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FULL PAPER

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Suzuki–Miyaura coupling reaction in water in the presence of robust palladium immobilized on modified magnetic Fe_3O_4 nanoparticles as a recoverable catalyst

Arefeh Dadras[1] | M. Reza Naimi-Jamal[1] | Firouz Matloubi Moghaddam[2] |
Seyed Ebrahim Ayati[2]

[1] Department of Chemistry, Research Laboratory of Green Organic Synthesis and Polymers, Iran University of Science and Technology, PO Box 16846-11314, Tehran, Iran

[2] Department of Chemistry, Laboratory of Organic Synthesis and Natural Products, Sharif University of Technology, PO Box 11155-9516, Tehran, Iran

Correspondence
M. Reza Naimi-Jamal, Department of Chemistry, Research Laboratory of Green Organic Synthesis and Polymers, Iran University of Science and Technology, PO Box 16846-11314, Tehran, Iran.
Email: naimi@iust.ac.ir

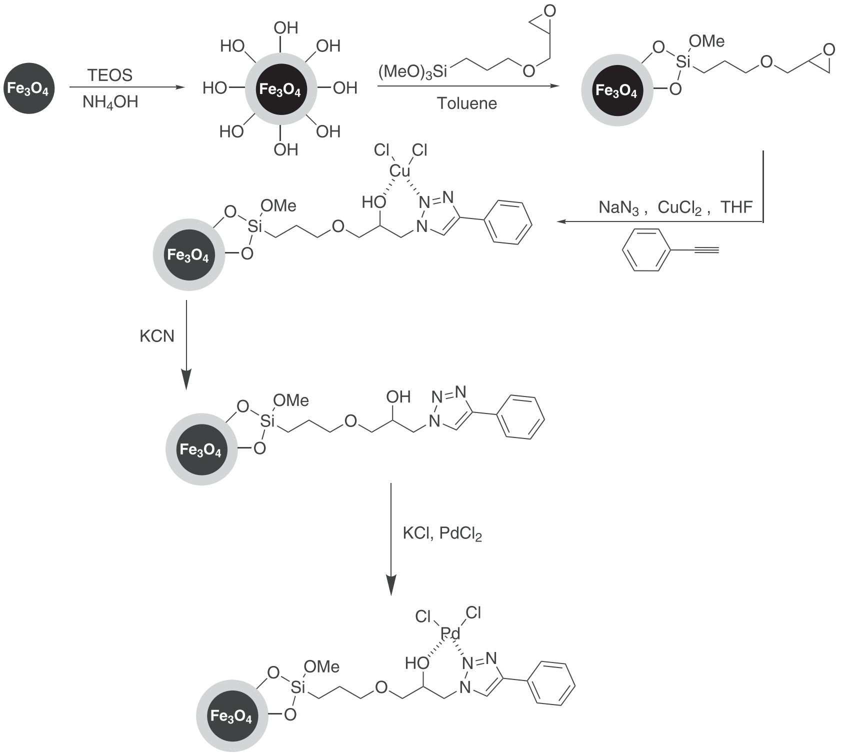
Funding information
Iran University of Science and Technology

Aryl halides and especially inactive aryl chlorides were coupled to benzenoid aromatic rings in a Suzuki–Miyaura coupling reaction in the absence of organic solvents and toxic phosphine ligands. The reaction was catalysed by a recoverable magnetic nanocatalyst, Pd@Fe_3O_4, in aqueous media. This method is green, and the catalyst is easily removed from the reaction media using an external magnetic field and can be re-used at least 10 times without any considerable loss in its activity. The catalyst was characterized using scanning and transmission electron microscopies, thermogravimetric analysis, inductively coupled plasma spectroscopy, Fourier transform infrared spectroscopy, CHN analysis, X-ray diffraction and vibrating sample magnetometry.

KEYWORDS
green chemistry, magnetic nanoparticle, nanomagnetic catalyst, palladium, Suzuki–Miyaura coupling reaction, water

