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Palladium stabilized by 3,4-dihydropyridine-functionalized magnetic Fe₃O₄ nanoparticles as a reusable and efficient heterogeneous catalyst for Suzuki reactions

Mozhgan pirhayati,^a Hojat Veisi^{*b} and Ali Kakanejadifard^a

A Pd supported on 3,4-dihydropyridine (Py)-functionalized Fe₃O₄ (Fe₃O₄/Py/Pd) hybrid material has been synthesized for the first time. Inductively coupled plasma (ICP), energy dispersive X-ray spectroscopy (EDX), transmission electron microscopy (TEM), scanning electron microscopy (SEM), and field emission scanning electron microscopy (FESEM) and Fourier transform infrared (FTIR) studies have been used to characterize the catalyst. The catalyst exhibited very high activity for Suzuki coupling reaction of several aryl halides with phenylboronic acids in aqueous phase at room temperature. The most interesting result of this work is the possibility to perform Suzuki reactions of aryl chlorides in the presence of the prepared catalyst. The yields of the products were in the range from 70% to 98%. In this process, the novel catalyst could be recovered in a facile manner from the reaction mixture by applying an external magnet device, and reused more than eight times without any significant loss in activity.

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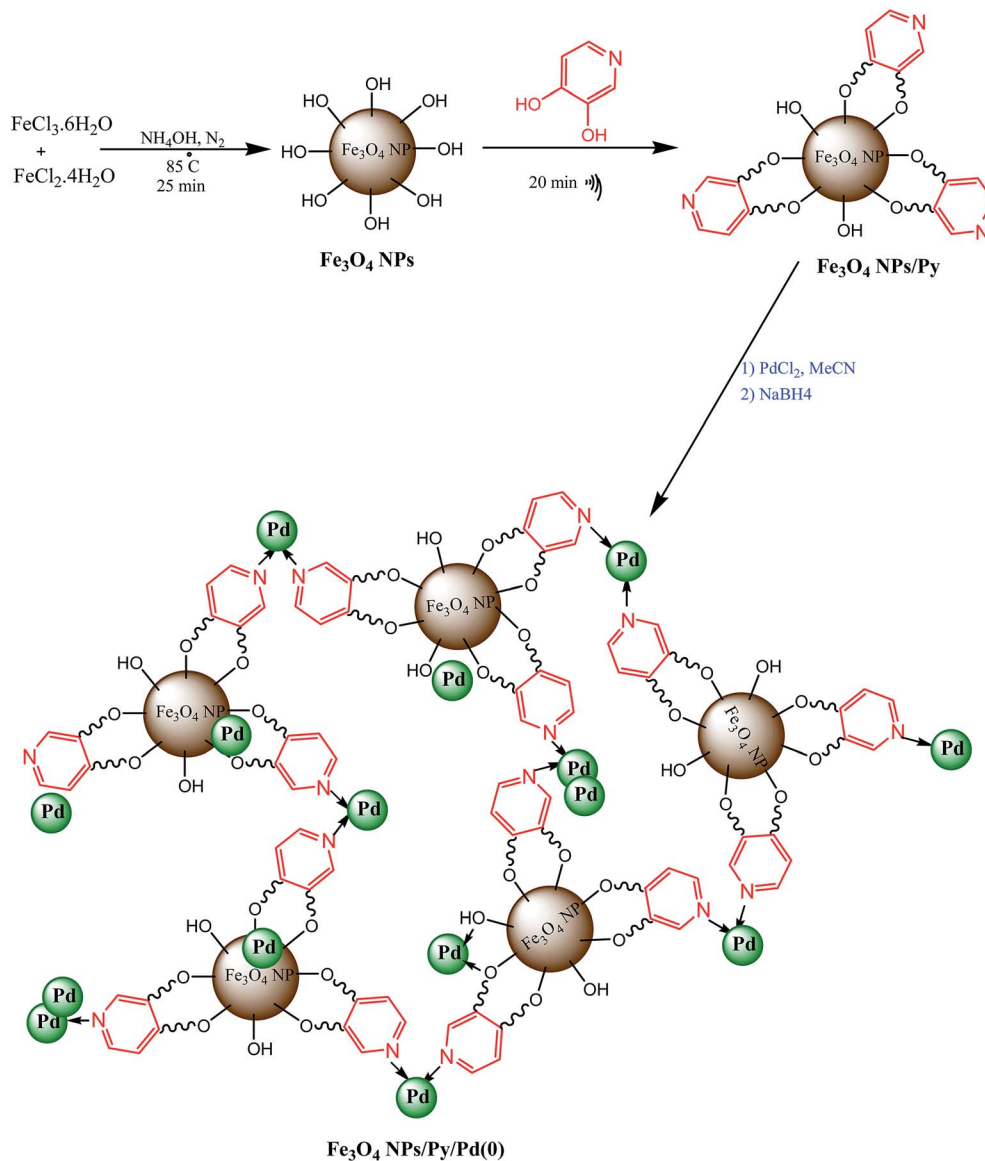
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1. Introduction

