# A novel phosphine-free and recyclable palladium organic–inorganic hybrid magnetic nanocatalyst for Heck cross-coupling reactions

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## Abstract

A palladium organic–inorganic hybrid magnetic nanocatalyst for the Heck-cross coupling reactions was developed. This newly synthesized phosphine-free PdMNPs catalyzed Heck-cross coupling reactions in short reaction times (20–30 min) and high to excellent yields (75–93%). The catalyst was separated simply by an external magnet and reused in 10 successive runs without significant decrease in catalytic activity. The structure of the catalyst was established by Fourier transform infrared, X-ray diffraction, scanning electron microscopy, transmission electron microscopy, energy-dispersive X-ray spectroscopy, vibrating sample magnetometer and thermo-gravimetric analysis analyses.

**Keywords** Heck reaction · PdMNPs · Cross-coupling · Nanocatalyst · Palladium

## Introduction

The Heck reaction or palladium-catalyzed arylation of olefins has received a prominent position among the transition metal catalyzed carbon–carbon bond forming in organic synthesis, in recent years. The Heck-cross coupling reactions are very broad in domain [1–6] and have been used in many areas such as molecular organic, natural products materials, polymers, pharmaceuticals, anti-oxidants, herbicides and industrial applications over the past few decades [7–11]. In most

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previous reports, the common ligands utilized for Heck-reactions are phosphine based. Since the phosphine ligands have several drawbacks such as difficulty of synthesis, expensive, toxic, air and/or moisture-sensitive, there has been great interest in developing phosphine free Pd catalyst for these reactions [12–18]. Palladium is a high-cost metal. Therefore, the development of easily accessible palladium catalyst for the Heck C–C coupling reaction, with high recyclability is a pivotal challenge for the synthetic chemists. The characteristics of ligand bonded to the Pd center play the most essential role in developing the reaction condition and high catalytic activity [19]. Furthermore, various catalysts utilized in the Heck-reaction are homogeneous which are faced with problems such as catalyst separation from the reaction concoction and furthermore the catalyst is not easily reused [20]. Recently, metal nanoparticles have gained considerable attentions in catalysis of organic reactions, in particular magnetic nanoparticles (MNPs) as a bridge between heterogeneous and homogenous catalysts are receiving more attentions due to high efficiency and simple recovery (green chemistry) from the reaction mixture by external magnetic field [21]. Therefore, eliminating the essential of tedious centrifugation and separation steps [22, 23]. To improve the chemical permanency as well as to attain some advantages such as the flexibility in surface modification, MNPs usually are coated with various organic or inorganic compounds, valuable metals and calcium hydroxyapatite $Ca_{10}(PO_4)_6(OH)_3$ (HAp) [24–32]. In addition, covalently combining an active site onto a great surface area of a solid through a flexible spacer which makes an organic–inorganic hybrid catalyst is known as a way to simulate homogenous reaction conditions together having the advantage of reusability [20, 33–38].

In this work, we report palladium chloride supported on HAp-encapsulated-$\gamma$-Fe$_2$O$_3$ (designate as PdMNPs (**4**) (Scheme 1) as an organic–inorganic hybrid supper magnetic nanocatalyst for the Heck-reaction of aryl halides with various olefins under phosphine-free conditions.
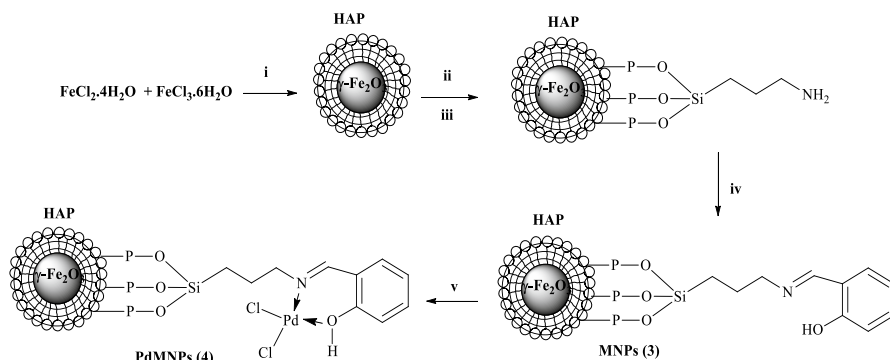


**Scheme 1**  (i) Ca(NO$_3$)$_2$, (NH$_4$)$_2$HPO$_4$, NH$_4$OH, (ii) calcination, (iii) 3-aminopropyltrimethoxysilane, toluene, reflux, 48 h, (iv) 2-hydroxy benzaldehyde, dry EtOH, reflux, 24 h, and (v) PdCl$_2$, EtOH, r.t., 12 h

## Experimental

### Apparatus and reagents

All materials were purchased from Merck and Fluka chemical companies and were used without any additional or further purification. The structures of MNP of Pd catalyst PdMNPs (**4**) were characterized by X-ray diffraction (XRD) (X-Pert MPD Philips diffractometer) with Co $K_\alpha$ ($\lambda = 1.7897$ Å) radiation. The thermal stability of the functionalized PdMNPs (**4**) was investigated by thermogravimetric analysis (TGA), differential scanning calorimetry (DSC) and differential thermal analysis (DTA). The thermogravimetric treatment of the specimen was scanned from 40 to 600 °C at the rate of 20 °C/min under Ar atmosphere by using TA-SDT Q600 instrument. $^1$H-NMR, and $^{13}$C-NMR spectra were performed on a Bruker Advance 300 and 400 MHz spectrometers in $CDCl_3$ using TMS as the internal standard. Fourier transform infrared (FT-IR) spectra were recorded on a Shimadzu FT-IR 8900 spectrophotometer operating in transmission mode on KBr pellets. The IR spectra in Nujol was recorded on a Thermo scientific model Nicolet is10 (USA) FT-IR spectrophotometer. The amount of palladium was determined on an ICP Varian VISTA-PRO (400–4000) inductively coupled plasma optical emission (ICP-OES) with axial injection. The morphology of PdMNPs (**4**) was performed using a TESCAN Model MIRA3 XMU VP-FESEM variable pressure field emission scanning electron microscope (FESEM) with scanning range from 3 to 30 keV. The magnetization measurement was carried out in a vibrating sample magnetometer/alternating gradient force magnetometer (VSM/AGFM, MDK Co., Ltd., Iran). The magnetization curves of the nanocatalysis were obtained in an external field up to 15 TESCAN model MIRA3 with detector SAMX. Melting points were determined on an Electrothermal IA9100 series. The ultraviolet–visible absorption spectra were recorded in the range 200–800 nm using SCINCO S4100 UV–Vis spectrophotometer. UV–Vis spectrophotometer SCINCO S4100 with diffuse reflectance accessory (integrated sphere) was used for spectrophotometric measurements and transmission electron microscopy (TEM) analysis was carried out by a Philips CM120 transmission electron microscope, operating at accelerating voltage of 100 kV with 100 mesh TEM grid.

