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Direct use of nanoparticles as a heterogeneous catalyst: Pd^0-doped $CoFe_2O_4$ magnetic nanoparticles for Sonogashira coupling reaction

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Abstract A magnetically separable nanocatalyst prepared by incorporating Pd nanoparticles onto $CoFe_2O_4$ magnetic nanoparticles was found to be very effective in catalyzing Sonogashira cross-coupling reactions. In this green synthetic process, it is not necessary to use an external linker to support the palladium nanoparticles onto the cobalt ferrite matrix. The catalyst is effective without the use of any ligand or copper additive. The reaction works smoothly in ethanol at 70 °C with both aryl iodides and bromides to produce corresponding product in high yield. After completion of the reaction, the catalyst could be easily separated using an external magnet and reused up to five catalytic cycles with sustained catalytic activity.

Keywords Magnetic nanoparticle · Nano-catalyst · Pd-$CoFe_2O_4$ · Sonogashira · Aryl halide · Alkyne

Introduction

In the recent past, magnetic nanoparticles (MNPs) have been extensively employed as alternative catalyst supports for a variety of organic transformations [1, 2]. The key advantage of magnetic nano-catalysts is their high surface area, which results in high catalyst loading capacity, high dispersion, and outstanding stability. Moreover, these catalysts have the green advantage of convenient and effective recycling, due to the ease of separation with the help of a magnet. Catalyst supported on super MNP has been found to catalyze many organic reactions quite effectively [1–3].

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Because of the sustained catalytic activity of palladium salts, several MNP-supported Pd-catalysts have been developed for promoting different organic reactions [4–10].

The Sonogashira coupling reaction is the most commonly used method for the selective sp^2–sp carbon–carbon bond formation reaction in organic synthesis and the products have found many applications in the area of natural products and the pharmaceutical industry [11–13]. In general, palladium along with copper (as a co-catalyst) is used for the Sonogashira cross-coupling reaction [14–16]. The addition of Cu salts assist the reaction but this has some serious drawbacks because of the formation of the self-coupling alkyne side product by Glaser oxidation reaction [17, 18]. Fewer reports on Cu-free Sonogashira reactions are also reported in the literature but they often require microwave activation or ultrasonic irradiation [19–23]. There are several reports on homogeneous Pd-catalyzed Sonogashira coupling reactions [24–38]. However, isolation of the costly and toxic Pd catalyst from the reaction mixtures is still a challenging task for the chemist. Therefore, heterogeneous palladium catalysts have been developed for this particular reaction [39–58]. However, the use of MNPs as support or a catalyst has distinct advantages over other heterogeneous catalysts [1, 2]. Le et al. [5] reported Sonogashira coupling reaction using Pd Schiff's base complex supported on functionalized cobalt ferrite MNPs as a catalyst using DMF as a solvent. A major disadvantage in most of the earlier reports is that it is very much necessary to use a linker to support the catalytically active metals onto the magnetic nano-support. We have recently reported a water-dispersible cobalt ferrite catalyst for various organic transformations [6, 7, 59–62]. We also developed a palladium-supported magnetic nanocatalyst for Suzuki coupling reactions [7]. In continuation of our work on green chemical synthesis using magnetic nanocatalysts, we wish to report herein a green catalytic route for ligand- and copper-free Sonogashira reactions using Pd nanoparticle-supported cobalt ferrite MNPs as a catalyst. The significance of our method is the direct use of MNP as a catalyst. Unlike other reports, we used no linker to support the palladium nanoparticles. The catalyst was found to be well dispersed in ethanol and can be separated easily form the ethanolic dispersion with the help of an external magnet.

