



Palladium nanoparticle supported on cobalt ferrite: An efficient magnetically separable catalyst for ligand free Suzuki coupling

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ABSTRACT

Synthesis of Pd nanoparticle supported on cobalt ferrite magnetic nanoparticles has been achieved by direct addition of Pd nanoparticles during synthesis of cobalt ferrite nanoparticles by ultrasound assisted co-precipitation in the absence of any surface stabilizers or capping agent. The catalytic performance of the Pd incorporated cobalt ferrite nanoparticles was examined in Suzuki coupling reaction in ethanol under ligand free condition. The reaction undergoes with low catalyst loading (1.6 mol%) and the catalyst could be recovered using an external magnet and reused for multiple cycles with sustained catalytic activity.

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1. Introduction

Recently, magnetic nanoparticles (MNPs) supported catalyst have been efficiently employed as heterogeneous catalysts for various organic transformations [1,2]. In particular, various magnetic nanoparticle-supported Pd-catalyst has been widely employed for promoting different organic reactions [3–11]. However, in most cases, palladium is immobilized on to the modified surface of the MNPs. The magnetic cores of these particles are generally capped with suitable capping agents rendering their stability and dispersibility to organic solvent. The catalysts species can be loaded onto the magnetic supports either by post modification of MNP shells or by co-precipitation during the MNPs synthesis [12]. The use of these magnetic nanoparticle catalysts can address the isolation and re-cycling problem encountered in many heterogenous and homogenous catalytic reactions [13–17]. Most importantly, the MNPs-supported catalysts show not only high catalytic activity but also a high degree of chemical stability and they do not swell in organic solvents. It is noteworthy that, although the surface coated MNPs offers good catalytic activity in many organic reactions, the coating may decrease magnetization and stability of the magnetic core by altering interparticle interactions which in turn reduce effective surface area and hence catalytic efficacy [2]. Iron oxide nanoparticles such as magnetite (Fe_3O_4) and maghemite ($\gamma\text{-Fe}_2\text{O}_3$) are commonly used for both catalyst supports and biomedical

applications [18]. However, other paramagnetic or ferromagnetic nanoparticles are less studied [19–23]. Although, the Fe_3O_4 could be easily prepared and has been efficiently utilized in many organic reactions [4,10,24,25], it is fairly reactive to acidic environment [9] and $\gamma\text{-Fe}_2\text{O}_3$ is also not thermally stable [26] and hence coating on the magnetic core is mandatory. On contrary, the CoFe_2O_4 is a typical ferromagnetic oxide with spinel structure which has high thermal stability, large magnetic anisotropy, moderate saturation magnetization, remarkable chemical stability and mechanical hardness [27,28]. Although the CoFe_2O_4 magnetic core as catalyst or support has been used recently [13,29–32], the surface of the CoFe_2O_4 magnetic particles was coated with the catalytic species in the presence of surface capping agents. Recently, we have reported the synthesis of highly stable CoFe_2O_4 MNPs without using organic capping agent or surface stabilizer [33]. Herein, we wish to prepare Pd incorporated CoFe_2O_4 nanoparticles by addition of Pd NPs to the reaction mixture during synthesis of CoFe_2O_4 by co-precipitation method under ultrasonic irradiation without using any surface stabilizer. The catalytic property of the synthesized magnetic palladium particles was evaluated for Suzuki coupling reaction.

The palladium-catalyzed Suzuki coupling reaction is generally performed under an inert atmosphere because the catalytic species are sensitive to oxygen or moisture [34]. There are also several reports in the literature for the Suzuki coupling reaction which have the attractive attributes such as the commercial availability, the air and water stability, and the nontoxic nature of boronic acids and catalysts [35]. Normally, homogenous catalysts used for Suzuki reaction are based on various Pd complexes [36–38] along with some ligands, such as phosphines [39], dibenzylideneacetone (dba)