1 | INTRODUCTION

Catalysts have many advantages in organic synthesis and are divided into two general categories, heterogeneous and homogeneous. Both have their own advantages and disadvantages. For example, homogeneous catalysts are more selective and because of being in the same phase as reactants, they may result in higher reaction rate and higher yields, but they are hard to separate from reaction media, and therefore they may contaminate the final product, which can be sometimes very harmful, especially in drug synthesis.[1,2] Metals supported on magnetic nanoparticles create a new approach in the world of catalysts.[3,4] By the development of such catalysts, it became possible to bring the advantages of both kinds of catalysts (homogeneous and heterogeneous) together in a single magnetic nanocatalyst.[5,6] This means one can profit from sustainability, along with high yields and easy work-up.[7,8] Because of nanoparticle size, they have a high ratio of surface area to volume, similar to a homogeneous catalyst. This property increases the interaction between the reaction components and so causes a marked increase in reaction rate and yield.[9–11] These heterogeneous catalysts remain insoluble in reaction media and, due to their magnetic characteristic, they can be easily removed using an external magnetic field.[12,13] Therefore, there is no concern about separation of such catalysts and pollution of products by toxic metals. Another important aspect is their robust structure, which results in reusability for several times that reduces environmental impact and increases economic advantages.[14] Immobilization of nanometals by strong sigma donor ligands not only minimizes metal leaching during a reaction, but also minimizes the agglomeration of nanometals and preserves the Fe_3O_4 magnetic core from over-oxidation.[15,16]



SCHEME 1 Synthesis of $Fe_3O_4@SiO_2@3$-glycidoxypropyltrimethoxysilanetriazole@Pd.

As is known, palladium is a precious metal and is useful in many organic transformations, especially in Suzuki coupling. Biaryl compounds are of high importance and have many applications, so scientists are still seeking for new ways to produce them in easier and affordable ways.[17–21]

The Suzuki–Miyaura C–C cross-coupling reaction nowadays is of high importance in organic synthesis.[22–28] This cross-coupling reaction is generally done with precious metal palladium in the presence of hazardous, toxic, flammable and expensive ligands such as hindered phosphines and carbenes in harmful organic solvents like dimethylformamide, dioxane and toluene, usually at high temperatures and with long reaction times and low yields.[29–34] Herein, we introduce Fe_3O_4 magnetic nanoparticles, functionalized by triazole as an efficient anchor for chelation of palladium. This catalyst has been successfully used in Suzuki–Miyaura C–C cross-coupling reactions.

2 | RESULTS AND DISCUSSION

$Fe_3O_4@SiO_2@3$-glycidoxypropyltrimethoxysilane triazole has been shown to be a strong ligand for chelating of copper ions, resulting in a robust catalyst for click reactions, without considerable leaching and with high reusability. It was prepared as demonstrated in Scheme 1. Silica-coated Fe_3O_4 magnetic nanoparticles were synthesized by a co-precipitation method,[35] functionalized using 3-glycidoxypropyltrimethoxysilane and then reacted with phenylacetylene, sodium azide and copper chloride.[36] To prepare the desired palladium catalyst, copper was then removed via reaction with KCN, and palladium was inserted by reaction with $PdCl_2$ and KCl (Scheme 1).

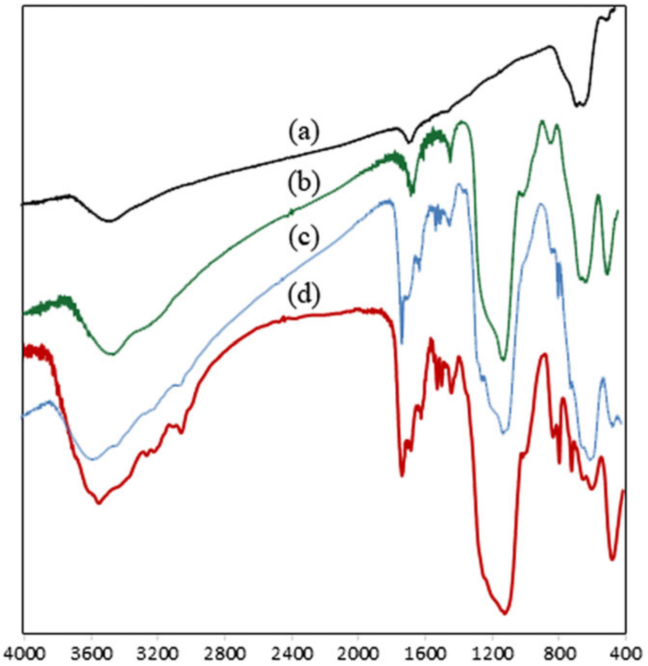


FIGURE 1 FT-IR spectra of (a) Fe_3O_4, (b) $Fe_3O_4@SiO_2$, (c) $Fe_3O_4@SiO_2@3$-glycidoxypropyltrimethoxysilanetriazole and (d) $Fe_3O_4@SiO_2@3$-glycidoxypropyltrimethoxysilanetriazole@Pd.

