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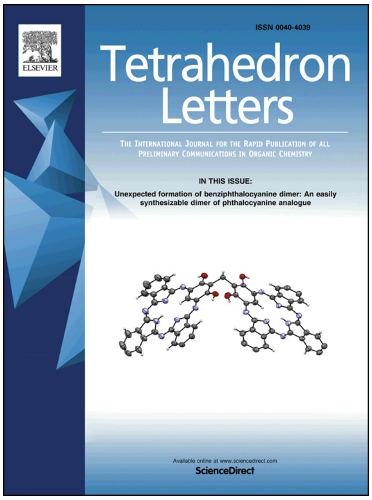

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Graphical Abstract

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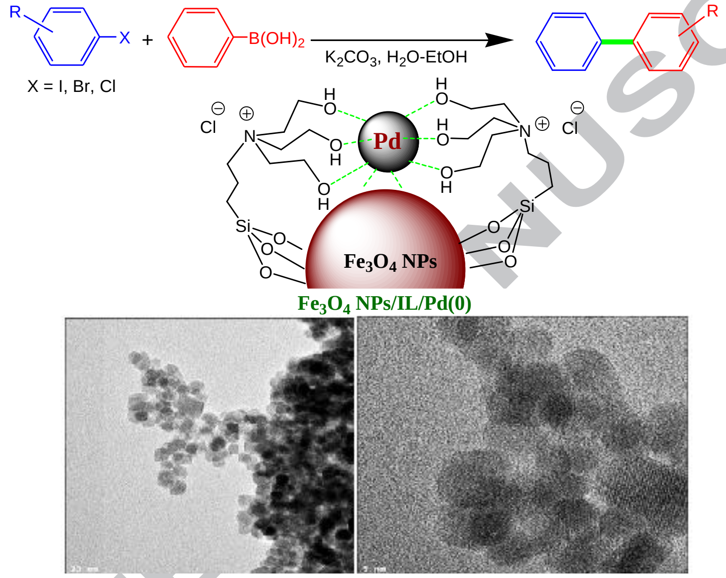

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Immobilization of palladium nanoparticles on ionic liquid-triethylammonium chloride functionalized magnetic nanoparticles: as a magnetically separable, stable and recyclable catalyst for Suzuki-Miyaura cross-coupling reactions

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ABSTRACT

A facile procedure was applied to successfully synthesize novel Pd nanoparticles immobilized on triethanolamine-functionalized magnetic nanoparticles [Fe_3O_4/IL/Pd]. Diverse characterizations (HR-TEM, XRD, FT-IR, TGA, EDX, FE-SEM, ICP, XPS and VSM) were carried out to identify intrinsic traits of the nanoparticles. At room temperature, Fe_3O_4/IL/Pd demonstrated high catalytic activity toward Suzuki-Miyaura cross-coupling reactions in aqueous solution. Based on the results, Fe_3O_4/IL/Pd acted as zwitterionic IL-type heterogeneous catalyst, which could be separated from the reaction mixture, conveniently. Moreover, it exhibited excellent recyclability for at least eight cycles without considerable loss of its activity.

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Introduction

Transition metals have had an important influence on development of organic chemistry by evolving different novel reactions, recently. Palladium, one of the precious noble metals, catalyzes various important coupling chemical transformations, such as Suzuki-Miyaura,[1] Heck-Mizoroki[2] and Sonogashira-Hagihara[3] reactions. Among these reactions, Suzuki-Miyaura reaction, that involves cross coupling between aryl, vinyl or alkyl (pseudo) halides and organoboron reagents, has turned out to be an extremely powerful synthetic method for formation of different types of compounds found in many building blocks of pharmaceuticals and natural products. However, homogeneous Pd catalysts suffer from some practical problems related to their separation and recycling, which leads to product contamination with metal, while Pd is high cost. Hence, heterogeneous Pd-based catalysts can be considered as a great alternative due to their air-stability, recoverability, reusability and non-residual assets.[4] Numerous solid supports, such as microporous polymers,[5] mesoporous silica,[6] metal oxides,[7] clays,[8] carbon nanofibers,[9] and molecular sieves[10], have been adopted for Pd-based heterogeneous catalysts, in which Pd complexes or nanoparticles are involved as the active species in coupling reactions.[11]

