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ARTICLE

Palladium Supported on Phosphinite Functionalized Fe_3O_4 Nanoparticles as a New Magnetically Separable Catalyst for Suzuki-Miyaura Coupling Reaction in Aqueous Media

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Mohammad Gholinejad,*[a] Mehran Razeghi,[a] Arash Ghaderi,*[b], Pullithadathil Biji[c]

A novel phosphinite functionalized magnetic (Fe_3O_4) nanoparticles having silica nanoshells, containing imidazolium ionic liquid moiety has been successfully synthesized and used as a support and stabilizer for palladium nanoparticles. The obtained compound was characterized by SEM, TEM, EDX, solid UV, VSM, XRD, XPS, FT-IR, and N_2 adsorption–desorption analyses. This magnetic composite has been applied as the catalyst in Suzuki-Miyaura coupling reaction of aryl halides (I, Br,Cl) with arylboronic acids in aqueous media under mild reaction conditions and low palladium loading. The air stable catalyst could be easily separated from the reaction mixture using an external magnet and reused for eight consecutive times with small drops in its catalytic activity.

Introduction

In recent years, transition metals have had an important impact on the development of organic chemistry by evolving different new reactions. Palladium is one of the precious noble metal which catalyzes various important coupling reactions such as Suzuki-Miyaura,[1] Heck-Mizoroki[2] and Sonogashira-Hagihara[3] reactions. Among the different palladium catalyzed reactions, the cross coupling between aryl, vinyl or alkyl (pseudo)halides and organoboron reagents, known as Suzuki-Miyaura reaction, is one of the substantial palladium catalyzed reactions for the formation of different types of compounds found in many building blocks of pharmaceuticals and natural products. From the green chemistry point of view, contamination of the products in Suzuki-Miyaura reaction with heavy and toxic palladium metal is very undesirable.[4] Furthermore, isolation and reusing expensive palladium catalysts are important from the economic standpoint. To address these challenges, many efforts have been made by heterogenization of the catalysts using immobilization of homogeneous palladium catalysts on different supports such as polymers,[5] modified silicas,[6] mesoporous materials[7] and ionic liqiuids.[8] Despite the significant progress in heterogenization of palladium catalysts, separation of these heterogeneous catalysts from the reaction mixture using conventional methods such as filtration or centrifugation is not an easy task. However, magnetic nanoparticles with unique physical properties such as high surface area, superparamagnetism and low toxicity have been distinguished as promising supports for stabilization of palladium nanoparticles.[9]

Ionic liquids (ILs) with special properties, such as non-volatility, non-flammability and a wide temperature range over the liquid phase, are classified as green solvents.[10] However, most of ionic liquids are expensive materials and their use as a solvent is not desirable economically. Nevertheless, by immobilization of ILs onto the surface of a solid support, organic reactions can proceed on the thin IL layer on the surface of the support and minimize the amount of the employed ILs.[11]

Recently, we have reported clay composite carrying phosphinite-functionalized ionic liquid moieties as a support for stabilization of palladium nanoparticles and its applications in Suzuki-Miyaura and Sonogashira-Hagihara coupling reactions.[12] Also, very recently, we have reported magnetic nanoparticles supported oxime palladacycle[13] and palladium nanoparticles supported on magnetic modified with carbon quantum nanodots[14] as efficient and separable catalysts for Suzuki-Miyaura coupling reaction. In continuation of our interest on magnetite supported palladium catalysts, herein, we wish to report the synthesis and characterization of phosphinite-functionalized magnetic nanoparticles containing imidazolium ionic liquid moiety for stabilization of palladium nanoparticles (Scheme 1) and its application as a catalyst in

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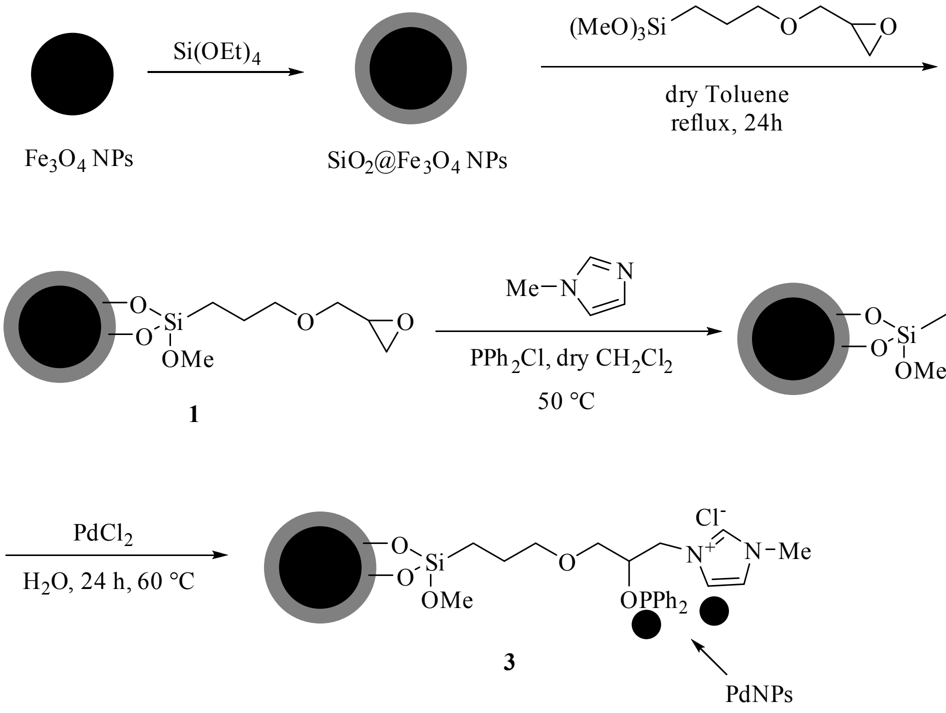
[a] *Department of Chemistry, Institute for Advanced Studies in Basic Sciences (IASBS), P. O. Box 45195-1159, Gavazang, Zanjan 45137-6731, Iran. Email: gholinejad@iasbs.ac.ir*

[b] *Department of Chemistry, College of Sciences, Hormozgan University, Bandar Abbas, 71961, Iran. Fax: +98-761-766-0032; Tel: +98-761-766-0042; Email: aghaderi@hormozgan.ac.ir*

[c] Nanotech Research, Innovation and Incubation Center, PSG Institute of Advanced Studies, Coimbatore-641 004, India.

