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Highly efficient polymer-stabilized palladium heterogeneous catalyst: Synthesis, characterization and application for Suzuki–Miyaura and Mizoroki–Heck coupling reactions

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Kiumars Bahrami, Department of Organic Chemistry, Faculty of Chemistry, Razi University. Kermanshah, Iran, 67149-67346. Email: kbahrami2@hotmail.com; k.bahrami@razi.ac.ir average diameter of 3–4 nm, on magnetic polymer is described. A new magnetic polymer containing 4'-(4-hydroxyphenyl)-2,2':6',2"-terpyridine (HPTPy) ligand was prepared by the polymerization of itaconic acid (ITC) as a monomer and trimethylolpropane triacrylate (TMPTA) as a cross-linker and fully characterized. Pd NPs embedded on the magnetic polymer were successfully applied in Suzuki–Miyaura and Mizoroki–Heck coupling reactions under low palladium loading conditions, and provided the corresponding products with excellent yields (up to 98%) and high catalytic activities (TOF up to 257 hr⁻¹). Also, the catalyst can be easily separated and reused for at least consecutive five times with a small drop in catalytic activity.

A suitable approach to stabilize palladium nanoparticles (Pd NPs), with an

KEYWORDS

Mizoroki-Heck reactions, palladium nanocatalyst, polymer-stabilized nanoparticles, Suzuki-Miyaura reactions, terpyridine ligand

1 | INTRODUCTION

The C-C bond-forming reactions have played a remarkable role in organic synthesis, since its origins in 1845 by Kolbe.^[1] The progress in C-C cross-coupling came from the use of reactive homogeneous and heterogeneous palladium catalysts for the reaction of aryl halides or vinyl halides with organometallic compounds (Suzuki, Corriu-Kumada, Hiyama, Negishi and Stille reactions), or with alkenes (Heck reaction), or with alkynes (Sonogashira reaction).^[2] Nowadays, Suzuki–Miyaura and Mizoroki– Heck reactions have become among the most robust and efficient synthetic protocols for the formation of C-C bonds. These reactions have enabled chemists to join two organic fragments using relatively mild conditions, allowing for the creation of delicate intricate organic scaffolds. Therefore, the Suzuki–Miyaura and Mizoroki–Heck reactions have been widely applied in the synthesis of many drugs, natural products and starting materials via both intermolecular and intramolecular reactions.^[3]

During the last few decades, major advances in homogeneous palladium-catalyzed C-C coupling reactions have been described by a number of research groups.^[4] Considering the extensive use of palladium in coupling reactions, and the high cost and toxicity of palladium on the other hand, there is a growing interest in applying heterogeneous and recoverable palladium catalysts, therefore the heterogenization of palladium catalysts is extremely important from both environmental and economic points of view.^[5–8]

In recent years, ultrafine noble metal nanoparticles have been broadly explored for the improvement of the catalysts' performance.^[9] It is confirmed that noble metal nanoparticles perform superior activity for catalysis due

to their extremely small size and high surface areas.^[10] However, high surface energies and large surface area of noble metal nanoparticles could lead to thermodynamically instability; therefore, protecting capping agents are often used to stabilize them in a nano region during their synthesis.^[11] There are several stabilizing agents, such as surfactants. polymers, porous organic polymers, dendrimers, micelles, and various ligands that are able to stabilize metal nanoparticles.^[12,13] In the case of noble metals, the most widely used methods to stabilize the metal nanoparticles and control their growth are to use polymers or ligands.^[14] It is observed that tridentate nitrogen ligands, including terpyridine-based ligands, increase the dispersion and stability of the metal nanoparticles due to the strong interaction of metal-nitrogen formation of two five-membered and the metallacycles.^[15,16]

Currently, polymer supports have found widespread use as stabilizing agents for noble metal nanoparticles. "Use of polymer-immobilized catalysts provides an essential technique for the green chemistry process of organic synthesis. In addition to the aspect of simplicity of catalyst recovery and recycling, it is even possible to apply the polymeric catalysts to the continuous flow system which can lead to an economical automation system."^[17-19]

Due to advantages of polymers as well as facile removal and recycling of the magnetic catalyst from the solution system, herein, we report the synthesis and characterization of a new magnetic polymer containing 4'-(4hydroxyphenyl)-2,2':6',2"-terpyridine (HPTPy) palladium complex, namely, MP-TPy/Pd. The catalytic activity of the MP-TPy/Pd was evaluated in the Suzuki-Miyaura and Mizoroki-Heck coupling reactions (Scheme 1).

