Full paper

Applied Organometallic Chemistry

Received: 3 November 2015 Revised: 23 November 2015 Accepted: 4 December 2015

(wileyonlinelibrary.com) DOI 10.1002/aoc.3424

Fe_3O_4@SiO_2@L-arginine@Pd(0): a new magnetically retrievable heterogeneous nanocatalyst with high efficiency for C–C bond formation

Arash Ghorbani-Choghamarani* and Gouhar Azadi

The surface of Fe_3O_4@SiO_2 nanoparticles was modified using L-arginine as a green and available amino acid to trap palladium nanoparticles through a strong interaction between the metal nanoparticles and functional groups of the amino acid. The proposed green synthetic method takes advantage of nontoxic reagents through a simple procedure. Characterization of Fe_3O_4@SiO_2@L-arginine@Pd(0) was done using Fourier transform infrared spectroscopy, thermogravimetric analysis, scanning electron microscopy, energy-dispersive X-ray spectroscopy, X-ray diffraction, vibrating sample magnetometry and inductively coupled plasma analysis. The catalytic activity of Fe_3O_4@SiO_2@L-arginine@Pd(0) as a new nanocatalyst was investigated in C–C coupling reactions. Waste-free, use of green medium, efficient synthesis leading to high yield of products, eco-friendly and economic catalyst, excellent reusability of the nanocatalyst and short reaction time are the main advantages of the method presented. Copyright © 2016 John Wiley & Sons, Ltd.

Additional supporting information may be found in the online version of this article at the publisher's web-site.

Keywords: C–C bond formation; Fe_3O_4@SiO_2@L-arginine@Pd(0); retrievable

Introduction

To design novel catalysts with high activity, selectivity and resistance to deactivation is one of the long-term goals for research scientists.[1] In chemistry, a heterogeneous catalyst refers to the form and phase of the catalyst differing from those of the reactants. The great majority of practical heterogeneous catalysts are solids. Among a number of advantages of heterogeneous catalysts can be listed ease of handling and recyclability.[2]

Fabrication of nanoparticles with desired properties through modification of their surfaces has attracted growing attention in recent years. There is an increasing interest in the synthesis, characterization and surface modification of magnetic nanoparticles because of their potential applications in biotechnology, biomedicine, environmental chemistry, material science and catalysis.[3–6] Magnetic nanoparticles are efficient, readily available and have high surface area resulting in high catalyst loading capacity and outstanding stability as heterogeneous supports for catalysts. They show the same and sometimes even higher activity than their corresponding homogeneous analogues.[7–9] Therefore, combining the attractive properties of nanotechnology with the above mentioned advantages of heterogeneous catalysts increases the importance of these catalysts.

Magnetic nanoparticles especially Fe_3O_4 coated with silica (Fe_3O_4@SiO_2) are emerging as interesting supports for the immobilization of homogeneous catalysts. Different from many traditional porous supports, nonporous magnetic nanoparticles induce the distribution of catalytically active sites throughout the outer surface; thus, the pore diffusion constraint is practically avoided.[10] Importantly, magnetic separation of the magnetic nanoparticles is more effective than filtration or centrifugation, easy, economical and promising for industrial applications.[11] Supported metal nanoparticles play a vital role in a wide range of applications, particularly in the scope of catalysis. Among the various metal nanoparticles, platinum group metals are used most extensively as catalysts for a great many industrial applications in hydrogenation,[12] hydroformylation,[13] carbonylation,[14] and so on. Over the past few decades, palladium nanoparticles have also been applied as useful catalysts for C–C coupling reactions like Suzuki–Miyaura coupling reactions on account of the economic benefits.[15] Loading palladium active species onto solid materials develops a cost-effective and green route for the wide applications of palladium-based catalysts in the areas of cross-coupling reactions. Carbon–carbon bond forming reactions such as the Suzuki–Miyaura cross-coupling reaction represent some of the most important transformations in organic synthesis, which are of great significance in the fields of agrochemicals, functional materials and pharmaceuticals. With the fast development of palladium-based catalysts, Suzuki–Miyaura reactions now can be carried out under rather mild conditions with great proficiency and selectivity.[16–18]

---

* *Correspondence to: Arash Ghorbani-Choghamarani, Department of Chemistry, Faculty of Science, Ilam University, PO Box 69315516, Ilam, Iran. E-mail: arashghch58@yahoo.com or a.ghorbani@mail.ilam.ac.ir*

Department of Chemistry, Faculty of Science, Ilam University, PO Box 69315516, Ilam, Iran

For the reasons mentioned above, in this paper we report the synthesis of a novel magnetic Fe_3O_4/silica nanoparticle-supported palladium (Fe_3O_4@SiO_2@L-arginine@Pd(0)) catalyst for the first time and evaluate the catalytic activity of the prepared catalyst. The Suzuki–Miyaura coupling reaction was employed as a model reaction.