Fe_3O_4 nanoparticles (NPs) tend to aggregate and are easily oxidized or dissolved in an acidic medium.[12] Coating Fe_3O_4 NPs with organic or inorganic surfactants is one solution of avoiding such limitations and improving physicochemical properties and colloidal stability.[13-15] Organic surfactants act as capping agents but they give bigger particle sizes. Inorganic capping agents, e.g. silica (SiO_2), have exceptional chemical and physical traits. In acidic solutions, SiO_2 is chemically stable and apt to modification.[16] Additionally, coating Fe_3O_4 particles with SiO_2 prevents agglomeration and protects the particles from dissolving in acidic solutions. SiO_2 covers the surface of Fe_3O_4 nanoparticles to form Fe_3O_4@SiO_2 core-shell nanoparticles.[17]

Thorough consideration of all these factors, and in continuation of our previous works[18,19], herein a novel nanocatalyst, i.e. Fe_3O_4/IL-supported Pd nanoparticle, will be described as a heterogeneous catalyst (Scheme 1) and its utilization in Suzuki-Miyaura cross coupling (Scheme 2) will be investigated. The catalyst was fabricated by immobilizing Pd NPs on triethanolamine-functionalized Fe_3O_4 magnetic NPs (MNPs) modified with chloropropyl. The triethanolamine groups on modified Fe_3O_4 act as strong and efficient stabilizers for the Pd NPs, which provide high activity and durability of the catalyst for the studied reaction. Using a magnet, the new catalyst can be well dispersed in the reaction medium, conveniently separated from the reaction mixture and utilized several times without considerable loss of its activity.

Experimental

Synthesis of Fe_3O_4

Fe_3O_4 MNPs were prepared according to Ref. 18a via co-precipitation of Fe (III) and Fe (II) ions with a molar ratio of 2:1 in presence of ammonium hydroxide. Generally, a mixture of $FeCl_3.6H_2O$ (5.838 g, 0.0216 mol) and $FeCl_2.4H_2O$ (2.147 g, 0.0108 mol) was dissolved in 100 mL deionized water at 85 $^{\circ}$C under N_2 atmosphere and intense mechanical stirring (500 rpm). After that, 10 mL of 25% NH_4OH was injected into the reaction mixture, quickly. Addition of the base to the Fe^{2+}/Fe^{3+} solution resulted in formation of the black precipitate of MNPs, instantly. The reaction was continued for another 25 min and the mixture

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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 deionized water.

Synthesis of the Fe_3O_4/IL

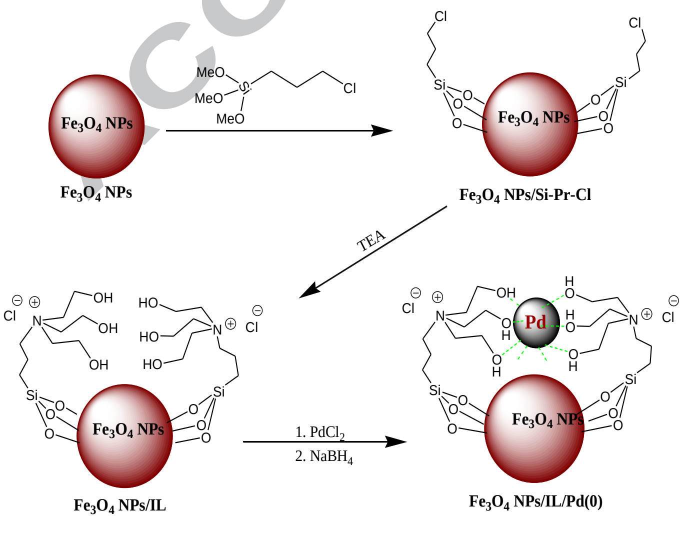
1.0 g of Fe_3O_4 NPs was dispersed in 80 ml of toluene by an ultrasonic bath for 25 min. Then, 1 ml (5 mmol) of 3-Chloropropyl-trimethoxysilane (CPTS) was added and the solution was stirred at 40 °C for 18 h. The chloropropyl-functionalized solid (Fe_3O_4/Si-Pr-Cl) was washed with toluene, separated by a magnet and dried in vacuum at 50 °C. The acquired Fe_3O_4/Si-Pr-Cl was suspended in ethanol (50 mL) with sonication about 20 min. Triethanolamine (1 mL) was added to the mixture under mechanical stirring and the reaction mixture was refluxed for 24 h. After cooling down to room temperature, the obtained solid was separated magnetically, washed with absolute ethanol several times and dried under vacuum at 50 °C.

