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Palladium-decorated *o*-phenylenediamine-functionalized Fe₃O₄/SiO₂ magnetic nanoparticles: A promising solid-state catalytic system used for Suzuki–Miyaura coupling reactions



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ABSTRACT

Palladium-supported *o*-phenylenediamine-functionalized Fe_3O_4 magnetic nanoparticles are presented. A convenient synthetic route for the nanocatalyst and also its application in Suzuki–Miyaura coupling of various aryl halides with phenylboronic acids are described. A high reaction yield (98%) was been obtained in a short reaction time (10 min) through use of this highly efficient nanocatalyst. From a mechanistic aspect, firstly, effective electronic interactions between heteroatoms such as oxygen and Pd(II) provide a suitable condition for covalent bonding by the ingredients in the Suzuki–Miyaura coupling reaction. Secondly, Pd(II) is converted to Pd (0) by use of sodium borohydride in the presence of triphenylphosphine in basic conditions, and then it plays a main role in the catalytic process. However, the most distinguished properties of this catalytic system are the ease of catalyst separation and great reusability. The palladium-supported *o*-phenylenediamine-functionalized Fe₃O₄ nanoparticles can be easily recovered by use of an external magnet and can reused at least ten times with no significant decline in catalytic activity. This novel system was structurally characterized by various analytical methods, and the results obtained are well interpreted in the context.

1. Introduction

In recent decades, heterogeneous catalysis systems have attracted much attention because of their diverse advantages in industrial applications, such as convenient separation from the reaction mixture and considerable reusability [1,2]. Among the various types of heterogeneous catalysis systems, researchers have focused mostly on nanoscale composites because of their huge active surface area and excellent functionalization capability [3,4]. One well-known nanoscale catalytic system (especially in recent decades) is magnetic nanoparticles (MNPs) such as iron oxide (Fe₃O₄) nanoparticles (NPs). Fe₃O₄ NPs with a core/shell structure have been extremely used for catalysis of different coupling reactions that include covalent bonding because of their traits such as superparamagnetism, huge active surface area, surface functionalization capability (through chemical bonding), heterogeneity, good functionalization capability (with other metallic or polymeric matrices), and excellent recyclability [5-8]. For instance, surface functionalization of Fe₃O₄ MNPs with ethylenediaminetetraacetic acid was reported by Magdalena et al. [9] in 2018. More recently, polyvinylpyrrolidone-modified silica-coated Fe₃O₄ MNPs were synthesized by a miniemulsion method and applied for absorption of hydrophobic substances by Wang et al. [10]. In that work, superparamagnetic Fe₃O₄ MNPs with high saturation magnetization were synthesized by a miniemulsion method, and then the SiO₂ shell was synthesized by the Stöber method. Since the silica network has a mesoporous structure, the silica-coated NPs could be applied for absorption purposes. The absorption capacity of the Fe₃O₄/SiO₂ MNPs was increased through the use of hybrid matrices or polymeric matrices such as polyvinylpyrrolidone. Moreover, several achievements regarding the preparation, characterization, and catalytic application of Fe₃O₄ MNPs have been reported by our research group [11-13]. In our previous work, co-deposition as one of the most efficient methods for preparation of Fe₃O₄ NPs was used in basic conditions. Then, the surfaces of the Fe₃O₄ NPs were well functionalized with some organic compounds through Pd-catalyzed covalent bonding or polymer modification. Afterward, they were suitably applied for different catalytic aims. Here we report another efficient catalytic system constructed from Fe₃O₄ MNPs (as a magnetic nanoscale core), a silica network (as an exterior shell), (3-chloropropyl)trimethoxysilane (CPTES; as a cross-linker), o-phenylenediamine (o-PDA; as a nitrogen source), and palladium (as the main

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active catalytic site).