RESULTS AND DISCUSSION 2

2.1 | Catalyst characterization

The stages of MP-TPy/Pd preparation are summarized in Scheme 2. Initially, HPTPy-itaconic acid (ITC) was prepared via esterification reaction of ITC and HPTPy. On the other hand, the Fe₃O₄@SiO₂ was modified by using 3-(trimethoxysilyl) propyl methacrylate (TMSPM). Then, polymerization of Fe₃O₄@SiO₂-TMSPM with HPTPy-ITC and TMPTA as a cross-linker was achieved in the presence of 2,2'-azobisisobutyronitrile (AIBN) as an initiator in MeOH/CH₃CN affording the final magnetic polymer. The MP-TPy/Pd was obtained by interaction of PdCl₂ with MP-TPy in EtOH as solvent and green reducing agent (Scheme 2). Moreover, Pd NPs can be successfully prepared on MP-TPy without the addition of external reducing agents because HPTPy ligands serve also as a reducing agent due to its nitrogen atoms.^[16]

The MP-TPy/Pd was extensively analyzed through some characterization techniques, including Fourier transform-infrared spectroscopy (FT-IR), transmission electron microscopy (TEM), scanning electron microscopy (SEM), thermogravimetric analysis (TGA), energydispersive X-ray spectroscopy (EDX), X-ray diffraction spectroscopy (XRD), X-ray photoelectron spectroscopy (XPS), vibrating-sample magnetometer (VSM), UV-Vis spectra analysis and inductively coupled plasma (ICP).

The FT-IR technique can be used to track the synthesis of MP-TPy/Pd (Figure 1). In the FT-IR spectrum of HPTPy, the following functional groups were identified: OH stretching vibrations (3386 cm^{-1}), sp² C-H stretching vibrations (3036 cm^{-1}) and C=N stretching frequency (1598 cm⁻¹). In the case of HPTPy-ITC, the band at 1740 cm^{-1} corresponds to C=O stretching of ester groups. The weak absorptions at 2856 cm^{-1} and 2926 cm^{-1} are attributed to the sp³ C-H stretching vibrations. The bands observed at 1592 cm⁻¹ and 3055 cm⁻¹ can be attributed to the C=N stretching frequency and C-H aromatic (pvridine rings) stretching vibration, respectively. The C=N bands of complex TPy-Pd in MP-TPy/Pd are shifted to a lower frequency (1583 cm⁻¹) in the FT-IR spectrum compared with that of TPy (1598 cm^{-1}). The lowering in frequency of the C=N peak is indicative of the interaction of TPy with Pd.^[20]

Figure 2(a) displays the SEM image of MP-TPy/Pd showing clearly the synthesized catalyst with irregular morphology of various particle sizes. The size of the palladium nanoparticles (Pd NPs) produced on the magnetic polymer was analyzed by TEM. The TEM images of the Fe₃O₄@SiO₂-TMSPM and MP-TPy/Pd are shown in Figure 2(b) and (c), respectively. The TEM images demonstrate the formation of small sized Pd NPs with an average diameter of 3-4 nm on MP-TPy/Pd. The TEM



7 examples (90-97% yields)

SCHEME 1 The MP-TPy/Pd catalyzed Suzuki-Miyaura and Mizoroki-Heck coupling reactions



SCHEME 2 Synthetic steps for the preparation of MP-TPy/Pd



FIGURE 1 Fourier transform-infrared (FT-IR) spectrum of HPTPy, HPTPy-ITC and MP-TPy/Pd

images also determined the magnetic nanoparticles cores, with sizes significantly larger than Pd NPs due to aggregation (~30 nm).