Green catalysis is a subchapter of green chemistry but probably the most important one generally. Catalysts are divided into two groups: most examples are homogeneous systems and the others are heterogeneous systems. Homogeneous catalysts have a number of other advantages, such as high selectivity, better yield, and easy optimization of catalytic systems by rectification of ligands and metals, but the difficulty of catalyst separation from the final product limits their use in industrial and synthetic applications. To address the separation problems in homogeneous catalysis, chemists and engineers have investigated a wide range of strategies resulting in the use of heterogeneous catalyst systems which appeared to be the best logical solution.¹ The benefit of heterogeneous catalysts is very simple separation from the reaction but, a substantial decrease in the activity of the immobilized catalyst is frequently observed due to the loss of the catalyst in the separation processes and/or diffusion factors. Consequently, we need a catalyst system that not only shows high activity and selectivity (like a homogeneous system) but also possesses the ease of catalyst separation and recovery (like a heterogeneous system). These goals can be achieved by nanocatalysts. Nanocatalysts bridge the gap between homogeneous and heterogeneous catalysis, preserving the desirable attributes of both systems. Recently,

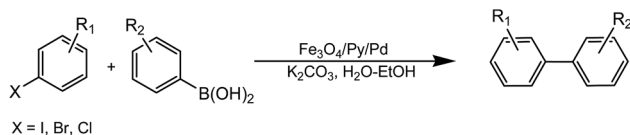
nanostructured catalysts have been extensively investigated due to their much higher activities than that of the corresponding bulk materials, however isolation and recovery of these tiny nanocatalysts from the reaction mixture is not easy.²⁻⁶ Conventional techniques (such as filtration) are not efficient because of the nano size of the catalyst particles so to overcome this issue, the use of magnetic nanoparticles has emerged as a viable solution. One of the attractive features of MNPs is the possibility of fast and cost-efficient separation by applying an external magnetic field, which makes them as the ideal candidates for practical use in catalysis process. This new direction in catalysis galvanized the academic research and led to the development of a great number of magnetic-based catalysts, especially magnetite (Fe₃O₄) that found application in the various reactions.⁷⁻¹⁶ Transition metal-catalyzed protocols, especially palladium reactions, have become powerful tools in chemical synthesis of many materials and compared with frequently used palladium(II) complexes catalysts, palladium nanoparticles were found to exhibit remarkable catalytic activities for Suzuki, Heck and Sonogashira cross-coupling reactions,¹⁷⁻²⁵ hydrogenation of many organic compounds,²⁶⁻²⁸ oxidation of hydrocarbon,²⁹ isomerization,³⁰ and decomposition of nitrogen monoxide,³¹ which have been extensively used in the synthesis of drugs and fine chemicals.³²⁻³⁷ There have been a variety of reports describing the use of magnetic nanocomposites for the immobilization of Pd nanoparticles, the catalytic activity of Pd nanoparticles can be retained, and the stability also can be improved to some extent.³⁸⁻⁴⁰ In continuing our attempts toward the extension of efficient and

^aDepartment of Chemistry, Faculty of Science, Lorestan University, Khorramabad, Iran^bDepartment of Chemistry, Payame Noor University (PNU), 19395-4697 Tehran, Iran.
E-mail: hojatveisi@yahoo.com



Scheme 1 Preparation of Fe₃O₄/Py/Pd(0) nanocatalyst.

environmentally benign heterogeneous catalysts,^{41–44} herein, we will report a simple preparation of palladium nanoparticles incorporated into Fe₃O₄/Py/Pd(0) nanocomposite as a new magnetically recoverable heterogeneous catalyst (Scheme 1). This recyclable heterogeneous catalyst was used to catalyze C–C coupling reaction in an aqueous solvent by Suzuki reaction (Scheme 2). Most important, the synthesized Fe₃O₄/Py/Pd(0) nanocomposite presented good magnetic property, and could be easily separated from the reaction mixture by using



Scheme 2 Fe₃O₄/Py/Pd(0) for Suzuki cross-coupling reaction.

a magnet. By utilizing this property, it could be reused for eight cycles without losing its catalytic activity, indicative of a potential application in industry.

2. Experimental

2.1. Preparation of the magnetic Fe₃O₄ nanoparticles (MNPs)

Magnetic nanoparticles were prepared *via* co-precipitation of Fe(III) and Fe(II) ions with a molar ratio of 2 : 1 in the presence of ammonium hydroxide. Generally, a mixture of FeCl₃·6H₂O (5.838 g, 0.0216 mol) and FeCl₂·4H₂O (2.147 g, 0.0108 mol) was dissolved in 100 mL deionized water at 85 °C under N₂ atmosphere and intense mechanical stirring (500 rpm). Afterwards, 10 mL of 25% NH₄OH was quickly injected into the reaction mixture in one section. The addition of the base to the Fe²⁺/Fe³⁺ salt solution resulted in the formation of the black precipitate of

MNPs instantly. The reaction continued for another 25 min and the mixture was cooled to room temperature. The magnetic nanoparticles as a dark solid were isolated from the solution by magnetic separation and washed several times by DI water.