### Synthesis of PdMNPs (4)

[$\gamma$-$Fe_2O_3$@HAp–Si–$(CH_2)_3$–$NH_2$] was synthesized by the literature report [24, 39] with some modifications and then was allowed to react with equimolar amount of 2-hydroxybenzaldehyde in dry ethanol for 24 h under Ar atmosphere. Afterwards, the solid product was magnetically separated by an external magnet and eluted with dry ethanol to produce the catalyst MNPs (**3**) (Scheme 1). A stirring blend of catalyst MNPs (**3**) (0.47 g) and $PdCl_2$ (0.084 g) in ethanol (15 mL) was kept at room temperature for 12 h. The resultant light brown precipitate was filtered, washed repeatedly with ethanol, and dried under vacuum at room temperature to produce catalyst PdMNPs (**4**) (0.5 g).

## General procedure for Heck cross-coupling

A mixture of aryl halide (1.0 mmol), olefin (1.5 mmol), TBAB (1 mmol, additive agent) PdMNPs (**4**) (0.0071 mmol), Et$_3$N (1.5 mmol) in DMF (2 mL) was stirred at 120 °C for 20 min. The progress of the reaction was monitored by TLC analysis. After the completion of the reaction, the catalyst was separated by an external magnet. Then, the catalyst was rinsed with DMF and resultant organic solution was evaporated under vacuum to produce a crude product which was purified by chromatography to furnish the desired products (Tables 2, 3, 4). The catalyst was washed by deionized water and EtOH (three times), dried at 100 °C and reused for the next run.

## NMR data for the selected products

### (E)-Methyl 3-(4-acetylphenyl) acrylate (4a)

Light-yellow solid, m.p. = 34–37 °C (lit. 32–36 °C [47]); FT-IR (KBr, cm$^{-1}$); 3045, 2959, 2922, 2854, 1713, 1686, 1551, 1427, 1097, 1036, 810; $^1$H NMR (400 MHz, CDCl$_3$): $\delta_H$ = 8.0 (d, $J$ = 8.4 Hz, 2H), 7.74 (d, $J$ = 16.0 Hz, 1H), 7.64 (d, $J$ = 8.4 Hz, 2H), 6.56 (d, $J$ = 16.0 Hz, 1H), 3.86 (s, 3H), 2.65 (s, 3H); $^{13}$C (100 MHz, CDCl$_3$); $\delta_C$ = 197.4, 167.0, 143.3, 138.7, 138.0, 128.9, 128.2, 120.3, 52.0, 26.8.

### (E)-Methyl 3-(4-methoxyphenyl)-2-methylacrylate (4b)

Pale-yellow oil (84%); FT-IR (KBr, cm$^{-1}$): 3010, 2954, 2842, 1708, 1604, 1444, 1309, 1251, 1180, 1177, 1027, 945, 827; $^1$H NMR (300 MHz, CDCl$_3$): $\delta_H$ = 7.69 (s, 1H), 7.52 (d, $J$ = 8.85 Hz, 2H), 6.92 (d, $J$ = 8.85 Hz, 2H), 3.86 (s, 3H), 3.84 (s, 3H), 2.17 (d, $J$ = 1.2 Hz, 3H); $^{13}$C (75 MHz, CDCl$_3$); $\delta_C$ = 170.5, 148.8, 137.7, 129.4, 127.4, 125.0, 112.9, 54.9, 52.0, 14.2.

### (E)-Methyl 3-(4-acetylphenyl)-2-methylacrylate (6b)

Light-yellow solid (87%), m.p. = 80–82 °C; FT-IR (KBr, cm$^{-1}$); 3012, 2920, 2852, 1720, 1681, 1627, 1602, 1556, 1434, 1357, 1305, 1263, 1114, 956, 838; $^1$H NMR (400 MHz, CDCl$_3$): $\delta_H$ = 7.98 (d, $J$ = 8.0 Hz, 1H), 7.70 (s, 1H), 7.49 (d, $J$ = 8.0 Hz 1H), 3.73 (s, 3H), 2.63 (s, 3H), 2.13 (s, 3H); $^{13}$C (100 MHz, CDCl$_3$); $\delta_c$ = 196.8, 169.8, 141.5, 138.3, 136.4, 129.8, 128.6, 127.4, 53.3, 27.5, 14.2.

## Result and discussion

### Synthesis of PdMNPs (4)

PdMNPs were synthesized by the conventional co-precipitation method with some modifications [24, 40–43]. Initially, Fe$_3$O$_4$ nanoparticles were synthesized

by using $FeCl_2 \cdot 4H_2O$ and $FeCl_3 \cdot 6H_2O$ as starting materials and ammonia as a precipitating agent. Based on our previous report [41] after coating a layer of hydroxyapatite on the surface of the $Fe_3O_4$ nanoparticles and its calcinations at 400 °C, it was functionalized by 3-aminopropyltrimethoxysilane to produce an organic–inorganic hybrid. Then, the prepared hybrid was reacted with 2-hydroxy-benzaldehyde to produce a bi-dentate ligand for functionalized core–shell magnetic nanocatalyst. Finally, surface-bound ligands were complexed with palladium(II) by using $PdCl_2$ to furnish PdMNPs (**4**) (Scheme 1).