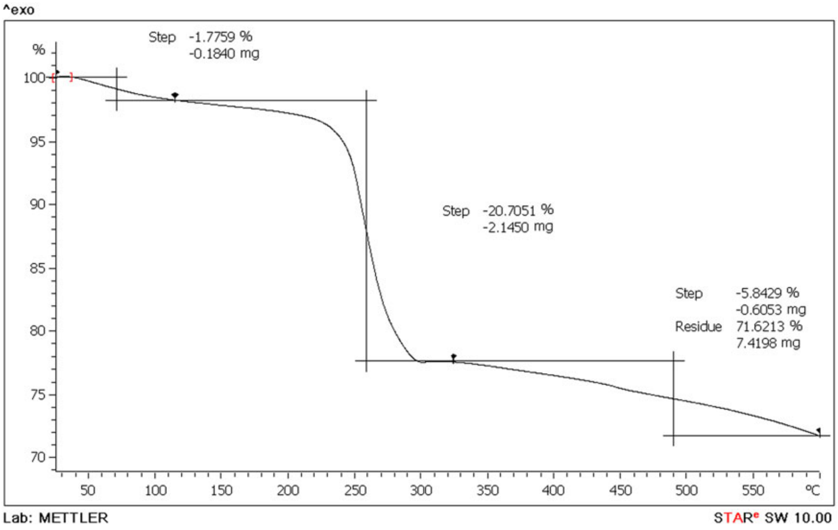


FIGURE 2 TGA curve of the catalyst

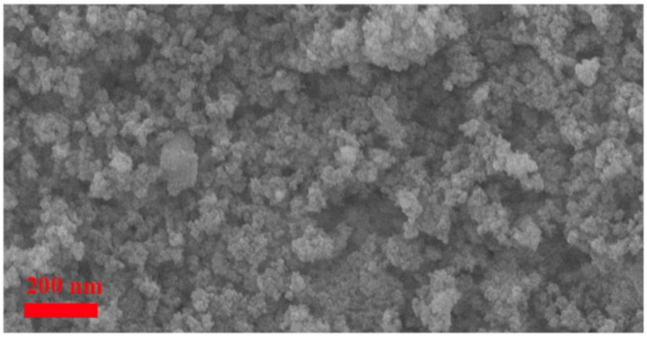


FIGURE 3 SEM image of the catalyst

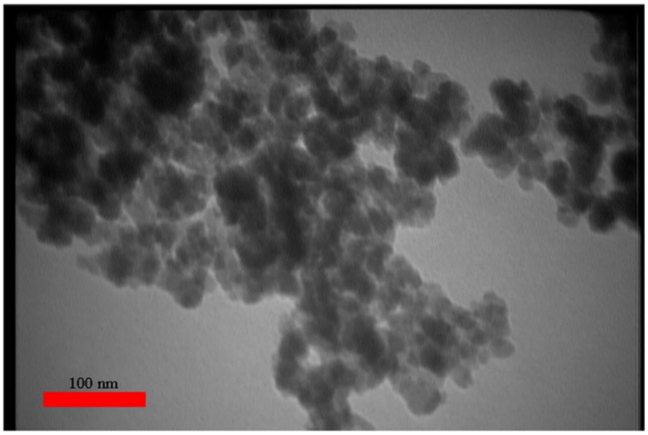


FIGURE 4 TEM image of the catalyst

The catalyst was characterized using Fourier transform infrared (FT-IR) spectroscopy (Figure 1). The peaks at 650 and 1100 cm^{-1} correspond to Fe—O and Si—O stretching vibrations of Fe_3O_4 and SiO_2, respectively (Figure 1a,b). The peaks at 2950 and 2930 cm^{-1} are attributed to C—H stretching vibrations and indicate the presence of alkylsilane groups on $Fe_3O_4@SiO_2$ (Figure 1 c,d). As can be seen in Figure 1(d), there is a small shift of hydroxyl group band to lower wavelengths that is a reasonable effect of the interaction between Pd and hydroxyl groups of the catalyst.

According to the thermogravimetric analysis (TGA) curve (Figure 2), decomposition of organic groups starts at 250 °C and completes at 600 °C, which corresponds to approximately 30% of the weight (1.15 mmol g^{-1}) of the catalyst and is a good indication for immobilization of triazole groups on the magnetic core. The weight loss before 250 °C corresponds to removal of adsorbed water. The stability of the catalyst up to 250 °C indicates that the catalyst has a good thermal stability.