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[40] and carbenes [41]. Some homogeneous Pd catalyzed methodologies for Suzuki reaction under ligand free condition have also been developed [42–46]. However, high cost of the Pd complexes and difficulty in recovery of the catalyst make these procedures embarrassing. Due to the inherent advantages of recovery and reuse, several Pd-based heterogeneous catalysts for Suzuki reaction have been developed. Various supports such as carbon [47], clays [48,49], zeolites [50–52], mesoporous silica [53] and metal oxides [54] were used for immobilization of Pd complexes or nanoparticles for Suzuki coupling reactions. The serious drawback in many of these cases is that additional steps must be taken to remove the leached metals and ligands released from the decomposed catalyst. The use of magnetic nanoparticle supported Pd-catalysts have also been addressed in recent times for the Suzuki coupling reaction [4,5,11,55–59] so that the catalysts can be easily separated magnetically and reused. However, the use of toxic organic chemicals such as toluene, DMF, dioxane and xylene is required either in preparation of the catalyst or to catalyze the reactions. Moreover, in most cases, specific functionalization procedures were inevitably adopted to anchor the active Pd species onto the magnetic support. Therefore, developing an efficient and ligand free Suzuki coupling reaction with Pd-based MNPs in a green chemical process is of our special interest. In this article, we report the direct use of CoFe_2O_4 MNPs to support Pd NPs without using any protecting or functionalizing agent and useful in Suzuki cross-coupling reaction under ligand free and aerobic conditions. The new catalyst is well-dispersed in reaction medium (ethanol), highly efficient, environmentally benign, magnetically recoverable and reusable without considerable change in activity.

2. Experimental

The chemicals and solvents used are of reagent grade purchased from Merck Chemicals and used as purchased. The palladium acetate was purchased from Sigma–Aldrich Pvt. Ltd.

2.1. Synthesis of Pd NPs

Prior to incorporation of palladium into CoFe_2O_4 MNPs, palladium nanoparticles (Pd NPs) were synthesized. Then the Pd NPs were incorporated into CoFe_2O_4 MNPs during their synthesis by ultrasonication assisted co-precipitation method.

Pd NPs with narrow size distribution were synthesized following the method reported by Wang et al. [60]. $\text{Pd}(\text{OAc})_2$ (0.05 g, of 2.2×10^{-4} M) was added into poly (ethyleneglycol) (4 g of PEG-400, 2.0×10^{-4} M). The reaction mixture was then stirred in a magnetic stirrer at 80°C for 1 h. The resulting light yellow homogeneous solution was further stirred for 2 h at the same temperature during which the color of the solution slowly turned from light yellow to gray dark, indicating the formation of Pd NPs. The as-synthesized PEG stabilized Pd NPs was then solidified by cooling at room temperature. The Pd NPs were then dispersed in dry ethanol by sonication. The dispersion was further centrifuged at 14,000 rpm at 10°C and the separated particles were washed properly with ethanol. The particles were dried under vacuum and preserved for further use.

2.2. Synthesis of Pd incorporated CoFe_2O_4 magnetic nanoparticles (Pd– CoFe_2O_4 MNPs)

The Pd incorporated CoFe_2O_4 nanoparticles were synthesized by adding Pd NPs in to the reaction mixture of CoFe_2O_4 during its synthesis. The CoFe_2O_4 NPs were synthesized following our previously reported sonochemical assisted co-precipitation method [33,61]. For this, two aqueous solutions of FeCl_3 (9.3 mmol, 50 mL) and $\text{CoCl}_2 \cdot 6\text{H}_2\text{O}$ (4.2 mmol, 50 mL) in distilled de-ionized water

were mixed in a 200 mL flat bottom flask and placed in an ultrasonic bath. An aqueous NaOH solution (3 M, 25 mL) was added drop-wise under argon atmosphere with continuous ultrasonic irradiation (frequency 40 kHz and power of 40 kW). Prior to mixing, all these three solutions were sonicated for 30 min to remove dissolved oxygen. The temperature of the sonicator bath was raised up to 60°C and the mixture was further sonicated for 30 min in air atmosphere. The black precipitate formation was observed during that time. To the reaction mixture, was then added the dispersion of the as-synthesized Pd NPs in ethanol and the reaction temperature was slowly brought to 80°C . The mixture was further kept under sonication for 1 h and then slowly cooled down to room temperature. The black precipitate was then separated by centrifugation at 15,000 rpm for 15 min, washed several times with both distilled water and ethanol and kept overnight in an incubator at 60°C . The precipitate was then further dried in an oven at 100°C for nearly an hour and subsequently kept in highly evacuated environment (10^{-2} bar) for another 1 h. At this stage the product (Pd doped CoFe_2O_4) contains some associated water which was then removed by heating the product at 200°C for 6 h and preserved in desiccator for further analysis. The whole procedure was repeated twice to check the reproducibility. The synthesized sample by this method was denoted as Pd– CoFe_2O_4 MNPs.

