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A polymer-supported salen-palladium complex as a heterogeneous catalyst for the Mizoroki-Heck cross-coupling reaction

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Abstract

In this work, the catalytic performance of a polymer-supported Pd(II)-salen complex (PS-Pd-salen) as an effective and environmentally friendly catalyst for the Mizoroki-Heck C-C cross-coupling reaction is presented. The PS-Pd-salen complex was employed as a catalyst for Mizoroki-Heck reactions of an aryl halide with various terminal alkenes (Styrene, Methyl acrylate, Ethyl acrylate, n-butyl acrylate, tert-Butyl acrylate) under phosphine free conditions. Moreover, a range of Mizoroki-Heck reactions using different polar solvents, co-solvents, and bases has been investigated. Aryl iodides and bromides with terminal alkene are well activated in C-C coupling reactions. All products were isolated by column chromatography as liquids/white to off-white crystalline solids and confirmed by ¹H and ¹³C NMR spectroscopy. The catalyst could be easily separated by filtrations and reusability of catalyst was also assessed under optimized conditions. The hot filtration test revealed that the catalyst was truly heterogeneous, very active and stable under the reaction conditions and could be reused up to fifth cycles with analogous activities to that of the fresh catalyst. High catalytic activity at a low concentration (30 mg) and flexibility

under mild reaction conditions, simple product work-up towards Mizoroki-Heck reactions indicated that PS-Pd-salen was an efficient catalyst for C-C coupling reactions.

Keywords: PS-Pd-salen, Heterogeneous catalysis, Mizoroki-Heck, Cross-Coupling.

1. Introduction

In recent years, Carbon-Carbon bond formation reactions have gained enormous significance for their use in research, chemical intermediates, natural products, bioactive compounds [1] and pharmaceutical industries for the preparation of fine chemicals and pharmaceutically active compounds [2,3]. The complex organic molecules are usually synthesized by Stille, Suzuki, Mizoroki-Heck reaction. The Pd-catalyzed Heck reactions are well-known as important methods to construct C-C bond formation of aryl or alkyl halides with olefins in modern chemical transformations with attractive features such as functional group compatibility, easy accessibility, air, and water stability. There has been significant progress in this field and research is still continuing [4–6].

Bearing in mind the prominence of C-C coupling reactions, a large number of homogeneous palladium catalysts with a variety of subsidiary ligands, such as phosphorus ligands [7], N-heterocyclic carbenes [8,9], P,O based ligands [10] and bis(thiourea) ligands [11], pincer [6] and, bipyridine [6], phosphines [12] and acyclic diaminocarbene [13], etc. in organic solvents under homogeneous conditions have been described. Conversely, these homogeneous protocols have some limitations such as separation of product and catalyst, tedious workup, recyclability, the use of rare and costly ligands, and contamination of palladium in the products, etc. [14]. Furthermore, the presence of remaining palladium, in the final products often remains at an undesirable level, which really limits the use of products in food, pharmaceuticals, and food, be cosmetics. [15]. problems can side-stepped by developing etc. These cheaper

and environmentally friendly Pd-heterogeneous catalysts. A number of attempts have been made to dangle Pd over various supports such as polymer, [16,17], charcoal [18], functionalized silica [19–25] and supporting Pd on various inorganic and organic materials, like metal oxides [26–29], nanoparticle [30-34], clay [35], zeolites, [36-39], carbon materials [40,41]. The drawbacks of these processes/supports include calcination at high temperature or polymerization of petrochemical and costly feedstocks. Taking into account of all these problems and the growing environmental importance on materials and processes, ample efforts have been made to easily accessible polystyrene-supported catalysts [42]. Polymer-supported Pd(II) complexes have been established as the most broadly considered catalytic systems for the Mizoroki-Heck C-C-coupling reactions [6]. The key feature of a system is that the catalyst can be easily separated from the reaction mixture through a simple filtration process upon completion of the reaction [43]. Therefore PS-Pd(II) has followed one of the principles of green chemistry which enables the catalyst to reused in the next cycle [44]. Commonly, the collision possibility of Pd with substrates has been enhanced by anchoring, palladium species on the surface of solid matrices with a larger specific surface area [45,46]. In heterogeneous catalysis palladium discharge during the reaction, is a usual problem for these surface adsorbed palladium catalysts owing to the feebler coordination of Pd(0) with solid supports at high temperatures. To avoid leaching, the solid support with distinct ligands has been extensively used in catalysis. Nevertheless, the synthesis of special chelating groups and alteration of solid matrices are usually challenging [47,48].