Because of the great importance of biphenyl derivatives as intermediates in materials science, pharmaceuticals, polymers, and agrochemicals, several methods have been reported for the synthesis of biphenyl compounds [14-16]. Among the different strategies, the Suzuki-Miyaura coupling reaction is a powerful synthetic method for preparation of biphenyls from aryl halides and phenylboronic acids because of the mild reaction conditions and functional group tolerance [17-19]. Usually, coupling reactions are conducted with a soluble Pd/organic complex as the homogeneous catalyst, but tedious workup procedures, low catalytic activity (due to wasting), and contamination by residual metals in the final product are the major drawbacks of this method. However, it seems that use of heterogeneous Pd-containing catalysts is the best solution to address the aforementioned deficiencies [20-28]. Recently, several methods have been reported in which organic and inorganic solid supports (such as silica, carbon, zeolite, polymer, and ionic liquids) were used for preparation of heterogeneous Pd catalysts [29,30]. In this regard, we present a novel Pd-supported magnetic nanocatalyst (Fe₃O₄/o-PDA-Pd) as a heterogeneous nanocatalyst with superparamagnetic behavior, and then we investigate its activity in catalyzing Suzuki–Miyaura coupling reactions under mild conditions. Among the various types of heterogeneous catalysis systems, Fe₃O₄-based systems are the most applicable because of the ease of the separation process and recycling. From a physical aspect, their magnetic property provides a substantial opportunity to recycle and reuse them several times with a low amount of waste. Also, a larger active surface area is provided through dispersion of these NPs in comparison with integrated polymeric systems. Thus, lower ratios of the catalyst work as well as relatively large quantities of other types of these catalytic systems. From a chemical aspect, there are two advantages of this catalytic system. First, the effective electronic interactions between the loaded Pd(II) and heteroatoms in the structure of the aryl halides and phenylboronic acid increase the probability of contact between the molecules. Second, the convenient conversion of Pd(II) to Pd(0) on the NP surfaces leads to good execution of the coupling reactions. Additionally, the chance of producing byproducts is increased because of the longer reaction times. Thus, this is considered a important benefit of the Fe₃O₄/o-PDA-Pd nanocatalyst, which catalyzes the coupling reactions in a short reaction time (10 min). Here we report that a high reaction yield (98%) is obtained in a very short reaction time (10 min) through use of the Fe₃O₄/o-PDA-Pd nanocatalyst (0.01 g) at room temperature (Fig. 1).

2. Materials and methods

2.1. Materials and equipment

All solvents, chemicals, and reagents were purchased from Merck, Sigma, and Aldrich. Melting points were measured with an Electrothermal 9100 apparatus and are uncorrected. Fourier-transform infrared (FT-IR) spectra were recorded with a Shimadzu IR-470 spectrometer by the KBr pellet method. ¹H and ¹³C nuclear magnetic resonance (NMR) spectra were recorded with a Bruker DRX-500 Avance spectrometer at 500 and 125 MHz, respectively. Scanning electron microscopy (SEM) images were taken by a Zeiss Sigma microscope with a camera attached. Magnetic measurements of the solid samples were performed with Lakeshore 7407 and Meghnatis Kavir Kashan Co. (Iran) vibrating sample magnetometers. Elemental analysis of the nanocatalyst was performed by energy-dispersive X-ray (EDX) analysis with a Numerix DXP-X10P instrument. X-ray diffraction (XRD) measurements were performed with a DRON-8 X-ray diffractometer. K α X-ray photoelectron spectroscopy (XPS) was used for identification of reduced palladium, and the loading value of palladium in the catalyst was estimated by inductively coupled plasma (ICP) analysis with a Varian ICP-OES 730-ES instrument.

2.2. Synthesis

2.2.1. Preparation of chloropropyl-functionalized silica-coated Fe $_3O_4$ MNPs

In a round-bottomed flask (100 mL), as-prepared Fe_3O_4/SiO_2 MNPs (0.4 g) (prepared according to our previous reports [11–13]) were well dispersed in tetrahydrofuran (8.0 mL) (ultrasonication for 10 min). Then NaH (0.2 g, 8.33 mmol) was added to the flask, CPTES (3.0 mL) was added drop by drop at room temperature, and the mixture were well stirred for 12 h at 60 °C. Ultimately, $Fe_3O_4/SiO_2/CPTES$ MNPs were collected (with an external magnet), washed with ethanol and deionized water, and then dried at 60 °C.

2.2.2. Preparation of o-PDA-functionalized Fe₃O₄ MNPs

In a round-bottomed flask (100 mL), $Fe_3O_4/SiO_2/CPTES$ MNPs (0.3 g) were dispersed in ethanol (10 mL) (ultrasonication for 10 min). Then *o*-PDA (0.03 g, 0.277 mmol) was added and the mixture were stirred for 1 h at room temperature. The stirring was continued for an additional 12 h under reflux. Finally, the Fe_3O_4/o -PDA MNPs prepared were collected magnetically, washed with ethanol and deionized water, and then dried in a vacuum oven for 24 h.