Experimental

Synthesis of Pd nanoparticle-supported cobalt ferrite MNPs

Palladium nanoparticle-supported $CoFe_2O_4$ magnetic nano-catalyst was synthesized using our previously reported ultrasonic-aided co-precipitation technique without using any surface stabilizers or surface-coating agent [7]. Initially, the Pd nanoparticles were synthesized taking $Pd(OAc)_2$ and PEG-400 as raw materials by a reported procedure [63]. Then, $CoFe_2O_4$ MNPs were synthesized. For this, two aqueous solutions of $FeCl_3$ (1.5 g, 9.3 mmol, 50 ml) and $CoCl_2{\cdot}6H_2O$ (1 g, 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 KOH solution (3 M, 25 ml) was added drop-wise under a nitrogen atmosphere with continuous ultrasonic irradiation (frequency 40 kHz and power of 40 kW). Prior to mixing, all three of these solutions were sonicated for 30 min to remove dissolved oxygen. The temperature of the sonicator bath was raised to 60 °C and the mixture was further sonicated for 30 min in air atmosphere. Finally, Pd NPs, which was already synthesized, was dispersed in ethanol and added drop-wise over the $CoFe_2O_4$ reaction mixture and the reaction temperature was slowly brought to 80 °C and kept under sonication for an hour. The reaction mixture was slowly cooled down to room temperature. Black precipitate of Pd-incorporated $CoFe_2O_4$ was observed, which was further separated by centrifugation at 15,000 rpm for 15 min, washed several times with both distilled de-ionized water and ethanol and kept overnight in an incubator at 60 °C for ageing. The precipitate was then further dried in an oven at 100 °C for an hour and subsequently kept in a highly evacuated environment (10^{-2} bar) for another hour. The residual water in the product (Pd nanoparticle-doped $CoFe_2O_4$) was then removed by heating the product at 200 °C for 6 h and kept in a desiccator for further applications.

Characterization of Pd-incorporated $CoFe_2O_4$

The as-synthesized Pd nanoparticle-supported $CoFe_2O_4$ magnetic nanocatalyst were completely characterized by FT-IR (Shimadzu 1800 FT-IR Spectrometer), field-emission scanning electron microscopy (FESEM, Carl Zeiss, $\sum$IGMA), electron dispersive X-ray (EDX, Oxford INCA X-ray microanalysis), transmission electron microscopy (TEM, JEOLJEM 2,100–200 kV), X-ray diffraction measurement XRD (Philips-X pert Pro X-ray diffractometer with Cu-K α radiation having $\lambda = 1.5418$ A), BET single point surface area analysis (Micromeritics chemisorb 2720), VSM analysis (Lakeshore 7410 vibrating sample magnetometer).

Sonogashira reaction using $PdCoFe_2O_4$ nanoparticle as a catalyst

In a typical coupling reaction, halobenzene (1 mmol), alkyne (1.1 mmol), K_2CO_3 (2 mmol), and Pd-$CoFe_2O_4$ MNPs (5 mol% by its weight, 17 mg) were taken in dry ethanol (5 ml) in a Schlenk tube under nitrogen atmosphere. The reaction mixture was heated at 70 °C for the appropriate time. The reaction was monitored using TLC. After completion of the reaction, the catalyst was separated using a magnet. The ethanol part was evaporated under vacuum to get the crude product. The crude product was further purified by column chromatography in 230–400 silica mesh using ethyl acetate and petroleum ether (0–2 %) as eluent. Separated magnetic catalyst was dried in an oven at 100 °C and kept in a desiccator for further use.

*1-Methyl-4-(2-phenylethynyl) benzene (**1a**)*

^{1}H NMR ($CDCl_3$, 300 MHz): δ 7.56–7.54 (m, 2H), 7.45 (d, $J = 9$ Hz, 2H), 7.36–7.35 (m, 3H), 7.17 (d, $J = 9$ Hz, 2H), 2.39 (s, 3H); ^{13}C NMR ($CDCl_3$, 75 MHz): δ 138.3, 131.5, 131.4, 129.1, 128.3, 128, 123.4, 120.1, 89.5, 88.7, 21.5.

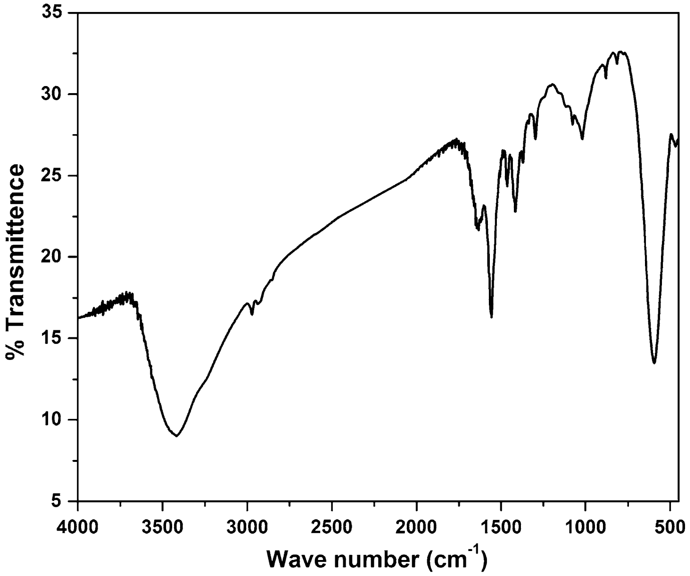


Fig. 1 FT-IR of Pd-CoFe$_2$O$_4$ MNPs

*1, 2-Diphenylethyne (**1b**)*

^{1}H NMR (CDCl$_3$, 300 MHz): δ 7.58–7.55 (m, 4H), 7.38–7.36 (m, 6H); ^{13}C NMR (CDCl$_3$, 75 MHz): δ 131.6, 128.3, 128.2, 123.2, 89.3.

