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PII: S0040-4020(17)30540-9
DOI: 10.1016/j.tet.2017.05.054
Reference: TET 28720

To appear in: *Tetrahedron*

Received Date: 8 October 2016
Revised Date: 11 May 2017
Accepted Date: 12 May 2017

Please cite this article as: Khazaei A, Khazaei M, Nasrollahzadeh M, Nano-Fe_3O_4@SiO_2 supported Pd(0) as a magnetically recoverable nanocatalyst for Suzuki coupling reaction in the presence of waste eggshell as low-cost natural base, *Tetrahedron* (2017), doi: 10.1016/j.tet.2017.05.054.

Graphical Abstract

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Nano-Fe_3O_4@SiO_2 supported Pd(0) as a magnetically recoverable nanocatalyst for Suzuki cross-coupling reaction in the presence of waste eggshell as low-cost natural base

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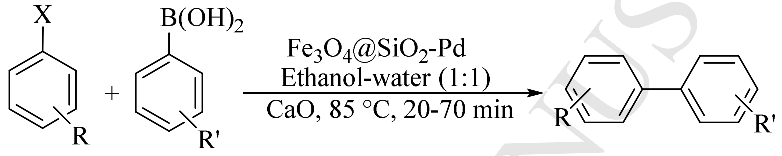
Ardeshir Khazaei*, Marzieh Khazaei and Mahmoud Nasrollahzadeh



X = Br & I.
R = H, 1-Naphthyl, 4-CH_3, 4-OCH_3, 4-CN, 2-CH_3-4-NO_2, 4-NO_2
R' = H, 4-C_2H_5

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Nano-Fe_3O_4@SiO_2 supported Pd(0) as a magnetically recoverable nanocatalyst for Suzuki coupling reaction in the presence of waste eggshell as low-cost natural base

Ardeshir Khazaei[*,a], Marzieh Khazaei[a] and Mahmoud Nasrollahzadeh[b,c]

[a]*Faculty of Chemistry, Bu-Ali Sina University, Hamedan 6517838683, Iran*

[b]*Department of Chemistry, Faculty of Science, University of Qom, Qom 3716146611, Iran*

[c]*Center of Environmental Researches, University of Qom, Qom, Iran*

Abstract—In this study, a simple and efficient protocol was used for the synthesis of the nano-Fe_3O_4@SiO_2 supported Pd(0) (Fe_3O_4@SiO_2-Pd). SiO_2 nanoparticles were prepared by the simple method from rice husk biomass as the source of biosilica. The Fe_3O_4@SiO_2-Pd was characterized by a series of techniques such as SEM, EDS, XRD, TEM, ICP-AES, FT-IR and VSM. The Fe_3O_4@SiO_2-Pd was used as a magnetically recoverable nanocatalyst for Suzuki coupling reaction in the presence of waste eggshell as low-cost solid base. The present method has significant advantages, such as use of natural and waste materials, use of an inexpensive catalyst, simple experimental procedure and low catalyst loading. In addition, the magnetically recoverable nanocatalyst can easily be recovered from the reaction system by using an external magnet and reused several times with insignificant loss of catalytic activity.

1. Introduction

Palladium-catalyzed Suzuki coupling reaction of aryl halides with arylboronic acids is one of the most valuable synthetic methods for preparation of symmetric and nonsymmetric biaryls,[1] which has been extensively used in the synthesis of pharmaceuticals,[2] ligands,[3] polymers,[4] and advanced materials.[5] Many of the palladium catalysts have been used as homogeneous catalysts for Suzuki coupling reaction.[6] Beside the advantages of homogeneous catalytic systems, they could not be used for the large-scale applications in liquid phase reactions. It causes greater difficulties such as purification of the final product, recycling of the catalyst and deactivation by aggregation into palladium particles. Activity and recovery in catalysis science are two important parameters. Hence, homogenous catalysts are not acceptable from a “green chemist's” point of view.[7] Some heterogeneous palladium catalysts show lower reactivity than homogeneous ones because of leaching of palladium from the supports[8] but can be recycled and recovered. Thus, there is a need to design of new heterogeneous catalysts that can retain the activities and selectivities of homogeneous catalysts. Nano science enables us to scale down the size of particles and make nanoparticles with unique properties.[9] Many types of nanoparticles have been synthesized for use as catalysts in reactions.[10] The synthesis of magnetic nanoparticles that show high activity in addition to being easily recovered, separated, and reused in reactions are the ideal catalyst from a “green chemist's” point of view.[11] Especially Fe_3O_4 nanoparticles have attracted many attentions because of their unique properties.[12]

In this study, in order to develop the use of an environmentally friendly catalyst, we decided to introduce Rice-husk as a suitable and naturally support for stabilization of palladium magnetic nano-particles

Rice-husk is considered as an agriculture waste material.[13] It has become a source for preparation of elementary silicon[14] and a number of silicon compounds,[15] especially silica[16], silicon carbide[17] and silicon nitride.[17b] So we used Rice-husk as a source of silica (Scheme 1). SiO_2 nanoparticles were prepared and used for synthesis of nano-Fe_3O_4@SiO_2-Pd (Scheme 2). Eggshell, a plentiful natural food source, is consumed worldwide because it contain essential amino acids and minerals. Most of the eggshell waste is commonly disposed without any pretreatment. Eggshell is totally biodegradable, recyclable and biocompatible.[18] Eggshells are included of a network of protein fibers, associated with crystals of calcium carbonate, calcium phosphate and magnesium carbonate and also organic substances and water. They are comprised of more than 90% $CaCO_3$.[19] In this study, CaO derived from eggshell was used as natural solid base for Suzuki