2.2.3. Preparation of the Pd-supported o-PDA-functionalized Fe_3O_4 magnetic nanocatalyst

In a round-bottomed flask (100 mL), Fe₃O₄/o-PDA MNPs (0.2 g) were well dispersed in dry acetone (20 mL) and mixed with palladium acetate (0.23 g, 1.28 mmol) by vigorous stirring for 12 h at room temperature. The fabricated Fe₃O₄/o-PDA–Pd magnetic nanocatalyst was then magnetically isolated from the reaction mixture, washed three times with acetone and deionized water, and dried at 50 °C.

2.2.4. General procedure for the synthesis of compounds **3a–3l** via a Suzuki–Miyaura cross-coupling reaction catalyzed by the Fe_3O_4/o -PDA–Pd nanocatalyst

In a round-bottomed flask (100 mL), Fe_3O_4/o -PDA–Pd MNPs (0.01) were dispersed in dichloromethane (5.0 mL) and ethanol (2.0 mL) by ultrasonication for 20 min at room temperature. Then aryl halides **1** (1 mmol), phenylboronic acid **2** (1.2 mmol), NaBH₄ (0.005 g, 0.1 mmol), K₂CO₃ (0.21 g, 1.5 mmol), and PPh₃ (0.0026 g, 0.1 mmol) were added to the flask and the mixture were stirred for 10 min at room temperature. After completion of the reaction, the magnetic nanocatalyst was conveniently isolated by use of an external magnet, and excess



Fig. 1. Schematic of a Suzuki–Miyaura coupling reaction catalyzed by Fe₃O₄/o-PDA–Pd nanoscale system (r.t.: room temperature).

dichloromethane (2.0 mL) was added to the flask. Deionized water (5.0 mL) was then added, and after much stirring the organic phase was separated and dried with $MgSO_4$ salt. The crude product was purified by column chromatography. Evaporation of the solvent gave the pure desired products **3a**–**3l**.

2.3. Characterization of selected products

Biphenyl (**3a**): FT-IR (KBr) (ν_{max} , cm⁻¹): 3041, 1573, 1469, 1454, 1427, 1338, 1298, 1168, 1010. ¹H NMR (500 MHz, CDCl₃, δ , ppm): 7.34 (2H, t, J = 7.4 Hz, H–Ar), 7.44 (4H, t, J = 7.8 Hz, H–Ar), 7.62 (4H, d, J = 7.3 Hz, H–Ar). ¹³C NMR (125 MHz, CDCl₃, δ , ppm): 140.8, 129.6, 128.0, 127.2.

Biphenyl-4-carbaldehyde (**3b**): ¹H NMR (500 MHz, CDCl₃, δ , ppm): 7.40–7.52 (3H, m, H–Ar), 7.75 (2H, d, J = 7.6 Hz, H–Ar), 7.86 (2H, d, J = 6.8 Hz, H–Ar), 7.98 (2H, d, J = 6.8 Hz, H–Ar), 10.05 (1H, s, CHO).

Biphenyl-4-methanol (**3e**): ¹H NMR (500 MHz, CDCl₃, *δ*, ppm): 4.54 (2H, d, J = 9.4 Hz, CH₂), 5.24 (H, t, J = 9.5 Hz, OH), 7.31–7046 (5H, m, H–Ar), 7.59–7.65 (4H, m, H–Ar). ¹³C NMR (125 MHz, CDCl₃, *δ*, ppm): 62.6, 126.3, 126.5, 127.0, 127.2, 128.8, 138.5, 140.1, 141.8.

3. Results and discussion

3.1. Preparation

First, Fe₃O₄ MNPs were synthesized from FeCl₃·6H₂O and FeCl₂·4H₂O by co-deposition in basic conditions, and then surface coating by a silica network was conducted with use of tetraethyl orthosilicate [31,32]. The Fe₃O₄/SiO₂ NPs were then treated with CPTES, and nucleophilic addition of the NH₂ group in *o*-PDA occurred to produce the Fe₃O₄/SiO₂/*o*-PDA nanocatalyst [33]. Finally, Pd was loaded onto the synthesized Fe₃O₄/SiO₂/*o*-PDA by slow addition of palladium acetate in dry acetone and stirring for 30 min at 80 °C to prepare the Fe₃O₄/SiO₂/*o*-PDA-Pd magnetic nanocatalyst (Scheme 1). It was easily recovered by use of an external magnet, and it can be used at

least ten times without significant decrease in the catalytic activity. To the best of our knowledge, this is the first report of the design, preparation, and characterization of $Fe_3O_4/SiO_2/o$ -PDA–Pd and its application as a heterogeneous catalyst in a coupling reaction (Fig. 1).