2.3. Characterization

The as-synthesized nanoparticles were characterized by scanning electron microscopy (SEM, LEO 1430 VP), field emission scanning microscopy (FESEM, Carl Zeiss, SIGMA), transmission electron microscopy (200KV TEM, JEOL JEM2100) and X-ray diffraction measurement (XRD, Bruker AXS D8). The formation cobalt ferrite particles were first ascertained by electron dispersive X-ray (EDX, Oxford INCA X-ray microanalysis) analysis combined with the scanning electron microscope (SEM). For SEM or FESEM analysis, the sample in ethanol dispersion was fixed on aluminum stub, air dried and then mounted in the instrument. In SEM analysis, the sample was scanned by electron beam at an accelerating voltage of 10–20 kV and a working distance of 10–15 mm using secondary electron detector. The image was captured at the resolution of 1–100 nm with the magnification of 15–30K \times . In FESEM, the sample was scanned by electron beam at low accelerating voltage of 2–5 kV at a working distance of 2–4 mm using inlens detector. The image was taken at the resolution of 300–100 nm with the maximum magnification of 200K \times . The sample for TEM analysis was prepared by taking a micro drop of dilute ethanolic solution of the particles deposited on a carbon-coated copper grid (400 mesh size) and allowed to dry in air. The nanoparticle formed was observed at bright field TEM images at the resolution of 300–20 nm with the magnification of 50–200K \times . The crystalline nature of the nanoparticles formed was further investigated by HRTEM and SAED pattern. The magnetic properties of the Pd– CoFe_2O_4 MNPs were analyzed in a vibrating sample magnetometer (VSM, Lakeshore 7410). The VSM measurement was done by taking 0.02 g of solid sample fixed to the tips of the vibrating rod and analyzed at room temperature. The IR spectrum was recorded in the range from 400 to 4000 cm^{-1} , using FT-IR spectrophotometer (Perkin Elmer Spectrum One) on KBr pellet. The UV–vis measurement was done using a Varian made Carry 50 UV–vis Spectrophotometer. The specific surface area and porosity were measured in a Backman Coulter Surface Area and Pore Size Analyzer (SA 3100). For this, the sample was first degassed for 2 h at 200°C and then BET analysis was performed.

The products in Suzuki reaction were characterized by comparing the NMR (Varian 400 MHz FT-NMR) and Mass (LCMS; Waters Q-ToF Premier) spectra with those reported in literature.

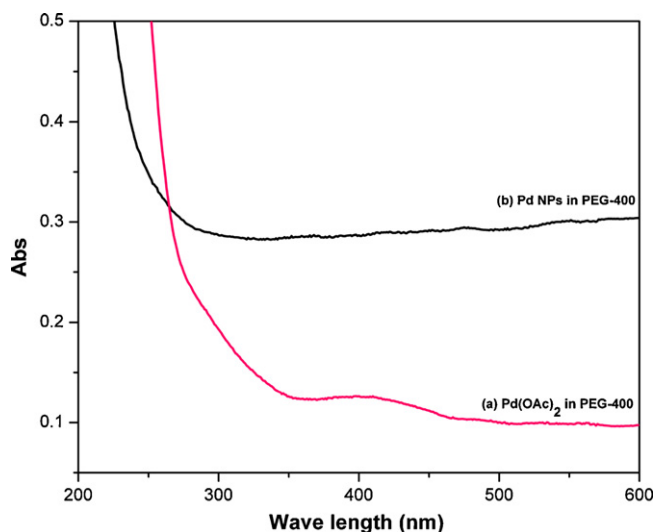


Fig. 1. UV-vis spectra of (a) Pd(OAc)₂ in PEG-400, and (b) Pd NPs in PEG-400.

2.4. General procedure for Suzuki reaction catalyzed by Pd–CoFe₂O₄ MNPs

In a typical reaction, to a solution of 0.5 mmol of the aryl halide in 5 mL of dry ethanol was added 0.75 mmol of phenyl boronic acid, 133 mg of Na₂CO₃ (1.25 mmol) followed by 2 mg of the as-synthesized catalyst (1.6 mol%). The mixture was then stirred under

reflux condition in oil bath for 6–12 h. The reaction was monitored by thin layer chromatography (TLC). After completion of reaction, the reaction mixture was cooled to room temperature and the catalyst (MNPs) was recovered by external magnet and washed with ethanol. The combined organic layer was dried over anhydrous sodium sulfate (Na₂SO₄) and evaporated in a rotary evaporator under reduced pressure. The crude product was purified by flash chromatography on silica gel (230–400 mesh) with hexane as eluting solvent.