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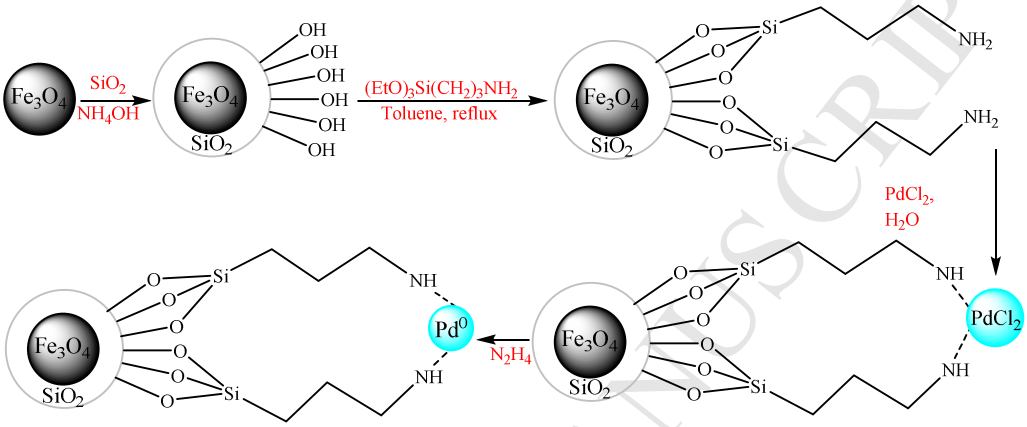
[*] Corresponding author. Tel.: +98 81 38257407; Fax: +98 81 38257407.

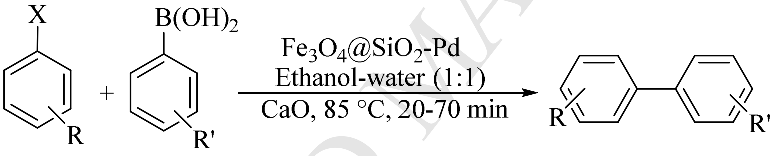
E-mail address: Khazaei_1326@yahoo.com (A. Khazaei).

coupling reaction in the presence of Rice-husk supported Fe_3O_4 stabilized palladium magnetic nanoparticles (Scheme 3).

Scheme 1. The synthesis of silica from Rice-husk as a naturally support for stabilization of palladium magnetic nanoparticles.



Scheme 2. The synthesis of palladium magnetic nanoparticles as a green catalyst for Suzuki coupling reactions.



X = Br & I.
R = H, 1-Naphthyl, 4-CH_3, 4-OCH_3, 4-CN, 2-CH_3-4-NO_2, 4-NO_2
R' = H, 4-C_2H_5

Scheme 3. The Suzuki cross-coupling reactions by $Fe_3O_4@SiO_2$-Pd.

2. Result and discussion

The catalyst was prepared using a simple and effective method and characterized by SEM, EDS, XRD, TEM, FT-IR and VSM.

Through this study we used the N_2H_4 as a reducing agent for the reduction of Pd(II) to Pd(0) and its application for the preparation of the $Fe_3O_4@SiO_2$-Pd. Figure 1 shows the UV-vis analysis of Pd(II) and Pd(0). After the addition of N_2H_4, the yellow color of the Pd^{II} solution immediately changed into dark brown which indicated that Pd(II) was converted to Pd(0).

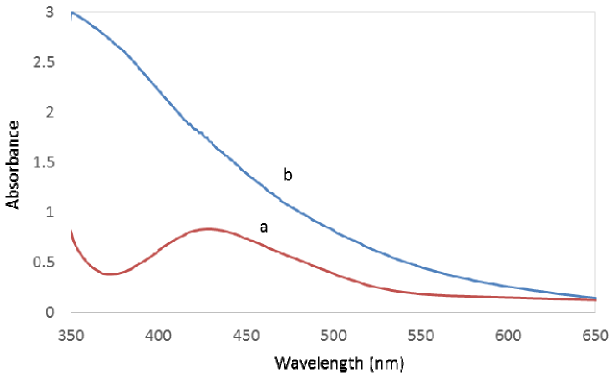


Figure 1. The UV-vis analysis of Pd(II) (a) and Pd(0) (b).

The XRD pattern of the CaO, SiO_2, Fe_3O_4, $Fe_3O_4@SiO_2$ and $Fe_3O_4@SiO_2$-Pd are given in Figure 2. The powder diffraction pattern of the $Fe_3O_4@SiO_2$-Pd is analyzed. No characteristic peak for Pd NPs was observed in the pattern of the $Fe_3O_4@SiO_2$-Pd, indicating that the amount of Pd is too low or the Pd NPs were highly dispersed on the $Fe_3O_4@SiO_2$ support.

FT-IR spectra of the CaO, SiO_2, Fe_3O_4, Fe_3O_4@SiO_2, Fe_3O_4@SiO_2@NH_2 and Fe_3O_4@SiO_2-Pd are given in Figure 3. The FT-IR analysis of the Fe_3O_4@SiO_2, Fe_3O_4@SiO_2@NH_2 and Fe_3O_4@SiO_2-Pd confirm that there was no change in functional groups after the immobilization of Pd NPs on the Fe_3O_4@SiO_2 surface.

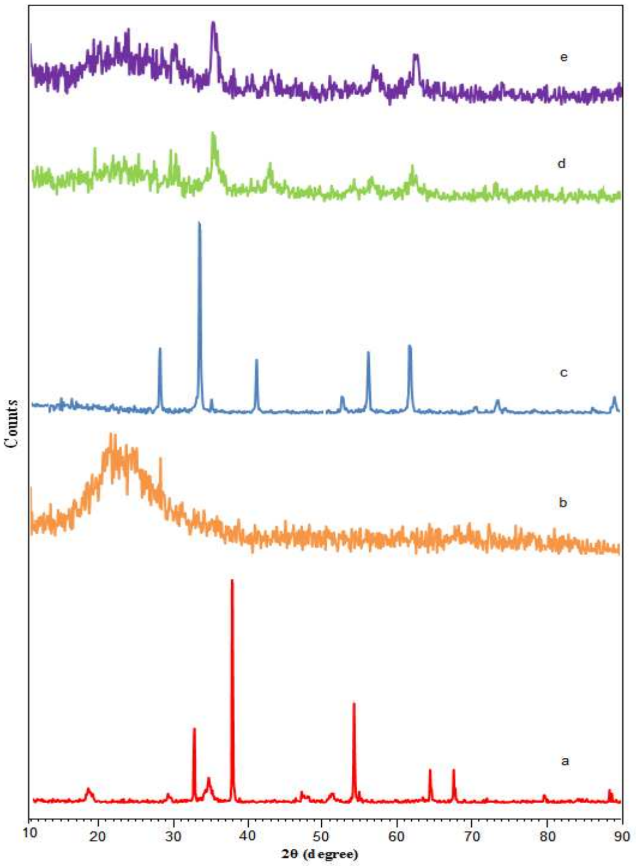


Figure 2. XRD patterns of the CaO (a), SiO_2 (b), Fe_3O_4 (c), Fe_3O_4@SiO_2 (d) and Fe_3O_4@SiO_2-Pd (e).