Conversion of PdCl₂ to Pd NPs using EtOH as reducing agent has been well documented and recognized.^[21] In addition, the nitrogen-based ligands can also be regarded as a reducing agent.^[16] In this regard, the synthesis of the Pd (0) catalyst was initially monitored by UV–Vis spectroscopy (Figure 3). In UV–Vis spectroscopy, the $PdCl_2$ solution showed a distinct peak at approximately 425 nm, indicating the existence of the Pd (II) ion. During the formation of Pd NPs on the polymer containing HPTPy ligand, the UV–Vis spectrum showed conversion of Pd (II) to Pd (0) by the absence of the peak at 425 nm.^[22]

The formation of Pd (0) nanoparticles was also confirmed by the color changes of the magnetic polymer from brown to dark gray during the synthesis of catalyst in EtOH within 24 hr (Figure 4). The color changes are due to interaction of terpyridine ligands of the polymer with PdCl₂.^[23]

The thermal behaviour of the nanocatalyst was investigated by TGA in oxidative (air) environment. The TGA thermogram for the magnetic polymers is shown in Figure 5. The polymer displayed excellent thermal stabilities up to 300°C in air. It presented maximum decomposition rate temperature above 300°C, and weight loss of ~84% between 300°C and 450°C is mainly assigned to the decomposition of the polymer shell and HPTPy entrapped in polymer.

Figure 6 presents the XRD pattern of MP-TPy/Pd. The diffraction peaks at the Bragg angles of 40.10° , 46.66° and 68.14° correspond to the 111, 200 and 220 facets of



FIGURE 2 (a) Scanning electron microscopy (SEM) image of MP-TPy/Pd, (b) transmission electron microscopy (TEM) image of Fe₃O₄@SiO₂-TMSPM and (c) TEM image of MP-TPy/Pd



FIGURE 3 UV–Vis spectrum of MP-TPy/Pd and PdCl₂ solution in EtOH

elemental palladium in MP-TPy/Pd.^[24] The XRD pattern also contains peaks at 2θ values 30.05°, 35.94°, 53.41°, 57.38° and 62.98° related to the (220), (311), (422), (511) and (440) that agree with the structure of Fe₃O₄ NPs.^[25]

The EDX technique can be used for the elemental analysis of the nanocatalysts, therefore successful synthesis of MP-TPy/Pd can be inferred from this technique. EDX spectra show the presence of Fe, Si, C, O, N and Pd in magnetic polymer-Pd (Figure 7).

The magnetic properties of Fe_3O_4 NPs and magnetic polymer were determined by VSM. As expected, the magnetization of magnetic polymer is smaller than that of Fe_3O_4 NPs (Figure 8). Nonetheless, the magnetization of magnetic polymer is still large enough for the catalyst separation from the reaction mixtures.

The MP-TPY/Pd was also studied by XPS, and high-resolution XPS results confirmed the presence of Pd (0) and Pd (II) on the catalyst (Figure 9). The peaks at 335.5 eV (Pd $3d_{5/2}$) and 340.5 eV (Pd $3d_{3/2}$) are assigned to Pd (0), whereas peaks at 336.5 eV (Pd $3d_{5/2}$) and 342.0 eV (Pd $3d_{3/2}$) are assigned for Pd (II) species present



FIGURE 4 The color change of the magnetic polymer, magnetic polymer (a), preparation of Pd catalyst after 1 min (b), after 2 hr (c), and after separating with a magnet (d)



FIGURE 5 Thermogravimetric analysis (TGA) thermogram of the magnetic polymer

on the polymer.^[26] The XPS spectrum shows that Pd (0) was predominant on MP-TPy/Pd as the area under the peak of Pd (II) is relatively small.

