux conditions. Gratifyingly, an excellent yield of 92% 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 2 h. (Entry 4, Table 1) Hence water was selected as the best suitable solvent for the Mizoroki-Heck coupling reaction using Pd-SILP-Fe₃O₄@SiO₂ as a catalyst under reflux conditions.

Table 1 Solvent optimization for the Mizoroki Heck coupling

Entry	Solvent	Time (h)	Yield (%) ^a
1	DMF	12	NR ^b
2	DMF	2	92
3	MeOH	2	91
4	Water	2	95
5	EtOH	2	89
6	MeCN	2	87

Reaction conditions: Iodobenzene (1 mmol), styrene (1.1 mmol), Et₃N (2 mmol), Pd-SILP-Fe₃O₄@SiO₂ (0.1 g), solvent (5 mL), ^aIsolated yield, ^bRoom temp.

Next, considering the importance of the base, we investigated the best suitable base for the reaction. A model reaction was executed using different bases such as NaOH, KOH, DABCO, Et₃N, DBU, K₂CO₃, etc. It was observed that Et₃N is the best suitable base with the highest yield of 95%. (Entry 4, Table 2)

Table 2 Optimization of base for the Mizoroki-Heck coupling

Entry	Base	Time (h)	Yield (%) ^a
1	NaOH	3	86
2	KOH	3	85
3	K ₂ CO ₃	2.5	88
4	Et ₃ N	2	95
5	DABCO	4	80
6	DBU	4	81

Reaction conditions: Iodobenzene (1 mmol), styrene (1.1 mmol), Base (2 mmol), Pd-SILP-Fe₃O₄@SiO₂ (0.1 g), water (5 mL), reflux, ^aIsolated yield, ^bRoom temp.

Table 3 Optimization of catalyst loading for Mizoroki-Heck coupling

Entry	Catalyst loading (mg)	Catalyst Loading (mol% Pd)	Time (h)	Yield (%) ^a	TON	TOF (min ⁻¹)
1	80	0.0017	2	95	55882	465
2	60	0.0013	2	95	73076	608
3	50	0.0010	2	95	95000	791
4	40	0.00084	3	92	109523	608
5	30	0.00063	4	88	139682	582
6	20	0.00042	5	61	145238	484

Reaction conditions: Iodobenzene (1 mmol), styrene (1.1 mmol), Pd-SILP-Fe₃O₄@SiO₂, Et₃N (2 mmol), water (5 mL), reflux, ^aIsolated yield.

Optimization of the catalyst loading was done by employing the different amounts of catalyst for the model reaction. It was observed that only 50 mg of catalyst was sufficient to carry out the reaction efficiently (Entry 3, 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, which indicates the role of Pd-SILP-Fe₃O₄@SiO₂ as catalyst.

Finally, model reaction has been carried out at various temperatures to investigate the optimum temperature. It was observed that 90 °C is the optimum temperature for the model reaction above which yield remains constant while below it yield decreases sharply. (Entry 4, Table 4)

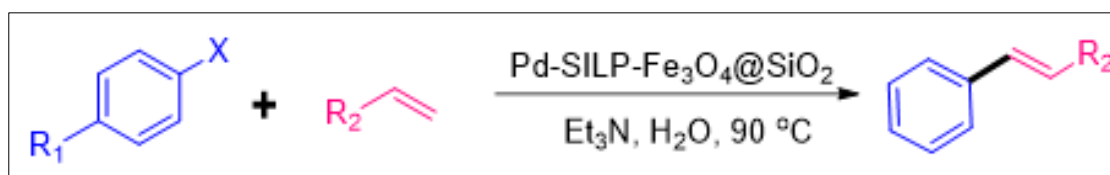
Table 4 Temperature optimization for the Mizoroki-Heck coupling

Entry	Temperature (°C)	Time (h)	Yield (%) ^a
1	110	2	95
2	100	2	95
3	90	2	95
4	80	2	90
5	70	4	64
6	60	4	50