The scanning electron microscopy (SEM) image of the catalyst (Figure 3) shows nanoparticles with spherical morphology and an average size of around 50 nm. The TEM image of the catalyst is shown in Figure 4, which indicates a core–shell structure of the catalyst.

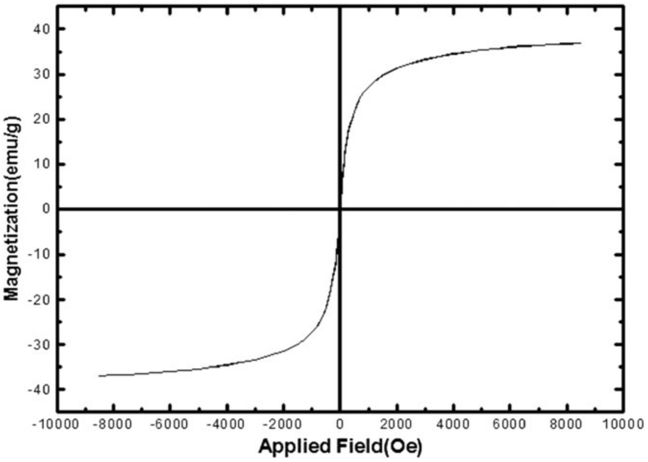


FIGURE 5 VSM curve of the catalyst

TABLE 1 Optimizing of base, solvent and temperature in model reaction[a]

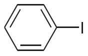
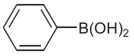
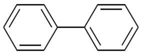
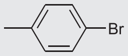
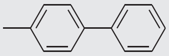
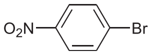
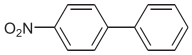
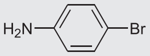
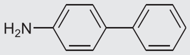
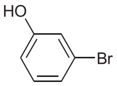
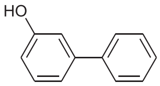
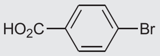
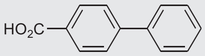
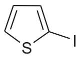
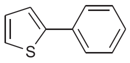
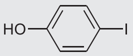
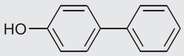
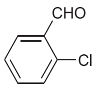
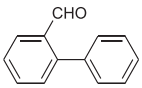
Entry	Base	Catalyst (mmol%)	Solvent	Temp. (°C)	Yield (%)[b]
1	—	1.2	H_2O	80	NR
2	K_2CO_3	—	H_2O	100	NR
3	K_2CO_3	1.2	H_2O	80	98
4	Na_2CO_3	1.2	H_2O	80	30
5	Li_2CO_3	1.2	H_2O	80	25
6	K_2CO_3	0.6	Toluene	100	Trace
7	K_2CO_3	1.2	Toluene	100	Trace
8	K_2CO_3	0.6	H_2O–*t*-BuOH[c]	80	7
9	K_2CO_3	1.2	H_2O–*t*-BuOH[c]	80	18
10	K_2CO_3	0.6	H_2O	100	40
11	K_2CO_3	0.6	H_2O	80	40

[a] Reaction conditions: *p*-bromobenzene (0.5 mmol), phenylboronic acid (0.6 mmol), base (0.6 mmol), solvent (2 ml) and reaction time of 3 h.

[b] GC yield.

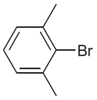
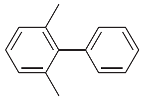
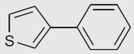
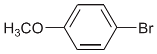
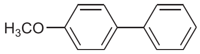
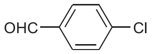
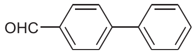
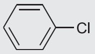
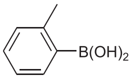
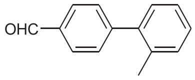
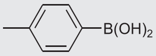
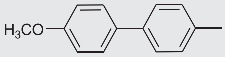
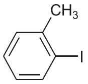
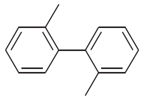
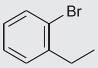
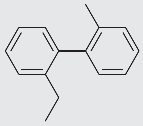
[c] Ratio of H_2O to *t*-BuOH is 2:1.