Experimental

Materials

All reactants were purchased from Merck Chemical Company and Aldrich and used without further purification. Fourier transform infrared (FT-IR) spectra were recorded as KBr pellets using a Bruker VRTEX 70 model FT-IR spectrophotometer. Powder X-ray diffraction (XRD) patterns were collected with a Rigaku-Dmax 2500 diffractometer with nickel filtered Cu Kα radiation (λ = 1.5418 Å, 40 kV). Supermagnetic properties of the catalyst were measured with a vibrating sample magnetometer (MDKFD) operating at room temperature. Thermogravimetric analysis (TGA) was carried out with a Shimadzu DTG-60 instrument.

General procedure for C–C coupling reaction of aryl halides with $NaBPh_4$

A mixture of aryl halide (1 mmol), sodium tetraphenylborate ($NaPh_4B$; 0.5 mmol), Na_2CO_3 (3 mmol), Fe_3O_4@SiO_2@L-arginine@Pd(0) (5 mg, 1.4 mmol% Pd) and poly(ethylene glycol) (PEG; 1 mL) as solvent was added to a 10 mL pressure-safe vial and stirred at 100 °C. After completion of the reaction (monitored using TLC), the catalyst was removed using an external magnet. The reaction mixture was diluted with water and the resultant mixture extracted with diethyl ether to isolate the products. The combined organic layers were dried over anhydrous Na_2SO_4, and the solvent was evaporated under reduced pressure.

General procedure for C–C coupling reaction of aryl halides with phenylboronic acid

A mixture of aryl halide (1 mmol), phenylboronic acid (1 mmol), Na_2CO_3 (3 mmol), Fe_3O_4@SiO_2@L-arginine@Pd(0) (5 mg, 1.4 mmol % Pd)) and PEG (1 mL) as solvent was added to a 10 mL pressure-safe vial and stirred at 100 °C. The reaction mixture was stirred for an appropriate time. After completion of the reaction (monitored using TLC), the catalyst was separated by applying an external magnet. The reaction mixture was diluted with water and the resultant mixture extracted with ethyl acetate to isolate the products. The combined organic layers were dried over anhydrous Na_2SO_4, and the solvent was evaporated under reduced pressure.

Results and discussion

Continuing our work on functionalizing magnetic nanoparticles with various derivatives for catalysis applications,[19–21] in the research reported here we decided to demonstrate the preparation of a novel magnetic nanoparticle by anchoring L-arginine on the surface of silica-coated iron oxide nanoparticles (Fe_3O_4@SiO_2@L-arginine). Then treatment of Fe_3O_4@SiO_2@L-arginine with $Pd(OAc)_2$ provides Fe_3O_4@SiO_2@L-arginine@Pd(0).

Preparation of Fe_3O_4@SiO_2

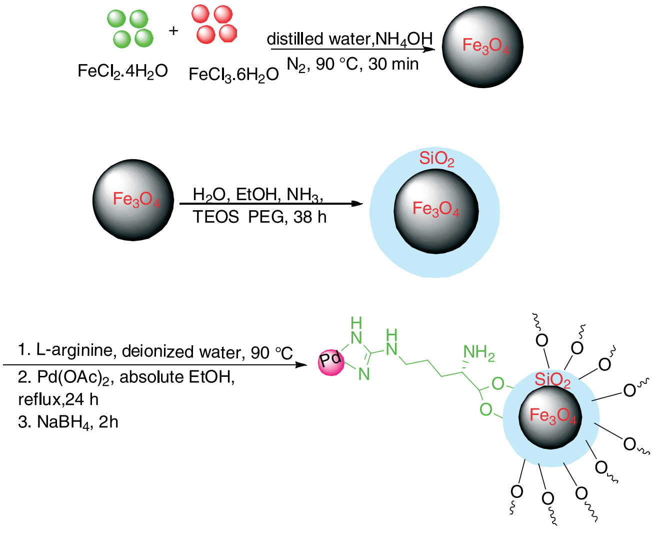
Fe_3O_4 was readily synthesized using a chemical co-precipitation method similar to a previously reported one,[22] followed by a SiO_2-coating procedure. Briefly, 2.00 g of the obtained Fe_3O_4 was dispersed in a mixture of 50 mL of ethanol, 20 mL of deionized water and 10.0 mL of concentrated aqueous ammonia solution, followed by the addition of 3.36 g of PEG and 2 mL of tetraethylorthosilicate (TEOS). This solution was stirred mechanically for 38 h at room temperature. Then the product, Fe_3O_4@SiO_2, was separated using an external magnet, washed with deionized water and ethanol three times and dried at room temperature.