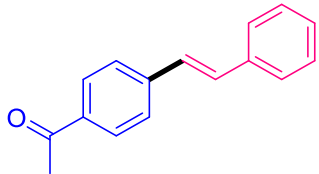
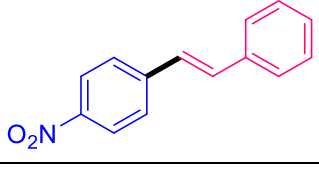
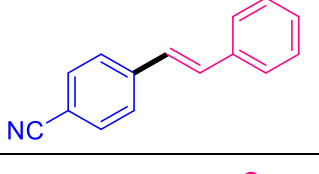
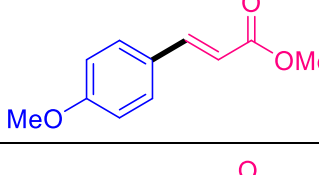
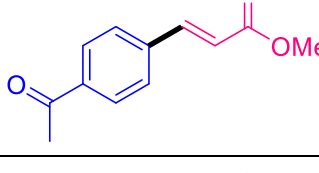
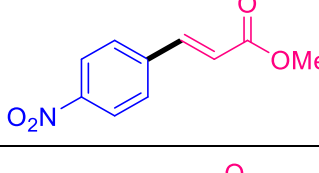
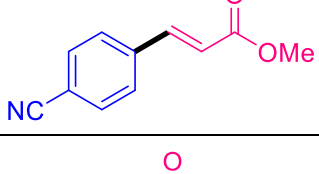
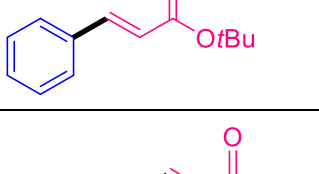
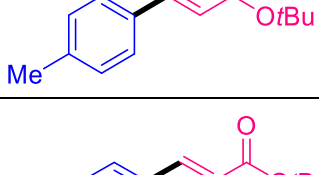
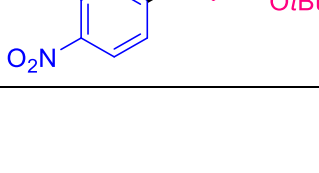
Reaction conditions: Iodobenzene (1 mmol), styrene (1.1 mmol), Pd-SILP-Fe₃O₄@SiO₂ (0.05 g), Et₃N (2 mmol), water (5 mL), ^aIsolated yield.

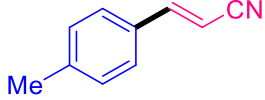
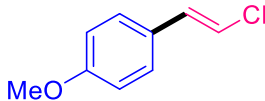
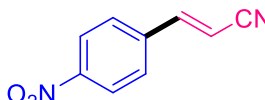
With optimized reaction conditions in hands, the generality of the method was tested by performing Mizoroki-Heck coupling between diversely substituted aryl halides and a variety of alkenes. A reaction of styrene with aryl iodide afforded a higher yield of 95% with a high turn-over frequency of 47500 h⁻¹ (Entry 1, Table 5), whereas aryl chloride displayed a lower yield of 71% with a lower turn-over frequency (14200 h⁻¹) (Entry 5, Table 5). Aryl halides with electron-withdrawing groups afford higher yields (Entries 3-5, 8-9, 12, 15, Table No. 5) than those with electron-donating groups (Entries 2, 11, 13-14, Table 5). Next, to explore the generality of the protocol, a variety of alkenes such as methyl acrylate, *tert*-butyl acrylate and acrylonitrile were employed for the coupling reactions. It was observed that all the coupling reactions with aryl iodides work smoothly with the excellent yield of the product, while aryl bromides and chlorides afforded a moderate yield. Synthesized compounds were characterized by various spectroscopic methods.

Table 5 Mizoroki-Heck coupling of a different aryl halide with alkenes



Entry	R ₁	X	R ₂	Product	Time (h)	Yield (%)	TOF (h ⁻¹)
1	H	I	Ph		2	95	47500
2	OMe	I	Ph		2	92	46000

3	COMe	I	Ph		2	96	48000
4	NO ₂	I	Ph		2	96	48000
5	CN	Cl	Ph		5	71	14200
6	OMe	I	CO ₂ Me		2	91	45500
7	COMe	I	CO ₂ Me		2	92	46000
8	NO ₂	I	CO ₂ Me		2	94	47000
9	CN	I	CO ₂ Me		2	94	47000
10	H	Cl	CO ₂ tBu		5	67	13400
11	Me	I	CO ₂ tBu		2	92	46000
12	NO ₂	Br	CO ₂ tBu		4	89	22250

13	Me	I	CN		2	94	47000
14	OMe	Br	CN		4	88	22000
15	NO ₂	Cl	CN		4	78	12000

Reaction conditions: Aryl halide (1 mmol), styrene/acrylate/acrylonitrile (1.1 mmol), Pd-SILP-Fe₃O₄@SiO₂ (0.05 g, 0.001 mol% Pd), Et₃N (2 mmol), 90 °C, H₂O (5 mL) ^bIsolated yield.