Preparation of Fe_3O_4/IL/Pd(0)

Fe_3O_4/IL was dispersed in CH_3CN (30 mL) in an ultrasonic bath for 30 min. Then, a yellow solution of $PdCl_2$ (30 mg in 40 mL acetonitrile) was added to the dispersed Fe_3O_4/IL solution and the mixture was stirred for 12 h at room temperature. After that, Fe_3O_4/IL/Pd(II) was separated by magnetic decantation and washed by ethanol to remove the unattached substrates. Fe_3O_4/IL/Pd(II) was reduced to Fe_3O_4/IL/Pd(0) by sodium borohydride. The final product (Scheme 1) was washed by ethanol and dried at room temperature. The Pd content of the catalyst was estimated by ICP-AAS to be 0.21±0.001 mmol g^{-1}.

Suzuki-Miyaura coupling reactions

Catalytic activity of the synthesized Fe_3O_4/IL/Pd(0) nanocomposite was investigated for Suzuki-Miyaura reaction. The novel nanocatalyst (0.2 mol%), the aryl halides (1.0 mmol), phenylboronic acid (1.1 mmol), K_2CO_3 (2.0 mmol) and EtOH/H_2O (1:1) (3 mL) were added to a round bottomed flask and stirred for the desired time at room temperature (Scheme 1). The reaction was monitored by thin layer chromatography (TLC, n-hexane/acetone; 4:1). When the reaction was completed, 5 mL of ethanol was added and an external magnet removed the catalyst. Further purification was achieved by column chromatography.



Scheme 1. **Preparation of the Fe_3O_4/IL/Pd catalyst.**

Results and discussion

Characterization

In this paper, we aimed to design a new hybrid magnetic nanocomposite with ionic nature and lipophilic feature. Fe_3O_4 particles were fabricated according to the aforementioned procedure, and were subsequently functionalized with 3-chloroproplytriethoxysilane (CPTES) to obtain chloropropyl-functionalized magnetic nanoparticles (Fe_3O_4/Si-Pr-Cl). Ultimately, upon the reaction of the MNPs with triethanolamine, their surfaces conducted an ionic nature through triethylammonium chloride formation. The ionic liquid (IL)-bonded on Fe_3O_4 NPs was then navigated using $PdCl_2$ and its subsequent reduction by $NaBH_4$ led to the corresponding Pd nanoparticles being supported on the magnetic nanoparticles (Fe_3O_4/IL/Pd). Finally, the mixture was collected by an external magnet and dried by vacuum. The reactions undergone for the synthesis of the catalyst are shown in Scheme 1. Additionally, the Pd content of the catalyst as estimated by ICP-AAS to equal 0.21±0.001 mmol g^{-1}. Characterization of the catalyst was achieved through FTIR, XRD, FE-SEM, EDS, HR-TEM, XPS, TGA, ICP and VSM.

Fig. 1 depicts the fourier transform infrared (FTIR) spectra of Fe_3O_4, Fe_3O_4/IL and Fe_3O_4/IL/Pd). In curve a, absorption peaks located at about 582 cm^{-1} and 637 cm^{-1} are characteristics of Fe-O bonds that are present in Fe_3O_4 NPs. The peaks appeared at 1625 and ~3400 cm^{-1} correspond to surface-adsorbed water and hydroxyl groups.[20]