TABLE 2 Suzuki–Miyaura C–C cross-coupling reactions catalysed by palladium immobilized on modified magnetic Fe_3O_4 nanoparticles[a]

Entry	Aryl halide (1)	Arylboronic acid (2)	Product (3)	Time (h)	Yield (%)[b]
1				3	98
2		**2a**		3	98
3		**2a**		3	97
4		**2a**		3	92
5		**2a**		3	94
6		**2a**		3	96
7		**2a**		3	96
8		**2a**		3	97
9[c]		**2a**		4	72

(Continues)

TABLE 2 (Continued)

Entry	Aryl halide (1)	Arylboronic acid (2)	Product (3)	Time (h)	Yield (%)[b]
10		**2a**		3	93
11	**1 g**	**2a**		3	95
12		**2a**		3	90
13	**1c**	**2a**	**3c**	3	97
14[c]		**2a**		4	80
15[c]		**2a**	**3a**	4	75
16[c]	**1 l**			4	78
17	**1 k**			3	90
18		**2b**		3	98
19		**2b**		3	96

[a] Reaction conditions: aryl halide (0.5 mmol), arylboronic acid (0.6 mmol), K_2CO_3 (0.6 mmol), catalyst (0.01 g), H_2O (2 ml), 3 h at 80 °C.

[b] GC yield.

[c] Reaction time = 4 h.

To investigate the amount of Pd loaded on the catalyst support, inductively coupled plasma (ICP optical electron spectrometry was used. The amount was estimated to be about 13.2 wt% (1.2 mmol g^{-1}). The ICP result proved that there was a good Pd loading on the catalyst. No Cu emission wavelength was detected. This means that all Cu atoms were replaced by Pd ones.

According to CHN analysis, the content of carbon, nitrogen and hydrogen in the catalyst was determined as 18.98, 3.02 and 2.30 wt%, respectively. This is in good agreement with the structure of the catalyst, indicating that a high level of alkylsilane groups (about 15.8 mmol C per gram of catalyst) had been coated successfully on the magnetic nanoparticles.

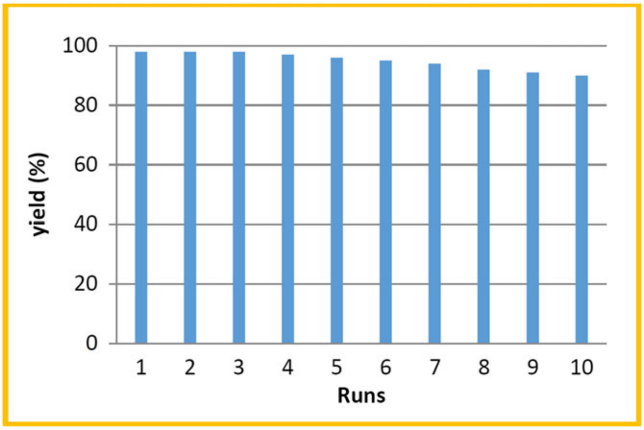


FIGURE 6 Reuse study of the catalyst in model reaction

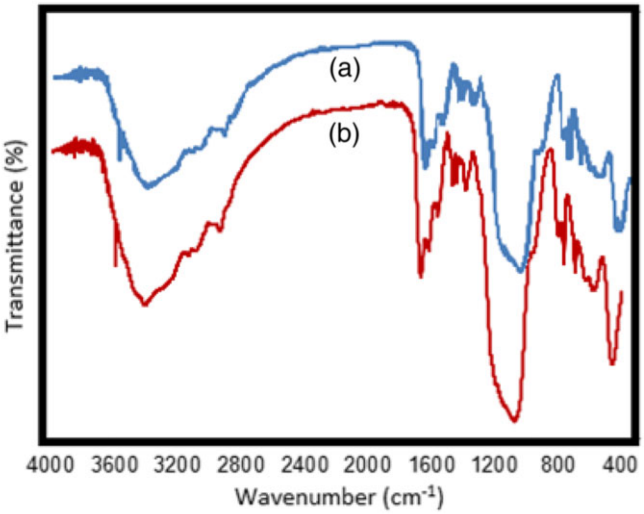


FIGURE 7 FT-IR spectra of the catalyst: (a) after reaction; (b) before reaction

The magnetic property of the catalyst was investigated at room temperature using vibrating sample magnetometry (VSM). According to Figure 5, the saturation magnetization of the catalyst is about 37 emu g^{-1} with a magnetic field within the range − 10 000 to 10 000 Oe. For a magnetic catalyst, this magnetization value is enough to allow it to be separated from reaction media by applying an ordinary external magnetic field.

After careful characterization of the catalyst, its usefulness in Suzuki–Miyaura reactions was investigated. For optimizing temperature, time, solvent and suitable base for these coupling reactions, phenylboronic acid and *p*-bromobenzene were chosen as model reactants. The results are summarized in Table 1. The reaction was monitored using TLC, and the yields were determined by GC. From Table 1, it is obvious that in the absence of a base or catalyst, no reaction occurs (Table 1, entries 1 and 2). Inorganic strong bases like NaOH are unsuitable, as they destroy the catalyst; therefore, alkali metal carbonates as weak bases were investigated (Table 1, entries 3–5). Potassium carbonate seems to be the most efficient base among those investigated (Table 1, entry 3). Water, toluene and a mixture of water and *t*-BuOH were investigated, and it was found that water was the best solvent. When the amount of the catalyst based on palladium was increased from 0.60 to 1.20 mmol%, the yield increased from 40 to 98% at the same time (compare entries 11 and 3).