3. Results and discussion

3.1. Synthesis of Pd incorporated CoFe₂O₄ MNPs

The formation of Pd NPs was observed from UV-vis spectrophotometric measurement (200–600 nm) as shown in Fig. 1 and subsequently by FESEM and TEM (Fig. 2(a–d)). The complete disappearance of peak at 400 nm in the UV-vis measurement revealed the full conversion of Pd (II) to palladium nanoparticles (Pd NPs). The SEM morphology visualized the presence of PEG-stabilized very uniform narrow size distributed Pd NPs of spherical morphology with the elemental contributions from Pd, C and O in the EDX spectra (Fig. 2b). The high magnification TEM image of Pd NPs showed that Pd NPs of 5–10 nm sizes were formed and clustered together.

The CoFe₂O₄ MNPs were synthesized by a combined sonochemical and co-precipitation technique in aqueous medium without any surfactant or organic capping agent. The synthesis was carried out in an alkaline pH with repeated ultrasonic irradiation.

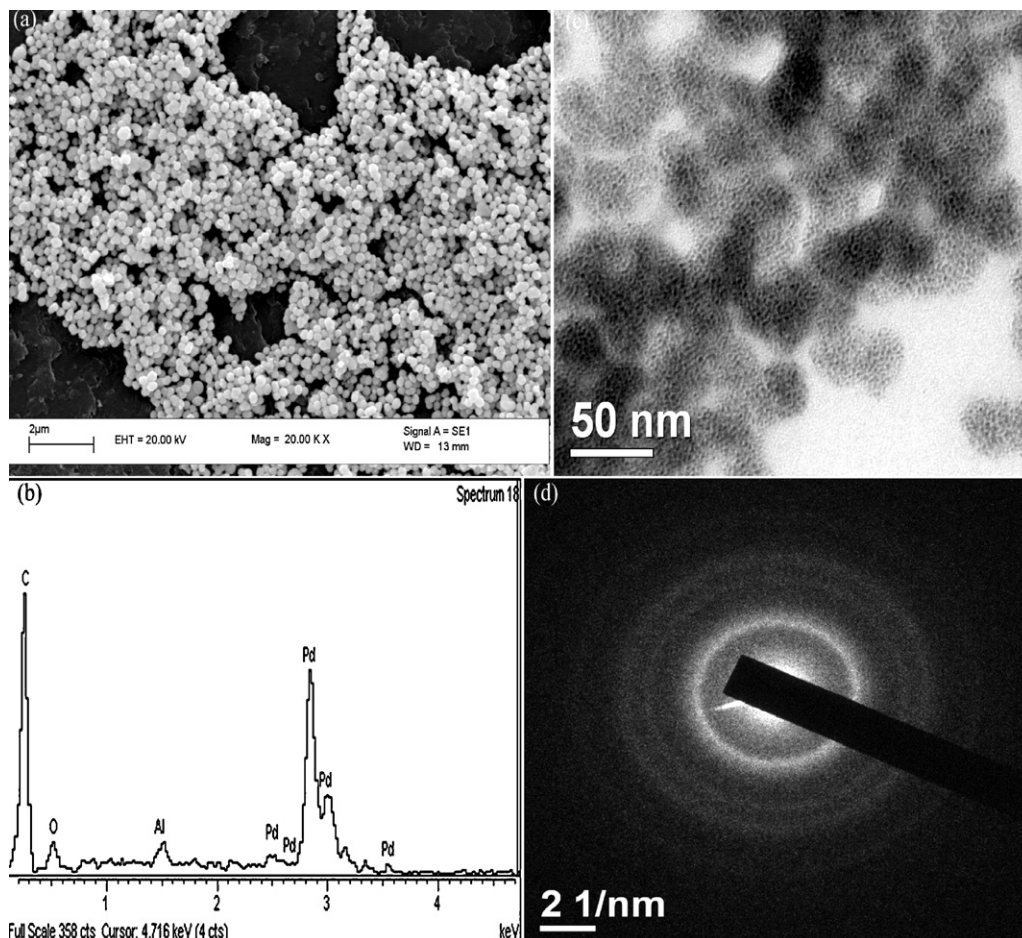


Fig. 2. SEM with EDX (a and b) and TEM image with SAED (c and d) of Pd NPs.