## Characterization of PdMNPs (4)

### X-ray diffraction (XRD)

The phase and crystallite structure of PdMNPs (**4**) were studied using XRD. The diffraction peaks appeared at $2\theta = 30.2°, 35.3°, 37.3°, 41.6°, 46.8°, 54.7°, 67.6°$ and $74.7°$ are related to the planes of (002), (220), (112), (311), (111), (200), (511) and (440) (Fig. 1), the resulted patterns can be referred to $\gamma$-$Fe_2O_3$ (JCPDS No. 39-1346) and hydroxyapatite (JCPDS No. 24-0033). No other phases were detected, indicating the phase purity of the sample. The average crystallite size of PdMNPs (**4**) sample was estimated from the most intense peak (111) using the Scherer formula [44]:
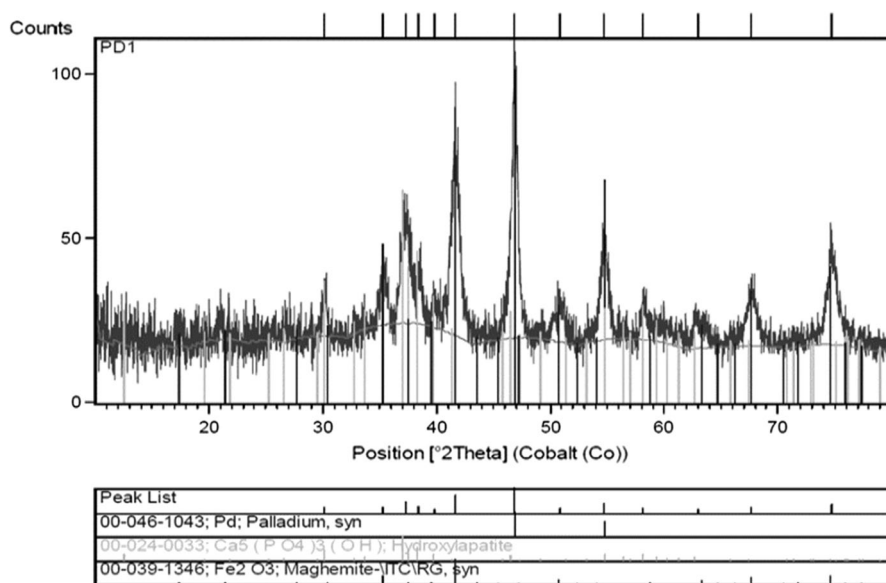


**Fig. 1** The X-ray diffraction spectrum of the PdMNPs (**4**). Powder XRD analysis was carried out on a Philips X-Pert MPD diffractometer with Co $K_\alpha$ ($\lambda = 1.7897$ Å) radiation at room temperature over $2\theta$ range 10°–80° at a scan rate of 0.1° $2\theta/s$

$$D_C = \frac{K\lambda}{\beta_{1/2}\cos\theta}.$$

Here $D_C$ is the crystallite diameter, K is the Scherrer constant (0.89), $\lambda$ is the X-ray wavelength (0.15418 nm), and $\beta_{1/2}$ is the full width at half maximum of the diffraction peak and $\theta$ is the diffraction angle of the peak. The average crystallite size of PdMNPs (**4**) was estimated to be around 21.3 nm.
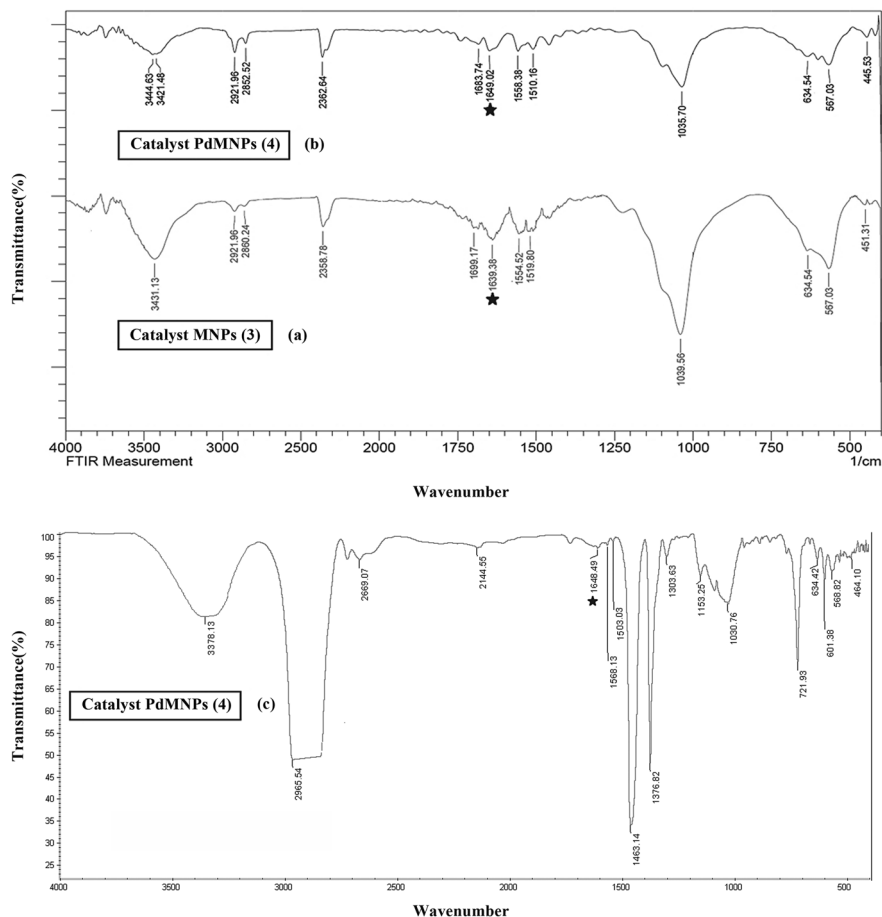


**Fig. 2** FT-IR spectrum of the catalyst MNPs (**3**) and PdMNPs (**4**). The FT-IR spectra (**a**, **b**) of the samples were recorded on a Shimadzu FT-IR 8900 spectrophotometer operating in transmission mode on KBr pellets. The samples were mixed with KBr and compressed into a pellet and placed into an IR cell. The spectra were recorded in the range of 400–4000 $cm^{-1}$ with a resolution of 4 $cm^{-1}$ at room temperature. Spectrum **c** was recorded in nujol

### Fourier-transform infrared spectroscopy (FT-IR)

FT-IR spectrum of the prepared nanocatalyst is shown in Fig. 2b (in KBr). The absorption peak at 445 cm$^{-1}$ can be assigned to the Fe–O absorption in the maghemite [45]. The O–P–O surface phosphate groups in the hydroxyapatite shell emerged at 567 and 604 cm$^{-1}$ which were in overlap with Fe–O stretching. The P–O stretching emerged at 1035 cm$^{-1}$. The bands at around 1510 and 1558 cm$^{-1}$ are associated to the aromatic C=C stretching also a band at 1649 cm$^{-1}$ produced by C=N double bond, verify that the organic linker exactly immobilized onto the surface. Note that the C=N band is shifted to a higher wave number compared to the C=N stretching frequency of MNPs (**3**) (Fig. 2a) (1649 cm$^{-1}$ rather than 1639 cm$^{-1}$). It is implying that C=N and OH groups are coordinated to Pd through the lone pair of N and O. FT-IR spectrum of the catalyst was also recorded in nujol (Fig. 2c). The bands related to OH (3378 cm$^{-1}$) and C=N (1648 cm$^{-1}$) groups of the ligand are evident in the spectra.