2.2. Preparation of the $\text{Fe}_3\text{O}_4/\text{Py}$

The obtained MNPs powder (500 mg) was dispersed in 50 mL ethanol/water (volume ratio, 1 : 1) solution by sonication for 20 min, and 3,4-dihydropyridine (Py) (250 mg) was added to the mixture. The mixture was stirred for 5 h at 40 °C. The suspended substance was separated with centrifugation. The settled

product was re-dispersed in ethanol by sonication and then was isolated with magnetic decantation for 5 times. The precipitated product ($\text{Fe}_3\text{O}_4/\text{Py}$) was dried at room temperature under vacuum.

2.3. Preparation of the $\text{Fe}_3\text{O}_4/\text{Py}/\text{Pd}(0)$

The $\text{Fe}_3\text{O}_4/\text{Py}$ (500 mg) were dispersed in CH_3CN (30 mL) by ultrasonic bath for 30 min. Subsequently, a yellow solution of PdCl_2 (30 mg) in 30 mL acetonitrile was added to dispersion of $\text{Fe}_3\text{O}_4/\text{Py}$ and the mixture was stirred for 10 h at room temperature. Then, the $\text{Fe}_3\text{O}_4/\text{Py}/\text{Pd}(0)$ was separated by magnetic

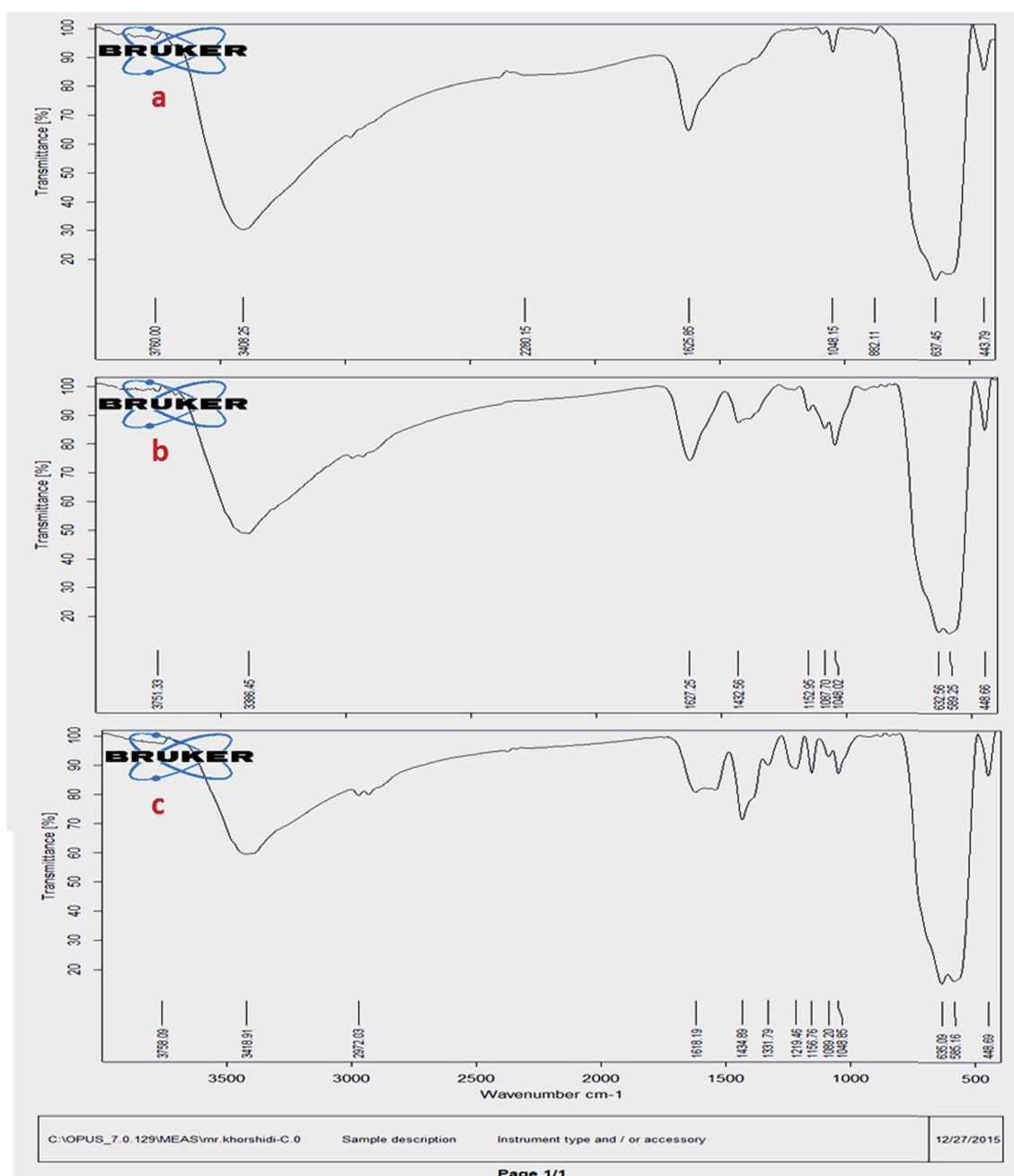


Fig. 1 FT-IR spectra of (a) Fe_3O_4 , (b) $\text{Fe}_3\text{O}_4/\text{Py}$, and (c) $\text{Fe}_3\text{O}_4/\text{Py}/\text{Pd}$.