Preparation of Fe_3O_4@SiO_2@L-arginine@Pd(0)

In the second step, Fe_3O_4@SiO_2@L-arginine nanocatalyst was synthesized using the following procedure. An amount of 1 g of Fe_3O_4@SiO_2 was suspended in deionized water (20 mL) and sonicated until it became highly dispersed. Then, 2 g of L-arginine was added and the mixture stirred at 90 °C for 15 h. Fe_3O_4@SiO_2@L-arginine nanoparticles were separated from the aqueous solution by applying an external magnet, washed with distilled water several times and then dried in an oven overnight. The whole synthesis was done under nitrogen atmosphere. In the last step, incorporation of palladium onto the Fe_3O_4@SiO_2@L-arginine nanocomposite was carried out by mixing the Fe_3O_4@SiO_2@L-arginine (0.5 g) and $Pd(OAc)_2$ (0.25 g) in absolute ethanol (30 mL). The mixture was refluxed for 24 h. Pd (II) ions were adsorbed onto the magnetic nanocarrier and reduced by $NaBH_4$ to produce Fe_3O_4@SiO_2@L-arginine@Pd(0). Finally, the synthesized Fe_3O_4@SiO_2@L-arginine@Pd(0) nanosolid as a black powder was separated from the suspension using magnetic decantation, washed with absolute ethanol and dried under vacuum at room temperature (1).

Catalyst characterization

The surface structure of the materials was confirmed using FT-IR spectroscopy. As shown in Fig. 1, the presence of vibration bands at 559–588 and 3400 cm^{-1}, which are due to Fe–O and OH, respectively, demonstrates the existence of Fe_3O_4 components in all of the synthesized materials. The sharp band at 1090 cm^{-1} is due to



Scheme 1. General route for the fabrication of Fe_3O_4@SiO_2@L-arginine@Pd(0).

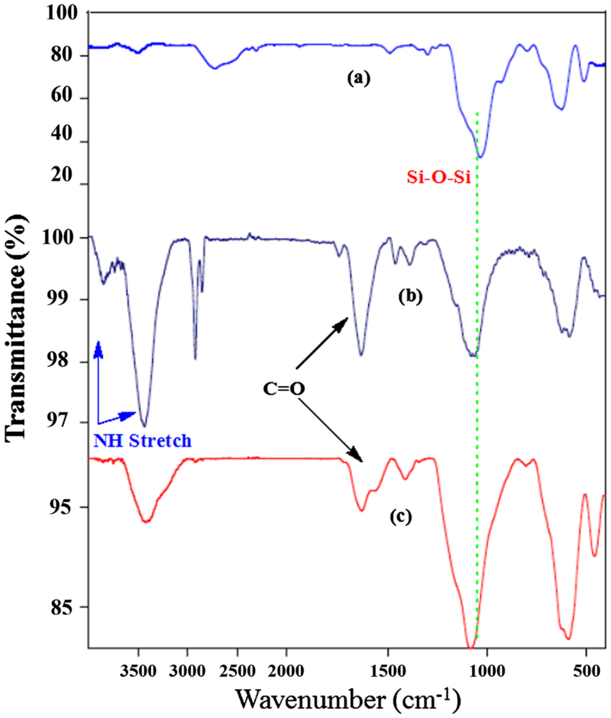


Figure 1. Comparison FT-IR spectra of (a) Fe_3O_4@SiO_2, (b) Fe_3O_4@SiO_2@L-arginine and (c) Fe_3O_4@SiO_2@L-arginine@Pd(0).

Si–O–Si antisymmetric stretching vibration, being characteristic of the presence of a SiO_2 layer surrounding each Fe_3O_4 nanoparticle.[23] The peak at around 2856–2924 cm^{-1} corresponds to aliphatic C–H stretching of methylene groups, which is observable in the spectra of the samples. According to Zhang *et al.* the wavenumber separation, *D*, between the $\nu_{as}(COO^-)$ and $\nu_s(COO^-)$ FT-IR bands can be used to distinguish the type of the interaction between the carboxylate head and the metal atom.[24] In this study, *D* (1570–1409 = 161 cm^{-1}) is ascribed to bridging bidentate. FT-IR spectra show no major changes in the Fe_3O_4@SiO_2@L-arginine@Pd(0) (Fig. 1, curve (c)) vibration bands, only a slight difference in intensity of bands in the 1400–1600 cm^{-1} range can be noticed. Generally, these observations indicate the immobilization of L-arginine on the surface of Fe_3O_4@SiO_2.

The thermal stability of Fe_3O_4@SiO_2@L-arginine@Pd(0) nanoparticles was investigated using TGA. The thermogram is presented in Fig. 2. The weight loss below 200 °C is attributed to the removal of bound water. As the TGA curve of the prepared nanocatalyst shows, the organic parts are decomposed completely at 385 °C.