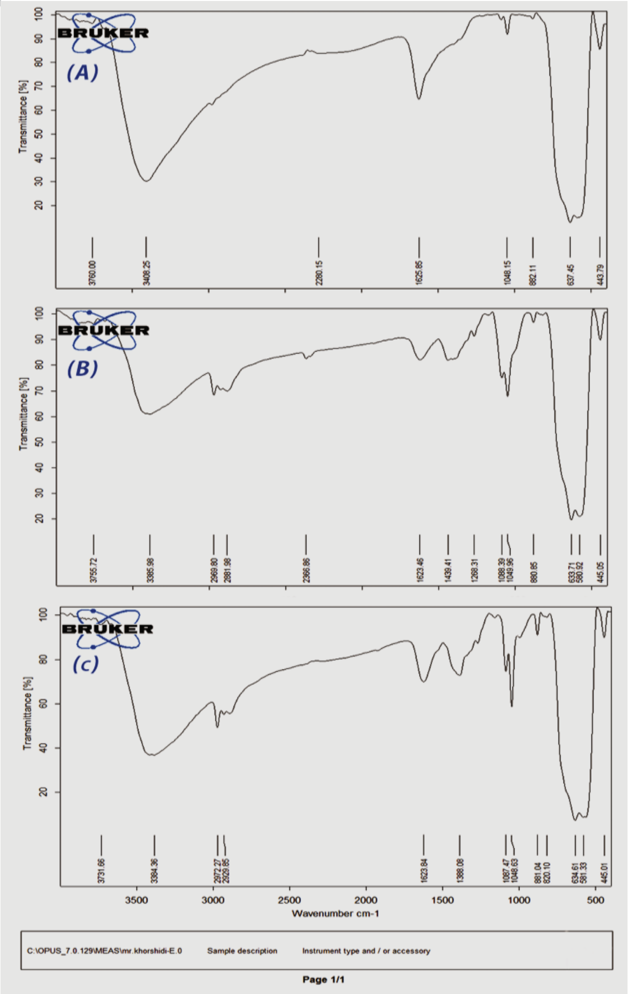


Fig 1. FT-IR spectra of (a) Fe_3O_4, (b) Fe_3O_4/IL and (c) Fe_3O_4/IL/Pd.

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In curve b, 1049 and 1088 cm^{-1} peaks are associated with Si-O-Si stretching mode while 956 cm^{-1} peak refers to Si-O bending mode of the silanol group.[21] These peaks state that silica has been properly functionalized on the Fe_3O_4 NPs.[22a] The FTIR spectra of Fe_3O_4/IL and Fe_3O_4/IL/Pd show Fe-O vibrations at similar wavenumbers. Three new absorption peaks around 2366, 2881 and 2969 cm^{-1} have emerged in the FT-IR spectra of Fe_3O_4/IL and Fe_3O_4/IL/Pd, which are characteristic of C-H stretching mode of the alkyl chain, demonstrating that ILs have been successfully immobilized on the surface of Fe_3O_4 NPs. Also, the peak located at 1439 cm^{-1}, in curve b, can be attributed to presence of quaternary amine, probably.[22b] In curve c, which relates to the Pd nanocatalyst, no dramatic changes in the FTIR spectrum is observed.

The room temperature magnetization curves, Fig. 2, proved that Fe_3O_4/IL/Pd nanoparticle is super paramagnetic. It is worth pointing out that reduction in the magnetization value of Fe_3O_4/IL/Pd, in comparison with Fe_3O_4 NPs, signifies successful immobilization of the organic groups on Fe_3O_4 surface. Even with this decrease in the saturation magnetization, the solid could still be effectively separated from the solution with a permanent magnet.

The nanostructure was further affirmed by HR-TEM analysis in Fig. 3, demonstrating that the particles are relatively uniform in diameter and spherical in shape. Though Fe_3O_4 NPs prefer to gather together due to their small size and magnetism, they have not aggregated. This observation indicates successful coating of the MNPs.

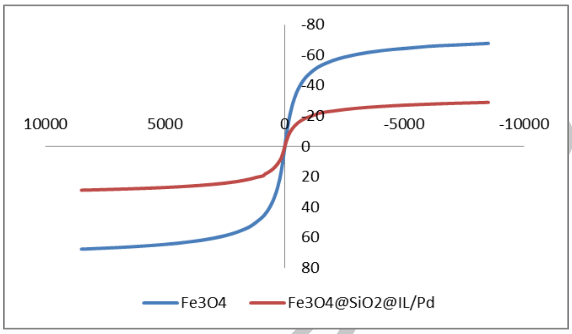

Fig. 2. VSM spectra of Fe_3O_4, Fe_3O_4/IL/Pd.

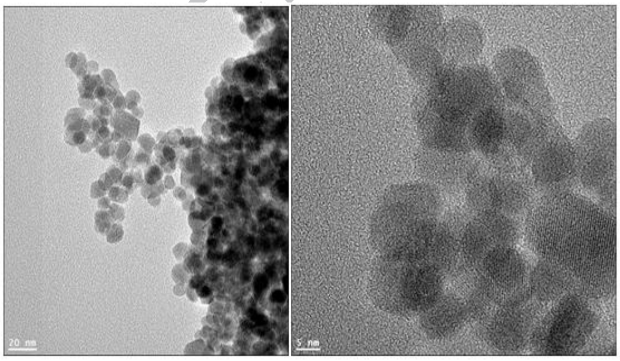

Fig. 3. HR-TEM image of Fe_3O_4/IL/Pd.