decantation and washed by CH_3CN , H_2O and acetone respectively to remove the unattached substrates. Scheme 1 depicted the synthetic procedure of $\text{Fe}_3\text{O}_4/\text{Py}/\text{Pd}(\text{II})$. The reduction of $\text{Fe}_3\text{O}_4/\text{Py}/\text{Pd}(\text{II})$ by sodium borohydride was performed. The final product $\text{Fe}_3\text{O}_4/\text{Py}/\text{Pd}(0)$ was washed by water and ethanol and dried in vacuum at 40°C . The concentration of palladium in $\text{Fe}_3\text{O}_4/\text{Py}/\text{Pd}(0)$ was 3.75 wt% (0.353 mmol g^{-1}), which was determined by ICP-AES.

2.4. Suzuki coupling reactions

Catalytic activity of the synthesized $\text{Fe}_3\text{O}_4/\text{Py}/\text{Pd}$ nanocomposite was tested through the Suzuki reaction of aryl halides with phenylboronic acid. In the typical experiment, a mixture of aryl halide (1.0 mmol), phenylboronic acid (0.134 g, 1.1 mmol), K_2CO_3 (0.276 mg, 2 mmol), and 7.0 mg $\text{Fe}_3\text{O}_4/\text{Py}/\text{Pd}$ nanocomposite ($7\text{ mg} \approx 0.021\text{ mol\% Pd}$) were added into 5 mL water/ethanol (1 : 1) solution in a 25 mL Schlenk tube. The mixture was then stirred for the desired time at room temperature. The reaction was monitored by thin layer chromatography (TLC, *n*-hexane/acetone; 4 : 1). After completion of the reaction, 5 mL ethanol was added, and the catalyst was removed by external magnet. Further purification was achieved by column chromatography.

3. Results and discussion

3.1. Catalyst characterization

The Fe_3O_4 particles were synthesized according to the literature using ferric chloride hexahydrate and ferrous chloride tetrahydrate upon addition of NH_4OH . The $\text{Fe}_3\text{O}_4/\text{Py}$ particles were prepared by coating 3,4-dihydropyridine (Py) on the surface of Fe_3O_4 particles. For the preparation of palladium loaded materials, $\text{Fe}_3\text{O}_4/\text{Py}$ particles were treated with a PdCl_2 (Scheme 1), and then a sodium borohydride was added. Finally, the mixture was collected by an external magnet, followed by drying in vacuum. The Pd content in $\text{Fe}_3\text{O}_4/\text{Py}/\text{Pd}$ catalyst was determined 3.75 wt% (0.353 mmol g^{-1}) by ICP-AES. The prepared catalyst was characterized by, FTIR, SEM, FESEM, TEM, ICP and EDX.

Fig. 1 shows Fourier transform infrared (FTIR) spectra for Fe_3O_4 , $\text{Fe}_3\text{O}_4/\text{Py}$, and $\text{Fe}_3\text{O}_4/\text{Py}/\text{Pd}$. The FTIR spectrum for the MNPs alone shows a stretching vibration at 3408 cm^{-1} which incorporates the contributions from both symmetrical and asymmetrical modes of the O–H bonds which are attached to the surface iron atoms.⁴⁶ The bands at low wave numbers ($\leq 700\text{ cm}^{-1}$) come from vibrations of Fe–O bonds of iron oxide, in which for the bulk Fe_3O_4 samples appear at 570 and 375 cm^{-1} but for Fe_3O_4 nanoparticles at 624 and 572 cm^{-1} as a blue shift, due to the size reduction.^{47–49} The presence of an adsorbed water layer is confirmed by a stretch for the vibrational mode of water found at 1625 cm^{-1} . The FTIR spectra of $\text{Fe}_3\text{O}_4/\text{Py}$ and $\text{Fe}_3\text{O}_4/\text{Py}/\text{Pd}$ show Fe–O vibrations in the same vicinity. The introduction of pyridine groups to the surface of MNPs is confirmed by the bands at 1627 , 1432 and 3000 cm^{-1} assigned to the C=N, C=C and C–H stretching vibrations respectively. The C=N signal appeared at 1627 cm^{-1} in curve b for the metal–ligand co-

ordination⁴⁸ presumably leads to a shift of this peak to lower frequency. This shift can be observed comparing curve c. This peak at curves b and c displayed the successful attachment of pyridine organic groups and subsequent coordination of Pd nanoparticles within the hybrid material.