Figure 3 shows SEM images and energy-dispersive X-ray spectroscopy (EDS) pattern of the nanocatalyst. It can be seen that Fe_3O_4@SiO_2@L-arginine@Pd(0) particles are spherical in shape with slight agglomeration. The presence of Si, O and Fe signals in the EDS pattern in Fig. 3 confirms that the iron oxide particles are loaded into silica, and the higher intensity of Si peak compared with Fe peaks shows Fe_3O_4 nanoparticles are trapped by SiO_2. The EDS analysis results confirm the elemental composition of the nanoparticles and the existence of Pd in the prepared nanocatalyst. The exact amount of Pd of Fe_3O_4@SiO_2@L-arginine@Pd(0) is found to be 2.82×10^{-3} mol g^{-1}, which was determined using inductively coupled plasma optical emission spectrometry.

The magnetic properties were characterized using vibrating sample magnetometry. The magnetization curve is shown in Fig. 4. The saturation magnetization of Fe_3O_4@SiO_2@L-arginine@Pd(0) is found to be *ca* 29 emu g^{-1}, which is lower than that of bare Fe_3O_4 magnetic nanoparticles (67.22 emu g^{-1}).[25] These results indicate that the magnetization of Fe_3O_4 decreases considerably when coated with SiO_2 and then Pd nanoparticles. Nevertheless, the catalyst can still be separated from solution using an external magnetic field.

The high-angle XRD pattern of the Fe_3O_4@SiO_2@L-arginine@Pd(0) nanocomposite is shown in Fig. 5. This result means that the nanocomposite has been successfully synthesized without damaging the crystal structure of the Fe_3O_4 core. The broad peaks from 18° to 24° cover the area ascribed to amorphous silica.

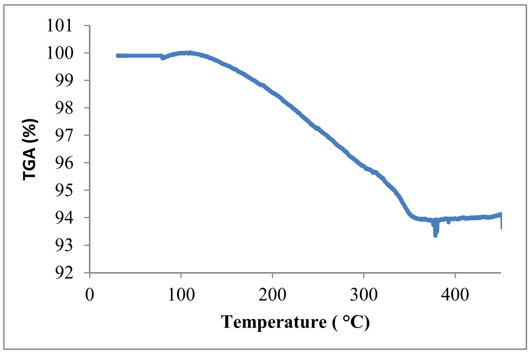


Figure 2. TGA curve of Fe_3O_4@SiO_2@L-arginine@Pd(0).

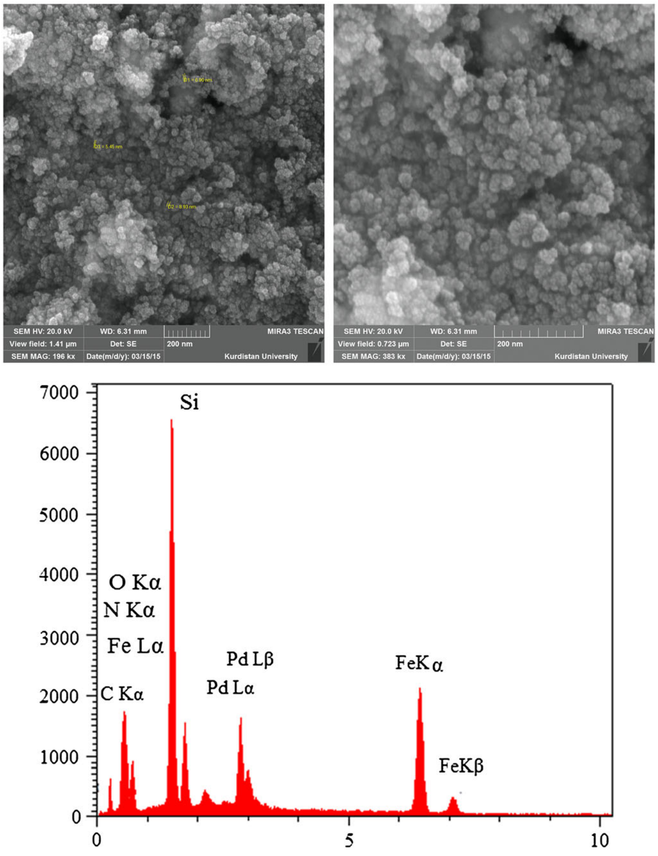


Figure 3. SEM images and EDS pattern of Fe_3O_4@SiO_2@L-arginine@Pd(0).