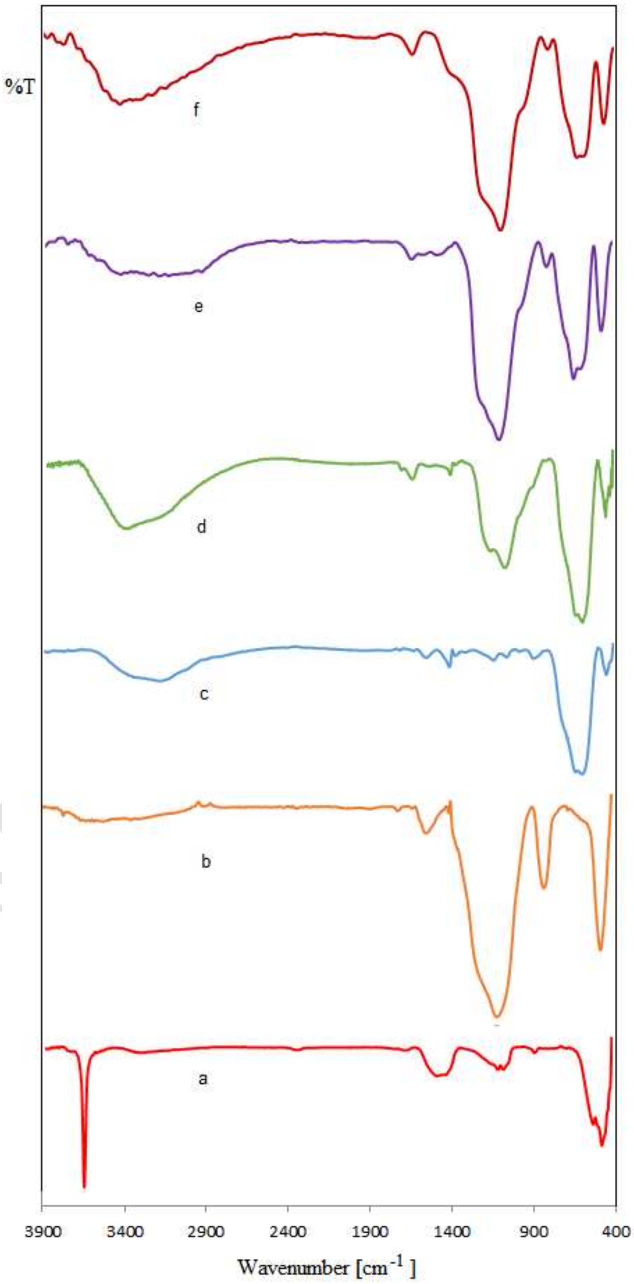


Figure 3. FT-IR spectra of the CaO (a), SiO_2 (b), Fe_3O_4 (c), Fe_3O_4@SiO_2 (d), Fe_3O_4@SiO_2@NH_2 (e) and Fe_3O_4@SiO_2-Pd (f).

The morphology of the CaO, Fe_3O_4, Fe_3O_4@SiO_2, Fe_3O_4@SiO_2@NH_2 and Fe_3O_4@SiO_2-Pd are characterized by SEM (Figure 4 and 5). For additional study on determinations of particle size of nanocatalyst, we used SEM analysis. The shapes and dimensions of the particles can be seen in Figure 4 and 5. The particles were found to be in spherical shape. The particles size in Fe_3O_4@SiO_2-Pd is estimated to be 31-73 nm.

The elemental composition of the CaO and Fe_3O_4@SiO_2-Pd was also analyzed by Energy Dispersive X-ray Spectroscopy (EDS) spectrum (Figure 6). It further confirmed the presence of Fe, C, Si and O elements in the Fe_3O_4@SiO_2-Pd.

The magnetic properties of the Fe_3O_4 and Fe_3O_4@SiO_2-Pd have been investigated by VSM system at room temperature, with the field sweeping from -10000 to +10000 Oe (Figure 7). Fe_3O_4 nanoparticles, shown super paramagnetic properties with saturation magnetization about 60 emug^{-1} and Fe_3O_4@SiO_2-Pd were 37 emug^{-1}. Compared with the Fe_3O_4 nanoparticles, the saturation magnetization of the magnetic nanoparticles catalyst clearly decreased because the diamagnetic contribution of the thick organic matter resulted in a low mass fraction of the Fe_3O_4 nanoparticles substance. Even with this reduction in the saturation magnetization, the solid could still be capably separated from solution with a permanent magnet.

According to the Transmission Electron Microscopy (TEM) images (Figure 8), the Pd NPs are well dispersed through the catalyst surface with an average diameter of 10-30 nm.