The triethanolammonium coating on the surface of Fe_3O_4 NPs was also confirmed by thermogravimetric analysis. As shown in Fig. 4, the weight loss of Fe_3O_4/IL is mainly divided into three temperature ranges: below 200 °C, 200-450 °C and above 450 °C. The weight loss during heating from 25 to 200 °C is attributed to the loss of moisture[23,24] and physically adsorbed solvents. Decomposition of covalently bonded organics led to a weight loss of around 3% at 200-450 °C. The results from TGA imply that the core/shell structure has been successfully modified with triethanolamine.

EDX analysis for the catalyst (Fig. 5) approved elemental composition of the modified nanoparticles and existence of Si, Fe, N, O, C and Pd in the NPs.

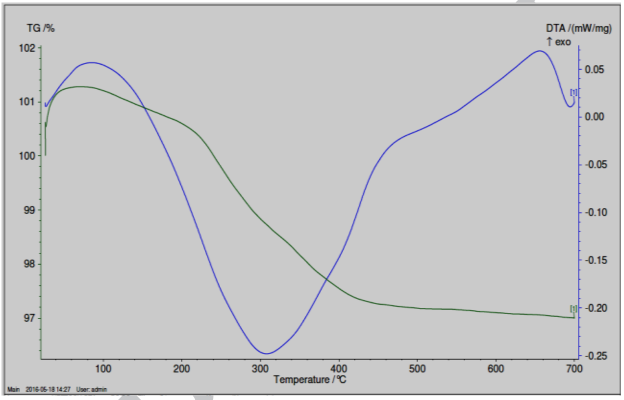

Fig. 4: TGA/DTG curves of Fe_3O_4/IL/Pd.

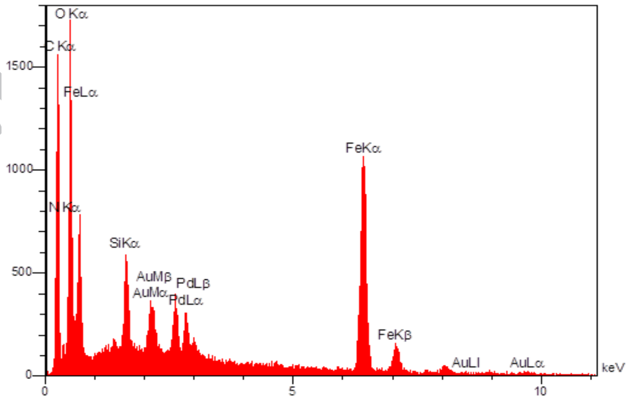

Fig. 5: EDX spectra of Fe_3O_4/IL/Pd.

The XRD patterns of Fe_3O_4/IL/Pd(0) are illusterated in Fig. 6. Strong characteristic diffractions at 2θ values of 30.09°, 35.44°, 43.07°, 53.43°, 57.06° and 63.2° corresponding to the (220), (311), (400), (422), (511) and (440) diffractions of Fe_3O_4 (JCPDS 89-3854) were detected in the sample, implying that the modified nanoparticles have been synthesized successfully without damaging the crystal structure of Fe_3O_4 core. Furthermore, apart from the original peaks, new peaks appearing at 2θ of 40.01°, 46.54° and 67.93° (weak peak), associated with (111), (200) and (220) crystalline planes of Pd in the spectrum, demonstrate that Pd element exists in the form of Pd^0 not Pd^{+2}. These three diffraction peaks are broad, which clarifies that the Pd composition is made of small nanocrystals and agrees well with the HRTEM analysis results.

The morphology and structure of Fe_3O_4/IL/Pd were investigated by field emission scanning electron microscopy (FE-SEM). It was approved that the catalyst was made of uniform nanometer-sized particles (Fig. 7).

X-ray photoelectron spectroscopy (XPS) is an influential instrument for investigating electronic characteristics of the species created on surfaces, including environment of electrons, states of oxidation and binding energy of metal core electrons.