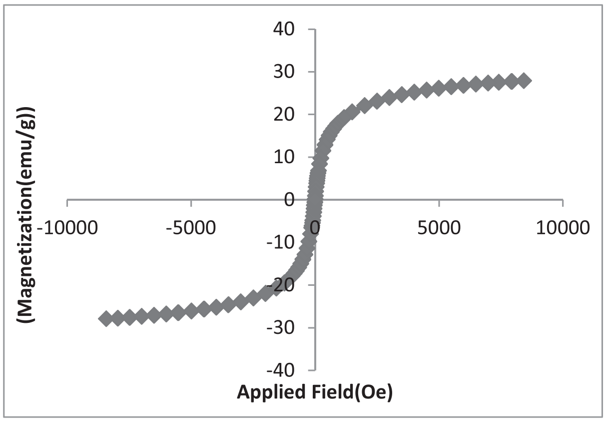


Figure 4. Vibrating sample magnetometry cure of $Fe_3O_4@SiO_2@$L-arginine@Pd(0).

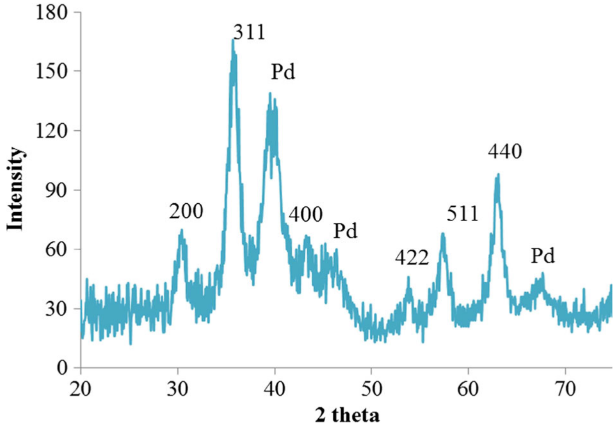


Figure 5. XRD pattern of $Fe_3O_4@SiO_2@$L-arginine@Pd(0).

Catalytic studies

After full characterization of $Fe_3O_4@SiO_2@$L-arginine@Pd(0), the catalytic activity of the prepared nanocatalyst was tested in the synthesis of biphenyl compounds. In order to get the best experimental conditions, the C–C coupling reaction was optimized with respect to solvent and base (2). The influence of various inorganic bases demonstrates that Na_2CO_3 and $NaHCO_3$ give the best yield only when PEG is used as solvent (Table 1, entries 5 and 6). Among the other solvents studied, only traces or no products are obtained.

Table 1. Optimization of base and solvent for synthesis of 4-nitrobiphenyl catalysed by $Fe_3O_4@SiO_2@$L-arginine@Pd(0)[a]

Entry	Solvent	Base	Time (min)	Yield (%)
1	DMSO	Na_2CO_3	50	No reaction
2	EtOH	Na_2CO_3	50	No reaction
3	H_2O	Na_2CO_3	50	Trace
4	Dioxane	Na_2CO_3	50	No reaction
5	PEG	Na_2CO_3	50	98
6	PEG	$NaHCO_3$	50	98
7	PEG	NaOH	50	No reaction
8	PEG	Et_3N	50	No reaction

[a] Reaction conditions: 1-bromo-4-nitrobenzene (1 mmol), $NaBPh_4$ (0.5 mmol), base (3 mmol), $Fe_3O_4@SiO_2@$L-arginine@Pd(0) (5 mg, 1.4 mmol% Pd), solvent (1 mL) at 100 °C.

Table 2. Synthesis of biphenyl in the presence of various amounts of catalyst at 100 °C[a]

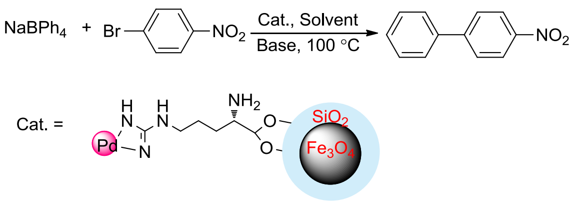
Entry	Catalyst (mg)	Time (min)	Yield (%)
1	0 (0 mmol%)	10	No reaction
2	1 (0.28 mmol%)	10	74
3	3 (0.8 mmol%)	10	80
4	5 (1.4 mmol%)	10	98
5	8 (2.2 mmol%)	10	98

[a] Reaction conditions: iodobenzene (1 mmol), $NaBPh_4$ (0.5 mmol), base (3 mmol), PEG (1 mL).

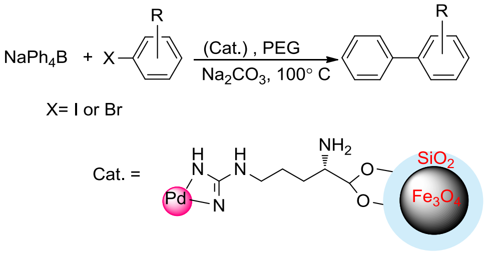
In order to determine a suitable catalytic amount of $Fe_3O_4@SiO_2@$L-arginine@Pd(0), we then examined various amounts of catalyst in the reaction of iodobenzene with $NaBPh_4$, starting from 1 mg up to 8 mg, for which the best result was obtained in the presence of 5 mg (1.4 mmol% Pd) of nanocatalyst. The results are summarized in Table 2. Also, the use of higher amounts of catalyst (8 mg) does not improve the result (Table 2, entry 5).