The transmission electron microscopy (TEM) image of the $\text{Fe}_3\text{O}_4/\text{Py}/\text{Pd}$ catalyst announced that the Pd nanoparticles with nearly spherical morphology were formed on the surface of the modified Fe_3O_4 nanoparticles (Fig. 2).

Field Emission Scanning Electron Microscope (FESEM) shows the image of the synthesized $\text{Fe}_3\text{O}_4/\text{Py}/\text{Pd}$ loaded magnetite nanoparticles. It was confirmed that the catalyst was made up of monotonic nanometer-sized particles (Fig. 3).

The existence of metallic Pd in the catalyst was also confirmed by the EDX detector coupled to the SEM which showed the presence of Fe, C, O and N in Fig. 4.

Fig. 5 shows a representative SEM image and corresponding elemental maps for the synthesized catalyst. It can be seen that Pd metal particles are well dispersed in the composite. The selected-area elemental analysis figure reveals the presence of C, O, Fe and Pd throughout the sample in a homogeneous manner, which confirms the regular uniformity of the prepared sample.

The XRD pattern of the $\text{Fe}_3\text{O}_4/\text{Py}/\text{Pd}$ is presented in Fig. 6. The characteristic diffraction peaks in the sample at 2θ of 30.3° , 35.7° , 43.4° , 53.8° , 57.2° and 62.8° are corresponded to the diffraction of (220), (311), (400), (422), (511), and (440) of the

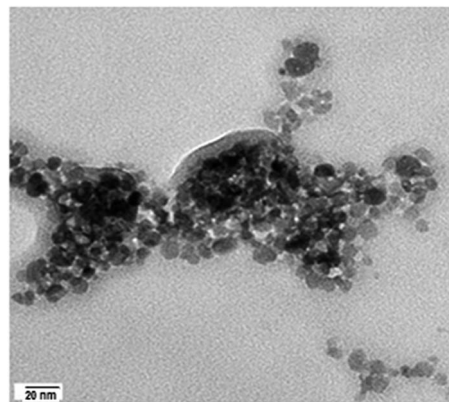


Fig. 2 TEM image of $\text{Fe}_3\text{O}_4/\text{Py}/\text{Pd}$.

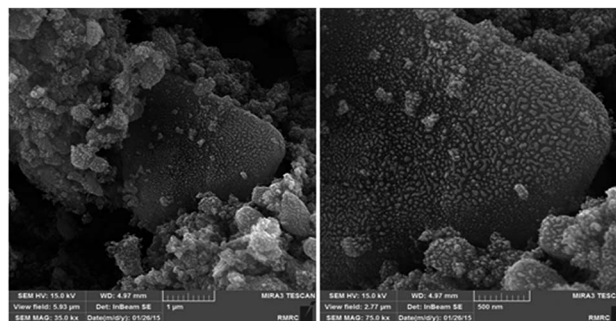


Fig. 3 FESEM images of $\text{Fe}_3\text{O}_4/\text{Py}/\text{Pd}$.

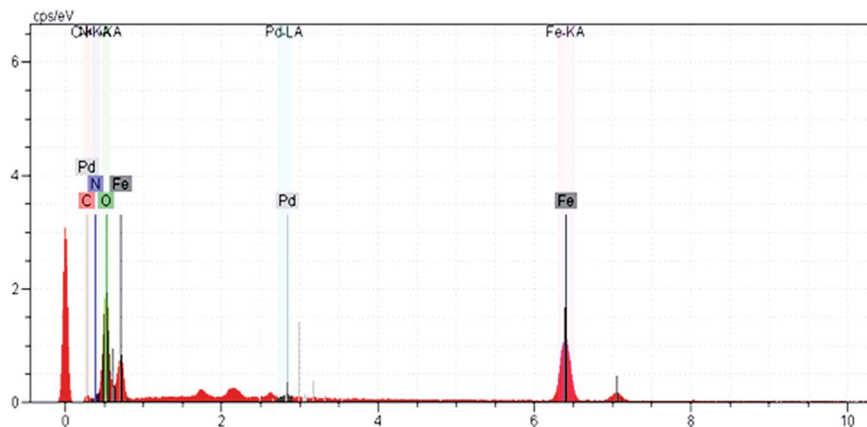


Fig. 4 EDX data for the catalyst.

Fe_3O_4 . The entire diffraction peaks match with the magnetic cubic structure of Fe_3O_4 (JCPDS 65-3107).⁵⁰ Typical diffraction peaks of Pd(0) correspond to (111), (200) and (220) are observed at 40.1° , 46.7° and 68.2° (JCPDS 87-0638) in the pattern. The results from XRD imply that the Pd nanoparticles have been successfully immobilized onto the surface of the magnetic particles.