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XPS elemental survey scans of the surface of the Fe_3O_4/IL/Pd catalyst is shown in Fig. 8. The peaks related to oxygen, carbon, nitrogen, silicon, iron and palladium are obvious in this spectrum. XPS analysis was also performed to determine Pd oxidation state. Results displayed presence of an intense doublet at binding energies (BEs) of 335.7 and 340.9 eV related to Pd(0), which correspond to Pd 3d5/2 and Pd 3d3/2 peaks, respectively. This result indicates that Pd is just present in its reduced form, which confirms successful reduction of Pd(II) to Pd(0) in the process.[25] The characteristic peaks corresponding to carbon (C 1s), nitrogen (N 1s) and iron (Fe 2p) are also clearly present in XPS elemental survey of Fe_3O_4/IL/Pd.

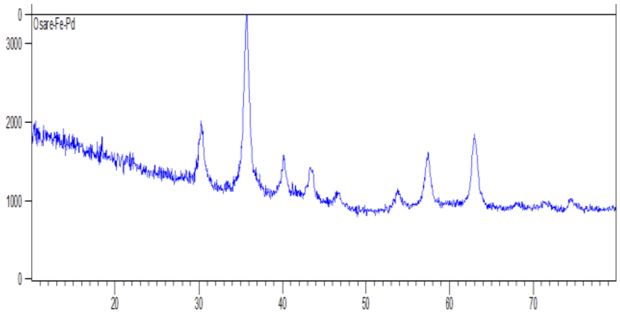


Fig. 6. XRD patterns of Fe_3O_4/IL/Pd.

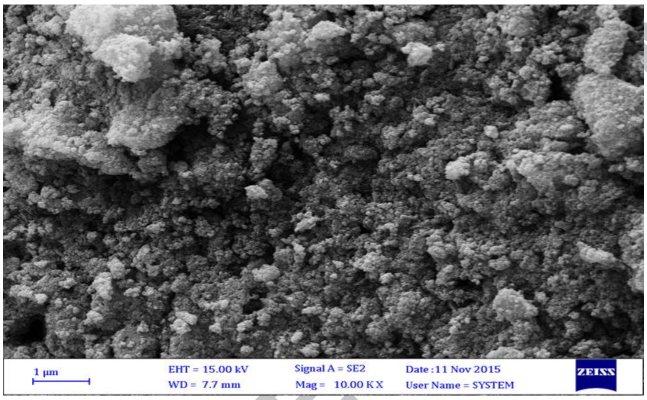


Fig. 7. FE-SEM image of Fe_3O_4/IL/Pd.

Evaluation of the catalytic activity of Pd NPs through Suzuki-Miyaura coupling reaction

Catalytic property of the Fe_3O_4/IL/Pd catalyst was tested via Suzuki cross-coupling reaction (Scheme 2). In order to develop a better catalytic system, influences of solvent, base and the amount of catalyst on Suzuki cross coupling were accurately probed at room temperature using the reaction of bromobenzene and phenylboronic acid, as the model reaction (Table 1). Solvent is known to play a vital role in the rate and the product distribution of Suzuki coupling reactions. Various solvents were screened and the reactions were conducted using H_2O/EtOH (1:1) as the best solvent. Among the evaluated bases, K_2CO_3 was found to be the most efficient base. As expected, no target product was detected in the absence of catalyst (Table 1, entry 10) and adding the catalyst to the mixture is necessary. Table 1 implies that decreasing the amount of the catalyst (Table 1, entries 8 and 9), decreases the yields, apparently. Therefore, 0.2% mol of the palladium catalyst suffices to complete the reaction (Table1, entry 7).

The Suzuki coupling reactions of various substituted aryl halides with phenylboronic acids were studied using 0.2 mol% of the magnetic catalyst at room temperature in air (Table 2). Aqueous ethanol was utilized as the reaction medium for environmental protection and economic advantage. Under the optimized circumstances, phenyl iodides, bromides and chlorides reacted actively with phenylboronic acid (Table 2, entries 1-17).