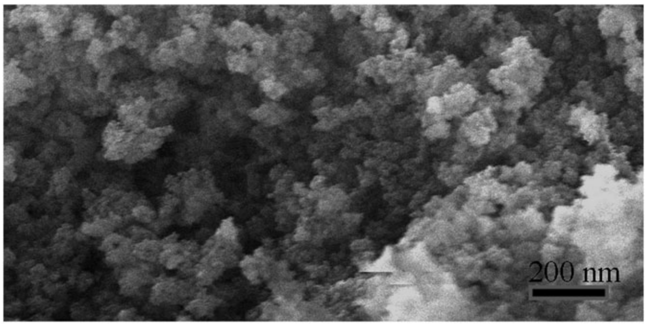


FIGURE 8 SEM image of recovered catalyst after reaction

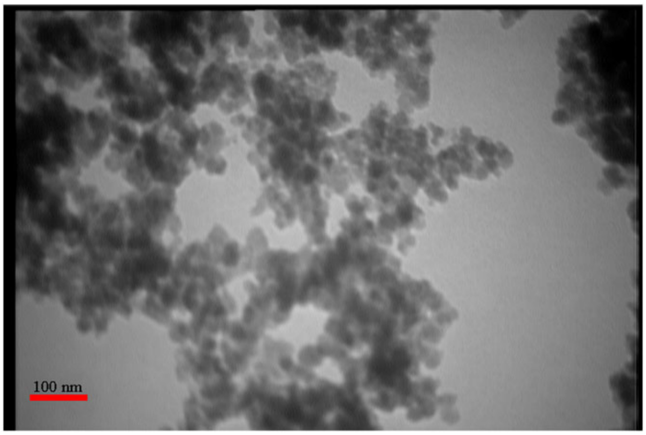


FIGURE 9 TEM image of recovered catalyst after reaction

After optimization of the reaction conditions, the scope of the method was investigated with other aryl halides and phenylboronic acid derivatives. The results are summarized in Table 2. Using this catalyst, aryl halides with both electron-donating and electron-withdrawing groups are easily coupled with phenylboronic acids (e.g. entries 3–6). Interestingly, generally challenging inactive aryl chlorides were also reacted with boronic acids to afford high yield of coupling products (e.g. entries 14–16).

In order to examine the reusability of the magnetic heterogeneous palladium catalyst, it was collected after each run by applying an external magnetic field,

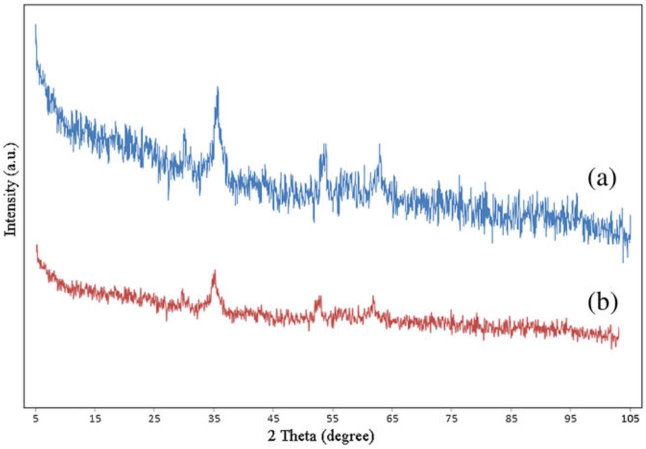


FIGURE 10 X-ray diffraction pattern of (a) the catalyst and (b) standard Fe_3O_4 sample

TABLE 3 Comparison of various catalysts for Suzuki–Miyaura coupling reaction of chlorobenzene and phenylboronic acid