2.2 | Catalytic studies

The catalytic activity of the prepared MP-TPy/Pd was evaluated in C-C formation via Suzuki–Miyaura and Mizoroki–Heck reactions. Initially, for the optimization of the Suzuki C-C coupling reaction, a reaction of iodobenzene with phenylboronic acid under different reaction conditions, such as different temperatures, solvents and bases, and in the presence of various amounts of MP-TPy/Pd was used as a model reaction (Table 1). The best result (98% yield) was achieved by using iodobenzene (1 mmol), phenylboronic acid (1.2 mmol) and K_2CO_3 (1.5 mmol) in the presence of the catalyst (0.01 g, 0.19 mol%) at 80°C for 2 hr in a mixture of EtOH/H₂O (2/ 1) as solvent (Table 1, entry 4).

Under these optimized conditions, the generality and scope of the procedure was assessed in the reaction of commercially available aryl halides with arylboronic acids, and the results are summarized in Table 2. As shown in Table 2, MP-TPy/Pd effectively catalyzed the coupling reaction between aryl halides possessing either electron-donating



FIGURE 7 Energy-dispersive X-ray spectroscopy (EDX) pattern of MP-TPy/Pd

or electron-withdrawing substituents with arylboronic acids performed to afford corresponding biaryl products in excellent yields. As expected, the Suzuki reaction of aryl chlorides required longer reaction times, because aryl chlorides are generally less reactive toward aryl bromides and iodides.

As an extension to the use of this, we also investigated the catalytic activities of MP-TPy/Pd for the Mizoroki –Heck C-C coupling reaction. Iodobenzene and styrene were selected as substrates to establish the best conditions for the preparation of the corresponding trans-stilbenes in the presence of different amounts of the catalysts and various bases and solvents at 100°C (Table 3). As can be seen from the table, the best result of 97% yield was obtained by carrying out the reaction with aryl halide (1 mmol), styrene (1.2 mmol) in the presence of 0.015 g (0.285 mol%) of MP-TPy/Pd and Et₃N (3 mmol), under solvent-free at conditions at 100°C (Table 3, entry 4).

In order to study the generality of this procedure, the reaction of other aryl halides with styrene were next studied. Table 4 contains the results of forming corresponding trans-stilbenes in the optimal conditions. As the table shows, donor- and acceptor-substituted aryl iodides have been reacted with styrene in mostly excellent yields.





FIGURE 8 Magnetization curves obtained by vibrating-sample magnetometer (VSM) of Fe_3O_4 nanoparticles (NPs) and magnetic polymer



FIGURE 9 The high-resolution X-ray photoelectron spectroscopy (XPS) scan spectrum over Pd 3d peak of MP-TPy/Pd

However, when iodobenzene was replaced by bromobenzene, the coupling reactions require longer reaction times. However, the scope of this methodology was found not to be effective to chlorobenzene (Table 4, entry 7).

The generally accepted mechanisms for Pd-catalyzed Suzuki–Miyaura and Mizoroki–Heck reactions are shown in Scheme 3. Both the mechanisms start with oxidative addition of the organohalide (\mathbb{R}^{1} -X) to the Pd (0) to form a Pd (II) complex.^[27–29]

Finally, the catalyst was easily separated from the reaction mixtures by using an external magnet, and washed twice with ethanol followed by water, and dried for the

TABLE 1 Optimization of conditions in the Suzuki–Miyauracoupling reaction^a

Entry	Cat. (mol%)	Base	Solvent	T (°C)	Yield (%) ^b	
1	0	K ₂ CO ₃	EtOH/H ₂ O (2/1)	80	0	
2	0.095	K ₂ CO ₃	EtOH/H ₂ O (2/1)	80	55	
3	0.152	K_2CO_3	EtOH/H ₂ O (2/1)	80	85	
4	0.19	K_2CO_3	EtOH/H ₂ O (2/1)	80	98	
5	0.19	Na ₂ CO ₃	EtOH/H ₂ O (2/1)	80	86	
6	0.19	Et ₃ N	EtOH/H ₂ O (2/1)	80	60	
7	0.19	K_2CO_3	H_2O	80	15	
8	0.19	K ₂ CO ₃	EtOH/H ₂ O (2/1)	r.t	20	