3.2. Characterization of the heterogeneous nanocatalyst

To investigate the structure of the Fe₃O₄/o-PDA-Pd nanocatalyst, FT-IR spectroscopy, EDX analysis, and XRD measurements were used. The size distribution and the general morphology of the particles were investigated by SEM and TEM. Moreover, to investigate the magnetic properties of the prepared samples, vibrating-sample magnetometry (VSM) was used. As can be seen in Fig. 2, the peaks at approximately 584 cm⁻¹ (in all the spectra shown) are from the stretching vibrations of the Fe–O bond and confirm the existence of the Fe₃O₄ magnetic core. In addition, the sharp bands at approximately 1085 and 1151 cm^{-1} (in spectra b-d) are attributed to the Si-O-Si asymmetric stretching vibration related to SiO₂ formation. In addition, the peaks at approximately 800 and 941 cm^{-1} are assigned to the stretching vibrations of Si–O and Si-OH bonds, respectively. In spectra c and d, the peaks at approximately 2923 cm⁻¹ are related to the stretching vibrations of the sp³hybridized C-H bond. Also, the asymmetric stretching vibrations of O-H and N–H groups appeared at approximately 3380 cm⁻¹. Moreover, the peaks at 1500–1620 cm⁻¹ in spectrum d are attributed to the aromatic C=C and C=N bonds, which prove the presence of o-PDA on the NP surfaces.

The sizes, spherical morphology, and uniformity of the Fe_3O_4 MNPs are clearly illustrated in the SEM image in Fig. 3a. In addition, some particle agglomeration occurred through silica coating of the MNPs by tetraethyl orthosilicate and CPTES, as illustrated in Fig. 3b and c. Most likely, this occurred because of the adhesive nature of the silicate compounds. The existence of Pd(0) NPs was proven by the SEM image of $Fe_3O_4/SiO_2/o$ -PDA MNPs. As can be seen in Fig. 3d, tiny particles of Pd (0) (after reduction by sodium borohydride and triphenylphosphine) are distributed on the surface of the larger NPs. Moreover, TEM images of



Scheme 1. Preparation route of Fe₃O₄/*o*-PDA–Pd nanocatalyst, r.t.: room temperature.



Fig. 2. FT-IR spectra of (a) Fe_3O_4 NPs, (b) Fe_3O_4/SiO_2 core/shell NPs, (c) Fe_3O_4/SiO_2 /chloropropylsilane NPs, and (d) $Fe_3O_4/SiO_2/o$ -PDA NPs.

Fe₃O₄/SiO₂ core/shell nanostructures revealed that silica coating of Fe₃O₄ MNPs was done well (dark areas indicate the core and light areas indicate the shell), as observed in Fig. 3e and f. Because there is more electron density around the metallic core, Fe₃O₄ appeared darker than the silica network in the TEM images. The presence of Pd(0) NPs was also proven by the TEM image in Fig. 3g, in which tiny dark spots are representative of Pd(0). However, to investigate the morphology and particle agglomeration after recycling of the nanocatalyst, an SEM image of Fe₃O₄/SiO₂/o-PDA MNPs was obtained after recycling nine times. As can be observed in Fig. 3h, the spherical NPs had been almost changed to laminate particles. It is probable that the core/shell structure was damaged during application of the reaction ten times. Also, the mean size of the NPs was 27 ± 0.4 nm. However, it is obvious that uniform particles with high monodispersity without aggregation would have better performance in catalytic processes because they could provide a larger active surface area.