*1-Methyl-4-(oct-1-yn-1-yl)benzene (**1c**)*

^{1}H NMR (CDCl$_3$, 300 MHz): δ 7.31 (d, $J = 9$ Hz, 2H), 7.1 (d, $J = 6$ Hz, 2H), 2.41 (t, $J = 6$ Hz, 2H), 2.34 (s, 3H), 1.75–1.18 (m, 8H), 1.05–0.85 (m, 3H); ^{13}C NMR (CDCl$_3$, 75 MHz): δ 137.2, 131.2, 128.8, 120.9, 89.5, 80.4, 31.2, 28.7, 28.5, 22.4, 21.2, 19.3, 13.9.

*Oct-1-yn-1-ylbenzene (**1d**)*

^{1}H NMR (CDCl$_3$, 300 MHz) δ: 7.5–7.36 (m, 2H), 7.35–7.2 (m, 3H), 2.41 (t, $J = 6$ Hz, 2H), 1.75–1.15 (m, 8H), 1.02–0.75 (m, 3H); ^{13}C NMR (CDCl$_3$, 75 MHz): δ 131.4, 128.0, 127.3, 124.0, 90.3, 80.4, 31.2, 28.6, 28.5, 22.4, 19.3, 13.9.

*1-Methyl-3-(oct-1-yn-1-yl)benzene (**1e**)*

^{1}H NMR (CDCl$_3$, 300 MHz): δ 7.38–7.05 (m, 4H), 2.43–2.38 (m, 2H), 2.32 (s, 3H), 1.63–1.33 (m, 8H), 0.92–0.90 (m, 3H); ^{13}C NMR (CDCl$_3$, 75 MHz) : δ 137.6, 132.0, 128.4, 128.2, 127.9, 123.7, 89.9, 80.5, 31.2, 28.6, 28.5, 22.4, 21.0, 19.3, 13.9.

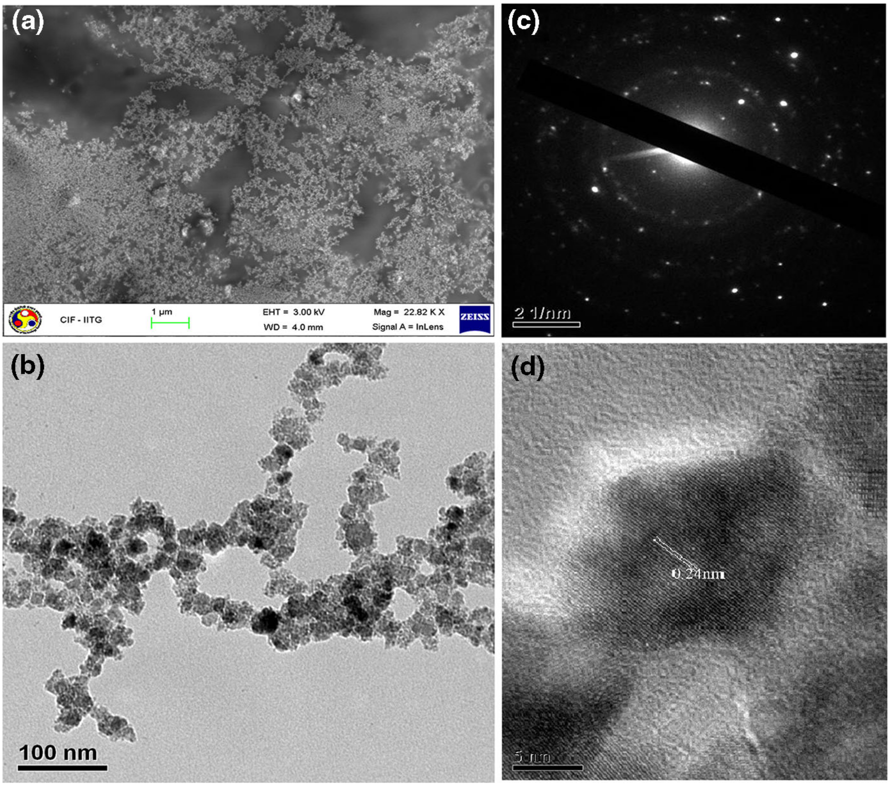


Fig. 2 **a** FESEM, **b** TEM image, **c** SAED pattern, and **d** HRTEM image of Pd-$CoFe_2O_4$ MNPs