†Electronic Supplementary Information (ESI) available: [FT-IR of Fe_3O_4@SiO_2 and ^1H NMR and ^{13}C NMR of all products]. See DOI: 10.1039/x0xx00000x

Suzuki-Miyaura coupling reaction in aqueous media under mild and low palladium loading conditions.



Scheme 1. The synthetic route toward the catalyst

Results and discussion

Fe_3O_4 NPs were prepared in a co-precipitation step based on the procedure of Massart *et al.* using $FeCl_3.6H_2O$ and $FeCl_2.4H_2O$ salts.[15] The prepared Fe_3O_4 nanoparticles were coated with a thin layer of silica using tetraethyl orthosilicate to impart core/shell Fe_3O_4 nanoparticles (SiO_2@Fe_3O_4 NPs). FT-IR analysis showed typical Si-O bond (Si-O-Fe) characteristics at 1090 cm^{-1} (Figure 1, supporting information).[16] The core/shell structure was further confirmed by TEM analysis (Figure 1). Further, SiO_2@Fe_3O_4 core/shell nanospheres were treated with 3-glycidoxypropyltrimethoxysilane to afford epoxy-functionalized SiO_2@Fe_3O_4 (**1**).

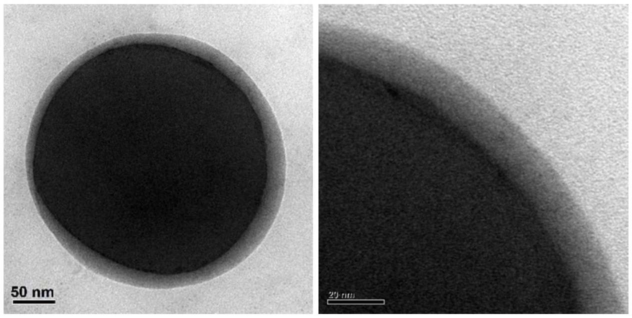


Fig. 1 TEM image of SiO_2@Fe_3O_4 NPs

Formation of material **1** was confirmed using thermogravimetric analysis which showed three step weight losses (Figure 2). First weight loss is related to water and physically adsorbed solvents. Second and third ones are related to the organic resides attached to the surface of the support. In order to add the ionic and phosphinite moieties, epoxy-functionalized SiO_2@Fe_3O_4 was reacted with 1-methyl imidazole and chlorodiphenylphosphine to afford material **2** which is referred to as Im-Phos-SiO_2@Fe_3O_4 throughout the text of this article. Thermogravimetric analysis of material **2** showed an increase in loading which is probably related to the added organic groups (Figure 3).

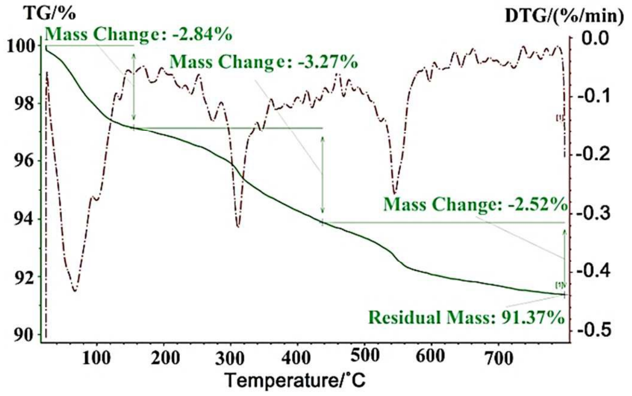


Fig. 2 Thermogravimetric diagram of the compound **1**

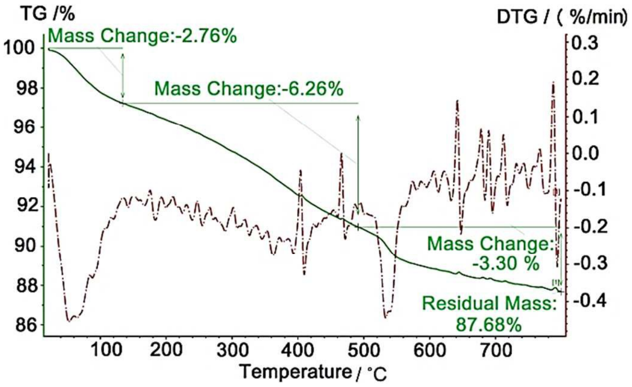


Fig. 3 Thermogravimetric diagram of the compound **2**

Finally, Pd NPs supported material (**3**) was easily obtained by dissolving and sonicating $PdCl_2$ in hot water followed by treating with Im-Phos-SiO_2@Fe_3O_4. Palladium loading on the composite **3** was determined using ICP analysis to be 0.32 mmolg^{-1}. SEM image of the material **3** showed the formation of uniform and mono-dispersed nanoparticles (Figure 4).