The results obtained from EDX analysis confirm the presence of iron, carbon, oxygen, nitrogen, silicon, and palladium in the structure of Fe_3O_4/o -PDA–Pd NPs (Fig. 4a). In addition, ICP analysis was used to determine the exact concentration of Pd, and the value obtained was 2.16 wt%, which confirms the value obtained by EDX analysis (Table S1 in the supporting information). The magnetic behavior of the Fe_3O_4/o -PDA–Pd NPs is shown by *M*–*H* curves at room temperature. The hysteresis loops of the superparamagnetic behavior can be clearly observed for the MNPs in the VSM analysis (Fig. 4b). Accordingly, saturation of the magnetization of the Fe_3O_4/o -PDA–Pd NPs occurred at 40.73 emu/g (curve II), whereas it was occurred at 50 emu/g for neat Fe_3O_4 NPs (curve I). As a result, this reduction in magnetization is mainly attributed to the existence of newly loaded layers on the surface of the NPs.



Fig. 3. SEM images of (a) Fe₃O₄ MNPs, (b) Fe₃O₄/SiO₂ MNPs, (c) Fe₃O₄/SiO₂/chloropropylsilane MNPs, (d) Fe₃O₄/SiO₂/o-PDA MNPs, TEM images of (e,f) Fe₃O₄/SiO₂/o-PDA MNPs after reduction of Pd by NaBH₄ and PPh₃, (h) SEM image of recovered Fe₃O₄/SiO₂/o-PDA MNPs after 9 times recycling, and (i) size-distribution diagram of the produced Fe₃O₄/o-PDA-Pd NPs.



Fig. 4. (a) EDX spectrum of the produced Fe₃O₄/o-PDA-Pd NPs, and (b) M – H curves of Fe₃O₄ NPs (I) and produced Fe₃O₄/o-PDA-Pd NPs (II).

For further investigation of the crystal structure of the Fe₃O₄/*o*-PDA–Pd NPs, the XRD pattern was obtained (Fig. 5). The crystalline peaks at diffraction angles $2\theta = 30.21^{\circ}$, 35.53° , 43.124° , 57.09° , and 62.82° represent the structure of Fe₃O₄ NPs (JCPDS card no. 01-075-1609), and are indicated by Miller indices in the spectrum. New peaks that could be attributed to the *o*-PDA layer and Pd are indicated by asterisks in the XRD pattern shown. The presence of these new peaks proves that new layers had been loaded onto the surface of the Fe₃O₄ NPs and influence the XRD pattern because of the well-defined crystal structures.

3.3. Catalytic activity

After characterization of the Fe₃O₄/o-PDA-Pd nanocatalyst, the catalytic properties of the catalyst were investigated for the synthesis of biphenyl derivatives by the Suzuki-Miyaura coupling reaction. For this purpose, the reaction of 4-iodobenzene (1.0 mmol, 0.11 mL) with phenylboronic acid (1.2 mmol, 0.15 g) was chosen as the model reaction for optimization of the reaction conditions (product 3a). Initially, the effect of the catalyst amount on the reaction yield was studied. As can be seen in Table 1, use of 0.01 g of the Fe₃O₄/o-PDA-Pd nanocatalyst is sufficient to complete the reaction in 10 min in the presence of NaBH₄, K₂CO₃, PPh₃, ethanol, and dichloromethane at room temperature. Since, Pd(0) plays the main role in the catalytic system, use of sodium borohydride in the presence the small amounts of PPh₃ as an assistant ligand is essential [34]. The amount of the catalytic active site (Pd) was estimated to about 0.203 mmol/g. We next studied the effects of the various effective factors on the model reaction (Table 1). The completion of the reaction was monitored by thin-layer chromatography. Furthermore, to highlight the great performance of the catalytic system, the results obtained in this work and in earlier work are briefly compared in Table 2 for the model reaction. As can be seen in Table 2, the results prove the superiority of the present catalytic system in saving time and energy and



Fig. 5. XRD patterns of the produced $\rm Fe_3O_4/{\it o}$ -PDA-Pd NPs (a), and $\rm Fe_3O_4$ NPs (JCPDS card No. 01-075-1609) (b).

Table 1

Optimization of the reaction conditions for the Suzuki–Miyaura coupling reaction catalyzed by the Pd-supported *o*-phenylenediamine-functionalized Fe₃O₄ magnetic nanocatalyst.

| Solvent | Temperature (°C) | Catalyst amount (g) | Time (min) | Yield ^a (%) |
|-------------------|------------------|---------------------|------------|------------------------|
| H_2O | 50 | 0.015 | 30 | Trace |
| Et ₂ O | r.t | 0.015 | 30 | 82 |
| EtOH | 50 | 0.015 | 30 | 79 |
| MeOH | 40 | 0.015 | 30 | 75 |
| DMF | 50 | 0.015 | 30 | 87 |
| DCM | r.t. | 0.02 | 30 | 98 |
| DCM | r.t. | 0.015 | 30 | 98 |
| DCM | r.t. | 0.01 | 30 | 98 |
| DCM | r.t. | 0.01 | 20 | 98 |
| DCM | r.t. | 0.01 | 10 | 98 |

DCM, dichloromethane; DMF, dimethylformamide; r.t., room temperature.