*1-Methyl-3-(non-1-ynyl)benzene (**1f**)*

^{1}H NMR ($CDCl_3$, 300 MHz): δ 7.25–7.1 (m, 4H), 2.41–2.39 (m, 2H), 2.33 (s, 3H), 1.65–1.28 (m, 10H), 0.92–0.9 (m, 3H); ^{13}C NMR ($CDCl_3$, 75 MHz): δ 137.7, 132.1, 128.5, 128.128.3, 128.0, 123.9, 90.0, 80.6, 31.7, 29.7, 28.9, 22.6, 21.1, 19.4, 14.0.

*1-Methyl-4-(non-1-yn-1-yl)benzene (**1g**)*

^{1}H NMR ($CDCl_3$, 300 MHz): δ 7.31(d, $J = 6$ Hz, 2H), 7.10 (d, $J = 6$ Hz, 2H), 2.41 (t, $J = 6$ Hz, 2H), 2.35 (s, 3H), 1.88–1.20 (m, 12H), 0.80 (m, 3H); ^{13}C NMR ($CDCl_3$, 75 MHz): δ 137.2, 131.3, 128.8, 120.9, 89.5, 80.4, 31.6, 29.6, 28.8, 28.7, 22.5, 21.2, 19.3, 13.9.

*1-Nitro-2-(phenylethynyl)benzene (**1h**)*

^{1}H NMR ($CDCl_3$, 300 MHz): δ 8.08 (d, $J = 9$ Hz, 1H), 7.72 (d, $J = 6$ Hz, 1H), 7.62–7.60 (m, 3H), 7.49–7.39 (m, 4H); ^{13}C NMR ($CDCl_3$, 75 MHz): δ 149.5, 134.5, 132.8, 132.0, 129.2, 128.5, 128.4, 124.7, 97.1, 84.7.

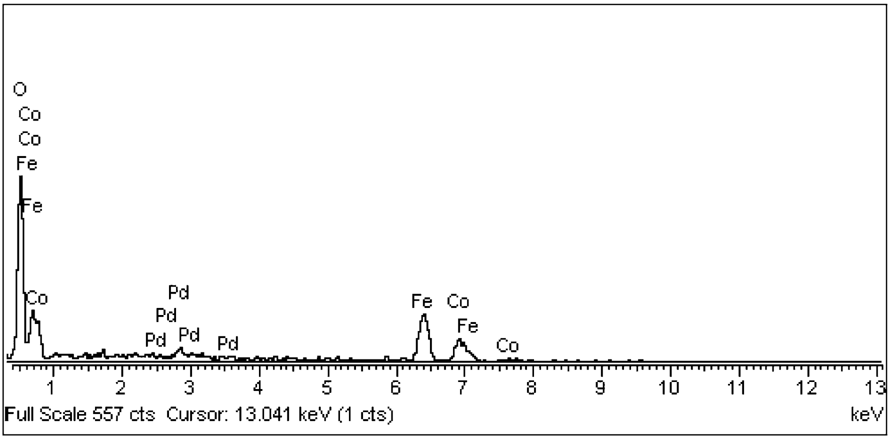


Fig. 3 EDX spectra of the Pd–$CoFe_2O_4$ MNPs

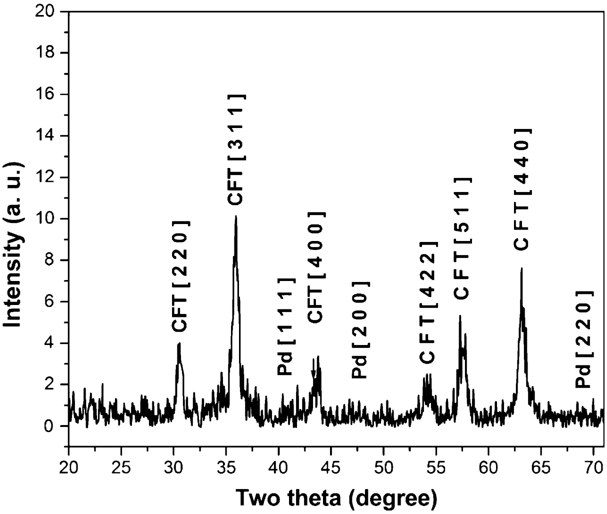


Fig. 4 Powered XRD pattern of Pd-$CoFe_2O_4$ MNPs (CFT stands for cobalt ferrite)