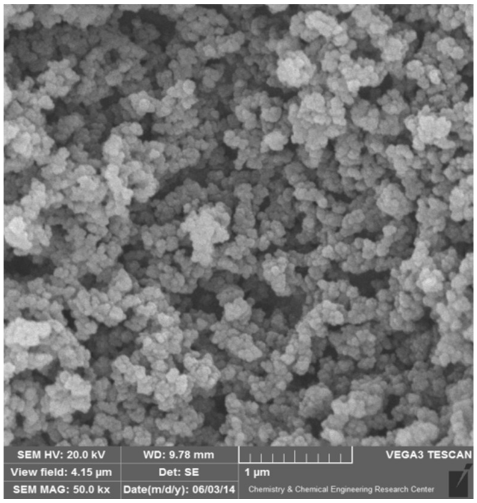


Fig. 4 SEM image of the prepared Pd NPs (**3**)

Solid state UV-Vis spectrum of the composite **3** did not show the characteristic peak of Pd(II) at 280 nm indicating the conversion of Pd(II) to Pd(0).[17] Moreover, increasing the absorption bands in the higher regions indicates the presence of nanoparticles in the structure of the material **3** (Figure 5).[18]

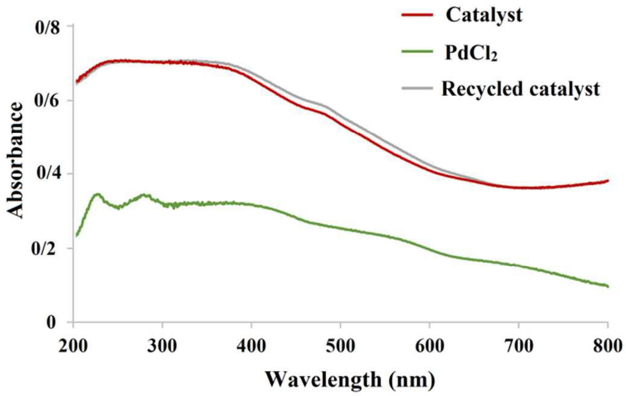


Fig. 5 Solid state UV-Vis spectra of the composite **3**

X-ray diffraction (XRD) analysis of the catalyst showed the presence of Pd nanoparticles by appearing Bragg's reflections related to palladium at 2θ= 40.1, 46.7, 68.1, and 82.1.[19] Also, Bragg's reflections related to spinel structure of Fe_3O_4 (JCPDS card no. 85-1436) and SiO_2 are evident in the diagram[20] (Figure 6).

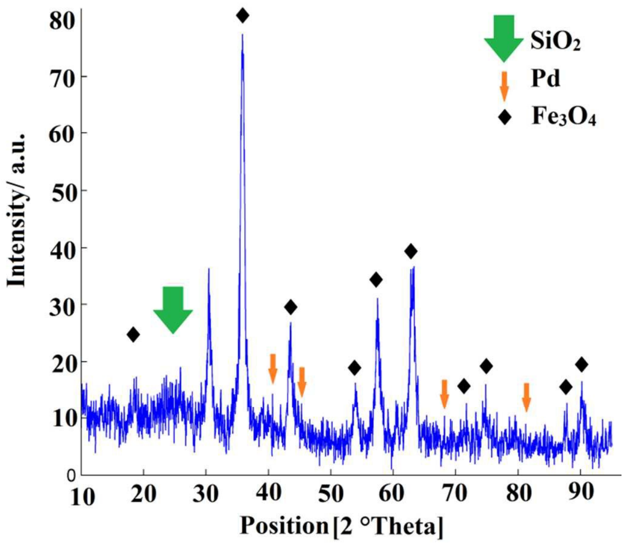


Fig. 6 XRD pattern of the material **3**

In order to get some information about the oxidation state of palladium in the composite, X-ray photoelectron spectrum (XPS) of the material was studied (Figure 7). The results showed the presence of two intensive doublets at 335 and 340 eV related to Pd(0) and peaks at 337 and 342 eV related to Pd(II) corresponding to Pd $3d_{5/2}$ and Pd $3d_{3/2}$, respectively. These results indicates that around 62% of palladium particles exists in the form of Pd(0).[21,22]

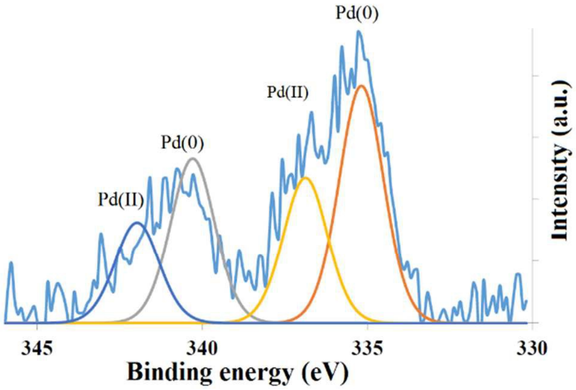


Fig. 7 XPS spectrum of the composite **3**

TEM images of the material **3** showed the attachments of palladium nanoparticles to the IL-modified Fe_3O_4 NPs (Figure 8).

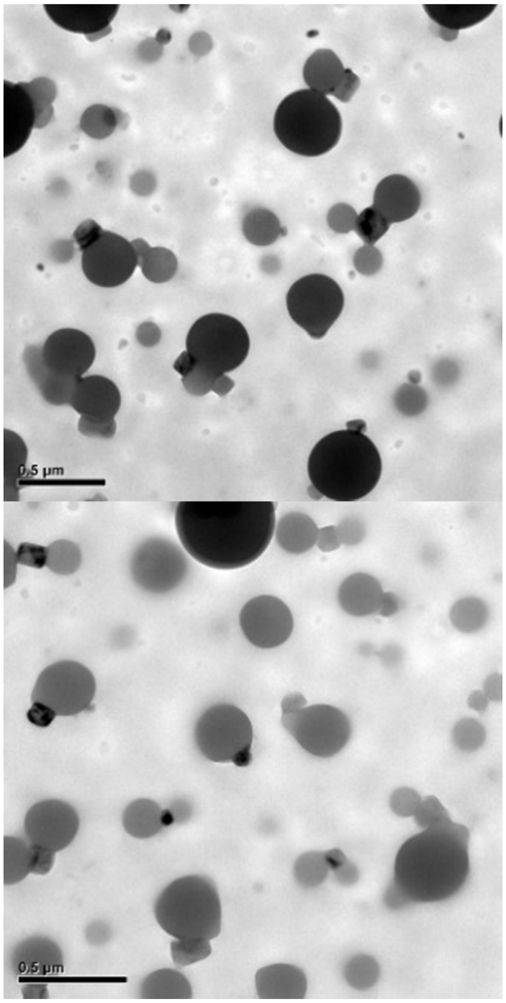


Fig. 8 TEM images of Pd NPs supported on IL-modified Fe_3O_4 NPs.

