

Pd Nanoparticles Immobilized on Supported Magnetic GO@ PAMPS as an Auspicious Catalyst for Suzuki–Miyaura Coupling Reaction

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Abstract A novel catalytic system based on palladium nanoparticles (Pd-NPs) immobilized onto the surface of graphene oxide (GO) modified by poly 2-acrylamido-2-methyl-1-propansulfonic acid decorated with magnetic Fe_3O_4 was designed, prepared and fully characterized. It was successfully examined as a highly efficient heterogeneous catalyst in the Suzuki-Miyaura cross coupling reaction. The results showed excellent catalytic activity for the cross coupling of aryl bromides, alkyl iodides as well as aryl chlorides as the challenging substrates. It was easily separated by an external magnet and reused without any pre-activation at least in seven consecutive runs without any loss in its catalytic activity as well as any detectable Pd leaching. This study demonstrates the great potential of polymericfunctionalized GO as a support owing to its high loading and suitable dispersing of Pd-NPs, for the development of metal-graphene nanocomposites in industrial scale.

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1 Introduction

Historically, from the date discovered, Pd-catalyzed C–C bond formation has always attracted much intention and stirred up the interest of synthetic organic chemists [1–9]. In addition, it has a significant impact on the academia as well as chemical industries, especially those working on the total synthesis of natural products or producing intermediates for the currently prescribed drugs, respectively [10, 11]. Transition metal-catalyzed cross-coupling reactions undoubtedly, are the most important processes for constructing carbon–carbon bonds [12]. Among them, the Pd-catalyzed cross-coupling reactions, and in particular

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"Suzuki–Miyaura reaction" [13–15] is the most admired and practically employed which led to awarding the 2010 Nobel Prize in Chemistry to Professor Akira Suzuki, shared with Richard Heck and Ei-ichi Negishi [16].

The increasing trend in Suzuki–Miyaura coupling is mostly due to the commercially or readily availability of the starting materials which are mostly non-toxic and easy to handle [17]. The biaryls as the products of Suzuki reaction are the involved as scaffold in various natural products. They are frequently used as suitable ligands and also are the key intermediates in the productions of different drugs, herbicides etc. [18–21].

The original Suzuki reaction is generally performed in the presence of relatively large amounts of palladium and copper in organic solvents which are cost-effective and environmentally inadmissible. However, this palladiumcatalyzed reaction has been extensively investigated during the years to improve the reaction conditions, thus a wide variety of modifications has been reported so far, including the utilization of Pd-nanoparticles (Pd-NPs) as the catalyst.

Catalysts based on Pd-NPs often suffer from two main drawbacks. The first one is extensive leaching of the active metal species during reactions which eventually leads the less catalytic activity. Secondly, aggregation of the MNPs which leads to increase the size of MNPs and their relative surface area becomes smaller, thus, their activities are reduced significantly. Therefore, choosing an appropriate support to obtain suitable sized Pd-NPs in order to avoid their leaching is still in much demand. Graphene has been proven as one of the best support for different metals because of its large specified surface area, excellent electrical conductivity and high chemical and thermal stability [22-24]. Many ongoing attempts are focused on deposition of various MNPs, metal oxides, polymers and chalcogenides on graphene oxide (GO) sheets due to its superior functionality [25–31].

The recovery of expensive Pd based catalysts by magnetic nanoparticles (Mag) without losing their catalytic activity is a prominent feature in the maintainable catalytic processes and green chemistry [32, 33].

In addition to the advantages of GO and Mag in catalytic systems, development of a suitable stabilizer for uniformly distribution of nanoparticles sizes as well as capping agent gives nanoparticles a high desirable stability. Consequently, to this purpose a variety of stabilizers were examined. In 2000, the first Pd(0) species immobilized onto a polymer was reported by El-Sayed et al. [34]. They prepared and applied PVP as catalysts in the coupling of aryl iodides with phenylboronic acid in aqueous media via Suzuki reaction. Furthermore, other polymeric stabilizers such as poly(amido-amine) dendrimers [34–38], polyvinylpyrrolidone [39], poly(amino acetanilide) composite [40], polypyrrole [41], poly(*p*-phenyleneethynylene) [42], porous ionic copolymer [43] and biopolymer complex [44, 45] were also used in the Suzuki–Miyaura reaction. Despite these noticeable achievements obtained in the field of polymeric stabilizers, the development of hydrophilic polymeric networks with functional groups such as –SO₃H, –COOH, –CONH₂, –OH, and –NH₂ for the protection of Pd-NPs has still remained a great challenge, especially in the case of Suzuki coupling reaction.