### Scanning electron microscopy (SEM)

The morphology and particle size of the PdMNPs were investigated by SEM micrograph (Fig. 3). The micrograph shows that the catalyst obviously showed the nano size of the particles and possesses a spherical shape. Also, the average size of the PdMNPs is around 23 nm (Fig. 3a, b) which is in good agreement with that of estimated by Scherrer's equation from XRD spectrum. Fig. 3c shows the presence of Pd in catalyst PdMNPs (**4**). The SEM image of the catalyst proved that after ten consecutive runs of the reaction, no change occurred in the shape and size of the nanoparticles (Fig. 3d).

The ICP-AES analysis was utilized for accurate determination of the palladium content in the synthesized PdMNPs (**4**). Analysis verified 0.71 mmol Pd g$^{-1}$ (7.54%) of the PdMNPs which is in consensus with the EDS consequence.

### Energy-dispersive X-ray spectroscopy (EDS)

EDS analysis spectrum for PdMNPs (**4**) presented in Fig. 4 reveals the existence of palladium in the structure. As is obvious from the Fig. 4 Ca, P, Fe, Si, Pd and Cl associated to the nanocatalyst structure, are seen in the spectrum. The proportion of palladium: chlorine: nitrogen in the spectrum is observed to be 4.03:1:2.15. The amount of palladium in the synthesized PdMNPs is 7.35% according to the EDS analysis, which is equivalent to 0.69 mmol of palladium per gram of PdMNPs.

### Vibrating sample magnetometer (VSM)

The magnetic property of the PdMNPs was studied using VSM technique (Fig. 5). Fig. shows the hysteresis loop of the PdMNPs at room temperature as the external magnetic field was changed from −10 to 10 KOe (−10,000 to 10,000 Oe). For super paramagnetic particles, the magnetization becomes zero when the external field approached zero. As it can be seen (Fig. 5) the hysteresis curve of PdMNPs
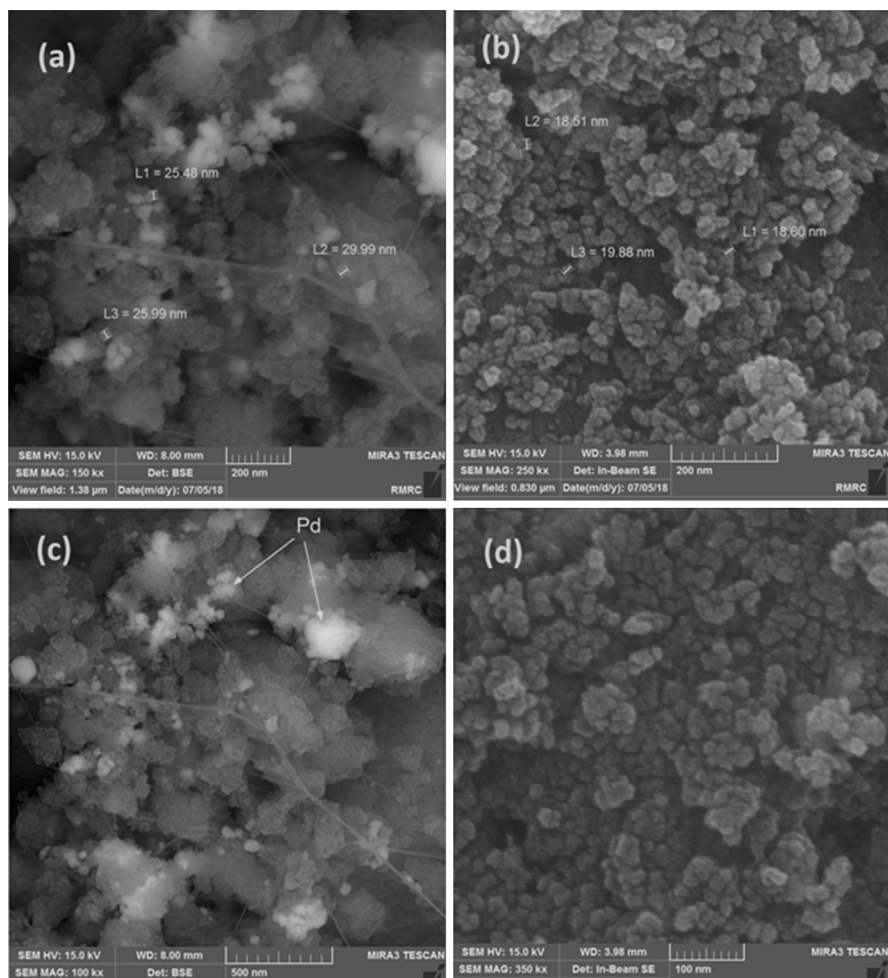
**Fig. 3** SEM image of the PdMNPs (**4**) (**a**, **b**) (nano particles with average size of 23 nm), SEM image shows the presence of palladium in MNPs (**c**), SEM image (after 10th cycle of the reaction) of the PdM-NPs (**4**) (**d**). Scanning electron microphotographs (SEM) were recorded by using a TESCAN Model MIRA3 XMU VP-FESEM variable pressure field emission scanning electron microscope (FESEM) with scanning range from 3 to 30 keV and an Au layer coating on carbon support

passed through the zero point of magnetization which confirms its super paramagnetic nature. The saturation magnetization (Ms) value of the synthesized PdMNPs is estimated to be approximately 24.65 emu g$^{-1}$.