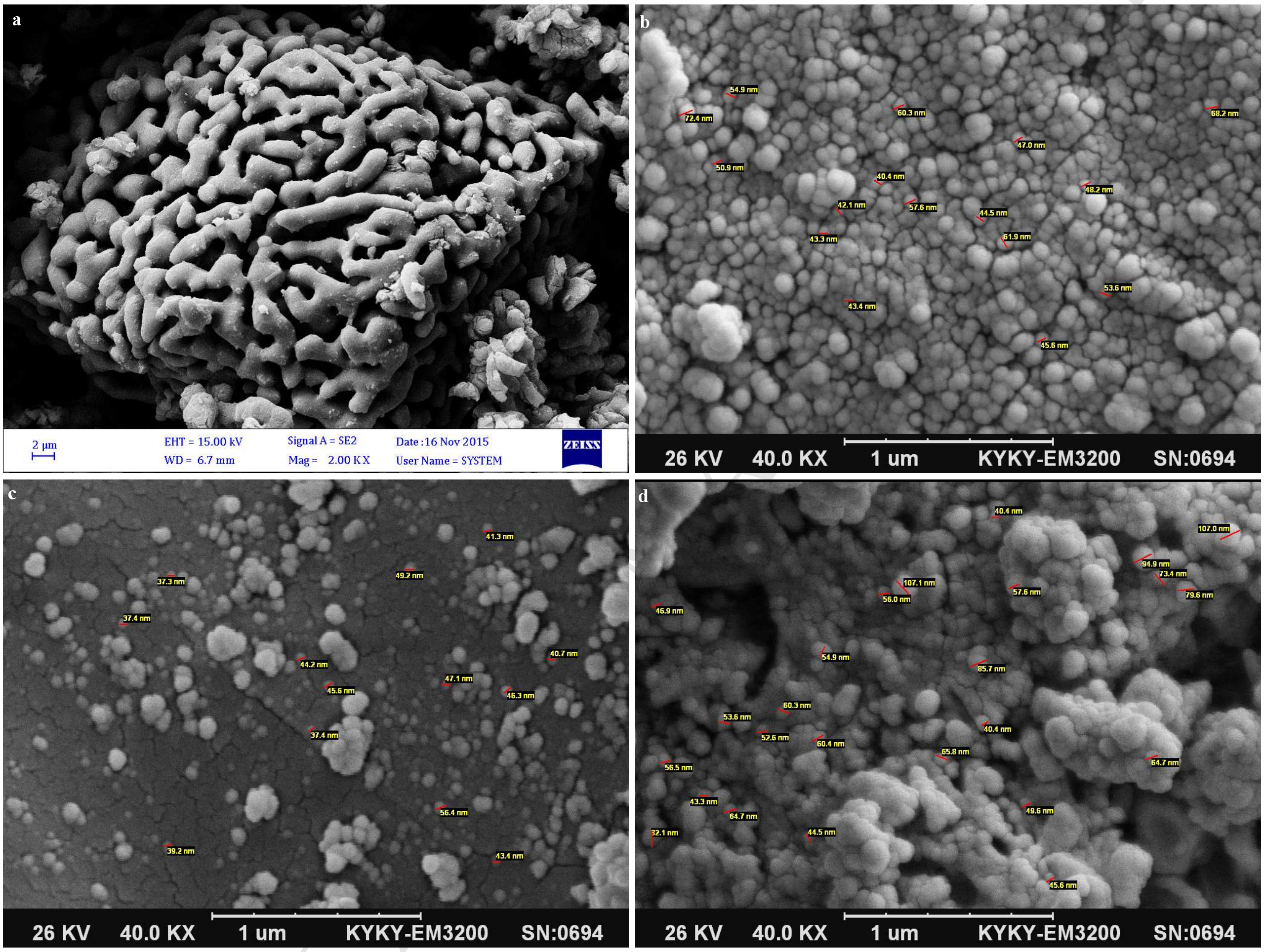


Figure 4. SEM images of the CaO (a), Fe_3O_4 (b), Fe_3O_4@SiO_2 (c) and Fe_3O_4@SiO_2@NH_2 (d).