^aReaction conditions: iodobenzene (1 mmol), phenylboronic acid (1.2 mmol), base (1.5 mmol), solvent (3 ml), under air atmosphere, 2 hr. ^bIsolated yields.

next run. Remarkably, recycling experiments confirmed the chemical stability and reusability of the catalyst, and the recovered catalyst can be used during four runs (Figure 10). To confirm this further, leaching of Pd during the course of the catalytic reactions was examined by ICP analysis. ICP of the recovered catalyst after five catalytic cycles indicated that 21% of palladium was leached into the reaction medium (0.1 g of the manufactured catalyst and the catalyst after the 5th run, containing 0.019 and 0.015 mmol of Pd, respectively).

To illustrate the efficiency of the present catalyst in comparison with some Pd-based nanocatalysts, we compared the results with respect to mol% of Pd, reaction time and yields of the products (Table 5). Table 5 shows that this catalyst is superior to some previously reported nanocatalysts in terms of yields and reaction times.

TABLE 2 Suzuki-Miyaura coupling reactions of aryl halides with phenylboronic acida

		R ¹	$x + R^2 - B(C)$	$HNPs-TPy/Port K_2CO_3$	$r_{\rm C}$ R^{1}	\mathbb{R}^2	
Entry	X	R ¹	R ²	Time (hr)	Yield (%) ^b	TOF (hr ⁻¹)	m.p. ^[ref.]
1	Ι	Н	Н	2	98	257	65-68 ^[32]
2	Ι	4-NO ₂	Н	2.5	95	250	112-115 ^[33]
3	Ι	Н	4-Me	2	98	257	44-46 ^[33]
4	Ι	4-NO ₂	3-NO ₂	2.5	92	242	183–187 ^[34]
5	Br	Н	Н	4	95	125	65-69 ^[32]
6	Br	Н	4-OMe	4.5	93	122	85-88 ^[32]
7	Br	Н	4-F	5	92	121	75-78 ^[32]
8	Br	4-Me	Н	4	92	121	45-47 ^[33]
9	Cl	Н	Н	10	92	48	63-67 ^[32]
10	Cl	Н	4-Me	10	92	48	49-51 ^[33]

^aReaction conditions: iodobenzene (1 mmol), phenylboronic acid (1.2 mmol), catalyst (0.19 mol%), base (1.5 mmol), solvent (3 ml), under air atmosphere. ^bIsolated yields.

TABLE 3 Optimization of reaction conditions^a

$\bigcirc -1 + \bigcirc \frown \frown \bigcirc - \frown \bigcirc$					
Entry	Cat. (mol%)	Base	Solvent	Yield (%) ^b	
1	0	NEt ₃	No solvent	0	
2	0.152	NEt ₃	No solvent	46	
3	0.19	NEt ₃	No solvent	75	
4	0.285	NEt ₃	No solvent	97	
5	0.285	K_2CO_3	DMF	90	

^aReaction conditions: iodobenzene (1 mmol), styrene (1.2 mmol), base (3 mmol), solvent (3 ml), at 100°C, under air atmosphere, 4 hr.
^bIsolated yields.

3 | EXPERIMENTAL

The materials were purchased from Merck and Fluka, and were used without any additional purification. All reactions were monitored by thin-layer chromatography (TLC). Melting points were determined using a Stuart Scientific SMP2 apparatus. FT-IR spectra were determined with a PerkinElmer 683 instrument. ¹H-NMR and ¹³C-NMR spectra were recorded with a Bruker (400 MHz) spectrometer in CDCl₃ and dimethylsulfoxide (DMSO) as solvent. TGA was carried out with a STA PT-1000 Linseis instrument (Germany) under air atmosphere at a heating rate of 10°C/min. SEM and EDX measurements were performed using a TESCAN-MIRA3 operated at 26 kV with the electron gun filament: tungsten. TEM observations were carried out with a Zeiss-EM10C (Germany) operating at 100 kV with samples on formvar carbon-coated grid Cu mesh 300. The elemental palladium content of the nanocatalyst was determined by Perkin Elmer Optima 7300D ICP. The XRD pattern was obtained using STOE STADI-P diffractometer (Cu Kalpha1 radiation wavelength = 1.54060 Å). The chemical compositions of the catalysts were performed using XPS a Kratos Axis Ultra DLS spectrometer with an Al K α as a source.