^a Isolated yield for product **3a**, via a coupling reaction between 4-iodobenzene (1.0 mmol) and phenylboronic acid (1.2 mmol) in the presence of NaBH₄ (0.1 mmol), K_2CO_3 (1.5 mmol), PPh₃ (0.1 mmol, 0.0026 g), and the solvent (5.0 mL).

in obtaining high reaction yields. However, to evaluate the scope and generality of this approach, the optimized reaction conditions were applied for the synthesis of the diverse aryl halide derivatives with phenylboronic acid, as summarized in Table 3. It is clearly observed that aryl iodides and aryl bromides are more reactive in the catalyzed Suzuki–Miyaura coupling reaction, as we expected. This means that the reaction catalyzed by Fe_3O_4/o -PDA–Pd NPs precisely proceeds by the Suzuki–Miyaura mechanism.

Table 2

Comparison of recent catalytic systems with the Pd-supported o-phenylenediamine (o-PDA)-functionalized Fe₃O₄ nanocatalyst for the model reaction.

| Catalyst | Conditions | Isolated yield (%) | Reference |
|--|--|-----------------------|-----------|
| PS-Pd(II)-furfural ^a | K ₂ CO ₃ , DMF, 80 °C, 300 min | 100 | [35] |
| PdCl ₂ -supported ILs | K ₂ CO ₃ , H ₂ O, 100 °C, 100 min | 100 | [36] |
| RGO/Pd composite | K ₃ PO ₄ , H ₂ O, 100 °C, 5 min | 100 | [37] |
| Pd-supported CS | K ₂ CO ₃ , DMF-H ₂ O (9:1), | 95 | [38] |
| particles | 90 °C, 90 min | | |
| Pd(P-Phos)Cl ₂ ^b | KOH, EtOH, r.t., 360 min | 95 | [39] |
| Pd-supported NHC | K ₂ CO ₃ , EtOH-H ₂ O (1:1), | 98 | [40] |
| | 90 °C, 150 min | | |
| Fe ₃ O ₄ /o-PDA-Pd | K ₂ CO ₃ , DCM, r.t., 10 min | 98 | This work |

CS, carbon sphere; DCM, dichloromethane; DMF, dimethylformamide; IL, ionic liquid; NHC, N-heterocyclic carbene; RGO, reduced graphene oxide, r.t., room temperature.

^a Pd-supported furfural-functionalized *p*-aminopolystyrene.

^b Pd–dipyridylphosphine chloride complex.

Table 3

Reaction of different aryl halides (I, Br, Cl) with phenylboronic acid catalyzed by the Pd-supported o-phenylenediamine-functionalized Fe₃O₄ nanocatalyst.

| R^1 | Х | Product | Time (min) | Isolated yield (%) | Melting point (°C) | | Reference |
|----------------------|----|---------|------------|--------------------|--------------------|------------|-----------|
| | | | | | Observed | Literature | |
| Н | I | 3a | 10 | 98 | 69–72 | 69–71 | [41] |
| 4-CHO | Ι | 3b | 30 | 95 | 59-62 | 57-59 | [41] |
| 4-OH | Ι | 3c | 60 | 95 | 160-163 | 162-163 | [43] |
| 4-CO ₂ H | Ι | 3d | 60 | 92 | 219-223 | 217-219 | [44] |
| 4-CH ₂ OH | I | 3e | 60 | 90 | 100-102 | 99 | [45] |
| Н | Br | 3f | 45 | 97 | 69–72 | 67–68 | [41] |
| 4-CHO | Br | 3g | 45 | 89 | 57-59 | 56-58 | [42] |
| 4-OH | Br | 3h | 90 | 90 | 160-164 | 162-163 | [43] |
| 4-CO ₂ H | Br | 3i | 90 | 89 | 224-226 | 219-223 | [44] |
| Н | Cl | 3j | 60 | 35 | 69–72 | 70–71 | [41] |
| 4-CHO | Cl | 3k | 90 | 55 | 57-59 | 57–58 | [42] |
| 4-CO ₂ H | Cl | 31 | 360 | 50 | 220-222 | 219-223 | [44] |