### Thermogravimetric analysis (TGA)

The thermal analysis method is a potent tool for characterizing a system (element, compound or mixture) by measuring changes in physico-chemical properties at high temperatures as a function of increasing temperature. Thermal stability of PdMNPs
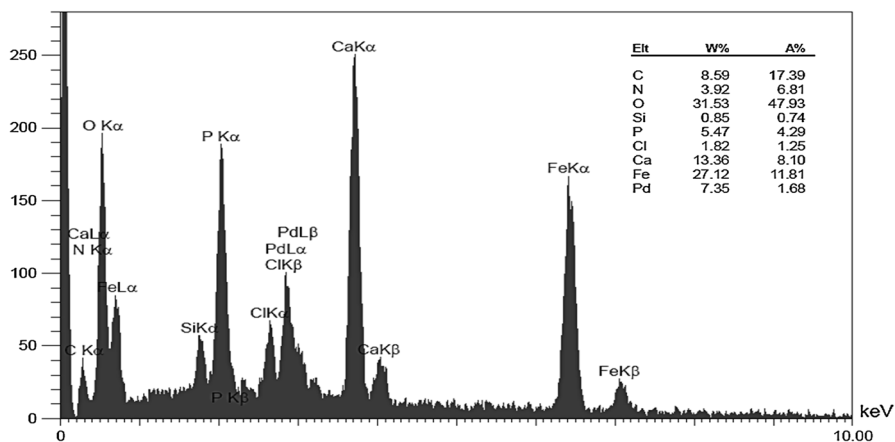
Fig. 4 EDS spectrum of the PdMNPs (**4**). The amount of palladium was determined on an ICP Varian VISTA-PRO (400–4000) inductively coupled plasma optical emission (ICP-OES) with axial injection
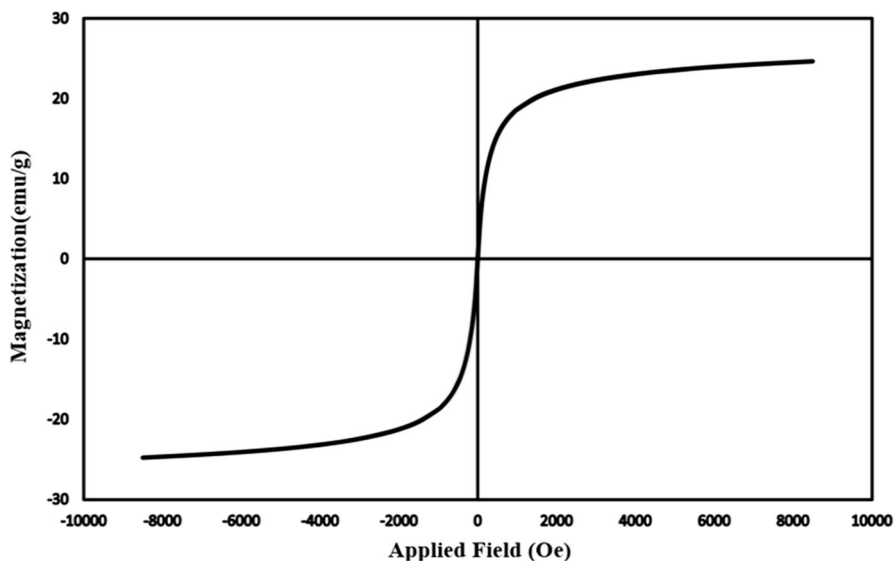


Fig. 5 Magnetization (M) as a function of field (H) for PdMNPs (**4**). The magnetization measurement was carried out in a vibrating sample magnetometer/alternating gradient force magnetometer (VSM/AGFM, MDK Co., Ltd., Iran). The magnetization curves of the nanocatalysis were obtained in an external field up to 15 TESCAN model MIRA3 with detector SAMX

(**4**) were performed by thermo gravimetric analysis (TGA), Differential thermal analyzer (DTA) and Differential scanning calorimetric (DSC) analyzer (Fig. 6). TGA with heating in a range altering from room temperature to 600 °C showed weight loss of 11.96%, which could be presumably related to the evaporation of the external water and decomposition of organic groups situated on the surface of PdMNPs (**4**).
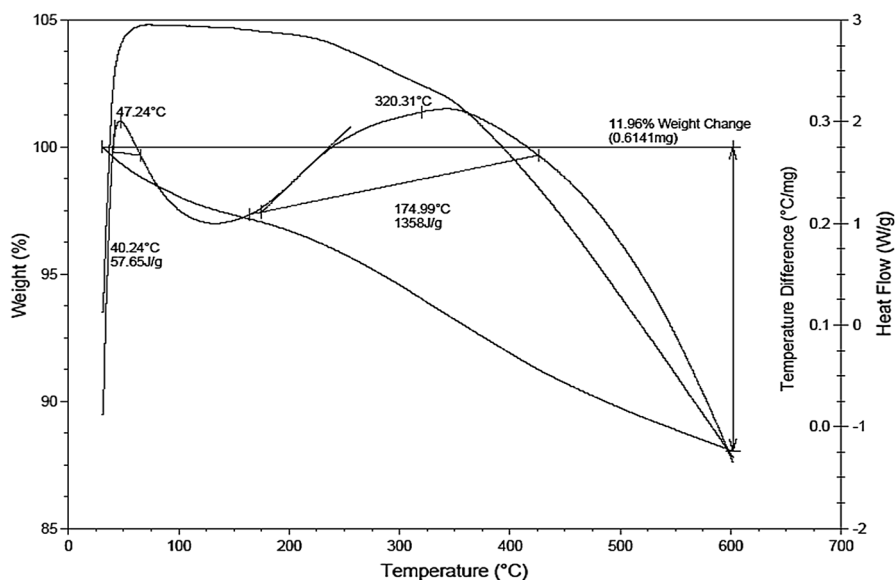
**Fig. 6** Total thermogram of the PdMNPs (**4**). Thermogravimetric analysis (TGA), differential scanning calorimetry (DSC) and differential thermal analysis (DTA) were measured by using TA-SDT Q600 instrument scanning from 40 to 600 °C at the rate of 20 °C/min under Ar atmosphere

## Diffuse reflection spectrometry analysis (DRS)

A different verification of permanency of PdMNPs (**4**) showed approximately the same diffuse reflectance spectra (DRS) before and after being used in the model reaction (Fig. 7). The experiments showed that PdMNPs (**4**) at high temperature were significantly remained constant without any changes. It is noteworthy that the PdMNPs (**4**) did not change much in catalysts weight and the efficiency of the products even after 10 times recovery. This fact is indicative of strong bonding between MNPs and palladium which lends support to the postulate of covalent bonds between these two components.