The presence of palladium species in the structure of the composite **3** was also confirmed by energy-dispersive X-ray spectroscopy (EDS) obtained from TEM analysis (Figure 9). It is worth mentioning that EDS analysis was also confirmed the presence of phosphorus in the structure of the material.

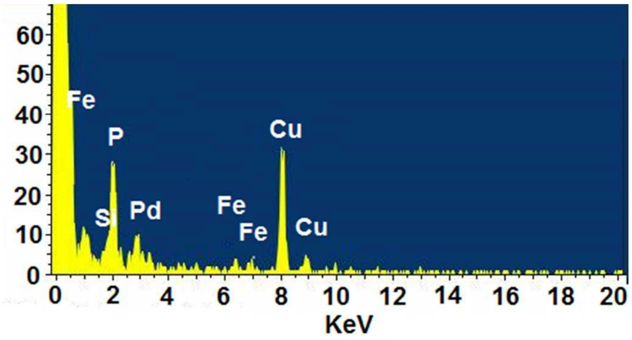


Fig. 9 EDS image of the material **3**

In order to obtain information about superparamagnetic property of the prepared materials, magnetization curves of Fe_3O_4 NPs, $SiO_2@Fe_3O_4$ NPs, Im-Phos-$SiO_2@Fe_3O_4$ (**2**), and the composite (**3**) was determined at room temperature (Figure 10).[22] In all four samples, zero coercivity and remanence on the magnetization loop was observed without the presence of hysteresis loop which confirmed superparamagnetic property and the ability of the material to be separated from the reaction mixture by an external magnet (Figure 10). It is worth mentioning that, the decrease in the magnetization value of the $SiO_2@Fe_3O_4$ (38 emug^{-1}) in comparison with Fe_3O_4 NPs (61 emug^{-1}) confirms the silica coating and formation of core/shell nanoparticles. Furthermore, a decreases in the magnetization value of the $SiO_2@Fe_3O_4$ functionalized phosphinite-imidazolium (**2**) (32 emug^{-1}), confirms the immobilization of organic groups on the surface. However, immobilization of palladium nanoparticles in the composite **3** does not change the magnetization compared to material **2**.

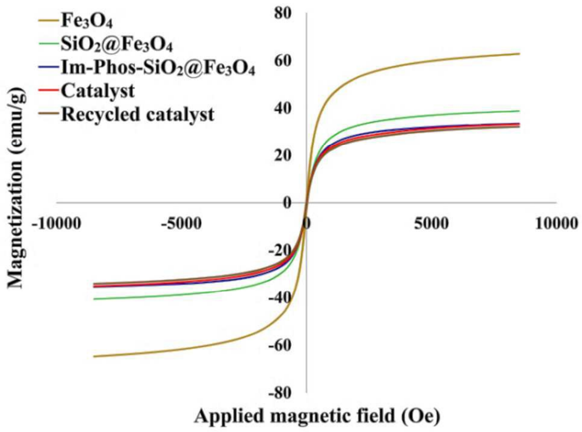
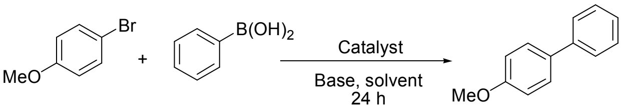


Fig. 10 Magnetization curves Fe_3O_4 NPs, $SiO_2@Fe_3O_4$, Im-Phos-$SiO_2@Fe_3O_4$,catalyst, and recycled catalyst after 3rd run.

The catalytic activity of the prepared material **3** was evaluated in Suzuki-Miyaura coupling reaction. In order to find the optimized reaction conditions, the reaction of 4-bromoanisole with phenylboronic acid was selected as the model reaction. The effect of different factors such as solvents, bases, amount of the catalyst and temperature were studied (Table 1). Initially, the reaction was studied using K_2CO_3 as a base in different solvents such as H_2O, DMF, EtOH, toluene, CH_3CN, THF, and a mixture of H_2O/EtOH. Results indicated that in aqueous ethanol (1:1) the reaction took place quantitatively in 1 h at 60 °C (Table 1, entry 6). By lowering the reaction temperature to 30 °C, the yield of the product was decreased to 84% (Table 1, entry 9). Using other bases such as DABCO, K_3PO_4, Et_3N, and NaOAc in H_2O/EtOH at 60 °C gave low yields for the reaction (Table 1, entries 10-16). In the absence of the catalyst, only 5% of the desired product was detected by GC (Table 1, entry 17).

Table 1. Optimization of the reaction conditions for the reaction of 4-bromoanisol and phenylboronic acid.[a]



Entry	Base	Solvent	Temp. (˚C)	Time (h)	Yield(%)[b]
1	K_2CO_3	H_2O	60	15	91
2	K_2CO_3	Toluene	60	15	7
3	K_2CO_3	DMF	60	15	2
4	K_2CO_3	CH_3CN	60	15	7
5	K_2CO_3	THF	60	15	1
6	K_2CO_3	H_2O/EtOH	60	1	100
7	K_2CO_3	EtOH	60	5	90
8	K_2CO_3	H_2O/EtOH	50	2	78[c]
9	K_2CO_3	H_2O/EtOH	30	24	84
10	Et_3N	H_2O/EtOH	30	24	5
11	DABCO	H_2O/EtOH	30	24	49
12	NaOAc	H_2O/EtOH	30	24	12
13	K_3PO_4	H_2O/EtOH	30	24	86
14	*t*-ButOK	H_2O/EtOH	30	24	97
15	*t*-ButOK	H_2O	30	24	70
16	*t*-ButOK	EtOH	30	24	88
17	K_2CO_3	H_2O/EtOH	60	24	5[c]