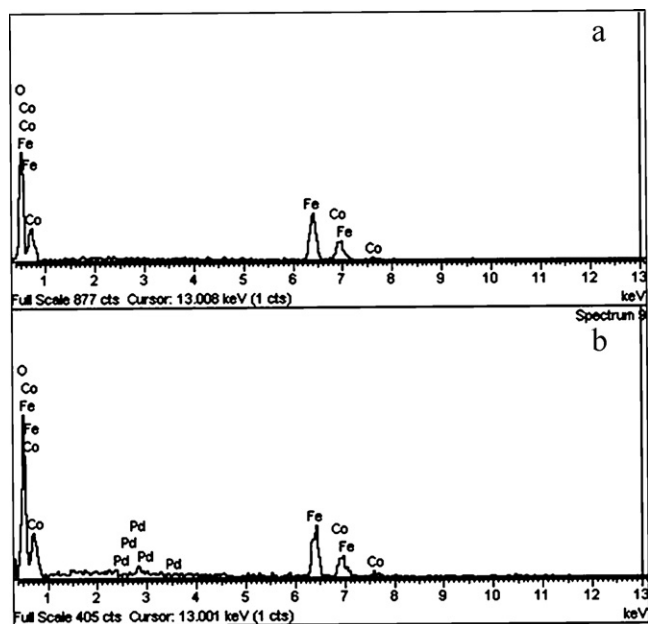


Fig. 3. EDX analysis of (a) CoFe_2O_4 MNPs and (b) $\text{Pd-CoFe}_2\text{O}_4$ MNPs.

After determining the elemental composition of the black particles of CoFe_2O_4 formed at the initial stage by EDX analysis, the as-synthesized Pd NPs were added. The EDX analysis of Pd incorporated CoFe_2O_4 MNPs ($\text{Pd-CoFe}_2\text{O}_4$ MNPs) (Fig. 3b) showed that the distribution of the elements (atomic percent) in the product was Co = 11.03%, Fe = 22.77%, O = 65.06% and Pd = 1.13%. The iron/cobalt ratio in the nanoparticles by EDX was found to be 2.06 which is very much close to the atomic ratio in the formula CoFe_2O_4

with 1% Pd incorporation. Similarly, the EDX analysis for CoFe_2O_4 MNPs (Fig. 3a) gave the elemental distribution of Co = 12.38%, Fe = 24.27%, O = 62.09% with the nearly same atomic ratios as in CoFe_2O_4 molecule.

We studied the morphology of the $\text{Pd-CoFe}_2\text{O}_4$ MNPs in FESEM and TEM measurements (Fig. 4a and b). Fig. 4b shows the TEM image of $\text{Pd-CoFe}_2\text{O}_4$ MNPs deposited on carbon coated copper grid at 100 nm resolution. The average particle sizes were measured in FESEM and TEM micrographs and were found to be in the range of 40–50 nm.

The XRD measurement of CoFe_2O_4 MNPs (Supporting Information) indicates the presence of all the characteristic peaks with relative intensities of all patterns matching well with a cubic spinel structure (JCPDS – International center diffraction data, PDF cards 3-864 and 22-1086) [62,63]. XRD measurement was carried out using $\text{Cu K}\alpha$ radiation ($\lambda = 1.54178 \text{ \AA}$) giving a scan from 10° to 70° (2θ) at a speed of $5^\circ/\text{min}$. The crystallite size for the nanoparticles obtained from the XRD pattern using scherrer's formula [64] was found to be $40 \pm 5 \text{ nm}$ which was consistent with the particle size obtained from the FESEM and TEM micrographs. The crystalline nature of the synthesized nanoparticles was inferred from HRTEM and SAED patterns (Fig. 4c and d).

The magnetic properties of the as prepared $\text{Pd-CoFe}_2\text{O}_4$ MNPs were investigated by VSM measurement. Fig. 5 shows the M–H loop taken at room temperature with a maximum applied field of $\pm 2 \text{ T}$. From the hysteresis loop both saturation magnetization (M_s) and coercivity values (H_c) were extracted. Coercivity, H_c of 1409 Oe with the corresponding saturation magnetization, M_s of 52.6 emu g^{-1} was obtained which indicates the ferromagnetism of the nanoparticles.

Next, the surface area and porosity of the $\text{Pd-CoFe}_2\text{O}_4$ MNPs were measured using Brunauer–Emmett–Teller (BET) equation [65] following the Barrett–Joyner–Halanda (BJH) method [65].