We are interested in Pd-catalyzed reactions [46–48]. We recently immobilized $PdCl_2$ on modified poly(styrene-comaleic anhydride) and used it as a highly active and recyclable catalyst for the Suzuki–Miyaura and Sonogashira reactions [49]. Very recently we disclosed the superiority of Pd(0) encapsulated nanocatalysts as an efficient catalytic systems for Pd-catalyzed organic transformations [50]. We also used the easily separable magnetic Fe₃O₄ as a component in our nano-catalytic systems [51–53].

Armed with these experiences, herein, we wish to reveal the design of a highly dispersed catalytic system in green environment which could be separated from the reaction mixture and recycled easily several times without appreciable loss of its catalytic activity.

In this line, we wish to introduce a novel catalytic system, denoted as $Pd/GO/Fe_3O_4/PAMPS$ including, Pd-NPs immobilized onto the surface of graphene oxide (GO) modified by poly 2-acrylamido-2-methyl-1-propansulfonic acid (PAMPS), decorated with magnetic Fe_3O_4 . This catalytic system was used successfully in Suzuki cross coupling reaction.

2 Experimental

2.1 Characterization

All chemicals were purchased from international commercial suppliers. The solvents were purified and dried using standard procedures. X-ray photoelectron analysis (XPS) was performed using a VG multilab 2000 spectrometer (ThermoVG scientific) in an ultrahigh vacuum. A Shimadzu model AA-680 atomic absorption spectrometer equipped with deuterium background correction was employed for the determination of amount of Pd. The elemental evaluation was performed using Energy-dispersive X-ray spectroscopy (EDX) (Philips XL-30). Transmission electron microscope (TEM) image of GO/Fe₃O₄/PAMPS/ Pd nanocomposite was taken using Philips CM-30 transmission electron microscope with an accelerating voltage of 150 kV. The crystalline phases of the nanoparticles were measured by X-ray powder diffraction (XRD) measurements (Siemens D5000 diffractometer). Fourier transform infrared (FT-IR) spectra were recorded using a BOMEM MB-series FT-IR spectrometer in the form of KBr pellets. Thermogravimetric analysis (TGA) was performed by a thermal analyzer instrument (TGA/DTA BAHR: STA 503) from 25 to 1000 °C at a heating rate of 10 °C/min under air. For investigation of the magnetic property, a vibrating sample magnetometer (VSM) from -10,000 to +10,000 Oe at room temperature was measured by Meghnatis Daghigh Kavir Company (MDK) Iran. ¹H-NMR spectra were recorded on a BRUKERDRX-300 AVANCE spectrometer. CDCl₃ and TMS were used as the solvent and internal standard, respectively. Melting points were measured on an Electrothermal 9100 apparatus and are uncorrected. Gas chromatography was performed on a Trace GC ultra from the Thermo Company equipped with FID detector and Rtx[®]-1 capillary column.

2.2 Preparation of the Catalyst System

2.2.1 Synthesis of GO

Graphene oxide was prepared via a modified Hummers' method from graphite powder, in accordance with previously reported method [54]. In brief, graphite powder (5 g) was suspended in deionized water (100 mL) and dispersed for 3 h using an ultrasonic bath. Then, KMnO₄ (1 g) was added to this suspension gradually under stirring for 15 min. This solution was stirred for 4 h then, diluted by addition of deionized water (250 mL) while the temperature kept below 50 °C. Then, H_2O_2 30% (10 mL) was added to this mixture till the color of the mixture changed into golden yellow. Finally, the obtained product was filtered and washed several times with HCl (0.1 M) for the removal metal ions, followed by addition of deionized water (250 mL) to decrease the acidity. The resulting GO solid was dried at 70 °C in a vacuum oven.