Entry	Catalyst	Solvent	Time (h)	Temp. (°C)	Yield (%)	Ref.
1	Fe_3O_4@SiO_2@3-glycidoxypropyltrimethoxysilanetriazole@Pd	H_2O	5	80	75	Present work
2	Pd(II)–$NiFe_2O_4$	EtOH–H_2O	15	80	40	[37]
3	MNP-supported di(2-pyridyl)methanol–Pd complex	DMF	20	100	<20	[38]
4	Dichloridobis{(4-diphenylphosphinylbenzenecarboxylic acid-4-[N-(3-trimethoxysilypropyl)amide]}palladium(II)	Dioxane	15	80	34	[39]
5	Pd/UiO-66 (MOF)	H_2O–EtOH	20	80	70	[28]
6	Fe_3O_4/SiO_2-met-Pd$(OAc)_2$	H_2O–EtOH	8	80	45	[40]
7	Ethylenediamine-functionalized graphene oxide-immobilized Pd complex	EtOH	20	80	87	[41]
8	Pd[tBuNH(S)NHP(O)(OiPr)$_2$S]$_2$Cl$_2$ complex	DMF	14	RT	64	[29]
9	Hollow Fe_3O_4-NH_2-Pd	H_2O–EtOH	10	80	74	[42]

washed two times with methanol, dried and reused. As shown in Figure 6, the catalyst can be used at least 10 times without any negligible reduction in its activity.

The structure of the catalyst was re-investigated after 10 cycles using by FT-IR spectroscopy, and no variation was seen for the catalyst structure (Figure 7). The Pd content was also determined by after 10 cycles using atomic absorption spectroscopy, and showed no significant loss of Pd (1.16 mmol g^{-1}).

SEM (Figure 8) and TEM (Figure 9) images of the catalyst after recovery give a good indication for the stability of the catalyst after 10 cycles.

Figure 10 shows the powder X-ray diffraction patterns of the catalyst and neat Fe_3O_4 sample. According to the diffraction peak positions and intensities, the modification does not affect the crystalline structure of the Fe_3O_4 particles.

In order to confirm that the progress of the reaction is due to the immobilized palladium (verifying the heterogeneous nature of the catalyst) and not leached homogeneous palladium in solution, a hot filtration test was conducted. After 1 h progress of the coupling reaction of iodobenzene with phenylboronic acid, the catalyst was collected using an external magnetic field, and the reaction was continued for the remaining time in the absence of the catalyst. No further conversion was observed in liquid phase, which is a good indication of the heterogeneity of the catalyst and verifies that there is no significant leaching.

A comparison between the efficacy of our reported catalyst and some other palladium-based catalysts for aryl chloride coupling is presented in Table 3 for the model reaction. It is apparent that our catalyst works well in reasonably short reaction times and under mild reaction conditions, in water as a green solvent.

3 | CONCLUSIONS

We have used palladium immobilized on Fe_3O_4 nanomagnetic core in C–C coupling reactions in the absence of poisonous ligands in water as a green medium in short reaction times with high yields and purity. Different derivatives of biaryl compounds were produced by reaction of phenylboronic acid derivatives and aryl halides. The ability of this catalyst to couple inactive aryl chlorides with phenylboronic acid is of high interest. The catalyst also was easily removed from reaction media using an external magnetic field, washed with methanol and reused for 10 cycles without considerable reduction in its reactivity. The stability of the catalyst to air, moisture and heat is another benefit of this catalyst. Easy and complete elimination of the catalyst from reaction media is a good reason for using this catalyst in pharmaceutical and drug synthesis.

4 | EXPERIMENTAL

4.1 | General

All chemicals and solvents were purchased from commercially available sources such as Sigma-Aldrich and Merck and there was no need for any additional purification. ^{1}H NMR and ^{13}C NMR spectra were recorded with a Bruker (Avance DRX-400) spectrometer in $CDCl_3$ as solvent at room temperature. Chemical shifts were measured in ppm relative to tetramethylsilane as an internal standard. An ABB Bomem MB-100 FT-IR spectrophotometer was used for obtaining FT-IR spectra of samples. The morphology of the catalyst was investigated using a Philips XL30 SEM instrument. TGA was conducted under a nitrogen atmosphere with a TGA Q 50 thermogravimetric analyser. CHN analysis was carried out with a LECO Truspec.