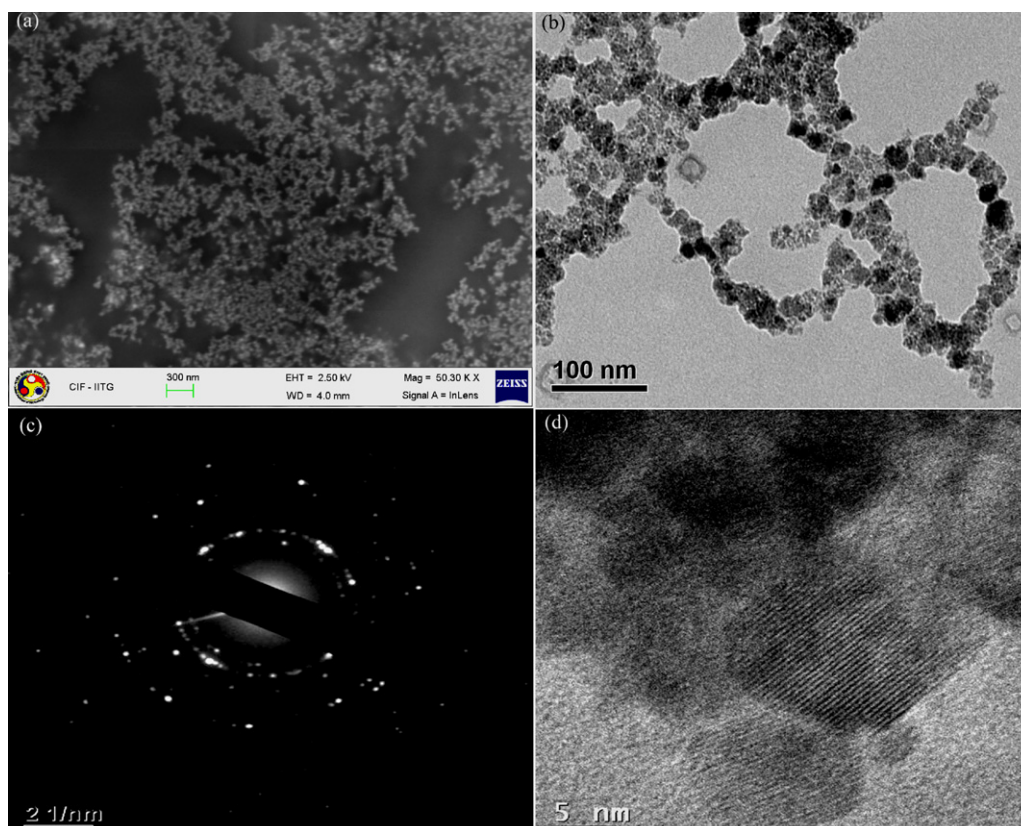


Fig. 4. (a) FESEM and (b) TEM image of $\text{Pd-CoFe}_2\text{O}_4$ MNPs with the (c) SAED pattern and (d) HRTEM image.

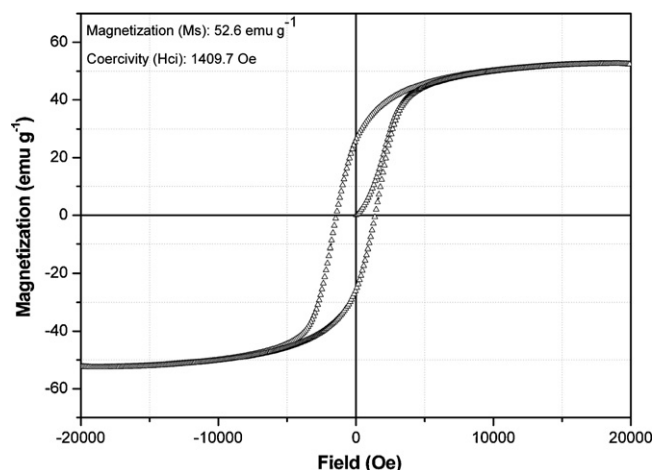


Fig. 5. M–H loop in VSM measurement of Pd–CoFe₂O₄ MNPs at room temperature.

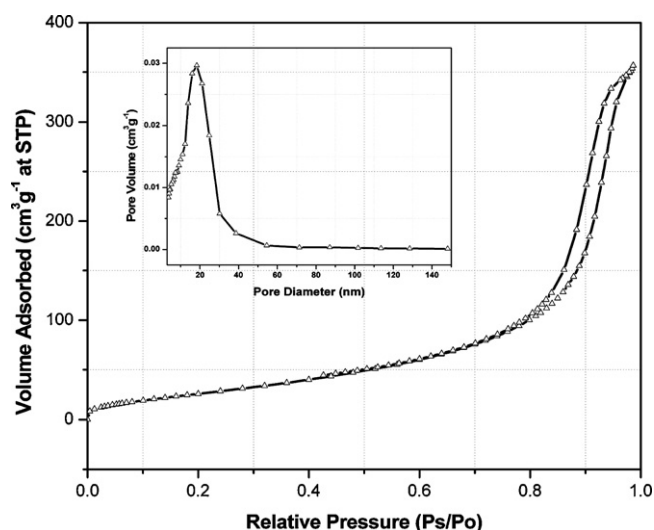


Fig. 6. (a) BET surface area and inset, (b) pore size distribution of Pd–CoFe₂O₄ MNPs.