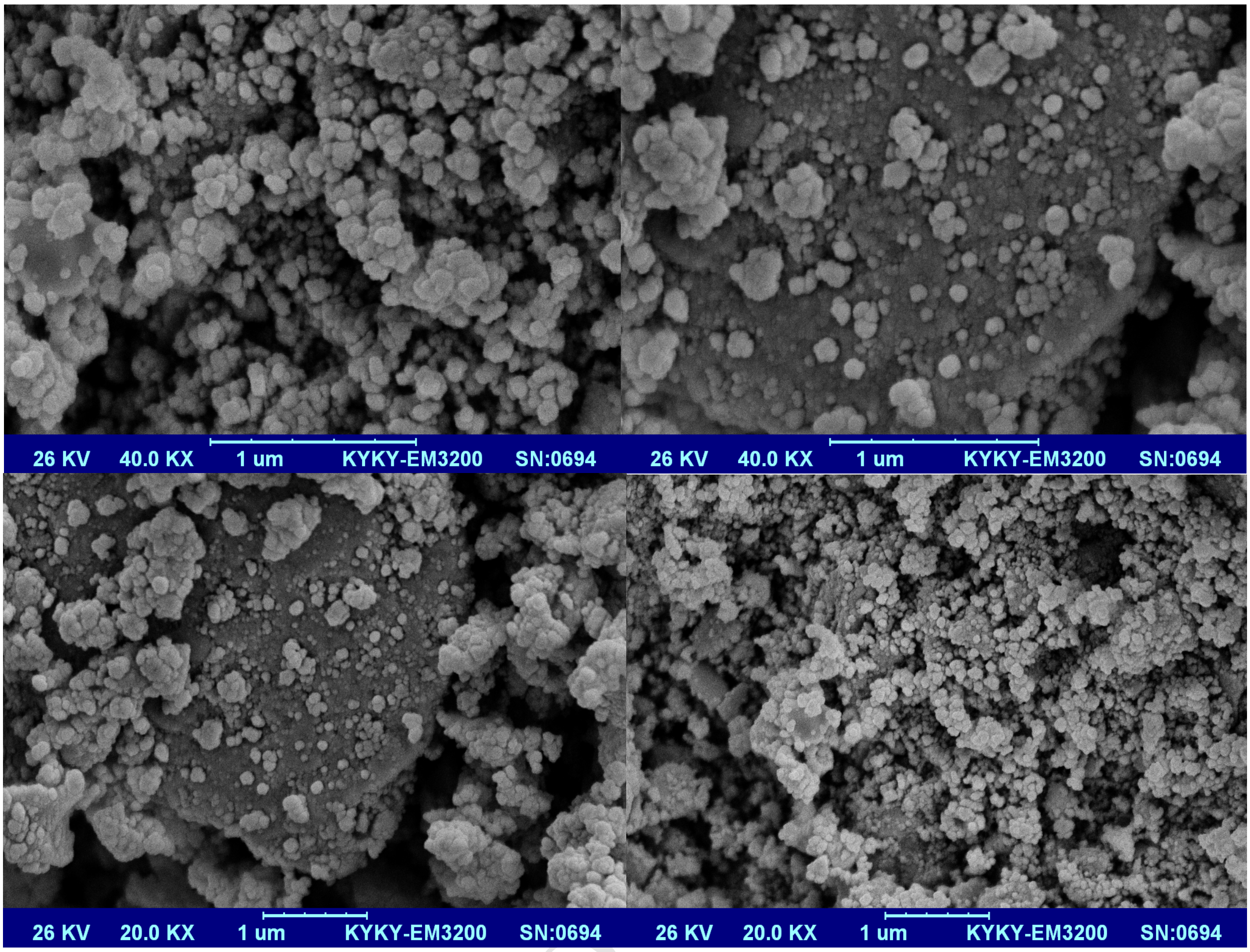


Figure 5. SEM images of the Fe_3O_4@SiO_2-Pd.

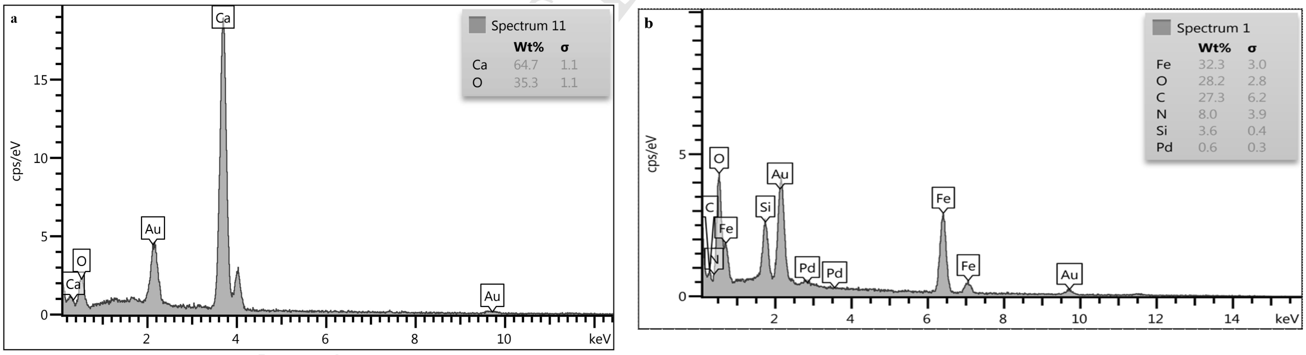


Figure 6. The EDX of the CaO (a) and Fe_3O_4@SiO_2-Pd (b).

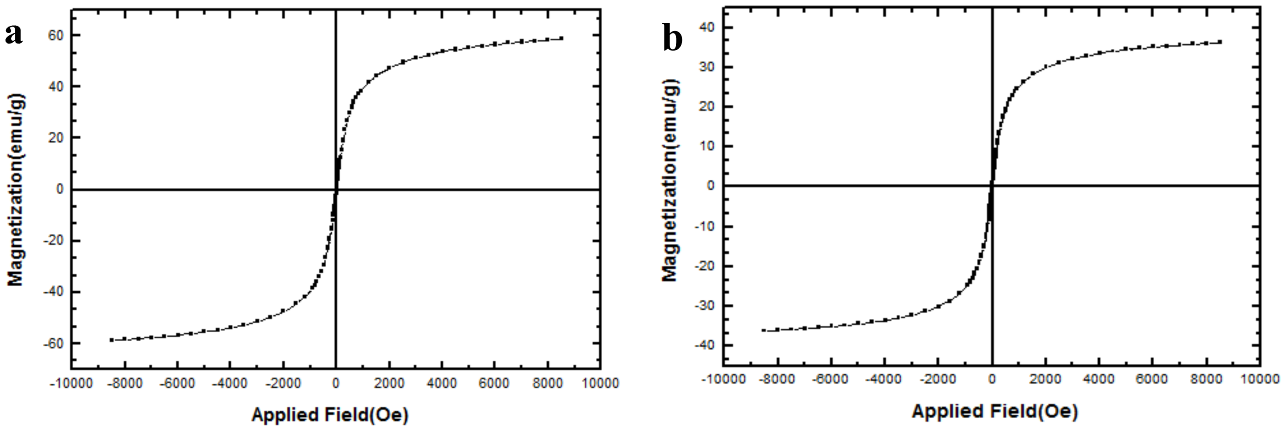


Figure 7. The vibrating sample magnetometer (VSM) analysis of the Fe_3O_4 (a) and $Fe_3O_4@SiO_2$-Pd (b).