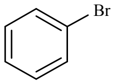
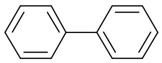
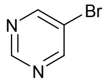
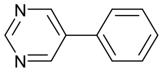
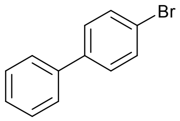
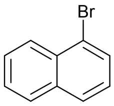
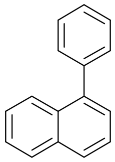
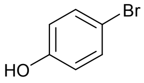
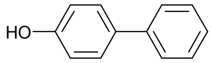
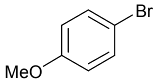
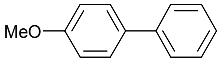
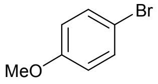
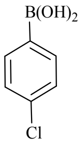
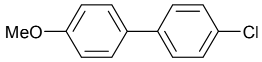
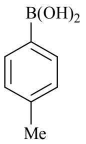
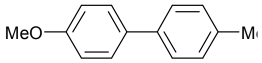
[a] Reactions performed on a 0.5 mmol scale. [b] GC yields. [c] Reaction in the absence of the catalyst.

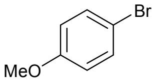
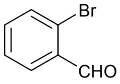
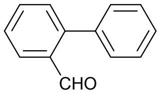
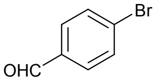
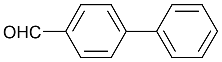
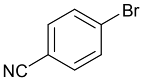
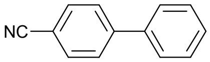
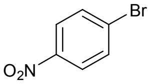
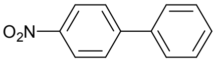
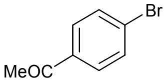
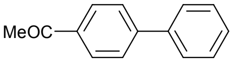
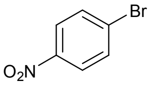
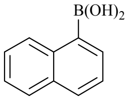
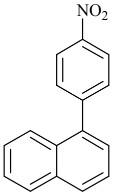
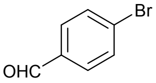
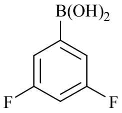
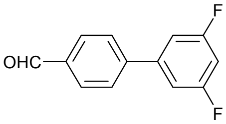
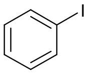
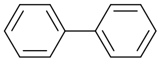
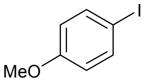
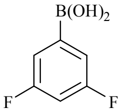
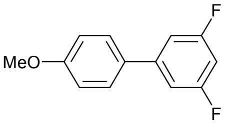
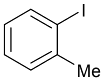
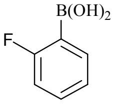
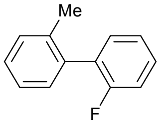
With the optimized reaction conditions in hand, the substrate scope of the Suzuki-Miyaura coupling reaction was evaluated employing different aryl halides and arylboronic acids (Table 2). Reactions of bromobenzene, 4-bromobiphenyl and 1-bromo naphthalene with phenylboronic acid proceeded well and the desired products were obtained in excellent yields (Table 2, entries 1, 3-4). Reaction of 5-bromopyrimidine as a heterocyclic aryl bromide with phenylboronic acid proceeded very well and corresponding coupling product were obtained in 97 % isolated yield (Table 2, entry 2). Also, reactions of aryl bromides containing electron donating group such as 4-bromophenol and 4-bromoanisole were performed efficiently giving the coupling products in 88-96% yields (Table 2, entries 5-7). Aryl bromides containing electron withdrawing groups such as 2-bromobenzaldehyde, 4-bromobenzaldehyde, 4-bromobenzonitril, 4-bromonitrobenzene, and 4-bromoacetophenone with phenylboronic acid were proceed smoothly and the desired coupling products were obtained in high to excellent yields (Table 2, entries 9-13). We have also studied the reactions of aryl iodides under the optimized reaction conditions at room temperature giving the coupling products in excellent isolated yields (Table 2, entries 16-20). Different arylboronic acids such as 1-naphthylboronic acid, 3,5-diflourophenylboronic acid, 2-fluorophenylboronic acid and 3-nitrophenylboronic acid were reacted efficiently with aryl bromides and iodides to give the products in high to excellent yields (Table 2, entries 7-8,14-15,17-18,20). We have also studied the reactions of aryl chlorides with phenylboronic acid under the optimized reaction conditions. However, the desired products were isolated in low yields. Therefore, the temperature of the reactions was raised to 120 °C and the solvent was switched to DMF. Under these conditions, aryl chlorides reacted effectively affording the corresponding biphenyl in 74-95% isolated yields (Table 2, entry 21-23).

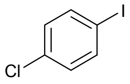
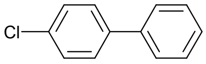
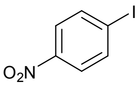
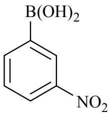
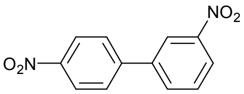
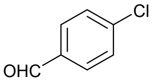
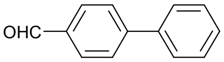
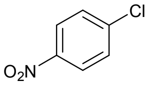
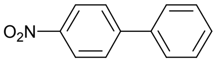
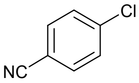
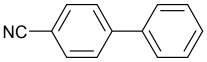
For showing the practical applicability of the catalyst, we have scaled up the reaction of 4-bromoanisol up to 10 mmol with 15 mmol phenylboronic acid under the optimized reaction conditions. Results indicated that the reaction performed effectively and the desired product was obtained in 87% isolated yield.