2.2.2 Synthesis of Magnetic GO

Magnetic GO was synthesized by dispersion of GO (1.5 g) and deionized water (150 mL) using an ultrasonic bath for 1 h. Then, the iron salt (1.2 g FeCl₃·6H₂O) was introduced to the mixture under vigorous stirring and purging of N₂ gas for 30 min. Following, FeCl₂·4H₂O (1.8 g) was added under N₂ atmosphere to the above mixture. Finally, to this mixture an ammonia solution (25%, 120 mL) was added, diluted by addition of 200 mL water and the suspension was refluxed for 2 h. The resultant GO/Fe₃O₄ as a black precipitate was separated by an external magnetic field and washed repeatedly with the water and ethanol, and then dried at 35 °C under vacuum overnight.

2.2.3 Synthesis of Magnetic GO Grafted by MAPTMS

In order to increase the stability and impeding the agglomeration of NPs, surface of GO/Fe₃O₄ sheets (1 g) was modified by 3-(trimethoxysilyl)propyl methacrylate (MAPTMS) (1.9 mL) as a silane coupling agent [55]. For this purpose, the above amounts of magnetic GO and MAPTMS was stirred in 20 mL toluene under a continuous flow of N₂ gas at ambient temperature for 24 h. Finally, the prepared surface modified GO sheets were collected by an external magnet and repeatedly washed with toluene for the total elimination of the extra MAPTMS and then dried overnight in an oven under vacuum at 35 °C for 24 h.

2.2.4 Polymerization and Synthesis of GO/Fe₃O₄/PAMPS Nanocomposite

For the polymerization of the desired monomers on the surface of modified GO, in a typical experiment, 2-acrylamido-2-methyl-1-propansulfonic acid (AMPS) (1.0 g) and methylenbisacrylamide (MBA) (0.147 g) were added to a flask containing 1 g GO suspended in 12 mL deionized water. Then, the mixture was purged under N₂ gas for 15 min to remove dissolved oxygen. Subsequently, 0.053 g azobisisobutyronitrile (AIBN) as an initiator was added to the reaction mixture, kept at 60 °C for 24 h to complete the polymerization. Finally, washing the synthesized polymer with ethanol and water (three times) and drying under a vacuum oven for 24 h at 50 °C afforded the GO/Fe₃O₄/PAMPS nanocomposite.

2.2.5 Synthesis of GO/Fe₃O₄/PAMPS/Pd Nanocomposite

For decoration of Pd-NPs, the mixture of GO/Fe₃O₄/ PAMPS (0.5 g) and PdCl₂ (0.1 g) was dispersed in H₂O (50 mL) using ultrasonic bath. After being sonicated about 30 min, the reaction left to stir for 12 h at room temperature. Then, excess amount of sodium borohydride (NaBH₄) solution as reducing agent was added dropwise to convert Pd(II) ions to Pd(0). Ultimately, GO/Fe₃O₄/PAMPS/Pd nanocomposite was obtained by an external magnet and washed several times with distilled water, ethanol and acetonitrile to remove unanchored Pd-NPs and finally dried in vacuum oven at 60 °C for 24 h. The content of Pd was estimated to be 1.1150 mmol/g based on atomic absorption spectroscopy (AAS).

2.3 Investigations on the Catalytic Activity

2.3.1 GO/Fe₃O₄/PAMPS/Pd Catalyzed Suzuki–Miyaura Reaction: General Procedure

To a 10 mL flask an appropriate aryl halide (1 mmol), suitable arylboronic acid (1.2 mmol), K_2CO_3 (3 mmol), the

above-mentioned catalyst (0.2–1 mol% Pd based on aryl halide) and 5 mL EtOH/water (1:1 V/V) were added. The mixture was stirred at reflux temperature (80 °C) for appropriate time. Upon completion of the reaction, the reaction mixture was cooled down to room temperature. Then, the solution was diluted with deionized water, and the catalyst was separated by using an external permanent magnet. The reaction solution was extracted with ethyl acetate and the organic phase was dried over MgSO₄, filtered and then the solvent was evaporated off under reduced pressure. The resulting residual was purified by column chromatography on silica gel (*n*-hexane/ethyl acetate) to give the corresponding pure products. All products were known and identified by FT-IR and ¹H NMR spectra with those of authentic samples which were found identical.