## Transmission electron microscopy (TEM)

TEM analysis of PdMNPs (**4**) is show in Fig. 8a. The present of ashy maghemite seeds that partially covered the smooth clusters of nanocatalyst is clear from the TEM. According to TEM image, the black palladium colloidal particles are well dispersed through the catalyst surface in average size distribution of 16.8 nm (Fig. 8b).
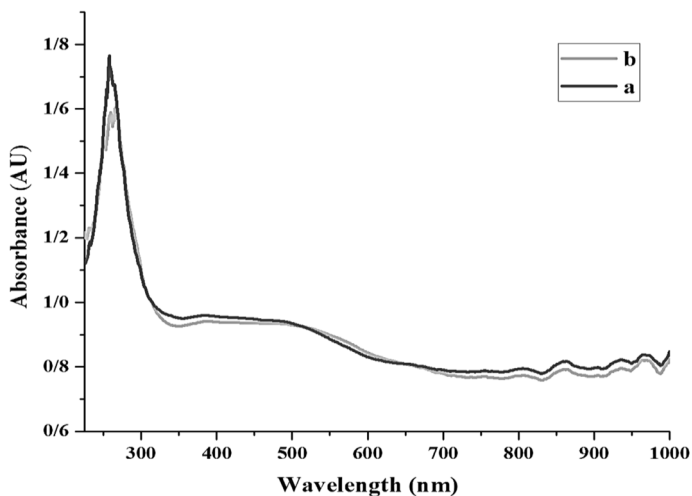
**Fig. 7** UV–Vis DRS spectra of PdMNPs (**4**) before (a) and after (b) using 10 consecutive runs in the model reaction. The ultraviolet–visible absorption spectra were recorded in the range 200–800 nm by using SCINCO S4100 UV–Vis spectrophotometer with diffuse reflectance accessory (integrated sphere)
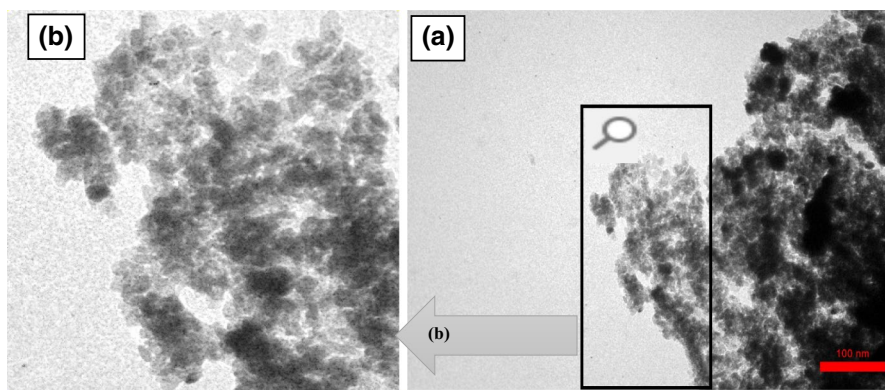


**Fig. 8 a** and **b** TEM micrographs of PdMNPs (**4**). TEM analysis was recorded using Philips CM120 microscope, operated with a 100 kV accelerating voltage with 100 mesh TEM grid

## Catalytic activity of PdMNPs (4) for the Heck-reactions

The Heck-coupling reaction of iodobenzene with methyl acrylate was chosen as the model reaction to evaluate the potential catalytic activity of PdMNPs (**4**). The optimization was performed with respect to solvent, base, temperature and additive by using PdMNPs as catalyst (Table 1). Due to the fact that in Heck reactions polar aprotic solvents are commonly used, $H_2O$, DMF, THF and EtOH/$H_2O$ solvents were selected. Among the solvents selected for the coupling reactions, DMF was preferred as the solvent of choice. When TBAB was added to the reaction

**Table 1** Optimization of the reaction parameters
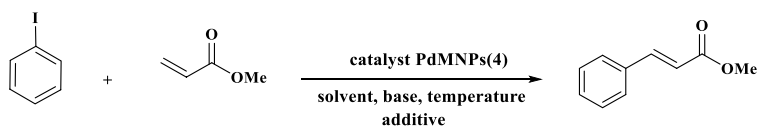


| Entry | Solvent | Base | Temperature (°C) | Additive | Time | Yield[a] (%) |
|---|---|---|---|---|---|---|
| 1 | H$_2$O | Et$_3$N | 100 | TBAB | 20 min | NR |
| 2 | Toluene | Et$_3$N | 110 | TBAB | 20 min | 60 |
| 3 | THF | Et$_3$N | 65 | TBAB | 20 min | 35 |
| 4 | EtOH/H$_2$O | Et$_3$N | 80 | TBAB | 20 min | NR |
| 5 | DMF | Et$_3$N | 120 | TBAB | 25 min | 93 |
| 6 | DMF | Et$_3$N | 120 | TBAB | 20 min | 93 |
| 7 | DMF | Et$_3$N | 120 | TBAB | 15 min | 85 |
| 8 | DMF | Et$_3$N | 120 | – | 20 min | NR |
| 9 | DMF | Et$_3$N | 100 | TBAB | 20 min | 75 |
| 10 | DMF | Et$_3$N | 50 | TBAB | 20 min | 30 |
| 11 | DMF | Et$_3$N | r.t. | TBAB | 20 min | NR |
| 12 | DMF | Na$_2$CO$_3$ | 120 | TBAB | 20 min | 78 |
| 13 | DMF | K$_2$CO$_3$ | 120 | TBAB | 20 min | 85 |
| 14 | DMF | K$_3$PO$_4$ | 120 | TBAB | 20 min | 64 |
| 15 | DMF | Bu$_4$NOH | 120 | TBAB | 20 min | NR |

Reaction conditions: iodobenzene (1.0 mmol), methyl acrylate (1.5 mmol), base (1.5 mmol), PdMNPs (**4**) (10 mg, 0.71 mol%), solvent (2 mL), TBAB (1 mmol)