Table 2. The reactions of structurally different aryl halides with arylboronic acids in the presence of the catalyst

$$Ar^1X + Ar^2B(OH)_2 \xrightarrow[\substack{K_2CO_3,\ EtOH:H_2O\ (1:1) \\ 30\text{-}120\ ^\circ C}]{\text{Catalyst (0.3 mol\%)}} Ar^1\text{-}Ar^2$$

Entry	Ar^1	$Ar^2B(OH)_2$	Time(h)	Temp. (˚C)	Product	Yield (%)	TON
1		$PhB(OH)_2$	18	60		90	300
2		$PhB(OH)_2$	2	60		97	323
3		$PhB(OH)_2$	24	60		93	310
4		$PhB(OH)_2$	12	60		89	296
5		$PhB(OH)_2$	24	60		94	313
6		$PhB(OH)_2$	24	60		96	320
7			24	60		88	293
8			24	60		89	296

							
9		$PhB(OH)_2$	24	60		81	270
10		$PhB(OH)_2$	4	60		98	326
11		$PhB(OH)_2$	1	60		96	320
12		$PhB(OH)_2$	24	60		88	293
13		$PhB(OH)_2$	2	60		97	323
14			6	60		98	326
15			2	60		93	310
16		$PhB(OH)_2$	5	30		90	300
17			2	30		93	310
18			24	30		87	290

19		$PhB(OH)_2$	1	30		98	326
20			12	30		98	326
21		$PhB(OH)_2$	48	120		74	246
22		$PhB(OH)_2$	48	120		95	316
23		$PhB(OH)_2$	48	120		78	260

[a]Reaction conditions: Aryl halide (1 mmol), arylboronic acid (1.5 mmol), K_2CO_3 (1.5 mmol), EtOH:H_2O (1:1, 2 mL), catalyst (0.3 mol%).

For getting information about heterogeneity or homogeneity of the catalyst, we have studied hot filtration test for the reaction of 4-bromoanisol and phenylboronic acid under the optimized reaction conditions. For this purpose, after 4 h the reaction mixture was filtered at the reaction temperature and filtrate allowed reacting for 24 h. GC analysis of reaction mixture after 4 h showed 43% conversion and GC analysis of reacted filtrate after 24 h showed 49% conversion to desired coupling product. Also, addition of Hg(0) to the reaction of 4-bromoanisol and phenylboronic (mercury test) caused decrease of the yield from 96% (Table 2, entry 6) to 35% after 24h. These results indicate that the catalyst acts mostly heterogeneously in these reactions.[23]

In order to test the recycling ability of this novel magnetic supported palladium catalyst, the coupling reaction of iodobenzene with phenylboronic acid under the optimized reaction conditions was studied. In each cycle, magnetically separable catalyst was easily separated using an external magnet, washed with ethanol and used directly for a subsequence round of the reaction. The catalyst is recyclable for at least eight consecutive times with small drops in catalytic activity (Figure 11).

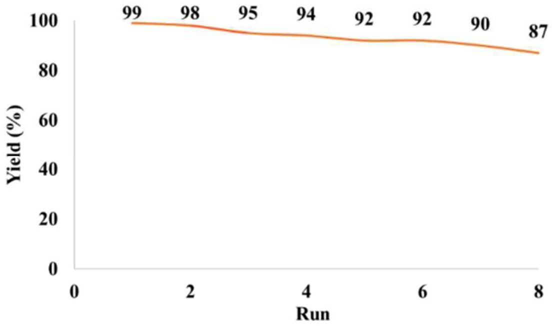


Fig. 11 Recycling of the catalyst for the reaction of iodobenzene with phenylboronic acid at room temperature

Leaching of palladium to the reaction mixture after 8th run was determined using ICP analysis to be 2.5% which indicated the stability of the catalyst during the reaction. In addition, thermogravimetric analysis of the catalyst after 8th run showed the presence of organic groups in the structure of the catalyst indicating its stability during the reaction courses (Figure 12).

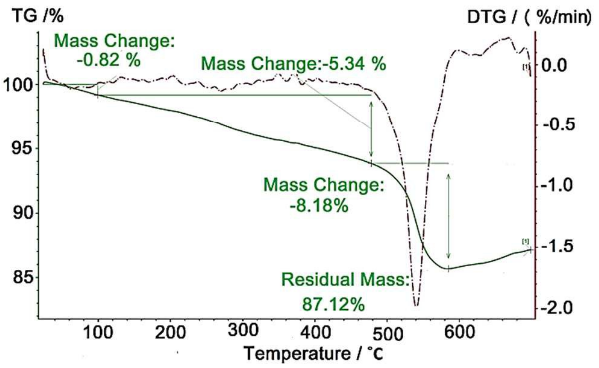


Fig. 12 Thermogravimetric diagram of recycled catalyst after 8th run

SEM image of the recycled catalyst after 3rd run showed that the morphology and structure of the catalyst has been preserved during the reaction (Figure 13). Solid UV-Vis spectrum of the reused catalyst after 3rd run (Figure 3) was the same as the fresh catalyst.

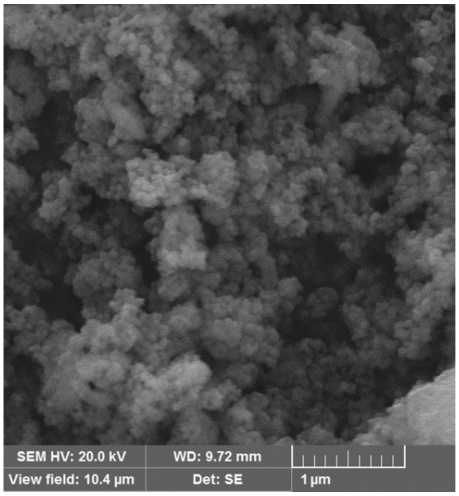


Fig. 13 SEM image of reused catalyst after 3rd run

TEM images of the reused catalyst after 3rd run showed preservation of the structures with highly mono-dispersed Pd NPs in the core/shell surface of magnetic nanoparticles (Figure 14).