The magnetic measurements were carried out by VSM at room temperature. The magnetization curves measured for $\text{Fe}_3\text{O}_4/\text{Py}/\text{Pd}$ is presented in Fig. 7. The magnetic saturation value is 55.6 emu g^{-1} . The decrease in the saturation magnetization is due to the presence of the organic shell and Pd nanoparticles on the Fe_3O_4 surface. Therefore, the above mentioned results indicated an easy and efficient way to

separate and recycle the prepared catalyst from the solution by an external magnetic force.

3.2. Catalytic activity

In continuation of our interest in environmentally benign chemical processes,^{41–44} after characterization of the prepared nanocatalyst to evaluate the catalytic ability of the composites, Suzuki cross-coupling reaction was carried out as model reactions (Scheme 2). It is well-known that the Suzuki cross-coupling reaction of arylhalides and phenylboronic acid provides an efficient route to form C–C bond under relatively mild conditions.⁴⁵ The $\text{Fe}_3\text{O}_4/\text{Py}/\text{Pd}$ catalyzed Suzuki reaction between phenylboronic acid and bromobenzene was chosen as a model reaction to evaluate the effects of solvent (nonpolar, protic and aprotic), base (Et_3N ,

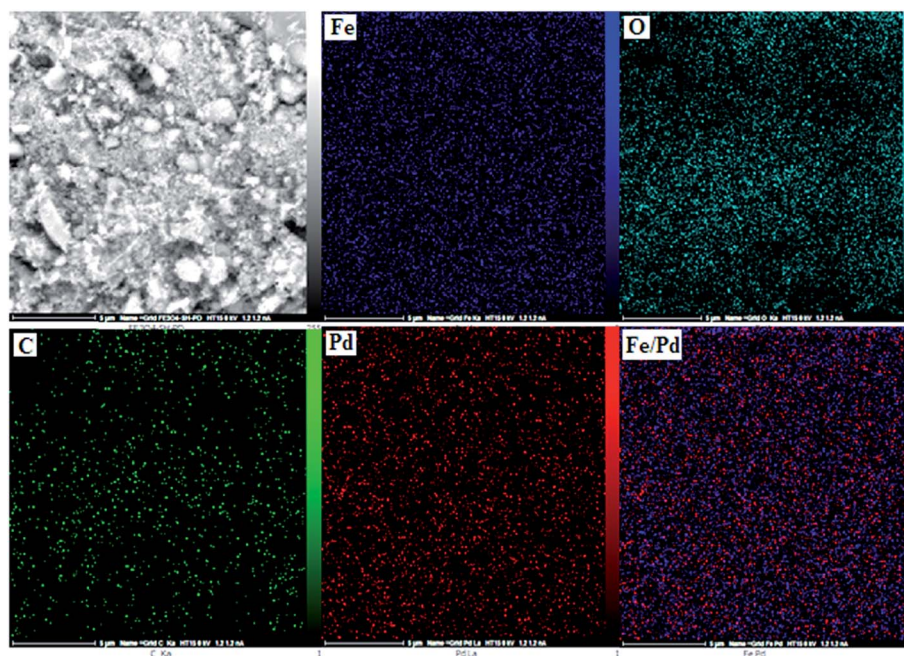
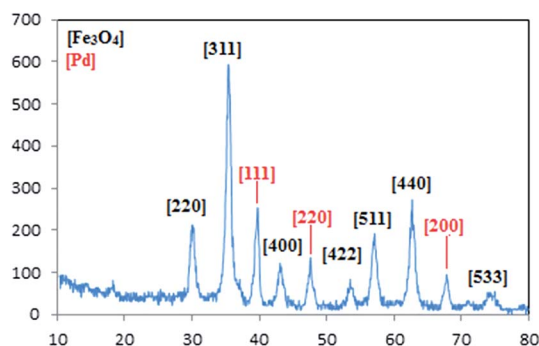
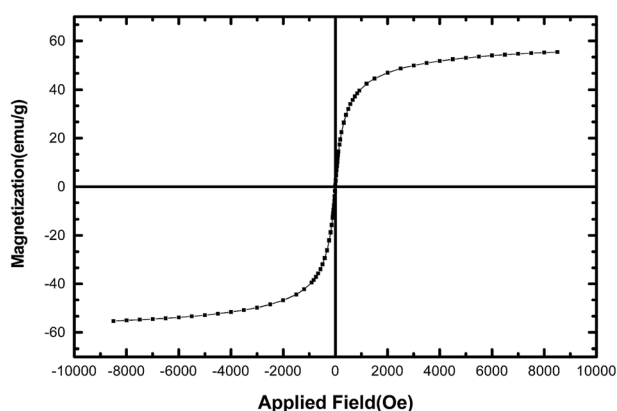


Fig. 5 SEM image of $\text{Fe}_3\text{O}_4/\text{Py}/\text{Pd}$ shows the presence of C, O, Fe, Pd and Fe/Pd atoms in the catalyst.

Fig. 6 XRD patterns of Fe₃O₄/Py/Pd.Fig. 7 VSM spectra of Fe₃O₄/Py/Pd.