*1-Methyl-4-(2-(2-nitrophenyl)ethynyl)benzene (**1i**)*

^{1}H NMR (CDCl3, 300 MHz): δ 8.07 (t, $J = 6$ Hz, 1H), 7.71–7.68 (d, $J = 9$ Hz, 1H), 7.60–7.43 (m, 4H), 7.18 (d, $J = 9$ Hz, 2H), 2.38 (s, 3H); ^{13}C NMR (CDCl3, 75 MHz): δ 149.4, 139.5, 134.4, 132.7, 132.3, 131.9, 131.5, 129.1, 128.2, 124.6, 119.2, 118.9, 97.5, 84.2, 21.6.

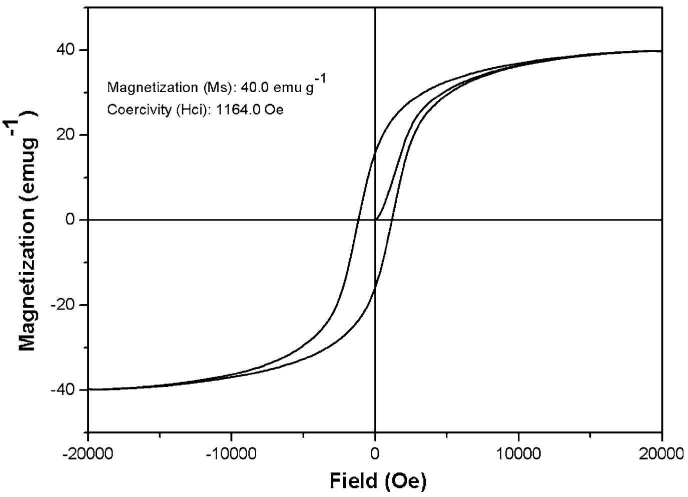
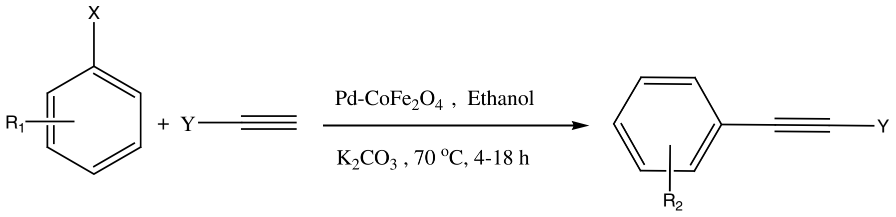


Fig. 5 M–H loop in VSM measurement of Pd-$CoFe_2O_4$ MNPs at room temperature



Scheme 1 Sonogashira reaction using Pd nanoparticles-supported $CoFe_2O_4$ MNPs

*1-tert-Butyl-4-(2-phenylethynyl)benzene (**1j**)*

^{1}H NMR (CDCl3, 300 MHz): δ 7.61–7.53 (m, 4H), 7.44–7.37 (m, 5H), 1.39 (s, 9H); ^{13}C NMR (CDCl3, 75 MHz): δ 151.4, 131.5, 131.3, 128.3, 128.0, 125.3, 123.5, 120.2, 89.5, 88.7, 34.7, 31.1.

*1-Fluoro-4-(2-phenylethylyn)benzene (**1k**)*

^{1}H NMR (CDCl3, 300 MHz): δ 7.55–7.51 (m, 4H), 7.38–7.35 (m, 3H), 7.06 (t, $J = 9$ Hz, 2H); ^{13}C NMR (CDCl3, 75 MHz): δ 164.1, 160.8, 133.5, 131.5, 128.3, 123.0, 119.3, 115.4, 88.9, 88.2.

*1-tert-Butyl-4-(2-(2-nitrophenyl) ethynyl) benzene (**1l**)*

^{1}H NMR (CDCl3, 400 MHz): δ 8.08 (d, $J = 6$ Hz, 1H), 7.71 (d, $J = 9$ Hz, 1H), 7.59–7.53 (m, 3H), 7.48–7.39 (m, 3H), 7.4 (d, $J = 9$ Hz, 2H), 1.34 (s, 9H); ^{13}C

Table 1 Sonogashira reaction between iodobenzene and phenylacetylene using $PdCoFe_2O_4$ nanoparticles