3.4. Suggested mechanism

A plausible mechanism for the Suzuki-Miyaura coupling reaction catalyzed by the Fe₃O₄/o-PDA-Pd nanocatalyst is illustrated in Scheme 2. First, it should be noted that effective electronic interactions between Pd(II) and heteroatoms of the ingredients in the Suzuki-Miyaura coupling reaction make them come close together. Then, in stage 1, the loaded Pd(II) on the surface of NPs is reduced to Pd(0) by NaBH₄ in the presence of K_2CO_3 , PPh₃, and phenylboronic acid **2**. The Pd(0) state was confirmed by the XPS peak at approximately 334.55 eV and also the XRD pattern (Figs. S7 and S8 in the supporting information). According to the literature, Pd(0) activates the C-X bond, and in the formation of C-Pd (II)-X, it is converted to Pd(II). In stage 2, the Suzuki coupling reaction starts with the oxidative addition of aryl halides 1 to Pd(0), and then carbonate ion assists the removal of halide from the surface of Pd(II) (stage 3). Afterward, a transmetalation reaction occurs between phenylboronic acid and the C-Pd(II)-CO3 intermediate to produce an Ar (C-Pd(II)-C)Ar' intermediate (stage 4). Finally, in stage 5, reductive elimination results in the Ar(C-Pd(II)-C)Ar' intermediate giving the Pd (0) complex with generation of related biphenyl (Ar-Ar').



Scheme 2. Plausible mechanism for Suzuki–Miyaura coupling catalyzed by ${\rm Fe_3O_4/0\text{-}PDA\text{-}Pd}$ nanocatalyst.

3.5. Recyclability of the nanocatalyst

Great reusability of the Fe₃O₄/*o*-PDA–Pd nanocatalyst is one of the most important advantages and makes it as an instrumental tool for commercial applications. For this aim, the nanocatalyst performance was carefully monitored in the model reaction (product **3a**) after recycling ten times. In this regard, after completion of the reaction, the NPs were magnetically isolated from the mixture and washed with ethanol, and were then dried and reused in subsequent reactions. The nanocatalyst can be reused at least ten times without any significant reduction in coupling reaction yield (Fig. 6). The observed reduction in catalytic activity probably originates from the *o*-PDA separation from the total structure of the nanocatalyst and deformation of the spherical core/shell structure of Fe₃O₄/*o*-PDA–Pd during the catalytic process. These claims were proven by FT-IR and XRD spectra of the nanocatalyst after recycling nine times (Figs. S9 and S10 in the supporting information).

4. Conclusions

In summary, a novel catalytic system constructed from Fe₃O₄ MNPs, a silica network, *o*-PDA, and palladium was designed and presented as an instrumental tool for facilitating the Suzuki–Miyaura cross-coupling reaction. This efficient catalytic system was completely characterized by FT-IR spectroscopy, SEM, TEM, EDX analysis, XRD spectroscopy, VSM, and ICP analysis. There are several advantages of applying this nanoscale system, such as convenient separation, good execution of the synthesis reactions under mild conditions (98% yield in 10 min at room temperature), and use of small amounts of this heterogeneous catalyst (Table 1). According to the SEM images, monodisperse MNPs with high



Fig. 6. Reusability diagram of Fe₃O₄/o-PDA-Pd nanocatalyst.

uniformity and spherical shape with an average size of 26 nm were obtained through a convenient synthetic pathway (Fig. 3). Also, VSM revealed the superparamagnetic behavior of the nanoscale catalytic system, which provides a great opportunity to easily separate the nanocatalyst and recover it for further reactions without any waste (Fig. 4b). The nanocatalyst was easily recovered by use of an external magnetic field and was reused efficiently an additional ten times without significant decrease in its catalytic activity. This is the first report on the design, preparation, functionalization, and characterization of the present magnetic nanocatalyst and also its performance as a heterogeneous catalyst in organic reactions.

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Appendix A. Supplementary data

Supplementary data to this article can be found online at https://doi.org/10.1016/j.jpcs.2019.109200.

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