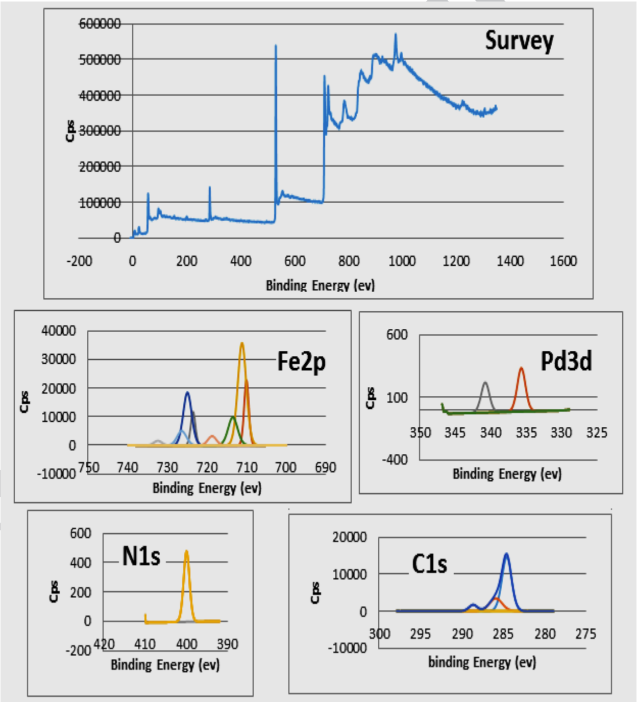
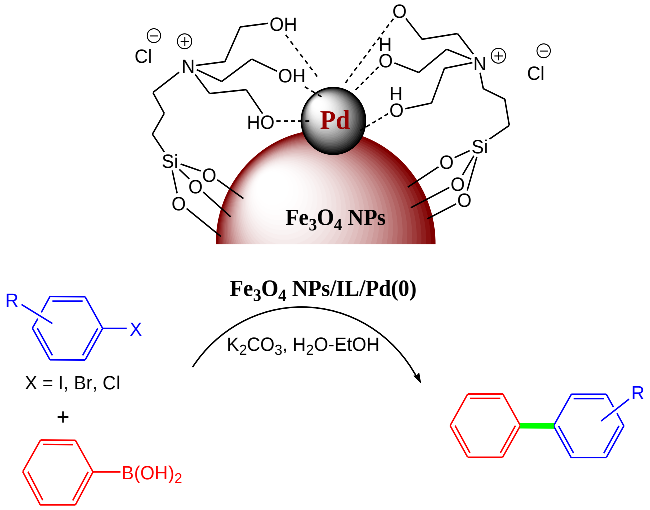


Fig. 8. XPS spectrum related to the elemental survey scan of Fe_3O_4/IL/Pd and the Fe2p, C1s, Pd3d, and N1s regions.



Scheme 2: Fe_3O_4/IL/Pd nanocatalyst for Suzuki-Miyaura cross-coupling reaction.

In the para-positions, aryl halides with electron-donating groups were less active than those with electron-withdrawing groups. A range of activated and deactivated aryl chlorides have also been investigated to study catalytic activity of the magnetic catalyst. According to the results, moderate yields were achieved at the given reaction condition (Table 2, entries 3, 6 and 9), as the bond energy of C–Cl in aryl chlorides is higher than that of C–Br in aryl bromides.

Table 1

Optimization of the reaction conditions in Suzuki-Miyaura coupling reaction of bromobenzene with phenylboronic acid.[a]

Entry	Pd (mol%)	Solvent	Base	Time (min.)	Yield (%)[b]
1	0.20	Toluene	K_2CO_3	60	65
2	0.20	DMF	K_2CO_3	80	80
3	0.20	EtOH	K_2CO_3	60	77
4	0.20	H_2O	K_2CO_3	90	55
5	0.20	$EtOH/H_2O$[c]	Et_3N	90	80
6	0.20	$EtOH/H_2O$[c]	NaOAc	60	65
7	0.20	$EtOH/H_2O$[c]	K_2CO_3	60	96
8	0.10	$EtOH/H_2O$[c]	K_2CO_3	60	65
9	0.15	$EtOH/H_2O$[c]	K_2CO_3	60	82
10	0.0	$EtOH/H_2O$[c]	K_2CO_3	40	0.0
11	0.2	$EtOH/H_2O$[c]	No base	90	Trace

[a] Reaction conditions: bromobenzene (1.0 mmol), phenylboronic acid (1.1 mmol), catalyst, base (2 mmol) and solvent (3 mL).

[b] Isolated yield.