A reaction of styrene with 4-iodoacetophenone afforded (*E*)-1-(4-styrylphenyl)ethan-1-one as a coupling product with 95% yield. (Entry 3, Table 5) The IR spectrum of the (*E*)-1-(4-styrylphenyl)ethan-1-one show carbonyl stretching frequency band at 1691 cm⁻¹. The absorption bands at 1588, 1407 cm⁻¹ are due to the C=C stretching frequency. Further, a band observed at 1616 cm⁻¹ is due to the presence of *trans* double bond, whereas C-H wag of *trans* double bond observed at 958 cm⁻¹. ¹H NMR spectrum of the same compound exhibited a singlet at δ 2.61 for methyl protons of the acetyl group. Two *trans* olefinic protons appeared as a two doublets at δ 7.13 and 7.23 ppm with a coupling constant *J* = 15.9 Hz. Two aromatic protons appeared as doublet between 7.95 ppm with coupling constant *J* = 8 Hz. Remaining eight aromatic protons appeared as three sets of multiplet between 7.28 - 7.32, 7.35-7.40 and 7.53-7.60 ppm for four protons, respectively. ¹³C NMR spectrum of the same compound displayed two remarkable signals at δ 26.58 and 197.49 ppm for methyl carbon and carbonyl carbon, respectively. A signal for the olefinic carbons was observed at δ 128.89 and 131.51 ppm, whereas signals appeared at δ 126.52, 126.84, 127.49, 128.35, 128.81, 136.01, 136.74, and 142.05 ppm represented aromatic carbons in the product. IR and NMR data are in agreement with the expected structure. Next, we switched over to the electron-withdrawing olefin, methyl acrylate and carried out its coupling with 4-iodoacetophenone under optimized reaction conditions.

The IR spectrum of methyl (*E*)-3-(4-acetylphenyl)acrylate (Entry 7, Table 5) depicted significant carbonyl stretching frequency band at 1721 and 1707 cm⁻¹ due to α-β unsaturated ester and ketone group, respectively. Absorption bands appeared around 1674, 1421 cm⁻¹ suggesting the presence of C=C in the compound. Further, band at 1620 cm⁻¹ is due to the presence of *trans* double bond, whereas C-H wag of *trans* double bond is observed at 956 cm⁻¹. ¹H NMR spectrum of the same compound displayed two singlets at δ 2.62 and 3.83 ppm for methyl protons of acetyl group and methoxy proton of acrylate, respectively. Two *trans* olefinic protons appeared as a doublet at δ 6.53 and 7.71 ppm with a coupling constant, *J* = 16 Hz. Further, two doublets at δ 7.61 and 7.97 ppm correspond to four aromatic protons with coupling constant, *J* = 8 Hz. ¹³C NMR spectrum of the same compound demonstrated signals at δ 26.68 and 51.90 ppm for methyl carbons. A significant signal observed at δ 197.29 and 166.94 ppm is due to the carbonyl carbon of the ketone and ester groups, respectively. A signals for the olefinic carbons were observed at δ 143.32, and 120.38 ppm, whereas signals for aromatic carbons were observed at δ 128.16, 128.88, 138.09, 138.74 ppm. All the spectroscopic data is in agreement with the expected structure.

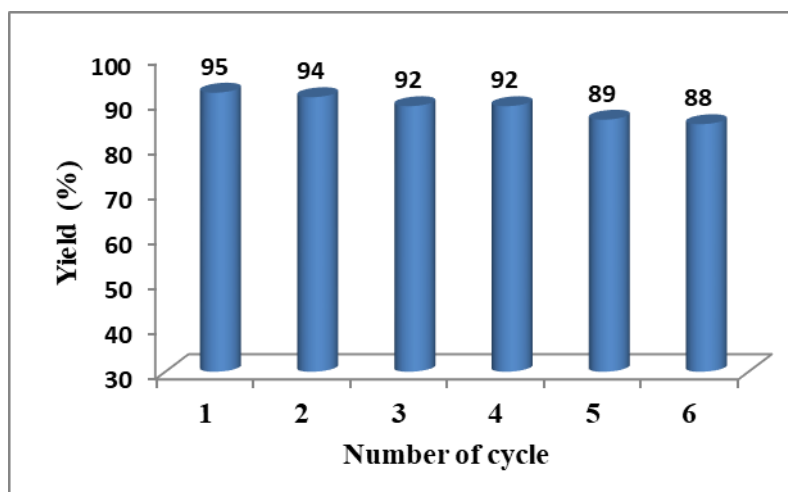
The catalytic efficiency of the synthesized catalyst Pd-SILP-Fe₃O₄@SiO₂ was compared with numerous recoverable, heterogeneous and Pd-SILP catalysts reported previously for the Mizoroki-Heck coupling of iodobenzene and styrene. From these results, it was observed that the catalyst, Pd-SILP-Fe₃O₄@SiO₂ was superior in terms of yield, metal loading, reaction time and turn-over number to most of the heterogeneous and Pd-SILP catalytic systems reported in the literature. Further, most of the literature reported high temperature (above 100 °C) for the Mizoroki-Heck coupling, whereas Pd-SILP-Fe₃O₄@SiO₂ is utilized at 90 °C (Entry 10, Table 6).