2.3.2 The Reusability Test

In order to investigate the reusability of desired nanocatalyst, the separated catalyst was washed with ethanol and water and reused in a model reaction involving 4-bromotoluene and phenyl boronic acid under already secured optimal optimized conditions.

3 Results and Discussion

Unsupported Pd-NPs have been extensively employed in various Pd catalyzed name reactions such as Suzuki [13], Heck [41], Sonogashira [56] and Negishi [57]. However, the utilization of supported Pd-NPs scarcely can be found in the chemical literature, although, the inherent tendency toward particle agglomeration makes the use of stabilizing agents or solid supports mandatory in most cases.

The purpose of this study is developing a new Pd-NPs immobilized onto a suitable support which is decorated with magnetic Fe_3O_4 for the ease of its separation by just an external magnet. In this line, we decided to design a novel magnetic Pd-NPs using GO and stabilizing it by the polymer.

Initially, water dispersed GO was performed from graphite, according to Hummer's method [54]. Then, magnetic GO was prepared by introducing iron salts as illustrated in Scheme 1. The surface of magnetic GO was modified using MAPTMS to provide the reactive C=C bonds. Subsequently, AMPS as monomer and MBA as cross–linker were polymerized onto the modified magnetic GO using AIBN as initiator for radical polymerization to produce the desired polymeric network. Finally, to this polymeric segment, Pd(II) salt was added with subsequent addition of NaBH₄ as reducing agent to obtain the expected GO/Fe₃O₄/ PAMPS/Pd catalyst. The characterization was started by measuring the Pd content of $GO/Fe_3O_4/PAMPS/Pd$ nanocomposite based on AAS analysis which found being 1.1150 mmol/g. The full characterization for proving the structure of the nano-size particles were achieved using FT-IR, XRD, XPS, TGA, TEM, VSM and EDX analysis.

For the better understanding how Pd-NPs immobilized on the surface of catalyst, another schematic was illustrated in Scheme 2. As one can see, modification the surface of GO with cross linked PAMPS carrying CONH₂ and SO₃H functional groups could immobilize Pd-NPs. PAMPS are believed to work as ligands, through nitrogen and oxygen atoms, thereby avoiding the need of additional ligand. In addition, hydrophilicity of this polymer was another important character for choosing PAMPS as polymeric segment.

Figure 1 shows the FT-IR spectra of the GO (a), GO/ Fe₃O₄ (b), GO/Fe₃O₄/MAPTMS (c), GO/Fe₃O₄/PAMPS (d) and $GO/Fe_3O_4/PAMPS/Pd$ (e) nanocomposite. The spectra of GO (Fig. 1a) demonstrates a broad band around 3400 cm⁻¹, which results from –OH groups of GO. Also, C-O stretching group of alkoxy and C=O stretching vibration of carbonyl were assigned at 1093 and 1623 cm^{-1} respectively. In the magnetic GO (Fig. 1b), the band at 570 cm⁻¹ is attributed to Fe–O stretching vibration. The spectra of modified GO using MAPTMS (Fig. 1c) showed a broad peak between 1060 and 1110 cm⁻¹, which was assigned to Si-O-Si. The bands at 1144 cm⁻¹ (C-O), 1645 cm⁻¹ (C=C), and 1725 cm⁻¹ (C-O) are characteristic of MAPTMS, and indicated the successful linkage of MAPTMS to the surface of GO sheet. After polymerization process, the presence of bands at 1644 cm^{-1} and 3250-3400 cm⁻¹ is due to CONH₂ and NH, respectively (Fig. 1d). In addition, the peak around $1109-1120 \text{ cm}^{-1}$ is attributed to S=O stretching of sulfonic acid. In Fig. 1e, the intensity of the peak at about 1644 cm^{-1} is weaker than that of GO/Fe₃O₄/PAMPS (Fig. 1d) due to the formation of a metal-ligand bond.