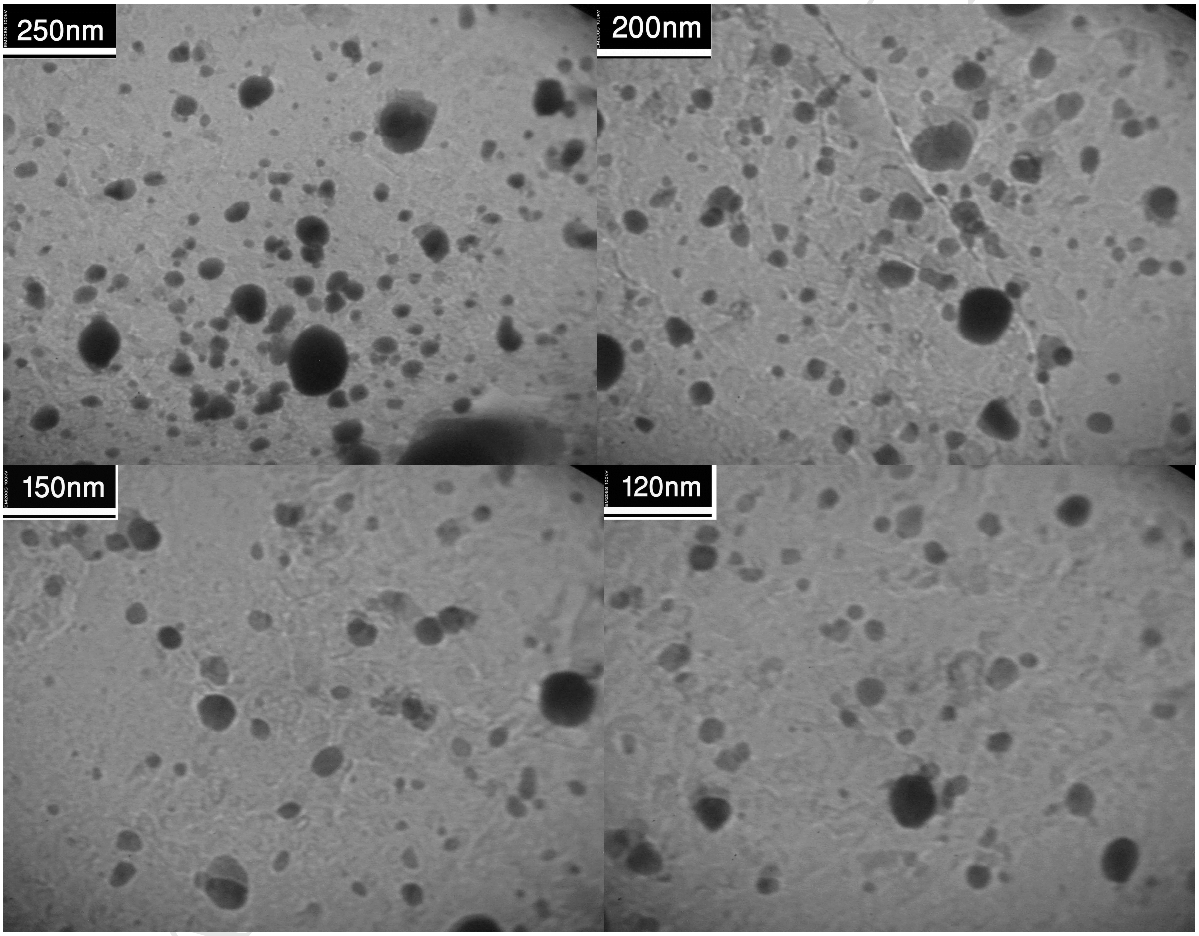
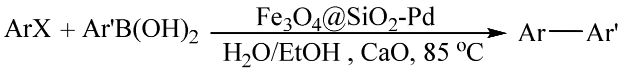


Figure 8. TEM images of the $Fe_3O_4@SiO_2$-Pd.

The palladium content in the $Fe_3O_4@SiO_2$-Pd determined by ICP-AES was 0.17 mmol g^{-1}.

The catalytic activity of the $Fe_3O_4@SiO_2$-Pd in the Suzuki coupling reaction of different aryl boronic acids with aryl halides was investigated (Scheme 4).

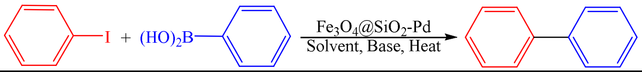


Scheme 4.

The coupling reaction of iodobenzene with phenyl boronic acid was carried out using $Fe_3O_4@SiO_2$-Pd under different conditions as a model reaction (Table 1). A preliminary survey of reaction conditions was conducted including the effects of the different solvents, temperatures, bases, and amount of catalyst. As shown in Table 1, no target product could be detected in the absence of $Fe_3O_4@SiO_2$-Pd even after 120 min (Entry 10). The best results were achieved with CaO as base in the presence of 0.03 mol% $Fe_3O_4@SiO_2$-Pd in H_2O/EtOH (1:1) at 85 °C (Table 1, entry 4). As the catalyst loading decreased from 0.03 to

0.01 mol%, yield was found to be decrease from 96% to 84%, respectively.

Table 1. Optimization of the Suzuki coupling reaction.



Entry	Solvent	Base	Catalyst (mol%)	Temp. (^oC)	Time (min)	Yield (%)
1	H_2O	CaO	0.03	90	25	92
2	EtOH	CaO	0.03	80	30	90
3	DMF	CaO	0.03	130	45	86
4	**H_2O/EtOH (1:1)**	**CaO**	**0.03**	**85**	**20**	**96**
5	H_2O/EtOH (1:1)	K_2CO_3	0.03	85	30	92
6	H_2O/EtOH (1:1)	Na_2CO_3	0.03	85	40	86
7	H_2O/EtOH (1:1)	NEt_3	0.03	85	85	65
8	H_2O/EtOH (1:1)	CaO	0.01	85	40	84
9	H_2O/EtOH (1:1)	CaO	0.02	85	30	92
10	H_2O/EtOH (1:1)	CaO	0.00	85	120	0

After the optimization study, the effect of electron withdrawing and electron donating functional groups in aryl iodides and bromides on the catalytic activity was examined in the Suzuki coupling reaction in the presence of $Fe_3O_4@SiO_2$-Pd as catalyst and CaO as base in H_2O/EtOH mixture. Various aryl halides were reacted with aryl boronic acids and converted into the corresponding coupling products. As shown in Table 2, the reaction of aryl halides bearing electron-withdrawing groups went to completion in longer reaction times than those with electron donating groups. In all the cases, aryl halides afforded excellent yields of the products. However, this method was not applicable for aryl chlorides (Table 2, entry 14).