In recent times, we found that palladium leaching could be noticeably reduced by trapping the palladium species in a salen moiety [49]. Additionally, the arrested palladium catalyst could be easily separated from the reaction mixture and reused, which could enhance the overall

production and curtail the waste generation, leads to green and ecological chemical transformation method.

Therefore, as an extension of our continuing research work in heterogeneous catalysis for organic transformations [49–52], in this study, we have focused on the exploration of a PS-Pd-salen complex as a heterogeneous catalyst in the Mizoroki-Heck C-C cross-coupling reaction. Catalyst reusability and hot filtration were also studied.

2. Experimental

2.1. Materials

All chemicals were reagent grade or analytical grade. 4-Vinylbenzyl chloride (used by washing with dil. NaOH), DMSO- d_6 , CDCl₃, Butyl acrylate, tert-Butyl acrylate were obtained from Sigma Aldrich (India), Palladium acetate, Ethylenediamine and o-phenyldiamine, benzaldehydes, from SDFCL and Aryl halide, Azobisisobutyronitrile (AIBN), Styrene, Methyl acrylate, Ethyl acrylate from Avra Synthesis, Pvt. Ltd. Ethanol purchased from Changshu Yangyuan chemical China, Acetonitrile, Chloroform, Tetrahydrofuran (THF) and Benzimidazole were acquired from Spectrochem Pvt. Ltd.

2.2. Characterization techniques

NMR spectra were measured on a Bruker 400 MHz instrument with TMS as the internal standard (¹H recorded 400MHz and ¹³C 100MHz) in DMSO-d₆ and CDCl₃ and FT-IR spectra were recorded on Shimadzu spectrometer using KBr pellets. Thermogravimetry analysis was carried out by a thermal gravimetric analysis instrument (TG/DTA thermoanalyser SII, 7200, Seiko, Japan). Brunauer–Emmett–Teller (BET) surface area was measured at the temperature of 77 K

liquid N₂ using a Quanta chrome nova-1000 instrument analyzer. Specific surface area, average pore diameter, and pore volume are measured using N₂ adsorption-desorption isotherms. The surface morphology and the elemental composition of the complex were studied by scanning electron microscope (Carl Zeiss EVO/18SH, UK) furnished with energy dispersive X-ray (EDX) facility. The amount of Pd loading in the PS-Pd-salen was confirmed by ICP-OES analysis (ICP-OES Perkin Elmer Optima 5300 DV).

2.3. Synthesis and characterization of polymer-supported palladium salen (PS-Pd-salen) complex

The polymer supported palladium-salen (PS-Pd-salen) complex was prepared as per the previous literature [49] the details synthesis procedure and characterization data is provided in the supporting information. In a usual reaction, a suspension of the $Pd(OAc)_2$ (0.224 g, 1 mmol) in 10 mL methanol was added drop-wise to a suspension of PS-salen ligand (0.893 g, 1 mmol) in 20 mL methanol. The mixture was stirred for 6 h at 60 °C, cooled and the solid product was separated by filtration followed by washing with 30 mL methanol. After drying in the oven, the PS-Pd-salen catalyst was obtained (Fig. 1).

CCK



Fig. 1 Preparation of polymer-supported Pd-salen complex (PS-Pd-salen) 1f.

2.4. General procedure for the Heck reaction catalyzed by PS-Pd-salen complex

In general procedure, 30 mg of PS-Pd-salen complex **1f** was added to the mixture of iodobenzene (1 mmol, 0.204 g), styrene or the alkyl acrylate (1.2 mmol), the base (2 mmol) in 5 mL of dimethyl formaldehyde and reaction mixture was heated at 110 °C for between 4-20 h, depending on the reaction.