The crystalline structures of GO/Fe₃O₄ (a), GO/Fe₃O₄/ PAMPS (b) and GO/Fe₃O₄/PAMPS/Pd (c) were characterized by powder X-ray diffraction (XRD) (Fig. 2). All these species have six strong diffraction peaks at 2θ =30.37, 35.71, 43.42, 53.79, 57.41, 63.05 corresponding to the crystal face (220), (311), (400), (422), (511) and (440) of Fe₃O₄ lattice [58]. The appearance of diffraction peaks at 2θ =40.12, 46.52 and 68.27 (weak peak) are due to the Pd (111), Pd (200) and Pd (220) lattice planes, respectively.

The XPS survey scan spectra of the GO/Fe₃O₄/PAMPS/ Pd catalyst, Fe and Pd 3d region is shown in Fig. 3. As displayed in Fig. 3a, the peaks corresponding to C 1s, N 1s, O 1s, Fe 2p and Pd 3p & 3d was clearly observed in the XPS survey spectrum. Figure 3b, c present the curve fitted Fe 2p and Pd 3d respectively. As shown in Fig. 3b, two peaks at 711.75 and 725.42 eV, related to Fe $2p_{3/2}$ and Fe $2p_{1/2}$



Scheme 1 General route for the synthesis of GO/Fe₃O₄/PAMPS/Pd nanocomposite



Scheme 2 Immobilization of Pd-NPs on the surface of PAMPS



Fig. 1 FT-IR spectra of **a** GO, **b** GO/Fe₃O₄, **c** GO/Fe₃O₄/MAPTMS, **d** GO/Fe₃O₄/PAMPS and **e** GO/Fe₃O₄/PAMPS/Pd nanocomposite



Fig. 2 XRD patterns of a GO/Fe₃O₄, b GO/Fe₃O₄/PAMPS and c GO/Fe₃O₄/PAMPS/Pd nanocomposite

respectively, which reveals the presence of Fe^{2+} in Fe_3O_4 [59]. The high-resolution XPS spectra of Pd 3d was collected and peaks at 335.48 and 340.94 eV were ascribed to Pd0 $3d_{5/2}$ and $3d_{3/2}$ respectively (Fig. 3c).

The magnetic property of the GO/Fe₃O₄/PAMPS/Pd catalyst was measured with a vibrating sample magnetometer (VSM) from -10,000 to +10,000 Oe at room temperature (Fig. 4). As expected, the saturation magnetization value (Ms) of resultant nanocomposite is 50 emu/g, which is lower than that of pure Fe₃O₄ NPs because the presence of GO and polymeric moieties. In addition, VSM measured by homemade instrument (Meghnatis Daghigh Kavir Company, Iran), does not show any hysteresis loop and perfect Langevin behavior which indicates its superparamagnetic characteristics. The magnetic character of GO/ Fe_3O_4 /PAMPS/Pd catalyst also facilitates the removal of the catalyst by a simple permanent magnet (See the photo in Fig. 4).

Thermogravimetric analysis (TGA) of GO/Fe₃O₄ (a) and GO/Fe₃O₄/PAMPS/Pd nanocomposite (b) was further used to study the composition of the resultant nanocomposite.

The TGA of both materials show three main weights loss. The first weight loss was occurred under 100 °C which attributed to desorption of water. The second weight loss from 200 to 300 °C is due to the dehydration process of surface oxygen and hydroxyl groups in GO. The final weight loss around 400–450 °C is related to the decomposition of graphene structure as well as decomposition of immobilized organic moieties on the surface of nanocomposite. Interestingly, the total mass loss of catalyst (Fig. 5b) was only 6.8% at temperatures below 200 °C and 20% at 650 °C which shows good thermal stability of the nanocomposite. The percentage of the remaining mass of GO/Fe₃O₄/ PAMPS/Pd was also compared with GO/Fe₃O₄. It was found about 17% which revealed the amount of loaded Pd and polymeric moieties in the structure of catalyst.