[c] 1: 1

As expected, electron rich aryl boronic acids provided coupling products in good yields (Table 2, entries 15-17). Steric hindrance of the substituent did not affect the product yield in Suzuki-Miyaura reaction of deactivated aryl halides using Pd NPs (Table 2, entry 15).

Table 2

Suzuki–Miyaura coupling reaction of different aryl halides with phenylboronic acid.[a]

Entry	RC_6H_4X	$R_2C_6H_4B(OH)_2$	X	Time(h)	Yield(%)[b]
1	H	H	I	0.25	96
2	H	H	Br	1.00	95
3	H	H	Cl	18.0	75
4	4-CH_3	H	I	0.25	95
5	4-CH_3	H	Br	0.75	92
6	4-CH_3	H	Cl	18.0	65
7	4-$COCH_3$	H	I	0.45	96
8	4-$COCH_3$	H	Br	0.80	96
9	4-NO_2	H	Cl	18.0	80
10	4-CH_3O	H	I	0.25	96
11	4-CH_3O	H	Br	0.75	92
12	4-NO_2	H	I	0.25	96
13	4-NO_2	H	Br	2.00	90
14	2-Me	H	I	0.50	80
15	4-NO_2	4-MeO	I	1.50	95
16	H	3-MeO	Br	1.50	90
17	H	2-OMe	Br	1.50	85

[a] Reactions were performed under aerobic conditions in 5 mL of $H_2O/EtOH$ (1:1), 1.0 mmol arylhalide,1.1 mmol phenylboronic acid and 2 mmol K_2CO_3 in presence of the catalyst

[b] Isolated yield

After completion of the reaction, the catalyst was recovered with the help of a magnet, washed with distilled water (to remove excess base) and ethanol and dried in an oven at 50 °C. The dried recovered catalyst was applied for eight cycles with no considerable loss of activity, successively. Catalyst reusability was investigated using iodoobenzene with phenylboronic acid as model substrates (Fig. 8).

Further, metal leaching, as another important factor for commercial application of noble metal catalysts, was studied by ICP analysis. The new Pd NPs showed exceptional stability throughout the catalytic runs against leaching and sintering so that they retained >90% of their activity even at the 8th cycle of catalytic reuse. To determine heterogeneity of the catalyst, a hot filtration test was conducted for the Suzuki reaction between iodoobenzene and phenylboronic acid using Fe_3O_4/IL/Pd under the same optimum conditions. After proceeding for 8 minutes, 65% yield was obtained from the reaction. Then, the catalyst was separated to be reused. There was no increase in yield of the desired product when the reaction was sustained for another 8 minutes after magnetic removal of the catalyst, verifying heterogeneous property of the catalyst.

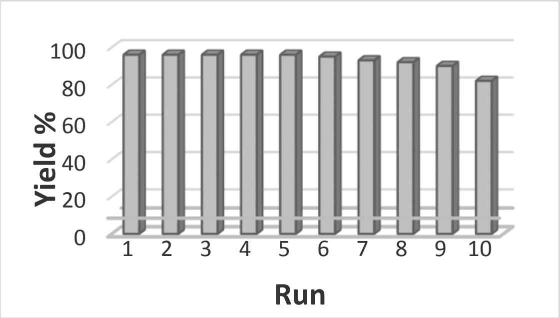


Fig. 8. Recycling of Fe_3O_4/IL/Pd in Suzuki reaction.

Conclusion

In the present study, a nanosized Fe_3O_4/IL/Pd catalyst with high magnetic and excellent dispersion characteristics was synthesized, successfully. The magnetic catalyst provided well decent reactivity and reusability in Suzuki reaction of aryl halides with phenylboronic acids. The magnetic catalyst could be easily recovered by an external magnet and reused eight times without significant loss of its activity. Additionally, the new magnetic catalyst is more economic and environment friendly because of its low Pd leaching after eight cycles. It is assumed that this novel heterogeneous magnetic nanocatalyst can be more widely applied to Pd-catalyzed reactions.

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Highlights

- A novel Fe_3O_4/IL/Pd nano structure was synthesized.
- Fe_3O_4/IL/Pd show good activity in the Suzuki reactions.
- The products were produced in excellent yields under mild conditions.
- Low palladium loading (~0.2 mol%) was used in the reaction.
- The catalyst can be reused several consecutive cycles.

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