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3.1 | Preparation of HPTPy

To a mixture of 4-anisaldehyde (0.12 ml, 1 mmol) and 2-acetylpyridine (0.22 ml, 2 mmol) were added KOH (0.15 g, 2 mmol) and 5 ml EtOH. The reaction mixture was stirred at room temperature for 2 min, ammonium hydroxide (2.9 ml, 2.5 mmol) was added and then stirring was continued for 8 hr. The resulting product was filtered and recrystallized from ethanol to produce 4'-(4-methoxyphenyl)-2,2':6',2"-terpyridine as white crystals in 85% yield (found: m.p. = 156° C).^[30] Then, 4'-(4-methoxyphenyl)- 2,2':6',2"-terpyridine (0.676 g, 2 mmol) was treated with 30% HBr in acetic acid (4 ml) at reflux conditions for 4 hr. After cooling to room temperature, the resultant solution was then basified to a pH-value of 10 by adding aqueous NaOH (20%) dropwise, and extracted repeatedly with CH₂Cl₂. The pH of the alkaline solution was then lowered with HCl (20%). The addition of HCl converts the soluble salt back into the water-insoluble HPTPy as white crystals. The precipitated product was then filtered and collected in 60% yield [found: m.p. = 290°C,^[30] IR (KBr): 3385,

TABLE 4 Coupling reactions of aryl halides with styrene^a

$R \xrightarrow{X} + \underbrace{\Box}_{\text{Et}_3\text{N, solvent-free, 100 °C}} \xrightarrow{R}$							
Entry	Х	R	Time (hr)	Yield (%) ^b	TOF (hr ⁻¹)	m.p. ^[ref.]	
1	Ι	Н	4	97	85	118-122 ^[35]	
2	Ι	4-NO ₂	4.5	92	80	150-152 ^[35]	
3	Ι	4-Me	4	95	83	115-118 [36]	
4	Br	Н	6	92	53	114-116 ^[35]	
5	Br	4-NO ₂	6.5	90	52	152-154 ^[35]	
6	Br	4-Me	6	90	52	115-117 ^[36]	
7	Cl	Н	24	Trace	_	-	

^aReaction conditions: aryl halide (1 mmol), styrene (1.2 mmol), catalyst (0.285 mol%), NEt₃ (3 mmol), under solvent-free conditions, 100°C. ^bIsolated yields.



SCHEME 3 The general mechanisms for Pd-catalyzed Suzuki–Miyaura and Mizoroki–Heck reactions



FIGURE 10 Recycling of the catalyst for the reaction of iodobenzene and phenylboronic acid

1594, 1526, 1460, 1175, 779 and 734 cm⁻¹]. ¹H-NMR (250 MHz, DMSO-d₆): $\delta = 9.03-9.06$ (d, J = 7.75 Hz, 2H), 8.93 (s, 2H), 8.78 (s, 2H), 8.45-8.50 (t, 2H), 7.91 (s, 4H), 6.93-6.97 (d, J = 7.75 Hz, 2H), 4.47 (br. s, OH). ¹³C-NMR (250 MHz, DMSO-d₆): $\delta = 160.21$, 151.23, 150.35, 146.08, 143.50, 132.12, 129.33, 128.40, 127.00, 124.17, 120.01, 116.45. MS: 327, 326, 325 (M⁺), 324, 308, 297, 296, 248, 247, 221, 220, 219, 218, 190, 163, 78, 51.

3.2 | Preparation of HPTPy-ITC

A mixture of ITC (0.065 g, 0.5 mmol) and HPTPy (0.325 g, 1 mmol) in DMSO (4 ml) was stirred at 100°C for 48 hr. After this time, EtOH (10 ml) and H_2O (5 ml) were added into the reaction mixture, and the precipitate collected by filtration and dried at 70°C.