From the N₂ adsorption–desorption isotherm of Pd–CoFe₂O₄ MNPs in Fig. 6, the BET surface area of the particles is 102 m² g^{−1} as calculated by linear part of the BET plot, which is much higher than CoFe₂O₄ nanoparticles [33,66]. The total pore volume at $P/P_0 = 0.98$ is 0.5427 cm³ g^{−1}. The BET isotherm is of type II and H3 hysteresis loop (BDDT/IUPAC classification) is the characteristic of mesoporous adsorbents [67].

The as synthesized MNPs and their ethanolic dispersion formed by this ultrasound promoted co-precipitation methods are quite

stable for longer period which is evident from the micrographs of electron microscopy analyzed after one month. The catalyst surface were further examined with the help of FT-IR spectra (Supplementary file), which shows two broad absorption peaks centered around 3419 cm^{−1} and 1620 cm^{−1} along with other characteristic peaks of spinel ferrite. These two peaks are due to excessive hydroxyl ions entrapped in the surface of the MNPs and create surface polarity. This may happen due to ultrasonic treatment during synthesis of the MNPs in aqueous medium and this surface property of the MNPs accounts for stable dispersion in ethanol. This behavior of the catalyst surface in case of CoFe₂O₄ MNPs synthesized by the same protocol has been reported in details in our previous report [33].

3.2. Suzuki reaction catalyzed by Pd incorporated CoFe₂O₄ MNPs

The catalytic activity of the synthesized Pd incorporated CoFe₂O₄ MNPs were examined for Suzuki cross-coupling reaction. Initial experiments were performed for the reaction of iodobenzene with phenyl boronic acid in the presence of a catalytic amount of CoFe₂O₄ MNPs. In general, phosphines are used as a promoting ligand for many Pd-catalyzed reactions [68]. We have carried out the reaction under phosphine-free condition in ethanol at reflux temperature in the presence of Na₂CO₃ under aerobic conditions.

To standardize the reaction conditions, we performed a series of reactions with several bases, solvents, temperatures and catalyst concentration to obtain the best possible combination. Initially, the reaction was performed using 0.5 mmol of iodobenzene, 0.75 mmol of phenyl boronic acid, and 1.25 mmol Na₂CO₃ in the presence of 1.6 mol% of Pd–CoFe₂O₄ MNPs by refluxing in ethanol and monitored by TLC. The reaction was completed in 12 h with a yield of 81%. When the reaction was carried out in water and ethylene glycol (EG) under the same reaction conditions, yields were very low i.e. 30% and 20% respectively. The reactions were also carried out under the same conditions using different bases such as K₂CO₃, K₃PO₄ and CsCO₃ and the yields were 80%, 68% and 30% respectively (Table 1: entries 4, 5, 6). The yields were not satisfactory in water and aqueous ethanol under the same reaction condition. The reaction at room temperature was found to be very slow and completion of reaction was observed only after 52 h with 72% yield. The results for optimum reaction condition are summarized in Table 1. Hence, an optimum of 1.6 mol% (0.16 mol% of Pd) of Pd–CoFe₂O₄ catalyst (based on iodobenzene) in the reaction mixture was ideal for achieving the best yield. We have analyzed the formation of biphenyl in the Suzuki reaction by using LCMS (Waters Q-ToF Premier LC MSMS system) equipped with TUV detector using dual wavelengths of 215 nm and 254 nm. We observed the 100% conversion of product and the TON for this conversion was found to be 6250.

Table 1
Suzuki reaction catalyzed by Pd incorporated CoFe₂O₄ MNPs (Pd–CoFe₂O₄ MNPs).^a

Entry	Catalyst concentration	Solvent	Base	Temperature (°C)	Time (h)	Yield (%) ^b
1	1.6 mol%	Ethanol	Na ₂ CO ₃	Reflux	12	81
2	2.4 mol%	Ethanol	Na ₂ CO ₃	Reflux	12	81
3	0.8 mol%	Ethanol	Na ₂ CO ₃	Reflux	12	78
4	1.6 mol%	Ethanol	K ₂ CO ₃	Reflux	12	80
5	1.6 mol%	Ethanol	K ₃ PO ₄	Reflux	12	68
6	1.6 mol%	Ethanol	Cs ₂ CO ₃	Reflux	12	30
7	1.6 mol%	aq.Ethanol	Na ₂ CO ₃	Reflux	12	60
8	1.6 mol%	Water	Na ₂ CO ₃	Reflux	12	30
9	1.6 mol%	Ethylene glycol	Na ₂ CO ₃	Reflux	12	20
10	1.6 mol%	Ethanol	Na ₂ CO ₃	30	52	72

^a Reaction condition: iodobenzene (0.5 mmol), phenyl boronic acid (0.75 mmol), base (133 mg), solvent (5 mL).