Transmission electron microscopy (TEM) images (Fig. 6) of GO (Fig. 6a, b) and GO/Fe₃O₄/PAMPS/Pd nanocomposite (Fig. 6c, d) were illustrated. The TEM images of GO sheets (Fig. 6a, b) demonstrated the flake-like shapes of graphene oxide. The high transparency of GO showed a few layers proved thin film of GO. As shown in figure (Fig. 6c, d), GO was successfully exfoliated in water and also show that the Fe₃O₄ nanoparticles are quasi-spherical, with average diameters of 16 nm. The Pd-NPs with mean size of 5 nm were dispersed in close contact with the surface of GO sheet. As shown in TEM images, Pd-NPs are not found outside the modified GO because of polymer network prevents the aggregation or agglomeration of Pd-NPs on the GO sheets. Owing to the high density of polymeric network and the presence of spherical Fe₃O₄ NPs, it is difficult to recognize Pd-NPs. In this regard, we tried to illustrate a closer sight of Pd-NPs at the bottom of the Fig. 6. In addition, EDX image (Fig. 7), also indicates the successful incorporation and presence of all the elements (O, C, N, Fe, Si and Pd) onto the GO sheets.

3.1 Catalytic Performance of GO/Fe₃O₄/PAMPS/Pd Nanocomposite

Heterogeneous palladium catalysts stabilized by polymers are extensively studied for the Suzuki–Miyaura crosscoupling reaction [60, 61]. However, to the best of our

Fig. 3 a Full range XPS spectrum of $GO/Fe_3O_4/PAMPS/Pd$ nanocomposite. b Fe 2p and c Pd 3d

60

40

20

0

-20

-40

-60

-10000

Magnetization (emu/g)



Fig. 4 Room-temperature magnetization *curve* of magnetic GO/ Fe_3O_4 /PAMPS/Pd nanocomposite

Fig. 5 TGA diagram of (a) GO/Fe $_3O_4$ and (b) GO/Fe $_3O_4$ /PAMPS/Pd nanocomposite



Fig. 6 Representative TEM images of GO (a, b) and GO/Fe₃O₄/PAMPS/Pd nanocomposite dispersed in water (c, d)



Fig. 7 EDX spectra of GO/Fe₃O₄/PAMPS/Pd nanocomposite

knowledge there are only a few reports on the application of magnetically separable Pd stabilized by hydrophilic polymers which catalyze the Suzuki reaction under green conditions [62–66].

To study the effects of solvent, optimal amount of catalyst and required time, we selected a model reaction. To the purpose, 4-bromotoluene was reacted with phenyl boronic acid in the presence our new catalytic system, using different amounts of catalysts, the required base and solvents diversel, finding the required times for each runs under examination (Table 1). As shown in Table 1, the best result was obtained in a mixture of H₂O and EtOH as solvent. This mixture of solvent provides a good interaction of hydrophilic polymer stabilized Pd-NPs with water soluble boronic acid and hydrophobic aryl halides which leads to an improvement in Suzuki reaction. With the previous experiments in hand, K₂CO₃ was selected as the most efficient base for the present catalytic system. Amount of catalyst and time of the reaction are two prominent parameters which investigated precisely in this work. The better conversion of 4-bromotoluene to the corresponding biphenyl was occurred with 0.4 mol% of catalyst in 2 h.

To screen the efficiency and limitation of our novel nanocatalyst, different substituted aryl halides and aryl boronic acids, bearing either electron- donating or 

Entry	Amount of catalyst (mol%)	T (°C)	Solvent	Time (h)	Conver- sion (%) ^a
1	0.4	80	H ₂ O	5	50
2	1.2	80	H ₂ O	5	28
3	2.8	80	H ₂ O	10	35
4	0.4	60	Toluene:H ₂ O	2	5
5	1.2	80	EtOH:H ₂ O	5	100
6	0.56	80	EtOH:H ₂ O	5	95
7	0.4	80	EtOH:H ₂ O	2	95
8	0.2	80	EtOH:H ₂ O	5	85
9	0.16	80	EtOH:H ₂ O	2	35
10	0.10	80	EtOH:H ₂ O	2	10
11	0.05	80	EtOH:H ₂ O	3.5	25

Reaction conditions: phenyl boronic acid (1.2 mmol), 4-bromotoluene (1 mmol), K_2CO_3 (3 mmol), GO/Fe₃O₄/PAMPS/Pd as catalyst, solvent (5 mL)