At the end of the reaction, the heterogeneous catalyst was recycled by simple filtration, washed with methanol and dried in a hot air oven. Further, the reaction mixture was extracted with chloroform (3X5 mL) and the combined organic layer was dried over sodium sulfate. The dried organic layer was filtered and concentrated under reduced pressure. The residue was purified by recrystallization with n-hexane or column chromatography on silica gel with ethyl acetate and n-hexane as an eluent. The isolated reaction products were confirmed by spectral analysis (Supporting Information).

Characterization data of the products:

1) (E)-1,2-diphenylethene; 4a/4b

GC-MS m/z: calcd. for C₁₄H₁₂: 180.0939, found 180.2624.¹H NMR (400 MHz, CDCl₃) δ = 7.57 (d, J = 7.42 Hz, 4H), 7.42 (t, J = 7.38 Hz, 4H), 7.32 (t, J = 7.35 Hz, 2H), 7.15 (s, 2H); ¹³C NMR (100 MHz, CDCl₃) 137.36, 128.73, 128.70, 127.64, 126.54.

2) (E)-1-methoxy-4-styrylbenzene; 4c

¹H NMR (400 MHz, CDCl₃) δ = 7.53 (m, 4H), 7.40 (t, J = 7.28 Hz, 2H), 7.28 (m, 1H), 7.12 (q, J = 38.16, 16.47 Hz, 2H), 6.95 (m, 2H), 3.86 (s, 3H); ¹³C NMR (100 MHz, CDCl₃) 159.33, 137.67, 130.17, 128.66, 128.23, 127.73, 127.23, 126.64, 126.27, 114.14, 55.34.

3) (E)-1-methyl-4-styrylbenzene; 4d

GC-MS m/z: calcd. for C₁₅H₁₄: 194.1096, found 194.2624. ¹H NMR (400 MHz, CDCl₃) δ = 7.50 (d, J = 7.68 Hz, 2H), 7.39 (d, J = 8.2 Hz, 2H), 7.3 (t, 2H), 7.18 (m, 1H), 7.12 (d, 2H), 7.10 (s, 2H), 2.39 (s, 3H); ¹³C NMR (100 MHz, CDCl₃) 137.6, 134.6, 129.4, 128.7, 127.7, 127.4, 126.4, 21.3.

4) (E)-1-nitro-4-styrylbenzene; 4e

¹H NMR (400 MHz, CDCl₃) δ = 8.31 (d, J = 8.86 Hz, 2H), 7.72 (d, J = 8.86 Hz, 2H), 7.64 (d, J = 7.80 Hz, 2H), 7.5 (m, 3H), 7.34 (d, 1H) 7.24 (d, 1H); ¹³C NMR (100 MHz, CDCl₃) 146.79, 143.86, 136.19, 133.33, 128.91, 128.86, 127.03, 126.87, 126.30, 124.16.

5) (E)-4-styrylbenzaldehyde; 4f

¹H NMR (400 MHz, CDCl₃) δ = 9.92 (s, 1H), 7.80 (d, J = 8.23 Hz, 2H), 7.59 (d, J = 8.23 Hz, 2H), 7.48 (d, J = 7.42 Hz, 2H) 7.33 (t, J = 7.30 Hz, 2H), 7.25 (t, 7.40 Hz, 1H), 7.18 (d, 1H), 7.04 (d

1H); ¹³C NMR (100 MHz, CDCl₃) 191.60, 143.44, 136.56, 135.35, 132.22, 130.25, 128.84, 128.68, 128.51, 124.36, 126.91.

6) (E)-4-styrylbenzonitrile; 4g

GC-MS m/z: calcd. for C₁₅H₁₁N : 205.0891, found 205.1858. ¹H NMR (400 MHz, CDCl₃) δ = 7.69 (q, 4H), 7.59 (m, 2H), 7.46 (t, J = 7.28 Hz, 2H), 7.38 (m, 2H), 7.31 (d, J = 16.28, 1H), 7.16 (d, J = 16.28 Hz, 1H); ¹³C NMR (100 MHz, CDCl₃) 141.85, 136.30, 132.65, 132.43, 128.87, 128.65, 126.92, 126.87, 126.74, 119.04, 110.60.