Table 6 Comparison of Pd-SILP-Fe₃O₄@SiO₂ with other supported and Pd-SILP catalysts for Mizoroki-Heck coupling

Entry	Catalyst ^{ref}	Reaction conditions	Time (h)	Yield (%)	TOF (h ⁻¹)
1	Pd cNPs/C@Fe ₃ O ₄ ²⁷	DMF, K ₂ CO ₃ , 100 °C, 0.73 mol%	10	99	135
2	PdO/GO ²⁶	DMSO, K ₂ CO ₃ , 120 °C, 10 mol%	12	88	205
3	MNP@SiO-SBA-PCA ²⁸	NMP, NaOAc, 120 °C 0.20 mol%	1	95	488
4	γ-Fe ₃ O ₄ @SiO ₂ (CH ₂) ₃ PDTC-Pd ²⁹	H ₂ O, NaOAc, RT, 0.08 mol%	1	97	1225
5	SBA-R/Im-NH ₂ -Pd ³⁰	H ₂ O, K ₂ CO ₃ , 90 °C, 0.025 mol%	0.67	98	1400
6	SBA-TMG-Pd ³¹	Et ₃ N, 140 °C 0.05 mol%	1.5	92	-
7	Pd/Ps-IL[Cl] ³²	H ₂ O, Et ₃ N, 100 °C, 0.2 equiv.	6	88	-
8	NHC-PdIL@SiO ₂ ³³	NMP, NaOAc, 140 °C	5	98	18300
9	PdFe ₃ O ₄ @PIL-NH ₂ ³⁴	Et ₃ N, 120 °C, 0.011 mol %	0.42	94	20,509
10	Pd-SILP-Fe ₃ O ₄ @SiO ₂ (present work)	H ₂ O, Et ₃ N, 90 °C, 0.001 mol%	2	95	47500

Reaction Conditions: Iodobenzene (1 mmol), styrene (1.1 mmol).

Finally, the reusability of the catalyst, Pd-SILP-Fe₃O₄@SiO₂ was investigated for the reaction between iodobenzene and styrene under optimized reaction conditions. The formed product was extracted from the reaction mixture using ethyl acetate and the catalyst, Pd-SILP-Fe₃O₄@SiO₂, was separated with the help of a bar magnet. The recovered catalyst was reused for at least 6 cycles without significant loss in the catalytic activity (Fig. 5).

**Figure 5** Reusability of Pd-SILP-Fe₃O₄@SiO₂ catalyst

4. Conclusion

We have explored Pd-SILP-Fe₃O₄@SiO₂ as a highly water dispersible, magnetically separable and robust heterogeneous catalyst for the synthesis of aryl alkenes through Mizoroki-Heck coupling of a variety of olefins and aryl halides. The Mizoroki-Heck coupling of aryl iodides, bromides and even less reactive chlorides with olefins produced corresponding coupling products in good to excellent yield. The reaction was carried out using water as a green solvent with very low loading (0.001 mol%) of the catalyst. Easy recovery and reusability of catalyst for at least 6 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/348wgk>

Compliance with ethical standards

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Disclosure of conflict of interest

The author declares no conflict of interest.