NaOAc and K₂CO₃) and amount of catalyst at room temperature. Optimization conditions studies are summarized in Table 1.

The reactions were conducted using H₂O/EtOH (1 : 1) as the best solvent. Among the bases evaluated, K₂CO₃ was found to be the most effective. The effect of catalyst loading was investigated employing several quantities of the catalyst ranging from 0.1 mol% to 0.3 mol% (Table 1, entries 6, 8 and 9). The best yield was obtained with 0.007 g (0.2 mol%) of the catalyst (Table 1, entry 6). To study the generality of this cross-coupling, the

Table 1 Optimization of the conditions for the Suzuki–Miyaura reaction of bromobenzene with phenylboronic acid^a

Entry	Solvent	Pd (mol%)	Base	Time (min)	Yield ^b (%)
1	DMF	0.2	K ₂ CO ₃	80	80
2	Toluene	0.2	K ₂ CO ₃	60	65
3	EtOH	0.2	K ₂ CO ₃	60	77
4	H ₂ O	0.2	K ₂ CO ₃	90	55
5	EtOH/H ₂ O ^c	0.2	NaOAc	60	65
6	EtOH/H ₂ O ^c	0.2	K ₂ CO ₃	40	98
7	EtOH/H ₂ O ^c	0.2	Et ₃ N	90	80
8	EtOH/H ₂ O ^c	0.1	K ₂ CO ₃	60	75
9	EtOH/H ₂ O ^c	0.3	K ₂ CO ₃	60	96
10	EtOH/H ₂ O ^c	0.2	No base	90	Trace

^a Reaction conditions: bromobenzene (1 mmol), PhB(OH)₂ (1.1 mmol), Fe₃O₄/Py/Pd, solvent (3 mL). ^b Isolated yield. ^c EtOH/H₂O = 1 : 1.

Table 2 Heterogeneous Suzuki–Miyaura reaction of aryl halides with phenylboronic acids catalyzed by Fe₃O₄/Py/Pd at room temperature^a

Entry	R ₁ C ₆ H ₄ X	R ₂ C ₆ H ₄ B(OH) ₂	X	Time (h)	Yield ^b (%)
1	H	H	I	0.16	98
2	H	H	Cl	12	70
3	H	H	Br	0.66	98
4	4-CH ₃	H	Cl	12	75
5	4-CH ₃	H	I	0.20	98
6	4-CH ₃	H	Br	1	96
7	4-COCH ₃	H	Br	0.8	96
8	4-COCH ₃	H	I	0.3	98
9	4-COCH ₃	H	Cl	12	65
10	4-CH ₃ O	H	I	0.3	98
11	4-CH ₃ O	H	Br	1.5	96
12	4-Cl	H	Br	1	96
13	3-NO ₂	H	I	0.5	96
14	3-NO ₂	H	Br	3	88
15	2-CHO	H	Br	5	70
16	2-Thienyl	H	I	1	96
17	2-Thienyl	H	Br	5	90
18	1-Naphthyl	H	I	2	96
19	H	4-NO ₂	Br	3	85
20	4-COCH ₃	4-NO ₂	Br	3	80
21	H	4-CH ₃	Br	1	92
22	4-COCH ₃	4-CH ₃	Br	1.5	92

^a Reactions were carried out under aerobic conditions in 3 mL of H₂O/EtOH (1 : 1), 1.0 mmol arylhalide, 1.1 mmol phenylboronic acids and 2 mmol K₂CO₃ in the presence of catalyst (0.007 g, 0.2 mol% Pd). ^b Isolated yield.

scope of the reaction was explored with various aryl halides (I, Br, Cl) and phenylboronic acids under the optimized conditions (Table 2, entries 1–22). Under the optimized conditions, phenyl iodides, bromides and chlorides all reacted efficiently with phenylboronic acid (Table 2, entries 1–15). Aryl halides with electron-withdrawing or releasing groups reacted with phenylboronic acid to afford the corresponding products in high yields. It was found that the yield when using an *ortho* substituted aryl bromide was lower (Table 2, entry 15) than those obtained with *para*- or *meta*-substituted aryl bromides (Table 2, entries 4–12, 13 and 14). Notably, heteroaryl halides such as 2-bromothiophene and 2-iodothiophene with phenylboronic acid gave the corresponding coupled products in 96% and 90% yields, respectively (Table 2, entries 16 and 17). The most interesting result of this work is the possibility to perform Suzuki reactions of aryl chlorides in the presence of prepared

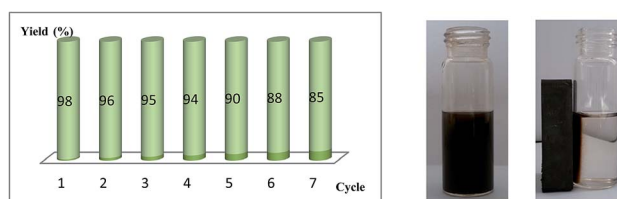


Fig. 8 (left) The recycling of the Fe₃O₄/Py/Pd for the Suzuki coupling reaction under similar conditions; (right) recycled Fe₃O₄/Py/Pd catalyst from reaction mixture.