7) (E)-1-(chloromethyl)-4-(4-methoxystyryl)benzene; 4h

¹H NMR (400 MHz, CDCl₃) δ = 7.52 (m, 4H), 7.38 (m, 2H), 7.28 (m, 2H), 7 (d, 1H), 6.91 (d, 1H), 4.62 (s, 2H), 3.85 (s, 3H); ¹³C NMR (100 MHz, CDCl₃) 159.48, 130.25, 128.99, 128.25, 127.81, 126.60, 126.53, 125.85, 114.31, 55.34, 46.20.

8) methyl cinnamate; 4i

GC-MS m/z: calcd. for $C_{10}H_{10}O_2$: 162.0681, found 162.068. ¹H NMR (400 MHz, CDCl₃) δ = 7.64 (d, J = 15.89 Hz, 1H), 7.4 (m, 2H), 7.30 (t, 3H), 6.38 (d, J = 16.21 Hz, 1H), 3.72 (s, 3H); ¹³C NMR (100 MHz, CDCl₃) 166.41, 143.85, 133.32, 129.27, 127.85, 127.04, 116.73, 50.68.

9) methyl (E)-3-(4-methoxyphenyl)acrylate; 4j

GC-MS m/z: calcd. for $C_{11}H_{12}O_3$: 192.0786, found 192.0786. ¹H NMR (400 MHz, CDCl₃) δ = 7.59 (d, J = 16.05 Hz, 1H), 7.4 (d, J = 8.49 Hz, 2H), 6.83 (d, J = 8.71 Hz, 2H), 6.25 (d, J = 15.60 Hz, 1H), 3.75 (s, 3H), 3.71 (s, 3H); ¹³C NMR (100 MHz, CDCl₃) 167.79, 161.39, 144.55, 129.74, 127.10, 116.35, 115.25, 114.33, 55.38, 51.60.

10) methyl (E)-3-(4-nitrophenyl)acrylate; 4k

GC-MS m/z: calcd. for $C_{10}H_9NO_4$: 207.0532, found 207.0840. ¹H NMR (400 MHz, CDCl₃) δ = 8.09 (d, J = 8.30 Hz, 2H), 7.68 (d, J = 8.51 Hz, 2H), 7.52 (d, 1H), 6.76 (d, 1H), 3.71 (s, 3H). ¹³C NMR (100 MHz, CDCl₃) 167.7, 148.1, 144,5, 129.7, 127.1, 116.3, 114.4, 51.6.

11) ethyl cinnamate; 4l

GC-MS m/z: calcd. for C₁₁H₁₂O₂ : 176.0837, found 176.2370. ¹H NMR (400 MHz, CDCl₃) δ = 7.67 (d, J = 15.91 Hz, 1H), 7.46 (m, 2H), 7.30 (t, J = 6.5, 3H), 6.38 (d, J = 15.95 Hz, 1H), 4.26 (q, 2H), 1.30 (t, 3H); ¹³C NMR (100 MHz, CDCl₃) 166.51, 144.10, 133.6, 129.4, 128.1, 127.6, 116.9, 60.1, 14.1.

12) ethyl (E)-3-(4-methoxyphenyl)acrylate; 4m

GC-MS m/z: calcd. for $C_{12}H_{14}O_3$: 206.094, found 206.2293, ¹H NMR (400 MHz, CDCl₃) δ = 7.59 (d, J = 16.05 Hz, 1H), 7.4 (d, J = 8.49 Hz, 2H), 6.83 (d, J = 8.71 Hz, 2H), 6.3 (d, J = 15.60 Hz, 1H), 4.2 (q, 2H), 3.75 (s, 3H), 1.28 (t, 3H); ¹³C NMR (100 MHz, CDCl₃) 167.4, 161.3, 144.2, 129.7, 127.7, 115.8, 115.3, 114.3, 60.3, 55.3, 14.4.

13) butyl cinnamate; 4n

GC-MS m/z: calcd. for $C_{13}H_{16}O_2$: 204.1150, found 204.2802. ¹H NMR (400 MHz, CDCl₃) δ = 7.62 (d, J = 16.15 Hz, 1H), 7.46 (m, 2H), 7.29 (t, 3H), 6.38 (d, J = 15.98 Hz, 1H), 4.14 (t, J = 6.63 Hz, 2H), 1.67 (m, 2H), 1.44 (m, 2H), 0.90 (t, J = 7.41 Hz, 3H); ¹³C NMR (100 MHz, CDCl₃) 166.7, 144.4, 133.9, 129.86, 128.3, 127.3, 118.0, 64.3, 30.8, 19.2, 13.6.