TABLE 5Catalytic performances of some Pd-based nanocatalystsfor Suzuki coupling of iodobenzene and phenylboronic acid

Entry	Conditions	Pd (mol%)	Time	Yield (%)
1	GO/NHC-Pd, Na ₃ PO ₄ ·12H ₂ O, H ₂ O, 100°C ^[37]	1	6 hr	91.6
2	Pd–HoMOF, KOH, DMF, 100°C ^[38]	0.4	1 hr	99
3	(Pd (II)–NHCs) _n @nSiO ₂ , K ₂ CO ₃ , DMF/H ₂ O (2:1), 60°C ^[39]	0.27	6 min	97
4	Pd NPs on polymer, K ₂ CO ₃ , H ₂ O, 25–100°C ^[23]	0.08	5 hr	83
5	Pd (II)-NiFe ₂ O ₄ , K ₂ CO ₃ , EtOH/ H_2O , 80°C ^[40]	0.5	3 hr	96
6	GO-CPTMS@Pd-TKHPP, K ₂ CO ₃ , EtOH/H ₂ O, 80°C ^[41]	10	15 min	99
7	Pd–IPG, NaOH, EtOH/H ₂ O, 60°C ^[42]	0.1	1 hr	99
8	MP-TPy/Pd	0.19	2 hr	98

3.3 | Preparation of Fe₃O₄ NPs

Fe₃O₄ NPs were prepared according to a reported literature procedure.^[31] FeCl₃·6H₂O (2.7 g) and FeCl₂·4H₂O (1 g) were dissolved in deionized water (100 ml) under inert gas of N₂ atmosphere. To this solution was added 11 ml of 25% NH₄OH while stirring vigorously under N₂. Then the mixture was heated to 60°C and stirred for 1 hr under N₂ atmosphere. After cooling to room temperature, the resultant nanoparticles were gathered using an external magnet and washed several times with distilled water. After drying, a black powder was obtained.

3.4 | Preparation of Fe₃O₄@SiO₂

The prepared Fe_3O_4 NPs (0.5 g) were dispersed in 20 ml of deionized water by ultrasonic treatment for 10 min. Then, to this mixture was added 80 ml of EtOH, 0.5 ml of tetraethyl orthosilicate (TEOS) and 1.5 ml of 25% NH₄OH at 30°C under mechanical agitation. After 24 hr, the final product was collected by an external magnet, washed with EtOH and deionized water, and dried at 50°C to afford Fe_3O_4 @SiO₂.

3.5 | Preparation of Fe₃O₄@SiO₂@TMSPM

The prepared Fe_3O_4 @SiO₂ (0.1 g) was dispersed in 10 ml of dry toluene by ultrasonic treatment for 15 min. Then, TMSPM (0.3 ml) was added to the mixture. At reflux temperature, the resulting mixture was stirred for 24 hr.

Finally, after air cooling, the mixture was collected by an external magnet and the solid obtained was dried at 50°C.

3.6 | Preparation of magnetic polymer containing HPTPy (MP-TPy)

Fe₃O₄@SiO₂@TMSPM (0.1 g) was dispersed in 15 ml MeOH/CH₃CN (40:60), and HPTPy-ITC (0.033 g) was added. The mixture was stirred at room temperature for 1 hr. To this mixture was added 0.9 ml of TMPTA and 0.06 g of AIBN as an initiator, and the final volume was adjusted with MeOH/CH₃CN (40:60) to 35 ml. The mixture was sonicated for 3 min and then purged with nitrogen. The resulting mixture was refluxed at 60–70°C for 24 hr. The products were collected by using the external magnetic field, washed with ethanol, deionized water and acetone, then dried in vacuum at 50°C.

3.7 | Preparation of MP-TPy/Pd

MP-TPy/Pd was prepared in a typical procedure as follows. The magnetic polymer (0.1 g) and $PdCl_2$ (0.003 g, 0.028 mmol) were refluxed in EtOH (5 ml) for 24 hr. The final catalyst was separated with a magnet, washed with EtOH and dried at 50°C. ICP showed 0.019 mmol of palladium is loaded on the 0.1 g MP-TPy/Pd (2.01 wt%).