In another study, recyclability and reusability of the catalyst was confirmed on the reaction of between iodobenzene with phenyl boronic acid. At the end of the reaction, catalyst was separated by an external magnetic field, washed with water and then and then reused. The catalyst was used without further cleansing after isolation. Afterwards the recycled catalyst was applied for alternative reaction. The catalyst was used over 5 runs without significant loss of activity (Table 3). To check the heterogeneity of catalyst, which is an important factor, the phenomenon of leaching was studied by Inductively Coupled Plasma Atomic Emission Spectroscopy (ICP-AES) analysis of the resulting reaction solution mixture. It was shown that palladium content of the used $Fe_3O_4@SiO_2$-Pd was the same as that of the fresh one (0.17 mmol g^{-1}). As shown in TEM images of the recycled catalyst after 5th recycle (Figure 9), no obvious change in morphology and size of Pd NPs were observed.

Table 2. Suzuki coupling of different aryl halides with aryl boronic acids in H_2O/EtOH in the presence of the Fe_3O_4@SiO_2-Pd using CaO as a base.

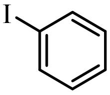
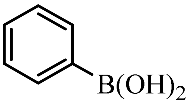
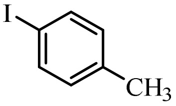
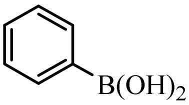
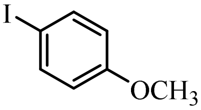
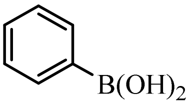
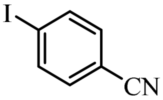
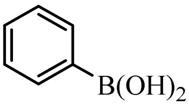
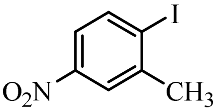
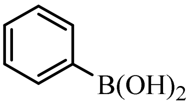
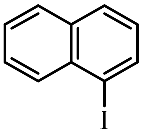
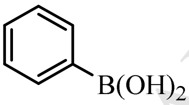
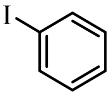
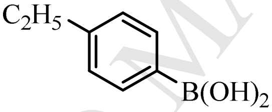
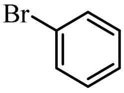
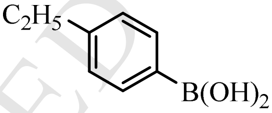
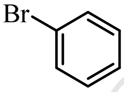
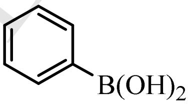
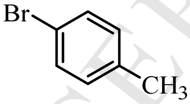
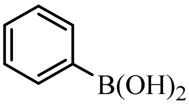
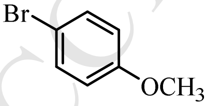
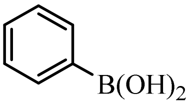
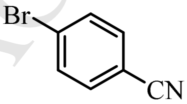
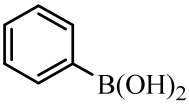
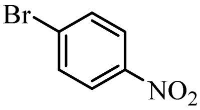
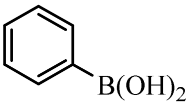
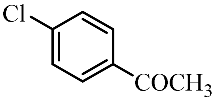
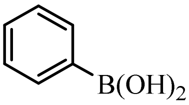
Entry	Aryl halide	ArB(OH)₂	Reaction time (min)	Yield (%)
1			20	96
2			30	92
3			26	93
4			50	89
5			25	91
6			35	90
7			24	93
8			38	90
9			30	90
10			45	88
11			40	90
12			65	85
13			70	87
14			100	No reaction

Table 3. Reusability of the $Fe_3O_4@SiO_2$-Pd in the Suzuki coupling of iodobenzene with phenyl boronic acid.[a]

Run	Yield (%)	Recovery of catalyst (%)
1	96	99
2	96	99
3	96	99
4	95	98
5	94	98

[a] Reaction conditions: Iodobenzene = 1.0 mmol, phenyl boronic acid = 1.1 mmol, catalyst = 0.03 mol%, CaO (2.0 mmol), H_2O/EtOH (1:1) 85 °C.

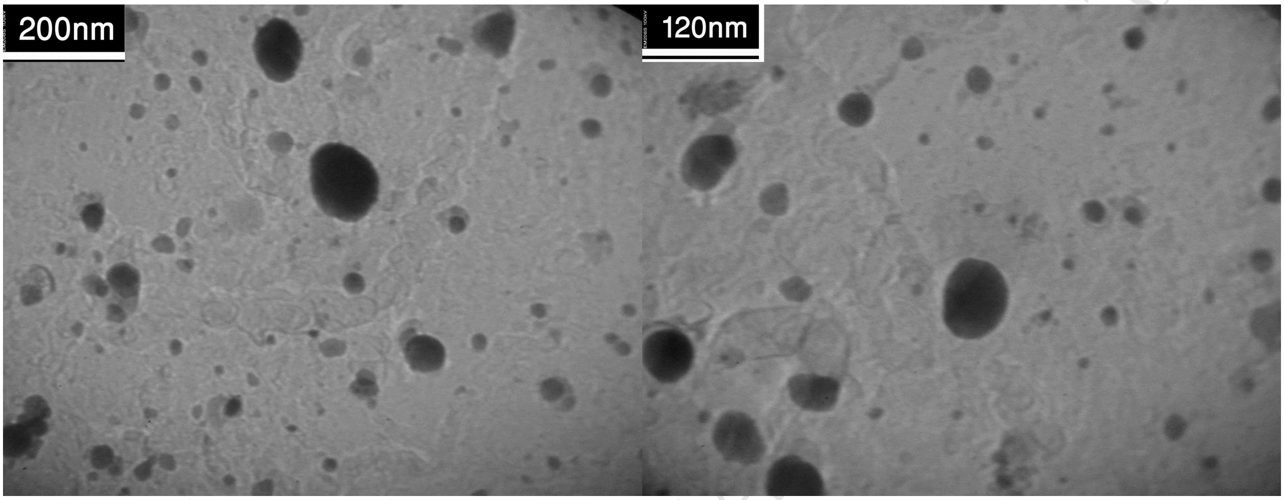


Figure 9. TEM images of the recycled catalyst after 5th recycle.