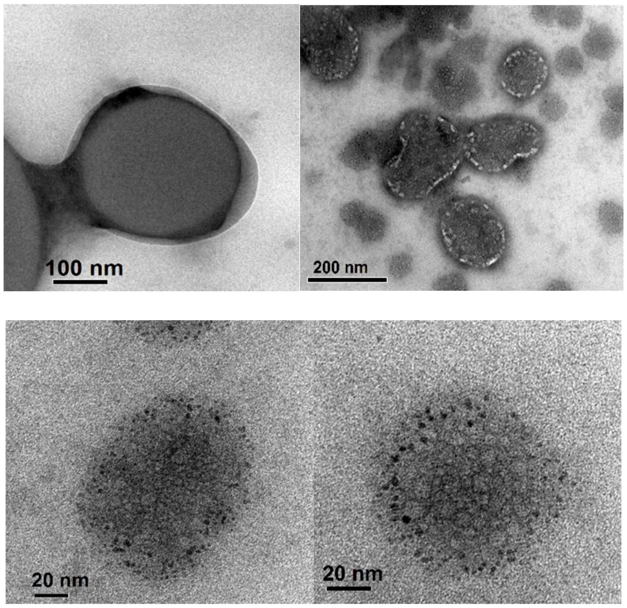


Fig. 14 TEM images of reused catalyst after 3rd in different magnifications

Additionally, EDS analysis of the reused catalyst after 3rd run confirmed the presence of Pd, Si, Fe, and P species in the catalyst structure (Figure 15).

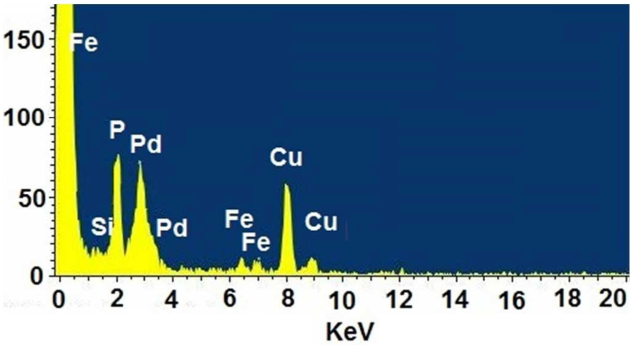


Fig. 15 EDS analysis of the reused catalyst.

FT-IR study of the catalyst after 3rd run confirmed its stability showing the Si-O-Fe bond as a strong peak at 1084 cm^{-1} (Figure 2, supporting information). Furthermore, X-ray diffraction (XRD) analysis of the reused catalyst after 3rd run showed that the structure has been preserved during the reaction. Presence of Pd, Fe_3O_4 and SiO_2 in catalyst structure was confirmed by XRD spectrum (Figure 16).

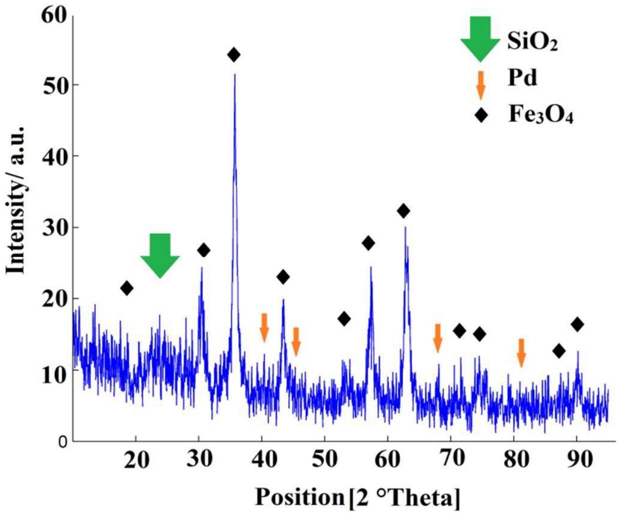


Fig. 16 XRD pattern of the reused catalyst after 3rd run

X-ray photoelectron spectroscopy (XPS) of the catalyst after 3rd run was also revealed the presence of the related peaks for Pd(0) (64%) and Pd(II) (36%) at 335-340 and 337-342 eV, respectively (Figure 17).

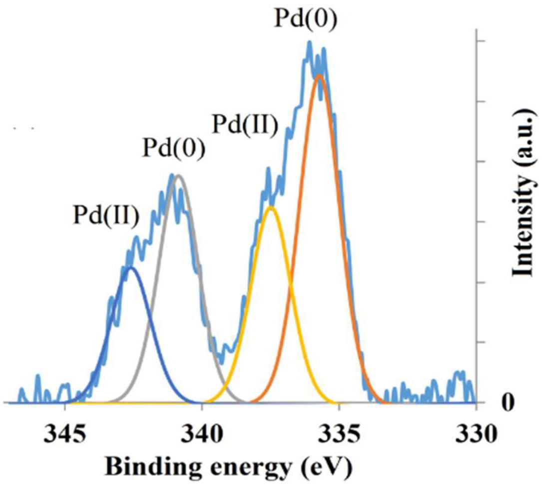


Fig. 17 XPS spectrum of the reused catalyst after 3rd run

Furthermore, study of superparamagnetic property of the recycled catalyst after 3rd run showed very slight decrease in the magnetization value (Figure 10). Finally, the nitrogen adsorption–desorption isotherm for catalyst and also the reused catalyst after 3rd run were studied (Figure 18). Results showed that both samples are same and possess type-III isotherms with H3 hysteresis loops. The BET surface area for catalyst and reused one are 44 and 46 m^2g^{-1}, respectively. According to BJH calculation, pore diameters for the catalyst and the reused catalyst were obtained to be 2.42 and 2.6 nm confirming the mesoporous structure of the materials.