Entry	Catalyst concentration (mol%)	Solvent	Base	Temperature (°C)	Time (h)	Yield[a] (%)
1	1	Ethanol	K_2CO_3	70	24	25
2	3	Ethanol	K_2CO_3	70	12	50
3	5	Ethanol	K_2CO_3	70	6	90
4	5	Ethanol	Na_2CO_3	70	8	70
5	5	Ethanol	K_2CO_3	RT	36	40
6	5	Ethylene glycol	K_2CO_3	80	12	80
7	5	DMF	K_2CO_3	110	12	80
8	5	DMF	Cs_2CO_3	110	12	84
9	5	Dioxane	Cs_2CO_3	90	12	77

Reaction condition: iodobenzene (1 mmol), phenylacetylene (1.1 mmol), base (2 mmol), solvent (5 ml)

[a] Isolated yield after column chromatography

NMR (CDCl3, 75 MHz): δ 152.6, 149.5, 134.5, 132.7, 131.8, 128.2, 125.4, 124.7, 119.3, 119.0, 97.5, 84.2, 31.1.

*1-Methoxy-4-(phenylethynyl)benzene (**1m**)*

^{1}H NMR ($CDCl_3$, 300 MHz): δ 7.54–7.47 (m, 4H), 7.35–7.34 (m, 3H), 6.89 (d, $J = 9$ Hz, 2H), 3.84 (s, 3H); ^{13}C NMR ($CDCl_3$, 75 MHz): δ 159.6, 133.0, 131.4, 128.3, 127.9, 123.5, 115.3, 113.9, 89.3, 88.0, 55.2.

*1-Nitro-4-(phenylethynyl)benzene (**1n**)*

^{1}H NMR ($CDCl_3$, 300 MHz): δ 8.22 (d, $J = 9$ Hz, 2H), 7.66 (d, $J = 9$ Hz, 2H), 7.58–7.57 (m, 2H), 7.41–7.39 (m, 3H); ^{13}C NMR ($CDCl_3$, 75 MHz): δ 146.9, 132.2, 131.8, 130.2, 129.2, 128.5, 123.6, 122.0, 94.6, 87.5.

*4-Methyl-2-(phenylethynyl)aniline (**1o**)*

^{1}H NMR ($CDCl_3$, 300 MHz): δ 7.64–7.48 (m, 2H), 7.45–7.3 (m, 3H), 7.22(s, 1H), 6.98 (d, $J = 6$ Hz, 1H), 6.67 (d, $J = 6$ Hz, 1H), 3.81 (s, 2H), 2.26 (s, 3H); ^{13}C NMR ($CDCl_3$, 75 MHz): δ 145.3, 132.1, 131.3, 130.5, 128.2, 128.0, 127.1, 123.3, 114.4, 107.8, 94.3, 85.1, 20.1.

*1,2-Dip-tolyl-ethyne (**1p**)*

^{1}H NMR ($CDCl_3$, 300 MHz): δ 7.42 (d, $J = 9$ Hz, 4H), 7.15 (d, $J = 9$ Hz, 4H), 2.37 (s, 6H); ^{13}C NMR ($CDCl_3$, 75 MHz): δ 138.1, 131.4, 129, 120.3, 88.8, 21.5.

Table 2 Sonogashira coupling reaction of aryl iodides using Pd-$CoFe_2O_4$ MNPs

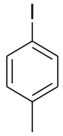
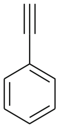
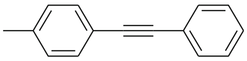
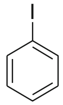
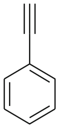
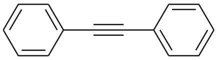
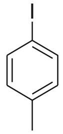
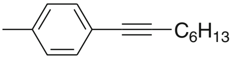
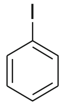
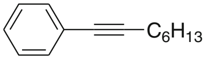
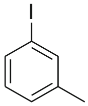
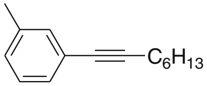
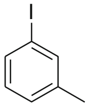
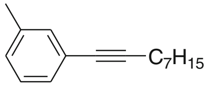
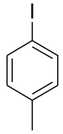
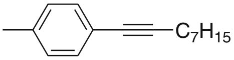
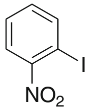
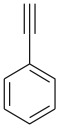
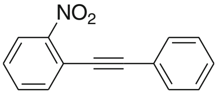
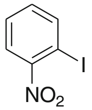
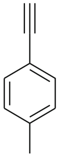
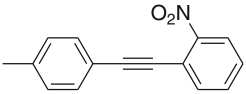
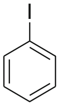
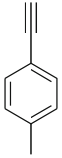
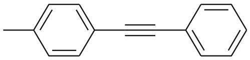
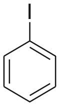
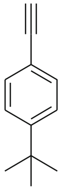
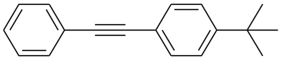
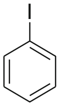
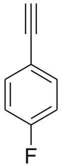
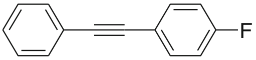
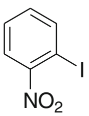
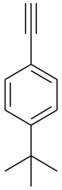
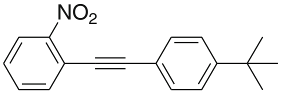
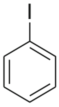
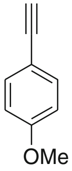
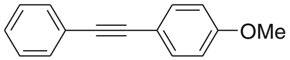
Entry	Aryl halide	Alkyne	Products	Time (h)	Yield (%)[a]
1			 1a	10	80
2			 1b	6	90
3		$\equiv-C_6H_{13}$	 1c	12	66
4		$\equiv-C_6H_{13}$	 1d	12	77
5		$\equiv-C_6H_{13}$	 1e	16	61
6		$\equiv-C_7H_{15}$	 1f	15	65
7		$\equiv-C_7H_{15}$	 1g	18	60
8			 1h	10	67
9			 1i	5	95