3. Conclusions

Here we demonstrated the feasibility to generate $Fe_3O_4@SiO_2$-Pd using a simple and efficient protocol. SEM, EDS, XRD, TEM, FT-IR and VSM techniques confirmed the formation of the $Fe_3O_4@SiO_2$-Pd. The Pd NPs were characterized via UV-vis spectroscopy. It was demonstrated that the prepared nanocatalyst was found very effective catalyst for Suzuki coupling reaction in the presence of waste eggshell as low-cost solid base. The nanocatalyst was readily recovered by using an external magnet and reused several times without significant loss of activity.

4. Experimental

4.1. Instruments and reagents

High-purity chemical reagents were purchased from the Merck and Aldrich chemical companies. All materials were of commercial reagent grade. ^{1}H NMR spectra were recorded on a Bruker Avance DRX-400 spectrometer at 400. FT-IR spectra were recorded on a Nicolet 370 FT/IR spectrometer (Thermo Nicolet, USA) using pressed KBr pellets. UV-visible spectral analysis was recorded on a double-beam spectrophotometer (Hitachi, U-2900) to ensure the formation of nanoparticles. X-ray diffraction (XRD) measurements were carried out using a Philips powder diffractometer type PW 1373 goniometer (Cu Kα = 1.5406 A°). The scanning rate was 2°/min in the 2θ range from 10 to 80°. Scanning electron microscopy (SEM) was performed on a Cam scan MV2300. The shape and size of the catalyst was identified by transmission electron microscope (TEM) using a Philips EM208 microscope operating at an accelerating voltage of 90 kV. EDS (S3700N) was utilized for chemical analysis of prepared nanostructures. Vibrating sample magnetometer (VSM) measurements were performed by using a SQUID magnetometer at 298 K (Quantum Design MPMS XL). The content of Pd in the catalyst was determined by ICP-AES (PROFILE SPEC, Leeman).

4.2. Preparation of CaO from eggshell waste

CaO as natural solid base was prepared by calcination method. Eggshells were collected, washed and dried. The dried eggshell was calcined at 700-900 ºC in air atmosphere for 4h. CaO was obtained as white powder. All calcined samples were kept in the close vessel to avoid the reaction with carbon dioxide and humidity in air before using.

4.3. Preparation of the magnetic Fe_3O_4 nanoparticles

Magnetic Fe_3O_4 nanoparticles were prepared using simple chemical coprecipitation described in the literature.[20] Typically, 11.3 g of $FeCl_3.6H_2O$ and 4.6 g of $FeCl_2.4H_2O$ were dissolved in 250 mL of deionized water in a round-bottom flask (500 mL) which was heated to 80 ºC until the solution was clear. Thereafter, under rapid mechanical stirring, 30 mL ammonia 25% in the mixture was stirred until a black homogeneous phase was formed, after being rapidly stirred for 2 h. The black precipitate form was isolated by magnetic decantation, and carefully washed with deionized water and then washed twice with acetone and dried at 60 ºC in vacuum.

4.4. Preparation of SiO_2 from Rice-husk

Rice-husk obtained from a local Industry in the north of Iran and washed several times with distilled water to remove any sticking materials and dried at 100 °C for 24 h. The Rice-husk (5.0 g) was acid-leached with 10% HCl and afterwards 30 wt.% sulfuric acid solution at 100°C for 3 h in a pyrex round-bottom flask equipped with a reflux condenser. Then, the resulting brown powder was filtered and washed repeatedly three times using deionized water to make it acid free and dried at 80 °C for 5 h. The resulted powder was calcinated at 650 °C for 3 h to obtain SiO_2.

4.5. Preparation of nanostructured silica-coated magnetic

Fe_3O_4 (1.0 g) was dispersed for 30 min in a premix of deionized water (40 mL), ethanol (80 mL) and ammonia 25% (4.0 mL) by ultrasonic treatment, then SiO_2 (1.0 g) was added and the mixture was under reflux for 12 h. The resulting product was separated from the reaction mixture with an external magnet, washed with deionized water and then washed three times with ethanol and dried at 65 ºC in vacuum.

4.6. Preparation of functionalized SiO_2 magnetic nanoparticles with 3-(triethoxysilyl)propylamine

SiO_2 magnetic nanoparticles (1.0 g) were added to the solution of 3-(triethoxysilyl)propylamine (0.44 g) in ethanol (5.0 mL), and then the resulting mixture was stirred under reflux conditions for 12 h. After the mixture was cooled to room temperature and the product was separated with an external magnet, washed with ethanol and deionized water and dried at 70 °C for 5 h.

4.7. Preparation of palladium magnetic nanoparticles

$PdCl_2$ (0.018 g in 100 mL) and previous step product (1.0 g) was mixed in 10 mL of deionized water and stirred under reflux conditions for 3 h. Then the product was separated with an external magnet and washed with deionized water three times. Then, the resulting product was dispersed in deionized water, and 0.4 mL of freshly prepared N_2H_4 (0.8 g in 100 mL) aqueous solution was added and stirred for 2 h. The reaction color changed to black, due to conversion of Pd(II) into Pd(0). The black nanoparticles were separated with an external magnet, washed with distilled water several times and then dried at 65 ºC for 6 h.

4.8. General procedure for the Suzuki coupling reaction

To a flask, a mixture of aryl halide (1.0 mmol [molar mass $\times 10^{-3}$ g]), aryl boronic acids (1.1×10^{-3} × molar mass g), CaO (0.112 g), H_2O (1.0 mL), ethanol (1.0 mL) and catalyst (0.117 g) were added. The reaction mixture was stirred for the required period of time at 85 °C until completion of the reaction, as monitored by TLC. After completion of the reaction, the mixture was cooled to room temperature and the catalyst separated from the reaction mixture with an external magnet. The resultant solution was extracted with n-hexane. The combined organic phase was dried with $CaCl_2$, solvent was removed, and the product was recrystallized with ethanol.

Acknowledgements

We gratefully acknowledge the Iranian Nano Council and Bu-Ali Sina University for the support of this work.

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