4.2 | General procedure for catalyst preparation

This catalyst was synthesized according to the procedure reported in the literature (Scheme 1).[36]

4.2.1 | Synthesis of Fe_3O_4@SiO_2

A solution of $FeCl_3$ (66.58 mmol, 10.8 g) and $FeCl_2$ (31.56 mmol, 4.0 g) was prepared in a three-necked flask in deionized water (50 ml). A solution of ammonium hydroxide (28% *v*/v) was added dropwise to the solution under an atmosphere of argon to adjust the pH to 10 and the solution was stirred for about 20 min at room temperature. The prepared magnetic nanoparticles were collected using an external magnetic field and washed with deionized water (30 ml) and then three times with ethanol (30 ml). The synthesized Fe_3O_4 nanoparticles were dispersed in ethanol (80 ml) for 20 min using ultrasonic irradiation (ultrasonic power: 100 W). These magnetic nanoparticles were coated with silica through the addition of 3 ml of tetraethyl orthosilicate (TEOS) to the solution. While the solution was stirring, 3 ml of ammonium hydroxide (28% *v*/v) was added to the mixture during 15 min. The mixture was stirred for 12 h at 40 °C. Finally, the silica-coated magnetic nanoparticles (Fe_3O_4@SiO_2) were collected using an external magnet and washed three times with ethanol (30 ml) and dried in a rotary evaporator under reduced pressure.[35]

4.2.2 | Synthesis of Fe_3O_4@SiO_2@3-glycidoxypropyltrimethoxysilane@triazole@cu

The synthesized Fe_3O_4@SiO_2 magnetic nanoparticles (2 g) were sonicated for 30 min in 10 ml of toluene. Then, 3-glycidoxypropyltrimethoxysilane (11.32 mmol, 2.5 ml) was added to the mixture while stirring and the mixture was refluxed for 48 h. The precipitate was washed with methanol (3 × 30 ml) and dried using a rotary evaporator under reduced pressure. Sodium azide (22.7 mmol, 1.5 g), copper(II) chloride (0.74 mmol, 0.1 g) and sodium ascorbate (0.76 mmol, 0.15 g) were dissolved in a mixture of tetrahydrofuran (THF) and water (80/20) in a round-bottom flask equipped with a magnetic stirring bar. Then, the modified magnetic nanoparticles (1.0 g) and phenylacetylene (18.2 mmol, 2 ml) were successively added to the mixture and stirred at 60 °C for 10 h. By applying an external magnet, the final product was extracted, washed with methanol (3 × 20 ml) and dried under reduced pressure.[36]

4.2.3 | Synthesis of Fe_3O_4@SiO_2@3-glycidoxypropyltrimethoxysilane@triazole

In order to exchange copper with palladium, potassium cyanide (1.5 g) was dissolved in water–methanol (1:1, 10 ml) and the solution was added to Fe_3O_4@SiO_2@triazole@Cu, which was synthesized in the previous step and stirred for 5 h at room temperature. Then, the catalyst was removed using an external magnetic field, washed with methanol and dried overnight at room temperature.

4.2.4 | Synthesis of Fe_3O_4@SiO_2@3-glycidoxypropyltrimethoxysilane@triazole@Pd

Potassium chloride (0.3 g) was dissolved in methanol and water (1:1, 10 ml) and palladium chloride (0.1 g) was added to the solution and the mixture was stirred vigorously for 4 h at room temperature. A transparent and clear reddish solution of [K_2PdCl_4] was obtained.

Fe_3O_4@SiO_2@triazole was dispersed in methanol (10 ml) and sonicated for 15 min. Then, the [K_2PdCl_4] solution was added and stirred vigorously for 24 h at room temperature. The resulting catalyst was removed using an external magnetic field and washed twice with methanol and dried under vacuum at 40 °C for 10 h.

4.3 | Typical procedure for C–C Suzuki–Miyaura cross-coupling reaction

Fe_3O_4@SiO_2@3-glycidoxypropyltrimethoxysilane@triazole@Pd (1.2 mmol% based on Pd, 10 mg) was added to a mixture of phenylboronic acid (0.6 mmol), aryl halide (0.5 mmol) and K_2CO_3 (0.6 mmol) in water (2 ml) and stirred for 3 h at 80 °C. The progress of the reaction completion was followed by TLC (EtOAc–*n*-hexane, 10:90). After completion of the reaction, the catalyst was removed using an external magnetic field and the products were extracted withy ethyl acetate. The solution was dried over $MgSO_4$ and the organic solvent was evaporated with a rotary evaporator.

The crude products were purified by flash chromatography with *n*-hexane–EtOAc. All products were known compounds and were identified by comparison of their physical and spectral data with those reported in the literature.

4.4 | Recycling of catalyst

In order to reuse the catalyst, the magnetic Pd(II) catalyst was collected using an external magnet, washed twice with methanol and air-dried overnight.

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ORCID

M. Reza Naimi-Jamal http://orcid.org/0000-0002-8305-7234
Firouz Matloubi Moghaddam http://orcid.org/0000-0002-8418-9888

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