^aCalculated by GC

electron withdrawing groups were reacted under secure optimal reaction conditions. These reactions all, proceeded smoothly, resulted in the desired corresponding cross coupled products in high to excellent yields. The results are summarized in Table 2. As it can be seen, when iodobenzene. 4-iodoanisole and 4-iodotoluene were used as reactants, desired coupling products were obtained in only 2 h with excellent yields (95–98%) in the presence of 0.2 mol% catalyst (Table 1, entries 1-3). Aryl bromides with electron-donating and electron-withdrawing groups such as 4-nitro, 4-methyl as well as bromobenzene, gave the coupling products in excellent yields (up to 95%) (entries 4-6). It is noteworthy to mention that the Suzuki reaction of aryl chlorides is more difficult than aryl bromides and aryl iodides because of strong C-Cl bond than that of C-Br and C-I and longer reaction time is required. However, by increasing the amount of catalyst loading to 1 mol% and extending the reaction time, the Suzuki reaction of aryl chlorides was completed in good yields (52-68%) within 24 h (entries 7-10). Furthermore, 4-tolylboronic acid as a coupling partner was subjected to various aryl halides and the results were mentioned in entries 11–16. Surprisingly, compare with phenyl boronic acid, 4-tolylboronic acid showed less efficient result with aryl bromides (Table 2,

entries 8–9) and superior result with aryl chloride (entry 10) in term of yield (75%) without using harmful solvents such as DMF or tetra butyl ammonium bromide (TBAB) or excess amount of catalyst. After completion of each reaction, all products were analyzed by ¹H NMR and FT-IR techniques and the corresponding peaks were observed.

3.2 Leaching

Another catalytic experiment was further conducted to estimate the impact of palladium leaching. For the purpose, a certain amount of catalyst was dispersed in the presence of K_2CO_3 and solvents (EtOH:H₂O). The mixture was stirred and then filtered to obtain a transparent solution. In the next step, the Suzuki coupling substrates such as phenyl boronic acid and bromobenzene were introduced to the above clean supernatant and the solution was heated to 80 °C and stirred. It was found that no biphenyl was detected even after 5 h, indicating that the coupling reaction catalyzed by heterogeneous catalyst not homogeneous leaching Pd.

3.3 Comparison

To evaluate the efficiency of the GO/Fe₃O₄/PAMPS/Pd catalyst, its catalytic activity was compared with some other Pd supported catalysts reported, previously. The results revealed that PAMPS cross linked by MAPTMS is a superior ligand to some of the previously reported catalysts in terms of using green solvent, less reaction times, ease of separation, recyclability, less Pd leaching and also better isolated yields (Table 3).

3.4 Recycles

The reusability of the GO/Fe₃O₄/PAMPS/Pd catalyst was evaluated by using it in the coupling of 4-bromotoluene with phenyl boronic acid as the model reaction under optimized reaction conditions. After completion of each cycle, the catalyst was separated easily by an external magnetic field and the residue was analyzed by GC. Next, fresh starting materials were then introduced to the flask containing magnetic catalyst and a new Suzuki coupling was started. The catalyst was recovered and reused for seven consecutive runs without any significant loss of its activity (Fig. 8).

4 Conclusion

In summary, we have developed a novel Pd NPs composite as denoted by $GO/Fe_3O_4/PAMPS/Pd$. It was efficiently used in Suzuki reaction of aryl halides with boronic acid in green media to give the cross-coupled products in high to excellent yields in relatively short reaction times. Worthy

Table 2 Suzuki reaction of various aryl halides with aryl boronic acids catalyzed by GO/Fe₃O₄/PAMPS/Pd