[a]Isolated yields after purification by chromatography

in DMF, showed high selectivity for the *trans*-isomer products in all cases, and no *cis* products were observed. It should be noted that DMF plays a role as an appropriate polar solvent and a reducing agent for converting Pd(II) to Pd(0) to perform carbon–carbon coupling reactions the postulate which is also supported by the literature report [46]. Among the selected bases Na$_2$CO$_3$, K$_2$CO$_3$, Et$_3$N, K$_3$PO$_4$ and Bu$_4$NOH, organic base Et$_3$N had the highest and K$_3$PO$_4$ the lowest yield and Bu$_4$NOH no product. The investigations at different temperature within 50–120 °C were performed for the model reaction, which eventually 120 °C was chosen as optimal temperature. Under the optimized conditions by using DMF and Et$_3$N at 120 °C the reaction times were diversified to get the quantitative yield of product within 20 min for the reaction of iodobenzene and methyl acrylate (Table 1, Entry 6). The coupling reaction of iodobenzene and methylacrylate did not proceed in the absence of TBAB (Table 1, Entry 8). However, the addition of 1 mmol TBAB/mmol substrate, furnished the desired product in

excellent yield. TBAB as additive sustains palladium nanoparticles stability and therefore enhances its activity.

Obtaining an impressive result in the PdMNPs (**4**) catalyzed Heck-reaction of iodobenzene with methyl acrylate under optimization condition (Table 1, Entry 6), the protocol was applied to different palladium-catalyzed coupling reactions of aryl halides carrying either electron-donating or electron withdrawing groups in aromatic rings with terminal olefins (methyl acrylate, methyl methacrylate, *n*-butyl acrylate and vinyl acetate (Table 2). In all cases, the *trans*-products were selectively produced with no detectable trace of *cis*-isomer. As shown in Table 2, all products were obtained in short reaction times and high to excellent yields in the presence of PdMNPs (**4**).

A comparison of the efficiency of present PdMNPs (**4**) catalyst and some heterogeneous and homogenous palladium catalysts is given in Table 3. Evidently, the present catalyst is superior in terms of reaction time, TON and recyclability (Table 3, Entry 6). As it is clear from the results this work prevail over drawbacks of some other works such as longer reaction time, difficult reaction conditions and elimination of phosphine ligands.

The optimized amount of catalyst for the model reaction was found to be 0.71 mol%. A decrease in the amount of nanocatalyst reduced the yield but an increase in its amount did not have any appreciable effect on the overall yield of product (Table 4).

## Recyclability of the catalyst

After completion of the reaction, the PdMNPs (4) was separated from the reaction mixture by an external magnet and washed several times with DMF to ensure that all the products were separated from the nanoparticles. The residue was washed three times with deionized water and ethanol for further purification and finally, dried at 100 °C in the oven and used in the next run. Recyclability of the catalyst for the model reaction is shown in Fig. 9. The catalytic system exhibited a remarkable activity and maintained its catalytic performance during 10 successive cycles without perceptible reduction in the catalytic activity.
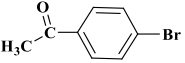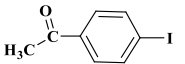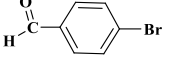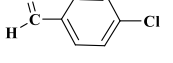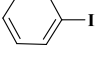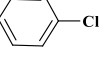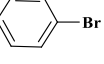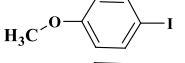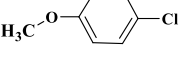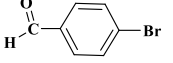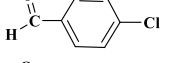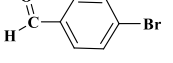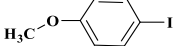
## Conclusion

A novel heterogeneous HAp-encapsulated-$\gamma$-Fe$_2$O$_3$-based Pd(II) organic–inorganic hybrid nanocatalyst was prepared and was used in the Heck cross-coupling reaction. This practical method gives rapid access to a range of Heck products under low palladium loadings, in lower reaction time and high to excellent yields. The catalyst is stable towards air and moisture and easily handled without any special precautionary measures and also benefits from several more advantages such as, easy recovery from the reaction system by using an external magnet, high recyclability in which 10 reuses did not result in appreciable decrease in its catalytic activities and avoiding the use of phosphine ligands.

**Table 2** Heck coupling reaction of aryl halides with olefines using PdMNPs (**4**)



X = I, Br, Cl   $R^1$ = CO$_2$M$_e$, CO$_2$B$_u$n, OAc
R = H, OMe, COMe COH   $R^2$ = H, Me
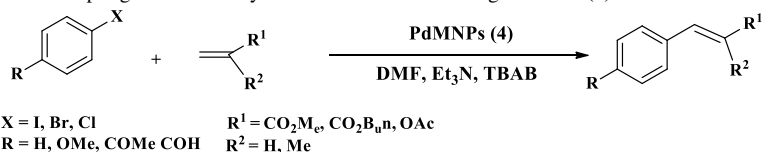
| Entry | Aryl halide | Alkenes | Yield[b, c] (%) | M.P (°C) | | TON[d] |
|---|---|---|---|---|---|---|
| | | | | Observed | Reported | |
| 1a |  | CO$_2$Me | 93 | 122-124 | 122-123 [47] | 131 |
| 2a |  | CO$_2$Me | 83 | 34-36 | 32-36 [48] | 117 |
| 3a |  | CO$_2$Me | 79 | 35-37 | 32-36 [48] | 111 |
| 4a |  | CO$_2$Me | 90 | 34-37 | 32-36 [48] | 127 |
| 5a |  | CO$_2$Me | 88 | 123-125 | 122-123 [47] | 124 |
| 6a |  | CO$_2$Me | 86 | 121-124 | 122-123 [47] | 121 |
| 7a |  | CO$_2$Me | 91 | 82-86 | 84-86 [48] | 128 |
| 8a |  | CO$_2$Me | 87 | 83-87 | 84-86 [48] | 122 |
| 9a |  | CO$_2$Me | 76 | 82-85 | 82-84 [48] | 107 |
| 10a |  | CO$_2$Me | 80 | 81-84 | 82-84 [48] | 112 |
| 1b |  | Me CO$_2$Me | 88 | Pale yellow-oil | Oil [49] | 124 |
| 2b |  | Me CO$_2$Me | 82 | Pale yellow-oil | Pale yellow-oil[50] | 115 |
| 3b |  | Me CO$_2$Me | 80 | Pale yellow-oil | - | 112 |
| 4b |  | Me CO$_2$Me | 84 | Pale yellow-oil | - | 118 |
| 5b |  | Me CO$_2$Me | 86 | Pale yellow-oil | - | 121 |