14) butyl (E)-3-(4-methoxyphenyl)acrylate; 40

GC-MS m/z: calcd. for $C_{14}H_{18}O_3$: 234.1256, found 231.2616. ¹H NMR (400 MHz, CDCl₃) δ = 7.59 (d, J = 16.05 Hz, 1H), 7.4 (d, J = 8.49 Hz, 2H), 6.83 (d, J = 8.71 Hz, 2H), 6.3 (d, J = 15.60

Hz, 1H), 4.14 (t, J = 6.63 Hz, 2H), 3.75 (s, 3H), 1.67 (m, 2H), 1.44 (m, 2H), 0.90 (t, J = 7.41 Hz, 3H); ¹³C NMR (100 MHz, CDCl₃) 167.4, 161.3, 144.2, 129.7, 127.7, 115.8, 114.3, 64.3, 55, 30.8, 19.2, 13.6.

15) tert-butyl cinnamate; 4p

GC-MS m/z: calcd. for $C_{13}H_{16}O_2$: 204.1150, found 204.2802. ¹H NMR (400 MHz, CDCl₃) δ = 7.59 (d, J = 16 Hz, 1H), 7.49 (m, 2H), 7.36 (m, 3H), 6.38 (d, J = 16 Hz, 1H), 1.54 (s, 9H); ¹³C NMR (100 MHz, CDCl₃) 166.5, 143.6, 134.6, 129.9, 128.8, 127.9, 120.1, 80.5, 28.2.

16) tert-butyl (E)-3-(4-methoxyphenyl)acrylate; 4q

GC-MS m/z: calcd. for C₁₄H₁₈O₃ : 234.1256, found 231.1920. ¹H NMR (400 MHz, CDCl₃) δ = 7.59 (d, J = 16.05 Hz, 1H), 7.4 (d, J = 8.49 Hz, 2H), 6.9 (d, J = 8.71 Hz, 2H), 6.25 (d, J = 15.90 Hz, 1H), 2.3 (s, 3H), 1.5 (s, 9H); ¹³C NMR (100 MHz, CDCl₃) 167.0, 144.5, 140, 129.74, 127.10, 128.0, 116.35, 119.2, , 80.1, 28.2, 21.5.

17) (1E,6E)-1,7-diphenylhepta-1,6-diene-3,5-dione; 4r

¹H NMR (400 MHz, DMSO-*d*₆) δ = 7.55 (d, J = 7.67Hz, 4H), 7.50 (d, J = 15.73 Hz, 2H), 7.42 (m, 6H), 6.70 (d, J = 15.73 Hz, 2H); ¹³C NMR (100 MHz, DMSO-d₆) 166.8, 139.8, 135.2, 130, 129.4, 128, 122.26, 44.

18) (E)-1-styrylnaphthalene; 4s

GC-MS m/z: calcd. for C₁₈H₁₄: 230.1096, found 230.2971. ¹H NMR (400 MHz, CDCl₃) δ = 7.86 (m, 4H), 7.76 (m, 4H), 7.57 (d, J = 7.6 Hz, 2H), 7.5 (m, 2H), 7.39 (t, J = 7.6 Hz, 2H), 7.31 (m, 3H); ¹³C NMR (100 MHz, CDCl₃)): δ 137.3, 134.8, 133.7, 133.0, 129.0, 128.7, 128.7, 128.3, 128.0, 127.7, 126.6, 126.5, 126.3, 125.9, 123.5.

3. **Results and discussion**

3.1. Catalytic application of polymer-supported Pd-salen complex (1f) in Mizoroki-Heck crosscoupling reaction

In order to study the efficacy of the polymer-supported Pd-salen complex (1f), was scrutinized for the C-C bond formation between the variety of olefins with aryl halides. The optimization of the reaction condition was carried out using iodobenzene (1 mmol, 0.204 g) with styrene (1.2 mmol, 0.124 g) by varying amount of catalyst, bases, solvents, temperatures and time. The experimental results are summarized in Table 1 and 2. In the beginning, the reaction was performed using ligand (Table 1, entry 1), complex (Table 1, entry 2) and without catalyst (Table 1, entry 3). The result clearly indicated that reaction does not occur in the presence of ligand and the palladium complex (PS-Pd-salen) is important for the C-C cross-coupling reaction (Table 1, entries 2,3). Further, the reaction was performed by varying the catalyst amount from 10-40 mg (Table 1, entries 4-7) and found the yield of product was enhanced 92% with 30 mg catalyst, (Table 1, entries 4-7). Conversely, an increasing amount of catalyst 40 mg, showed no appreciable effect on the yield of the coupling product (Table 1, entry 7).