References

- [1] Seechurn CCCJ, Kitching MO, Colacot TJ, Snieckus V. Palladium-catalyzed cross-coupling: a historical contextual perspective to the 2010 Nobel Prize Angew. Chemie Int. Ed., 2012 May; 51(21):5062-85.
- [2] Zapf A, Beller M. Fine chemical synthesis with homogeneous palladium catalysts: examples, status and trends. ChemInform, 2010 May; 33(51):101–109.
- [3] Nicolaou KC, Bulger PG, Sarlah D. Palladium-catalyzed cross-coupling reactions in total synthesis. Angew. Chemie Int. Ed., 2005 July; 44(29):4442-89
- [4] Rahimi L, Mansoori Y, Nuri A, Koohi-Zargar B, Esquivel D, A new Pd(II)-supported catalyst on magnetic SBA-15 for C-C bond formation via the Heck and Hiyama cross-coupling reactions. Appl. Organomet. Chem., 2021 February; 35(2):e6078.
- [5] Movassagh B, Ranjbari S, Kryptofix 5 as an inexpensive and efficient ligand for the palladium-catalyzed Mizoroki-Heck reaction. Appl. Organomet. Chem., 2018 February; 32(4):e4224.
- [6] Mizoroki T, Mori K, Ozaki A, Arylation of Olefin with Aryl Iodide Catalyzed by Palladium. Bull. Chem. Soc. Jpn., 1971 February; 44(2):581-581.
- [7] Heck RF, Nolley JP, Palladium-catalyzed vinylic hydrogen substitution reactions with aryl, benzyl, and styryl halides, J. Org. Chem., 1972 July; 37(14):2320–2322.
- [8] Cabri W, Candiani I, Recent developments and new perspectives in the Heck reaction. Acc. Chem. Res., 2002 January; 28(1):2–7.
- [9] Whitcombe NJ, Hii KK, Gibson SE, Advances in the Heck chemistry of aryl bromides and chlorides. Tetrahedron, 2001 August; 57(35):7449–7476.
- [10] Zhou C, Wang J, Li L, Wang R, Hong M, A palladium chelating complex of ionic water-soluble nitrogen-containing ligand: the efficient precatalyst for Suzuki–Miyaura reaction in water. Green Chem., 2011 June; 13:2100–2106.
- [11] Bourissou D, Guerret O, Gabbai FP, Bertrand G, Stable Carbenes, Chem. Rev., 2000 December; 100(1):39–92.
- [12] Nájera C, Gil-Moltó J, Karlström S, Falvello LR, Di-2-pyridylmethylamine-based palladium complexes as new catalysts for Heck, Suzuki, and Sonogashira reactions in organic and aqueous solvents. Org. Lett., 2003 April; 5(9):1451–1454.
- [13] Jones MW, Adlington RM, Baldwin JE, Pevelen DDL, Smiljanic N., New mononuclear Pd (II) complexes of sterically hindered bispyrazolylmethanes. Inorganica Chim. Acta, 2010 April; 363(6):1097–1101.
- [14] S. Haneda, C. Ueba, K. Eda and M. Hayashi, Imidazole and imidazoline derivatives as n-donor ligands for Palladium-catalyzed Mizoroki–Heck reaction, Adv. Synth. Catal., 2007 April; 349(6):833–835.
- [15] Cívicos JF, Alonso DA, Nájera C, Oxime–Palladacycle-catalyzed Suzuki–Miyaura arylation and alkenylation of aryl imidazolesulfonates under aqueous and phosphane-free conditions. European J. Org. Chem., 2012 July; 2012(19):3670–3676.
- [16] Andrade APS, Arantes LM, Kadooca JY, Carvalho RL, de Fátima Â, Sabino AA, Palladium complexes with tetradentate Schiff bases or their corresponding amines: synthesis and application in Heck reactions. ChemistrySelect, 2016 April; 1(5):886–890.
- [17] Feng L, Chong H, Li P, Xiang J, Fu F, Yang S, Yu H, Sheng H, Zhu M, Pd–Ni Alloy nanoparticles as effective catalysts for Miyaura–Heck coupling reactions. J. Phys. Chem. C, 2015 March; 119(21):11511–11515.