^b Isolated yield by column chromatography.

Table 2
Suzuki reaction catalyzed by Pd–CoFe₂O₄ MNP.^a

Entry	Aryl halide	Boronic acid	Time (h)	Product(s)	Yield (%) ^b
1			12		81
2			12		79
3			6		88
4			12		79
5			12		92
6			16		83
7			12		75
8			12		79
9			12		84
10			12		70
11			12		85
12			12		80

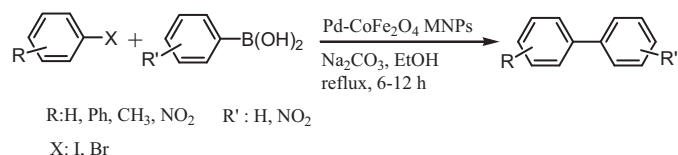
^a Reaction condition: 0.5 mmol of aryl halide, 0.75 mmol of boronic acid, 1.25 mmol of Na₂CO₃, 2 mg of Pd–CoFe₂O₄ MNPs, 5 mL ethanol, reflux.

^b Isolated yield by column chromatography.

After optimizing reaction conditions, the scope of the catalyst was further investigated for a variety of aryl halides and boronic acids (Scheme 1) and the results are summarized in Table 2.

After completion of the reaction, an external magnet was applied to concentrate the catalyst on the side of the reaction vessel. The reaction mixture was decanted holding the magnet on outside of the flask. Thereafter, the flask was washed with ethanol and combined ethanol layer was concentrated in a rotary evaporator under reduced pressure. The crude product was purified by flash chromatography in 230–400 mesh size silica using hexane as eluent. The products were characterized by using IR, NMR and mass (ESI-MS) spectroscopy data. After separation, the catalyst was dried in an oven at 120 °C for 6 h and kept under vacuum before next cycle of reaction.

To ensure complete removal of the magnetic catalyst we measured the EDX analysis in the ethanolic mixture after

**Scheme 1.** Suzuki reaction catalyzed by Pd–CoFe₂O₄ MNPs.

centrifugation of the liquid and no elemental contributions present in the Pd–CoFe₂O₄ MNPs was detected. We also checked for the Pd-leaching in the ethanolic mixture by the method of flame atomic absorption spectrometry (FAAS) [69] and did not get any contribution for leached Pd in the organic liquor (Procedure is given in Supplementary file).

The reusability of the magnetic catalyst was also examined by carrying out repeated runs on the same batch of the used 1.6 mol% Pd–CoFe₂O₄ MNPs catalyst in Suzuki reaction of 4-methyl iodobenzene and phenyl boronic acid (Table 3). After each cycle, nanoparticles were magnetically separated, washed, dried and used directly for the next round of reaction. The yield was not significantly decreased in the regenerated catalyst even

Table 3
Recyclability of Suzuki reaction with 1.6 mol% regenerated Pd–CoFe₂O₄ MNP catalyst.^a

Cycle	Yield at 6 h (%) ^b
1	87
2	86
3	83
4	81

^a Reaction condition: 0.5 mmol 4-methyl iodobenzene, 0.75 mmol phenyl boronic acid, 1.25 mmol Na₂CO₃, 5 mL dried ethanol, reflux.

^b Isolated yield after column purification.

after four consecutive cycles. It was also evident from the FESEM that, the morphology of the recovered MNPs remains unaltered (Supplementary file).

4. Conclusion

In conclusion, a facile magnetic catalyst of Pd incorporated CoFe₂O₄ NPs (40–50 nm) was developed and efficiently employed for Suzuki cross-coupling reactions. The reactions can be carried out using ethanolic dispersion of the catalyst under ligand free and aerobic conditions with low catalyst loading (1.6 mol%). The catalyst could be recovered by simple magnetic decantation and reused for multiple cycles with no significant loss of activity which will be of immense importance in industrial processes. Hence, these MNPs as catalysts are new development in using heterogenous catalysts for production of fine chemicals in liquid phase reactions.

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Appendix A. Supplementary data

Supplementary data associated with this article can be found, in the online version, at doi:10.1016/j.molcata.2011.10.022.

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