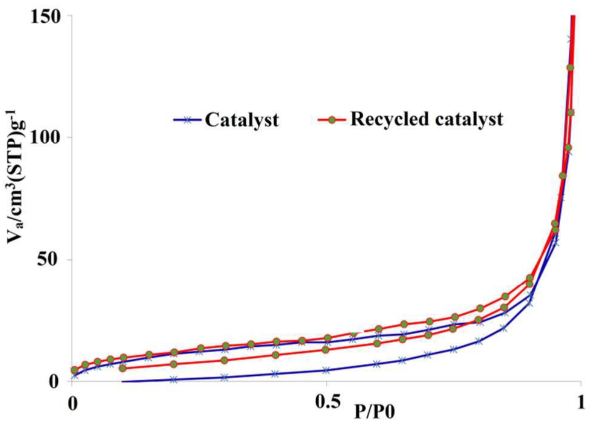


Fig. 18 N_2 adsorption/desorption isotherms of the catalyst and reused catalyst after 3rd run.

Conclusion

In conclusion, we have modified the surface of Fe_3O_4 with the phosphinite-functionalized ILs producing a novel solid material. This material which contains chelating groups has been used as the effective support for palladium nanoparticles. This inorganic-organic composite showed high catalytic activity in Suzuki-Miyaura coupling reaction of aryl halides with arylboronic acids in aqueous media. Reactions of aryl iodides and bromides were performed at room temperature and 60 °C, respectively. However, reactions of aryl chlorides were performed at higher temperature. The catalyst showed good stability and was recycled for several times with small decrease in its catalytic activity. The fresh and also recovered catalyst were characterized by spectroscopic and microscopic techniques.

Experimental Section

General

All chemicals were purchased from Sigma-Aldrich, Acros and Merck and were used without further purification. ^1H NMR spectra were recorded at 400 MHz and ^{13}C NMR spectra were recorded at 100 MHz in $CDCl_3$ using TMS as internal standard. Thermogravimetric analysis (TGA) was conducted from room temperature to 700 °C in an oxygen flow using a NETZSCH STA 409 PC/PG instrument. Transmission Electron Microscopy was carried out by JEOL JEM-2010, instrument (Japan). FT-IR spectra were recorded on a Bruker Vector 22. Energy dispersive X-ray analysis (EDX) was obtained using Carl Zeiss ΣiGMA instrument. Adsorption-desorption analyses were recorded using (BELsorp-max (Japan)). DRS-UV-Vis spectra was determined by Perkin-Elmer, Lambda 25 instrument. The content of copper and palladium in the catalyst was determined using atomic absorption spectrometry (Varian). X-ray diffraction (XRD) analysis were obtained using (Simens D-5000 diffractometer, Germany).

Synthesis of Fe_3O_4 nanoparticles:

Magnetite (Fe_3O_4) nanoparticles were prepared according to the reported method in the literature.[13,14] Typically, $FeCl_3.6(H_2O)$ (11.0 g) and $FeCl_2.4H_2O$ (4.0 g) were dissolved in 250 mL deionized water under argon with vigorous stirring using mechanical stirrer. Then, aqueous ammonia (25%, 40 mL) was added dropwise under argon atmosphere and mixture was stirred at 80 °C for 4 h. A black precipitate (Fe_3O_4) were collected by external magnet and washed three times with deionized water and ethanol and dried under vacuum.

Synthesis of silica-coated Fe_3O_4 nanoparticles

To the 30 min sonicated Fe_3O_4 nanoparticles (1 g) in ethanol (200 mL), were added tetraethyl orthosilicate (2 mL) and 6 mL aqueous ammonia (6 mL) and mixture was stirred for 24 h at room temperature. Produced $SiO_2@Fe_3O_4$ nanoparticles were separated by an external magnet and washed with H_2O (3×10 mL) and EtOH (3×10 mL) and dried under vacuum.

Synthesis of epoxy-functionalized magnetic nanoparticles (2)

Silica-coated Fe_3O_4 nanoparticles (1 g) were sonicated in 40 mL dry toluene and 3-glycidoxypropyltrimethoxysilane (4 mmol, 0.9 mL) was added. The resulting mixture was refluxed for 24 h under argon atmosphere. Then, the reaction mixture was subjected to magnetic separation, and obtained product (**2**) was washed sequentially with H_2O (3×10 mL) and EtOH (3×10 mL) and finally dried under vacuum.

Synthesis of Im-Phos-$SiO_2@Fe_3O_4$ (2)

The prepared epoxy-functionalized magnetic nanoparticles **2** (1 g) were sonicated in CH_2Cl_2 for 30 min. 1-Methyl imidazole (4 mmol, 0.33 g) and chlorodiphenylphosphine (4 mmol, 0.88 g) were added under argon protection and reaction was stirred at 50 °C for 24 h. Then, produced phosphinite-imidazolium functionalized magnetite was separated by external magnet and washed three times with deionized water (2×10 mL) and EtOH (3×10 mL) and dried under vacuum.

Synthesis of magnetite supported palladium nanoparticle catalyst (3)

The prepared $Fe_3O_4@SiO_2$-Im-Phos (**2**) (1 g) was sonicated in 15 mL H_2O. In another batch, $PdCl_2$ (0.45 mmol, 0.08 g) were sonicated in H_2O (10 mL) at 80 °C until dissolving $PdCl_2$ salt. Then, the aqueous solution of $PdCl_2$ was added to $Fe_3O_4@SiO_2$-Im-Phos (**2**) and the mixture was stirred at 60 °C for 24 h. Next, the mixture was subjected to magnetic separation and the solid was washed with H_2O (3×10 mL) and EtOH (3×10 mL) and dried under vacuum.

Acknowledgements

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Palladium Supported on Phosphinite Functionalized Fe_3O_4 Nanoparticles as a New Magnetically Separable Catalyst for Suzuki-Miyaura Coupling Reaction in Aqueous Media