The optimum amount of catalyst in hand, we have confirmed the effect of solvent on the C-C cross-coupling reaction (Table 2, entries 1-4). The result observed that DMF (Table 2, entry 2) as a good solvent compare to DMSO, H₂O and DMF/H₂O (Table 2, entries 1, 3, 4). The usual practice for the coupling reaction, the base plays a major role in C-C cross-coupling reaction. We have studied the effect of the base for Mizoroki-Heck cross-coupling reaction, with Et₃N and K₂CO₃ and the result summarized in Table 2, entry 5 and illustrated that K₂CO₃ showed better activity compared to Et₃N. To confirm the influence of temperature on our target reaction we have performed the reaction by varying the reaction temperature from 70 to 130 °C (Table 2, entries 6-

9). The result revealed that at 110 °C is sufficient to achieve the yield 92% (Table 2, entry 8), further increasing the temperature up to 130 °C, demonstrated no effect on the yield (Table 2, entry 9). With optimized parameters in hand, we have studied the role of duration reaction for the cross-coupling reaction. The model reaction was carried out by varying duration from 4-20 h (Table 2, entry 10-14) and favored that 10 h lead to maximum yield of the coupling product(Table 2, entry 12).

From the above results, we have confirmed the optimum reaction conditions: the catalyst amount (30 mg), solvent (DMF), base (K_2CO_3), temperature (110 °C) and reaction time (10 h) for the Mizoroki-Heck cross-coupling reaction.

Table 1. Optimization of the amount of catalyst for Mizoroki-Heck cross-coupling reaction^a

+ $\frac{PS-Pd-salen}{K_2CO_3, DMF, 130 °C}$							
En	try	Catalyst	Catalyst (mg)	20 h Time (h)	Yield ^b	TON	TOF
1	1	PS-salen	50	20	00		
2	2	PS-Pd-salen	50	20	90	947	47
3	3	No catalyst	Nil	20	00		
2	1	PS-Pd-salen	10	20	60	3000	150
4	5	PS-Pd-salen	20	20	81	2131	106
e	5	PS-Pd-salen	30	20	92	1614	80
7	7	PS-Pd-salen	40	20	92	1210	60

^a Reaction conditions: Iodobenzene (1 mmol, 0.204 g), styrene (1.2 mmol , 0.124 g), K₂CO₃ (2 mmol, 0.276 g) in DMF (5 mL) at 130 °C.

^bGC–MS conversion.

PS-Pd-salen

		+	Base				
Entry	Solvent	Base	Temp (°C)	Time (h)	Yeild ^b	TON	TOF
1	DMSO	K ₂ CO ₃	130	20	85	1491	74
2	DMF	K_2CO_3	130	20	92	1614	80
3	H_2O	K ₂ CO ₃	Reflux	20	60	1052	52
4	DMF/H ₂ O	K_2CO_3	Reflux	20	70	1228	61
5	DMF	Et ₃ N	130	20	65	1140	57
6	DMF	K_2CO_3	70	20	71	1245	62
7	DMF	K_2CO_3	90	20	78	1368	68
8	DMF	K_2CO_3	110	20	92	1614	80
9	DMF	K_2CO_3	130	20	92	1614	80
10	DMF	K ₂ CO ₃	110	4	81	1421	355
11	DMF	K ₂ CO ₃	110	8	87	1526	190
12	DMF	K ₂ CO ₃	110	10	93	1631	163
13	DMF	K ₂ CO ₃	110	12	93	1631	135
14	DMF	K ₂ CO ₃	110	20	92	1614	80

Table 2. Optimization of the reaction conditions for Mizoroki-Heck cross-coupling reaction^a

^a Reaction conditions: Iodobenzene (1 mmol, 0.204 g), styrene (1.2 mmol, 0.124 g), Base (2 mmol), PS-Pd-salen 30 mg, in Solvent (5 mL).^bGC–MS conversion.