Applying 5 mg (1.4 mmol%) of $Fe_3O_4@SiO_2@$L-arginine@Pd(0) and Na_2CO_3 as base in PEG as solvent at 100 °C are the best conditions for the C–C coupling reaction (Table 2, entry 4). We then explored the synthesis of various biphenyl derivatives under the established procedure, in order to probe the scope and generality of the process (3). The results are summarized in Table 3.

After successful synthesis of a wide range of biphenyl compounds with $NaBPh_4$, the catalytic activity of $Fe_3O_4@SiO_2@$L-arginine@Pd(0) was also probed in the Suzuki reaction of various aryl halides with phenylboronic acid. Initially the reaction between 1-bromo-4-nitrobenzene and phenylboronic acid as the model



Scheme 2. Synthesis of 4-nitrobiphenyl catalysed by $Fe_3O_4@SiO_2@$L-arginine@Pd(0).



Scheme 3. General scheme for the Suzuki reaction catalysed by $Fe_3O_4@SiO_2@$L-arginine@Pd(0).

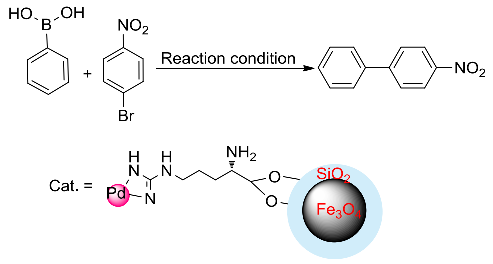
Table 3. C–C coupling reaction of aryl halides with $NaBPh_4$ using Fe_3O_4@SiO_2@L-arginine@Pd(0) as catalyst at 100 °C

Entry	X	R	Time (min)	Yield (%)	M.p. (°C)
1	Br	4-NO_2	50	98	110–113[26]
2	I	H	10	98	60–64[26]
3	I	4-OCH_3	90	96	84–86[27]
4	I	4-CH_3	40	93	40–41[26]
5	Br	4-CHO	20	97	55–57[26]
6	Br	4-NC	15	92	79–81[27]
7	Br	4-NH_2	60	91	55[26]
8	Br	H	40	98	60–64[27]
9	Br	2-$COCH_3$	40	95	Oil[28]
10	Br	3-CF_3	45	90	Oil[29]
11	Br	4-CO_2H	50	91	220–225[30]
12	Br	4-CH_3	120	94	40–41[27]
13	I	2-CO_2H	40	90	115–118[30]

[a]Reaction conditions: aryl halide (1 mmol), $NaBPh_4$ (0.5 mmol), Na_2CO_3 (3 mmol), catalyst (5 mg, 1.4 mmol% Pd), PEG (1 mL).

reaction was selected and the reaction was examined under various conditions (4).The results are presented in Table 4. Excellent yield of biphenyl compound in the model reaction is obtained with PEG as solvent in the presence of 5 mg (1.4 mmol % Pd) of catalyst and Na_2CO_3 as base at 100 °C. These were selected as optimized reaction conditions. It can be seen that when the model reaction is carried out at room temperature in PEG no product is obtained. When the reaction is conducted at 80 or 50 °C, a lower yield of the biphenyl product is obtained compared with reaction at 100 °C. The effects of solvent on product yields were also investigated (Table 4, entries 11–14). As can be seen, using other solvents such as EtOH, H_2O, dimethylsulfoxide (DMSO), dioxane and dimethylformamide (DMF) does not improve the yield of product or reaction time.

With these optimized conditions in hand, the scope of the substrate was explored with various aryl halides having different substituents (5). Various aryl halides were tested containing either electron-donating or electron-withdrawing groups such as Me, OMe, NO_2, CF_3, etc. As evident from Table 5, all the examined aryl halides couple with phenylboronic acid affording the corresponding products with good to excellent yields. Additionally, aryl chlorides were chosen as challenging substrates (Table 5, entries 11 and 12). However, the catalytic efficiency of Fe_3O_4@SiO_2@L-arginine@Pd(0) towards aryl chlorides is not satisfactory, which might be ascribed to the strength of the C–Cl bond.