**Table 2** (continued)

| Entry | Aryl halide | Alkene | Yield | mp / appearance | Lit. | TON |
|---|---|---|---|---|---|---|
| 6b | H₃C–C(=O)–C₆H₄–Br | =⟨Me, CO₂Me | 87 | 80-82 | - | 122 |
| 7b | H₃C–C(=O)–C₆H₄–I | =⟨Me, CO₂Me | 89 | 79-81 | - | 125 |
| 8b | H–C(=O)–C₆H₄–Br | =⟨Me, CO₂Me | 80 | Colorless oil | Oil [50] | 112 |
| 9b | H–C(=O)–C₆H₄–Cl | =⟨Me, CO₂Me | 76 | Colorless oil | Oil [50] | 107 |
| 1c | C₆H₅–I | $=\!\!-CO_2Bu^n$ | 90 | Colorless oil | Oil [51] | 126 |
| 2c | C₆H₅–Cl | $=\!\!-CO_2Bu^n$ | 85 | Colorless oil | Oil [49] | 119 |
| 3c | C₆H₅–Br | $=\!\!-CO_2Bu^n$ | 88 | Colorless oil | Oil [51] | 124 |
| 4c | H₃C–O–C₆H₄–I | $=\!\!-CO_2Bu^n$ | 91 | Colorless oil | Oil [51] | 128 |
| 5c | H₃C–O–C₆H₄–Cl | $=\!\!-CO_2Bu^n$ | 88 | Colorless oil | Oil [51] | 124 |
| 6c | H–C(=O)–C₆H₄–Br | $=\!\!-CO_2Bu^n$ | 82 | 106-109 | 108-109[52] | 115 |
| 7c | H–C(=O)–C₆H₄–Cl | $=\!\!-CO_2Bu^n$ | 80 | 106-107 | 108-109[52] | 112 |
| 1d | H–C(=O)–C₆H₄–Br | =–OAc | 72 | Colorless oil | Oil [53] | 101 |
| 2d | H₃C–O–C₆H₄–I | =–OAc | 53 | Colorless oil | Oil [53] | 74 |

Reaction conditions: aryl halide (1.0 mmol), alkene (1.5 mmol), Et₃N (1.5 mmol), PdMNPs (**4**) (10 mg, 0.71 mol%), DMF (2 mL), TBAB (1 mmol) added, at 120 °C

[b]Isolated yields after TLC purification by silica gel plates

[b]Reaction times 20–30 min

[c]Turn over number (TON) based on the number of mole of isolated product

**Table 3** Comparison of PdMNPs (**4**) catalyst with some heterogeneous and homogeneous catalysts for the Heck reaction of iodobenzene and methyl acrylate

| Entry | Catalyst | Loading | Time | Yield (%) | Reusability | References |
|---|---|---|---|---|---|---|
| 1 | Catalyst I-Pd | 300 mg | 24 h | 90 | No | [54] |
| 2 | PdNP/α-ZrPK | 0.1 mol% | 3 h | 98 | 6 Cycles | [55] |
| 3 | SBA-TMG-Pd | 0.01 mol% | 65 min | 91 | 7 Cycles | [49] |
| 4 | Pd(OAc)$_2$ | 4.45 mol% | 6 h | 78 | No | – |
| 5 | PdCl$_2$ | 5.63 mol% | 12 h | 62 | No | – |
| 6 | PdMNPs (**4**) | 0.71 mol% | 20 min | 93 | Successful in 10 cycles | This work |

**Table 4** Optimization the amount of applied supported PdMNPs (**4**) in the model reaction
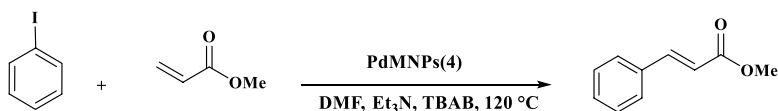
| Entry | PdMNPs (mg, mol%) | Time (min) | TON[a] | Yield[b] (%) |
|---|---|---|---|---|
| 1 | None | 20 | – | NR |
| 2 | 15, 1.1 | 20 | 85 | 94 |
| 3 | 10, 0.71 | 20 | 131 | 93 |
| 3 | 7, 0.5 | 20 | 170 | 85 |
| 4 | 5, 0.36 | 20 | 222 | 80 |

Reaction conditions: iodobenzene (1.0 mmol), methyl acrylate (1.5 mmol), Et$_3$N (1.5 mmol), PdMNPs (**4**) (as table), DMF (2 mL), TBAB (1 mmol), 120 °C

[a]Turn over number (TON) based on the number of mole of isolated product

[b]Isolated yields after TLC purification by silica gel plates

**Fig. 9** Recyclability of PdMNPs (**4**) in the model reaction. Reaction conditions: iodobenzene (1.0 mmol), methyl acrylate (1.5 mmol), Et$_3$N (1.5 mmol), PdMNPs (**4**) (10 mg, 0.71 mol%), DMF (2 mL), TBAB (1 mmol), 120 °C
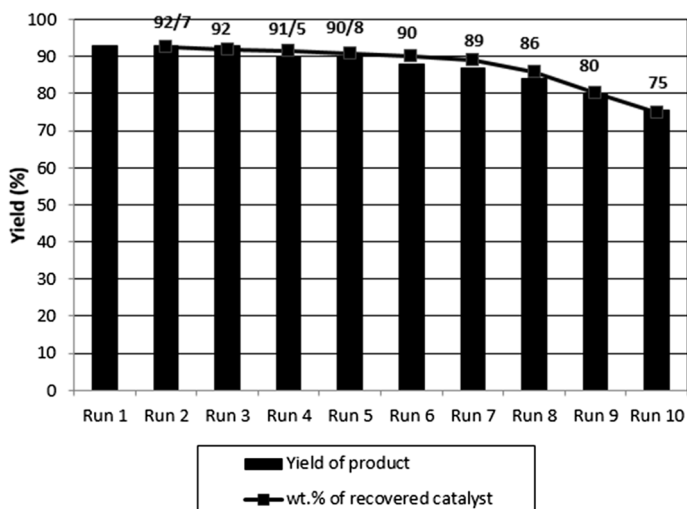
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