Table 2 continued

Entry	Aryl halide	Alkyne	Products	Time (h)	Yield (%)[a]
10			 1a	6	90
11			 1j	8	89
12			 1k	7	91
13			 1l	7	88
14			 1m	4	94

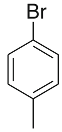
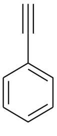
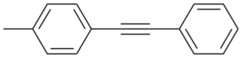
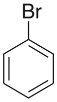
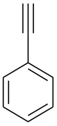
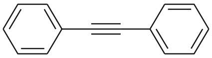
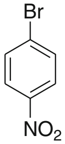
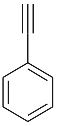
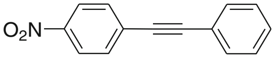
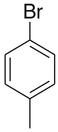
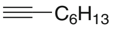
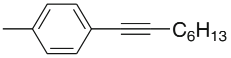
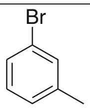
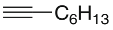
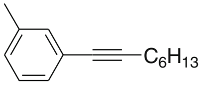
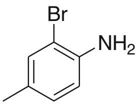
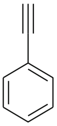
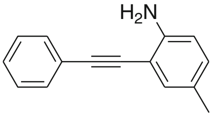
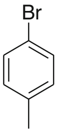
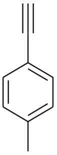
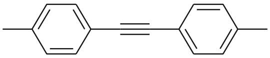
Reaction condition: Aryl bromide (1 mmol), alkyne (1.1 mmol), Pd-$CoFe_2O_4$ (5 mol%) and K_2CO_3 (2 mmol), ethanol (5 ml), 70 °C; [a] Isolated yield after column chromatography

Results and discussion

Synthesis and characterization of Pd-$CoFe_2O_4$ MNPs

The $CoFe_2O_4$ MNPs were synthesized by a combined sonochemical and co-precipitation technique in aqueous medium without any surfactant or organic capping agent [7, 64]. After confirming the formation of cobalt ferrite MNPs using

Table 3 Sonogashira coupling reaction of aryl bromide using Pd-incorporated $CoFe_2O_4$ MNPs

Entry	Aryl halide	Alkyne	Products	Time(h)	Yield(%)[a]
1			 1a	12	65
2			 1b	14	67
3			 1n	8	90
4			 1c	16	60
5			 1e	18	60
6			 1o	14	60
7			 1p	10	80

Reaction condition: Aryl bromide (1 mmol), alkyne (1.1 mmol), Pd-$CoFe_2O_4$ (5 mol%) and K_2CO_3 (2 mmol), ethanol (5 ml), 70 °C; [a] Isolated yield after column chromatography

EDX analysis, the presynthesized palladium nanoparticles were added to the cobalt ferrite MNPs. The entire process was carried out under ultrasonic irradiation. Two broad absorption peaks centered around 3,400 and 1,563 cm^{-1} along with other characteristic peaks of spinel ferrite was found in the IR spectrum (Fig. 1) [65, 66].