Finally, in order to show the uniqueness and simplification of the polymer-supported Pd-salen complex as a catalyst we have perform the Mizoroki-Heck cross-coupling reaction of variety of aryl halide with olefins (styrene, methyl acrylate, ethyl acrylate, butyl acrylate, tert. butyl acrylate and N,N'-Methylenebis(acrylamide)) Table 3 (entries 1-19). A number of important observations can be made. The reaction of styrene with aryl iodide achieved more product yield

(Table 3, entry 1) than with aryl bromide (Table 3, entry 2). The presence of electron rich (-OCH₃, -CH₃) or electron withdrawing substituents (-NO₂, -CHO, -CN) on the aryl halide, in the reaction with styrene, had no influence on the yield (Table 3, entries 3-7). Additionally, the reaction of iodobenzene with substituted styrene (4-Vinylbenzyl chloride) showed less product conversion (Table 3, entry 8). As we have observed the electron rich and electron withdrawing species of an aryl halide with styrene, we move further to check the effect of this group with a range of acrylate species (methyl acrylate, ethyl acrylate, butyl acrylate and tert. butyl acrylate) (Table 3, entries 9-17). The result exhibited tert. butyl acrylate (Table 3, entries 16,17) displayed, more yield compare to ethyl and butyl acrylate (Table 3, entries 9-15) this may due to the steric effect of the substitute.

Additionally, a compound with two terminal alkene groups, N,N'-Methylenebis (acrylamide) was tested with aryl halide and the product was isolated with a satisfactory yield of 54% (Table 3, 18). Finally, we have performed the reaction of 1-Bromonaphthalene with a terminal alkene (styrene) and achieved an acceptable conversion of the coupling product (Table 3, entry 19). The result revealed that the catalyst is efficient for the C-C cross-coupling reactions. The proposed mechanism for the Mizoroki-Heck reaction catalyzed by PS-Pd-salen is provided in supporting information Fig. S1.





1	Н	Ι	Ph	4 a	93	1631	163
2	Н	Br	Ph	4 b	85	1491	149
3	4-OCH ₃	Ι	Ph	4 c	88	1543	154
4	4-CH ₃	Br	Ph	4d	86	1508	150
5	$4-NO_2$	Br	Ph	4 e	93	1631	163
6	4-CHO	Br	Ph	4f	88	1543	154
7	4-CN	Br	Ph	4g	91	1593	159
8	Н	Ι	C ₆ H ₄ CH ₂ Cl	4h	70	1228	122
9	Н	Ι	CO ₂ Me	4i	79	1385	138
10	$4\text{-}OCH_3$	Ι	CO ₂ Me	4 j	87	1526	152
11	$4-NO_2$	Br	CO ₂ Me	4k	80	1403	140
12	Н	Ι	CO ₂ Et	41	76	1333	133
13	4-OCH ₃	Ι	CO ₂ Et	4m	80	1403	140
14	Н	Ι	CO ₂ ⁿ Bu	4n	90	1578	157
15	4-OCH_3	Ι	CO2 ⁿ Bu	40	94	1659	165
16	Н	Ι	CO ₂ ^t Bu	4p	92	1614	161
17	4-OCH ₃	1	CO_2 ^t Bu	4 q	98	1779	177
18	Н	Ι	(H ₂ C=CHCONH) ₂ CH ₂	4r	54 ^{c,d}	947	94
19	e		Ph	4 s	60	1052	105

^a Reaction conditions: aryl halide (1 mmol), olefine (1.2 mmol), K_2CO_3 (2 mmol) and catalyst (30 mg) in DMF (5 mL) at 110 °C, 10 h.

^bGC-MS conversion.

^c Isolated yields.