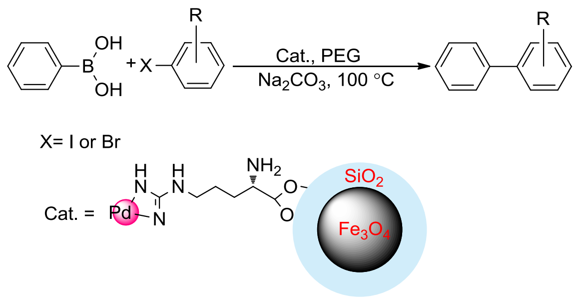


Scheme 4. General scheme for the Suzuki reaction catalysed by Fe_3O_4@SiO_2@L-arginine@Pd(0).

Table 4. Optimization of various parameters for synthesis of 4-nitrobiphenyl catalysed by Fe_3O_4@SiO_2@L-arginine@Pd(0)[a]

Entry	Solvent	Base	Temperature (°C)	Catalyst (g)	Time (min)	Yield (%)
1	PEG	Na_2CO_3	100	1	35	70
2	PEG	Na_2CO_3	100	3	35	75
3	PEG	Na_2CO_3	100	5	35	97
4	PEG	Na_2CO_3	100	0.00	35	No reaction
5	PEG	Na_2CO_3	Room temp.	5	35	No reaction
6	PEG	Na_2CO_3	80	5	35	80
7	PEG	Na_2CO_3	50	5	35	No reaction
8	PEG	Et_3N	100	5	35	Trace
9	PEG	KOH	100	5	35	No reaction
10	PEG	$NaHCO_3$	100	5	35	30
11	EtOH	Na_2CO_3	100	5	35	15
12	H_2O	Na_2CO_3	100	5	35	Trace
13	DMSO	Na_2CO_3	100	5	35	No reaction
14	DMF	Na_2CO_3	100	5	35	<5
15	Dioxane	Na_2CO_3	100	5	35	9

[a]Reaction conditions: aryl halide (1 mmol), $PhB(OH)_2$ (1 mmol), base (3 mmol).



Scheme 5. General scheme for the Suzuki reaction catalysed by Fe_3O_4@SiO_2@L-arginine@Pd(0).

To provide evidence about the heterogeneity of the catalytic reaction, we performed hot filtration for the synthesis of 4-methylbiphenyl with phenylboronic acid. In this experiment we obtain the product in half the time of the reaction, the yield being 60%. Then the reaction was repeated and in half time of the reaction, the catalyst was separated by applying an external magnet, and the filtrate was allowed to react further. We find that, after this hot filtration, no further reaction is observed. The yield of reaction in this stage is 65% that confirms the heterogeneity of the catalytic reaction.

As evident from the results, the procedure is uniformly effective for both electron-rich and electron-deficient aryl iodides and bromides and delivers products with good to excellent yields in short reaction time. In the final of our experimental work, the catalyst was subjected to successive reactions. As can be seen, this catalytic system can be recycled and reused up to five times without significant loss of activity (Fig. 6).

Table 5. Suzuki reaction of various aryl halides with phenylboronic acid catalysed by Fe_3O_4@SiO_2@L-arginine@Pd(0)^a

Entry	X	R	Time (min)	Yield (%)
1	Br	4-NO_2	35	97
2	I	H	15	91
3	I	4-OCH_3	55	90
4	I	4-CH_3	60	91
6	Br	4-NC	30	98
7	Br	H	30	92
8	Br	2-$COCH_3$	120	95
9	Br	3-CF_3	20	92
10	Br	4-OCH_3	45	90
11	Cl	4-CN	210	40
12	Cl	4-NO_2	40	10

^{a}Reaction conditions: aryl halide (1 mmol), phenylboronic acid (1 mmol), Na_2CO_3 (3 mmol), catalyst (5 mg, 1.4 mmol% Pd), PEG (1 mL).

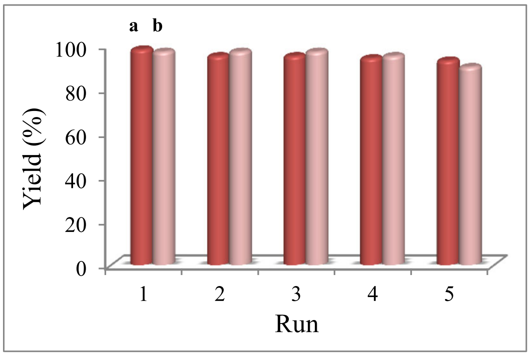


Figure 6. Recycling efficiency of Fe_3O_4@SiO_2@L-arginine@Pd(0) in the reaction of iodobenzene with $NaBPh_4$ (column a) and 1-bromo-4-nitrobenzene with phenylboronic acid (column b) at 100 °C.

Conclusions

In summary, Fe_3O_4@SiO_2@L-arginine@Pd(0) as a novel nanoparticle-supported and magnetically recoverable nanocatalyst has been fabricated, which is readily prepared from low-cost starting materials. The recyclable catalyst showed excellent activity for C–C bond formation and the whole process was carried out in a green medium. Operational simplicity, high yields of products, environmental friendliness, eco-friendliness, economic process and easy recovery of the catalyst using an external magnet are the key features of this methodology.