Table 3 Catalytic performance of different catalysts in the coupling reaction of iodobenzene and bromobenzene with phenylboronic acid

Entry	Catalyst (mol%)	Conditions	X	Time (h)	Yield (%)	Ref.
1	Bis(oxamato)palladate(II) complex (5)	Et ₃ N, <i>n</i> -Bu ₄ NBr, 120 °C	I, Br	2	78, 65	51
2	NHC–Pd(II) complex (0.2)	K ₃ PO ₄ ·3H ₂ O, H ₂ O, TBAB, 40 °C	I, Br	5, 6	98, 90	52
3	SiO ₂ -pA-Cyan-Cys-Pd (0.5)	K ₂ CO ₃ , H ₂ O, 100 °C	I, Br	5, 5.5	95, 88	53
4	Pd ₃ (dba) (1)	K ₃ PO ₄ , THF, 80 °C	Br	24	77.7	54
5	Pd-BOX (2)	K ₂ CO ₃ , DMF, 70 °C	I	6	100	55
6	γ-Fe ₂ O ₃ -acetamidine-Pd (0.12)	Et ₃ N, DMF, 100 °C	I, Br	0.5, 0.5	96, 96	56
7	Pd-isatin Schiff base-γ-Fe ₂ O ₃ (0.5, 1.5)	Et ₃ N, solvent-free, 100 °C	I, Br	0.5, 0.75	95, 90	57
8	Fe ₃ O ₄ /Py/Pd (0.02)	K ₂ CO ₃ , H ₂ O/EtOH, rt	I, Br	0.16, 0.66	98, 98	This work

catalyst with good yields (Table 2, entries 2, 4 and 9). The heterogeneity of the catalyst was evaluated to study whether the reaction using solid Pd catalysts occurred on the Fe₃O₄/Py surface or was catalyzed by Pd species leached in the liquid phase. To address this issue, two separate experiments were conducted with bromobenzene and phenyl boronic acid. In the first experiment, the reaction was terminated after 20 min; in this connection, the catalyst was separated from the reaction mixture by an external magnet and the reaction was continued with the filtrate for an additional 60 min. In the second experiment, the reaction was terminated after 20 min. In both cases, the desired product was obtained in the same yield (45%). Pd was not detected in the filtrate in either experiment by ICP-AES. These studies demonstrate that only the Pd bound to Fe₃O₄/Py during the reaction is active, and the reaction proceeds on the heterogeneous surface.

The recyclability of Fe₃O₄/Py/Pd was further studied because the recycling of the heterogeneous catalyst was an important issue for practical applications. The recovered catalyst was added to reaction mixture under the same conditions (Table 1) for eight cycles without a significant loss of yield and catalytic activity (Fig. 8, left side). This result also demonstrated that the palladium leaching of the catalyst was low. In order to regenerate the catalyst, after each cycle, it was separated by a magnet (Fig. 8, right side), and washed several times with deionized water and ethanol. Then, it was dried in oven at 50 °C. In continuation of our works, a blank test by Fe₃O₄@Pd was performed under same condition for this reaction coupling. Interestingly, we have found that the catalyst was not recoverable after two reaction cycles. So, this results shown that the 3,4-dihydroxypyridine ligands are responsible for stabilization of palladium nanoparticles and the good catalytic activity of the prepared catalyst.

The leaching of Pd into the reaction solution after five runs was determined by ICP analysis to be 1.35%, which indicates the stability of the catalyst during the reaction. To investigate the heterogeneity of the catalyst, we conducted a hot filtration test for the Suzuki reaction between bromoacetophenone with phenylboronic using Fe₃O₄/Py/Pd under same conditions. The reaction was allowed to proceed for 20 minutes (yield: 60%), and then the catalyst was separated. However, there is no increasing in yield of the desired product when the reaction was continued for further 1 h after the catalyst was magnetically separated, confirming the heterogeneous character of the catalyst.

A comparison of the activity of various Pd catalysts with Fe₃O₄/Py/Pd in the Suzuki coupling reaction published in the literature is listed in Table 3. From table, it can be seen that present catalyst exhibited higher conversions and yields compared to the other reported system.

4. Conclusion

The immobilized palladium on 3,4-dihydroxypyridine (Py)-coated Fe₃O₄ was found to be effective in the Suzuki coupling of various aryl halides and especially less reactive aryl chlorides with phenyl boronic acid. The benefits of this catalyst are the cheap and uncomplicated synthetic pathway, and mild and efficient C–C coupling reactions in green media. Notably, the recyclability of the catalyst by a external magnet, with no palladium leaching from Fe₃O₄/Py/Pd is good characteristics. It seems that 3,4-dihydroxypyridine have played an important role in stabilization of catalyst particles owing to its structural diversity.

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