^d N,N'-Methylenebis(acrylamide), ^e 1-Bromonaphthalene

The exclusive feature of a heterogeneous catalyst is its ability to be reused, mainly for industrial application. We have tested our PS-Pd-salen complex catalyst for recyclability, based on the model reaction at optimized reaction conditions. After the end of the reaction, the catalyst was separated by simple filtration from the reaction mixture and washed with excess distilled water to remove carbonate from the catalyst and further with methanol. The recovered PS-Pd-salen complex catalyst was dried in a hot air oven at 80 °C for 2 h and used for the next cycle at analogous reaction conditions. The recycle catalyst was compared with the fresh catalyst by FT-IR, to identify any change in the structure of the catalyst (Fig. 3). The result clearly demonstrated that there is no alteration in the catalyst, confirmed that catalyst is stable during the reaction even at high temperature. Furthermore, the catalyst recycles and reused up to fifth cycles without losing its activity (Fig. 4). The highly recyclable heterogeneous PS-Pd-salen catalyst was successfully used for the Mizoroki-Heck C-C cross-coupling reaction with good to the excellent yield of the product. Moreover, the true heterogeneous nature of the catalyst was confirmed by hot filtration test. The hot filtration test, the reaction was performed at optimized reaction condition for 2 h, the catalyst was removed and further proceed for 6 h. The result revealed that there is no progress in the reaction which confirmed the catalyst is true heterogeneous nature. The comparison of the PS-Pdsalen with a reported heterogeneous catalyst (Table 4) showed the result is comparable with literature reports. As per our previous report Suzuki-Miyaura C-C coupling reaction, we have found that PS-Pd-salen is also a stable catalyst for the Mizoroki-Heck reaction.

Entry	Heterogeneous Catalyst	Amount of catalyst	Time in (h)	Highest yield (%) ^{a,b}	Ref.
1	Nanostructured silica	500 mg	12	90 ^a	[53]
	Pyridine-Pd				
2	Pd-ethylthioglycolate	50 mg	24	99 ^a	[22]
	modified silica				
3	Pd-zinc oxide	9 mg	17	95 ^b	[33]
	nanoparticles				
4	TiO ₂ @Pd	1 mol%	10-24	94 ^b	[54]
	Nanoparticles				
5	D-glucosamine-derived	0.1 mol%	6-24	95 ^b	[1]
	pyridyltriazole@			S	
	Palladium				
6	PS-Pd-salen	25 mg	10	98ª	Present
					Work

Table 4. Comparison of r S-ru-salen with interature report	Table 4. C	mparison of PS-Pd-salen with literature repo	rts
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^aGC-conversion, ^bIsolated yield



Fig. 3 FT-IR spectra of the PS-Pd-salen (1) before reaction (2) after the reaction.



Fig. 4 Recyclability of PS-Pd-salen in Mizoroki-Heck reaction.

4. Conclusion

In present work, we have successfully used the polymer-supported Pd-salen (PS-Pd-salen) complex as a catalyst for Mizoroki-Heck reaction. The PS-Pd-salen as catalyst demonstrated not only good catalytic activity but also showed great thermal stability. The thermally stable catalyst used for high-temperature reaction and can be stored without any precautions. The low-cost polymer support used for the palladium metal increase the heterogeneous nature of the catalyst display recyclability up to five cycles. The applications of the catalyst were confirmed by the reaction of a variety of aryl halides (with both electrons rich and electron deficient groups) with terminal alkenes, including a bis-terminal alkene, giving good to excellent yields of the C-C cross-coupling product. The true heterogeneous nature of the catalyst was confirmed by the hot filtration test. Moreover, the present results of Mizoroki-Heck cross-coupling reaction are comparable with Suzuki-Miyaura catalyzed by PS-Pd-salen and the literature reports for Mizoroki-Heck cross-

coupling reaction. The protocol reveals a reasonable and modest substitute for conventional catalysts in synthetic organic chemistry.

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Accempters MANUSCRIPT

Highlights

- Polymer supported Pd-salen (PS-Pd-salen) complex was used for C-C cross coupling of Mizoroki-Heck reaction
- Variety of aryl halide and terminal alkenes with electron donating as well as electron withdrawing accomplished good to excellent yield of product
- Terminal alkene (Styrene, Methyl Acrylate, Ethyl Acrylate, n-Butyl Acrylate, tert-Butyl Acrylate) and bis terminal such as N,N'-Methylenebis(Acrylamide)) were studied
- Thermally stable catalyst showed recyclability for five runs without considerable loss in activity

Graphical abstract