Entry	R ₁	R ₂	Х	Amount of catalyst (mol%)	Time (h)	Yield (%) ^a	TON/TOF (h ⁻¹) ^b
1	Н	Н	Ι	0.2	2	100	500/250
2	4-Me	Н	Ι	0.2	2	100	500/250
3	4-OMe	Н	Ι	0.2	2	98	490/245
4	Н	Н	Br	0.4	2	96	240/120
5	$4-NO_2$	Н	Br	0.4	2	96	240/120
6	4-Me	Н	Br	0.4	2	95	237.5/118.7
7	Н	Н	Cl	1	18	60	60/3.3
8	Н	Н	Cl	1	24	65	65/2.7
9	4-Me	Н	Cl	1	24	52	52/2.2
10	$4-NO_2$	Н	Cl	1	24	68	68/2.8
11	Н	Me	Ι	0.2	2	95	475/237.5
12	4-Me	Me	Ι	0.2	2	95	475/237.5
13	4-OMe	Me	Ι	0.2	2	70	350/175
14	Н	Me	Br	0.4	7	62	155/22.1
15	4-Me	Me	Br	0.4	7	30	75/10.7
16	Н	Me	Cl	1	24	75	75/3.1

Reaction conditions: aryl boronic acid (1.2 mmol), aryl halide (1 mmol), K_2CO_3 (3 mmol), GO/Fe₃O₄/PAMPS/Pd as catalyst, EtOH:H₂O (5 mL), 80 °C

^aIsolated yield

^bThe TOF was defined as mol product mol⁻¹ Pd h⁻¹

Entry	Catalyst (Pd loading mol%)	Reaction conditions	Yield (%)	Time (h)	Refs.
	Me-Br + B(OH)2				
1	Poly(NIPAM-co-4-VP)-Pd (1)	K ₂ CO ₃ , H ₂ O, 60 °C	95	5	[63]
2	PNIPAM-HNT-Pd (1)	K ₂ CO ₃ , H ₂ O, 70 °C	82	4	[67]
3	G/MWCNTs/Pd (0.5)	K ₂ CO ₃ , EtOH:H ₂ O, 60 °C	90	1.5	[65]
4	rGO/Pd (0.5)	K ₂ CO ₃ , EtOH:H ₂ O, 60 °C	71	1.5	[65]
5	MWCNTs/Pd (0.5)	K ₂ CO ₃ , EtOH:H ₂ O, 60 °C	65	1.5	[65]
6	GO-NHC-Pd (1)	Cs ₂ CO ₃ , DMF:H ₂ O, 50 °C	89	1	[68]
7	GO-2N-Pd(II) (0.5)	K ₂ CO ₃ , EtOH, 80 °C	77	4	[69]
8	$\text{GO-NH}_2\text{-Pd(II)}(1)$	K ₂ CO ₃ , EtOH:H ₂ O, 80 °C	71	4	[70]
9	GO-NHC-Pd(II) (0.25)	K ₂ CO ₃ , EtOH:H ₂ O, 60 °C	94	20	[71]
10	GO/Fe ₃ O ₄ /PAMPS/Pd (0.4)	K ₂ CO ₃ , EtOH:H ₂ O, 60 °C	95	2	This work
	Br + B(OH)2	\rightarrow			
11	Poly(NIPAM-4-VP-AC)-Pd (0.05)	K ₂ CO ₃ , H ₂ O, Ar atmosphere, 90 °C	92	1	[72]
12	$\text{GO-NH}_2\text{-Pd(II)}(1)$	K ₂ CO ₃ , EtOH:H ₂ O, 80 °C	73	4	[70]
13	GO-NHC-Pd(II) (0.25)	K ₂ CO ₃ , EtOH:H ₂ O, 60 °C	93	3	[71]
14	GO/Fe ₃ O ₄ /PAMPS/Pd (0.4)	K ₂ CO ₃ , EtOH:H ₂ O, 60 °C	96	2	This work

Table 3 Comparison the results of selected coupling products using $GO/Fe_3O_4/PAMPS/Pd$ as catalyst with those obtained by some previous literatures



Fig. 8 Reusability of GO/Fe $_3O_4$ /PAMPS/Pd catalyst in the Suzuki reaction of 4-bromotoluene with phenyl boronic acid

to mention, this novel catalytic system worked equally well with less reactive aryl chlorides compared with the corresponding aryl bromides and aryl iodides. Furthermore, GO sheet provided a high surface area for uniform distribution of Fe₃O₄ NPs and magnetic character led to easy separation of the catalyst from the reaction mixture by using a simple external magnet. The catalyst was reused at least seven times without appreciable loss in its catalytic activity. Lack of metal leaching is a promising advantage for our novel catalyst proved by leaching test.

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