- [18] Astruc D, Palladium nanoparticles as efficient green homogeneous and heterogeneous carbon–carbon coupling precatalysts: A unifying view. *Inorg. Chem.*, 2007 March; 46(6):1884–1894.
- [19] Puthiaraj P, Pitchumani K, Palladium nanoparticles supported on triazine functionalised mesoporous covalent organic polymers as efficient catalysts for Mizoroki–Heck cross coupling reaction, *Green Chem.*, 2014 June; 16(9):4223–4233.
- [20] Van Doorslaer C, Wahlen J, Mertens P, Binnemans K, De Vos D, Immobilization of molecular catalysts in supported ionic liquid phases. *Dalt. Trans.*, 2010 April; 39(36): 8377–8390.
- [21] Gupta R, Yadav M, Gaur R, Arora G, Yadav P, Sharma RK, Magnetically supported ionic liquids: a sustainable catalytic route for organic transformations. *Mater. Horizons*, 2020 August; 7(12):3097–3130.
- [22] Burguete MI, García-Verdugo E, Garcia-Villar I, Gelat F, Licence P, Luis SV, Sans V, Pd catalysts immobilized onto gel-supported ionic liquid-like phases (g-SILLPs): A remarkable effect of the nature of the support. *J. Catal.*, 2010 January; 269(1):150–160.
- [23] Sonawane SA, Mhaldar PM, Chhowala TN, Pore DM, Novel palladium tagged ferrite nanoparticle supported ionic liquid phase catalyst for the efficient copper-free Sonogashira coupling. *J. Mol. Struct.*, 2022 December; 1269:133729–133239.
- [24] Movassagh B, Ranjbari S, Kryptofix 5 as an inexpensive and efficient ligand for the palladium-catalyzed Mizoroki-Heck reaction. *Appl. Organomet. Chem.*, 2018 April; 32(4):e4224.
- [25] Yu L, Huang Y, Wei Z, Ding Y, Su C, Xu Q, Heck reactions catalyzed by ultrasmall and uniform pd nanoparticles supported on polyaniline. *J. Org. Chem.*, 2015 August; 80(17):8677–8683.
- [26] Rahimi L, Mansoori Y, Nuri A, Koohi-Zargar B, Esquivel D, A new Pd(II)-supported catalyst on magnetic SBA-15 for C-C bond formation via the Heck and Hiyama cross-coupling reactions. *Appl. Organomet. Chem.*, 2021 February; 35(2):e6078.
- [27] Lakshminarayana B, Mahendar L, Ghosal P, Satyanarayana G, Subrahmanyam C, Nano-sized recyclable PdO supported carbon nanostructures for Heck reaction: Influence of Carbon Materials, *ChemistrySelect*, 2017 March; 2(9):2700–2707.
- [28] Tashrifi Z, Bahadorikhalili S, Lijan H, Ansari S, Hamedifar H, Mahdavi M, Synthesis and characterization of γ -Fe₂O₃@SiO₂-(CH₂)₃-PDTC-Pd magnetic nanoparticles: a new and highly active catalyst for the Heck/Sonogashira coupling reactions. *New J. Chem.*, 2019 May; 43(23):8930–8938.
- [29] Nasab MJ, Kiasat AR, Synthesis and characterization of bifunctional lipophilic and basic mesoporous organosilica supported palladium nanoparticles as an efficient and ecofriendly nanocomposite in aqueous Heck reaction. *RSC Adv.*, 2016 August; 6(85): 81614–81621.
- [30] Hagiwara H, Sugawara Y, Isobe K, Hoshi T, Suzuki T, Immobilization of Pd(OAc)₂ in ionic liquid on silica: application to sustainable Mizoroki-Heck reaction. *Org. Lett.*, 2004 July; 6(14):2325–2328
- [31] Corma A, García H, Leyva A, An imidazolium ionic liquid having covalently attached an oxime carbapalladacycle complex as ionophilic heterogeneous catalysts for the Heck and Suzuki–Miyaura cross-coupling. *Tetrahedron*, 2004 September; 60(38):8553–8560.
- [32] Karimi B, Enders D, New N-heterocyclic carbene palladium complex/ionic liquid matrix immobilized on silica: application as recoverable catalyst for the Heck reaction. *Org. Lett.*, 2006 February; 8(6):1237–1240.
- [33] Liu W, Wang D, Duan Y, Zhang Y, Bian F, Palladium supported on poly (ionic liquid) entrapped magnetic nanoparticles as a highly efficient and reusable catalyst for the solvent-free Heck reaction. *Tetrahedron Lett.*, 2015 April; 56(14):1784–1789.
- [34] Vucetic N, Virtanen P, Nuri A, Shchukarev A, Mikkola JP, Salmi T, Tuned bis-layered supported ionic liquid catalyst (silca) for competitive activity in the Heck reaction of iodobenzene and butyl acrylate. *Catalysts*, 2020 August; 10(9):963–981.