Acknowledgement

We gratefully acknowledge financial support of this work by Ilam University, Ilam, Iran.

References

[1] W. Zhang, X. Chen, T. Tang, E. Mijowska, *Nanoscale* **2014**, *6*, 12884.
[2] A. Baykal, E. Karaoglu, H. Sözeri, E. Uysal, M. S. Toprak, *J. Supercond. Nov. Magn.* **2013**, *6*, 165.
[3] M. Z. Kassaee, H. Masrouri, F. Movahedi, *Appl. Catal. A* **2011**, *395*, 28.
[4] T. Gelbrich, M. Feyen, A. M. Schmidt, *Macromolecules* **2006**, *39*, 3469.
[5] A. H. Lu, E. L. Salabas, F. Schuth, *Angew. Chem. Int. Ed.* **2007**, *46*, 1222.
[6] R. Mohammadi, M. Z. Kassaee, *J. Mol. Catal. A* **2013**, *380*, 152.
[7] D. H. Zhang, G. D. Li, J. X. Li, J. S. Chen, *Chem. Commun.* **2008**, 3414.
[8] F. Dehghani, A. R. Sardarian, M. Esmaeilpour, *J. Organometal. Chem.* **2013**, *743*, 87.
[9] M. Nasr-Esfahani, S. J. Hoseini, M. Montazerozohori, R. Mehrabi, H. Nasrabadi, *J. Organometal. Chem.* **2014**, *382*, 99.
[10] Y. Kong, R. Tan, L. Zhao, C. Li, D. Yin, *Green Chem.* **2013**, *15*, 2422.
[11] V. Polshettiwar, R. Luque, A. Fihri, H. Zhu, M. Bouhrara, J. M. Basset, *Chem. Rev.* **2011**, *111*, 3036.
[12] R. A. Reziq, H. Alper, D. Wang, M. L. Post, *J. Am. Chem. Soc.* **2006**, *128*, 5279.
[13] M. R. Didgikar, D. Roy, S. P. Gupte, S. S. Joshi, R. V. Chaudhari, *Ind. Eng. Chem. Res.* **2010**, *49*, 1027.
[14] M. Kim, J. C. Park, A. Kim, K. H. Park, H. Song, *Langmuir* **2012**, *28*, 6441.
[15] J. Sun, Y. Fu, G. Heb, X. Sun, X. Wang, *Appl. Catal. B* **2015**, *165*, 661.
[16] R. Gümüşada, N. Özdemir, M. E. Günay, M. Dinçer, M. S. Soylu, B. Çetinkaya, *Appl. Organometal. Chem.* **2014**, *28*, 324.
[17] S. Das, S. Bhunia, T. Maity, S. Koner, *J. Mol. Catal. A* **2014**, *394*, 188.
[18] X. Li, J. Zhang, X. Zhao, Y. Zhao, F. Li, T. Li, B. D. Wang, *Nanoscale* **2014**, *6*, 6473.
[19] A. Rostami, Y. Navasi, D. Moradi, A. Ghorbani-Choghamarani, *Catal. Commun.* **2014**, *43*, 16.
[20] A. Ghorbani-Choghamarani, G. Azadi, *RSC Adv.* **2015**, *59*, 9752.
[21] A. Ghorbani-Choghamarani, F. Nikpour, F. Ghorbani, F. Havasi, *RSC Adv.* **2015**, *5*, 33212.
[22] A. Ghorbani-Choghamarani, B. Ghasemi, Z. Safari, G. Azadi, *Catal. Commun.* **2015**, *60*, 70.
[23] M. Beygzadeh, A. Alizadeh, M. M. Khodaei, D. Kordestani, *Catal. Commun.* **2013**, *32*, 86.
[24] L. Zhang, R. He, H. C. Gu, *Appl. Surf. Sci.* **2006**, *253*, 2611.
[25] J. Safari, Z. Zarnegar, *J. Mol. Catal. A* **2013**, *379*, 269.
[26] http://www.chemspider.com.
[27] M. Samarasimhars, G. Prabhu, T. M. Vishwanatha, V. V. Sureshbabu, *Synthesis* **2013**, *45*, 1201.
[28] D. Zim, A. S. Gruber, G. Ebeling, J. Dupont, A. L. Monteiro, *Org. Lett.* **2000**, *18*, 2881.
[29] S. J. Hoseini, V. Heidari, H. Nasrabadi, *J. Mol. Catal. A* **2015**, *396*, 90.
[30] http://www.sigmaaldrich.com.

Supporting information

Additional supporting information may be found in the online version of this article at the publisher's web-site.