3.8 | General procedure for Suzuki-Miyaura cross-coupling reactions

ArX (1 mmol), ArB (OH)₂ (1.2 mmol) and K_2CO_3 (1.5 mmol) were added into a flask containing MP-TPy/Pd (0.01 g, 0.19 mol%) and EtOH/H₂O (2/1). The mixture was then stirred in an 80°C oil bath for an appropriate reaction time. The progress of the reaction was monitored by TLC. After completion of the reaction, ethyl acetate (10 ml) was added into the reaction mixture, the catalyst was separated by using an external magnet, and the organic solvent was evaporated to obtain a biaryl product.

Biphenyl (Table 2, entry 1): ¹H-NMR (400 MHz, CDCl₃): δ =7.53 (4H, d, J = 8 Hz), 7.37 (4H, t, J = 8 Hz), 7.28 (2H, t, J = 8 Hz). ¹³C-NMR (100 MHz, CDCl₃): δ = 141.27, 128.80, 137.0, 127.29, 127.21.

4-Methylbiphenyl (Table 2, entry 3): ¹H-NMR (400 MHz, CDCl₃): δ = 7.17–7.52 (9H), 2.32 (3H, s).

3,4'-Dinitrobiphenyl (Table 2, entry 4): ¹H-NMR (400 MHz, CDCl₃): δ =8.55 (1H, s), 8.40 (2H, d, J = 8 Hz), 8.42 (2H, d, J = 8 Hz), 8.37 (1H, d, J = 8 Hz), 8.02 (1H, d, J = 8 Hz) 7.86 (2H, d, J = 8 Hz), 7.76 (1H, t, J = 8 Hz). ¹³C-NMR (100 MHz, CDCl₃): 10 of 11 WILEY Organometallic Chemistry

 $\delta = 148.83, 148.02, 144.91, 140.48, 133.26, 130.32, 128.16, 124.51, 123.61, 122.35.$

3.9 | General procedure for Mizoroki -Heck cross- coupling reactions

A mixture of aryl halide (1 mmol), styrene (1.2 mmol), Et_3N (3 mmol) and MP-TPy/Pd (0.015 g, 0.28 mol%) was stirred at 100°C (oil bath temperature) under solvent-free conditions. After completion of the reaction, which was monitored by TLC, ethylacetate (10 ml) was added to the mixture reaction. The catalyst was separated by using an external magnet. Water (3 × 15 ml) was added to the ethylacetate phase and decanted. After evaporation of the solvent, the resulting crude products were purified in *n*-hexane/ethylacetate giving the pure products in high to excellent yields.

trans-Stilbene (Table 4, entry 1): ¹H-NMR (400 MHz, CDCl₃): δ = 7.60 (4H, d, *J* = 8 Hz), 7.44 (4H, t, *J* = 8 Hz), 7.31–7.37 (2H, m), 7.20 (2H, s).¹³C-NMR (100 MHz, CDCl₃): δ 137.38, 128.86, 128.76, 127.70, 126.59.

4 | CONCLUSIONS

In summary, magnetic polymer-supported Pd NPs have been prepared and fully characterized. As expected, MP-TPy/Pd exhibited excellent activity in Suzuki-Miyaura and Mizoroki-Heck cross-coupling reactions under low palladium loading conditions, and provided the corresponding products with excellent yields (up to 98%) and high catalytic activities (TOF up to 257 hr^{-1}). It is noteworthy that palladium ions are reduced to Pd NPs and stabled in the presence of ethanol as a green reducing agent and due to interaction with terpyridine-based ligand. Ultimately, we believe that this work offers several advantages in preparative procedures, including simplicity of product work-up and separation of the catalyst. In addition, MP-TPy/Pd, magnetically recoverable nanocatalyst, was reused for a consecutive five times with a small drop in catalytic activity, considering the high cost of palladium, reuse of the catalysts could lead to economical automation system.

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