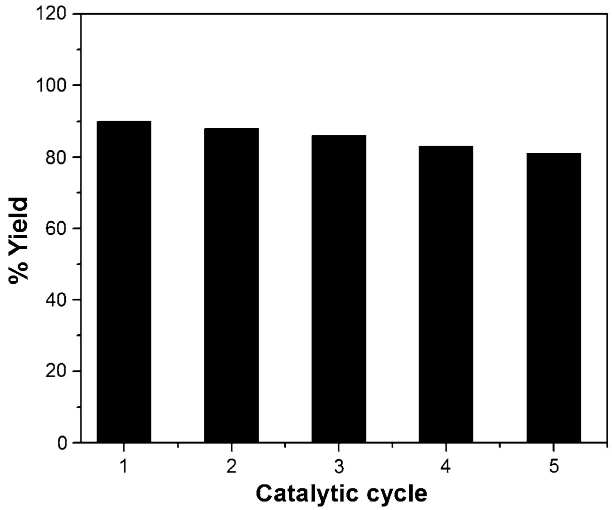


Fig. 6 Reusability of Pd-$CoFe_2O_4$ MNPs

These two peaks are due to excessive hydroxyl ions trapped in the surface of $CoFe_2O_4$ NPs, which gives its surface polarity and stability. The IR spectrum also exhibits another strong absorption peak at 590 cm^{-1}, which is due to the presence of an Fe–O bond. The nanocatalyst was further characterized using FESEM and TEM (Fig. 2a–d). The SEM picture indicates the spherical morphology of the nanoparticles. The image shows that the particles are almost homogeneously distributed throughout the sample. The elemental composition (weight percentage) of Pd-$CoFe_2O_4$ MNPs was determined using EDX analysis (Fig. 3) and found to be: Co = 20.18 %, Fe = 42.15 %, Pd = 3.81 %, and O = 33.86 %.

Powered XRD (Fig. 4) of the $CoFe_2O_4$ indicates the presence of all characteristic peaks of the cubic spinel structure (JCPDS–data cards 3–864 and 22–1086) [65–68]. Weak signals for Pd species in the XRD pattern were observed, which is due to the low percentage of palladium in the sample. From the XRD pattern of the Pd-$CoFe_2O_4$, average crystalline size of the nanoparticles was measured using Scherer's equations [69] and was found be 30 nm. The particle size determined from the XRD pattern was almost consistent with the SEM and HRTEM analysis.

Surface area of the Pd-incorporated $CoFe_2O_4$ was measured from BET single-point surface area determination, which was found to be 122 m^2 g^{-1}. To study the ferromagnetic property, VSM measurement of the Pd-$CoFe_2O_4$ nanocatalyst was undertaken. From the M–H loop (Fig. 5) taken at room temperature with a maximum applied field of ±2 T, both saturation magnetization (Ms) and coercivity values (Hc) were extracted. Coercivity, Hc was found to be 1,164 Oe with the corresponding Ms value of 40.0 emu g^{-1} which indicates the ferromagnetic nature of the nanostructure material.

Sonogashira coupling reaction using Pd-$CoFe_2O_4$ MNPs

The as-synthesized Pd-incorporated $CoFe_2O_4$ nanoparticles were utilized as a magnetically separable catalyst for the Sonogashira coupling reaction (Scheme 1). Initial experiments to evaluate the catalytic performance of the nanocatalyst were carried out between iodobenzene and phenylacetylene. For standardization of the reaction condition, a series of reactions using different combinations of solvent, base, and catalyst concentration were carried out (Table 1).

During our investigation, we found that the catalyst can be dispersed very well in water or alcohol. Hence, initial experiments were carried out in ethanol as a solvent. The reaction was carried out by heating iodobenzene (1 mmol), phenylacetylene (1.1 mmol), and K_2CO_3 (2 mmol) at 70 °C (bath temperature) in the presence of 1 mol% of Pd-$CoFe_2O_4$ catalyst. The yield of the reaction was found to be 25 % after 24 h of reaction. Hence, the amount of catalyst was increased gradually up to 5 mol%. Finally, the use of 5 mol% of catalyst could produce the desired product in 90 % yield after 6 h of reaction. The reaction was further examined using different solvents as well as base. After performing several experiments, we found ethanol and K_2CO_3 to be the best possible combinations of solvent and base, respectively, for this reaction.

After optimization, the method was extended to a variety of iodobenzenes and alkynes. The results are presented in Table 2. In general, the catalyst works well for this reaction. It was observed that both aromatic as well as aliphatic alkynes react efficiently under the reaction condition. However, the reaction takes a much longer time in the case of aliphatic alkynes.

Having had success in promoting Sonogashira coupling for aryl iodides, the reaction was tested for aryl bromides. Results are presented in Table 3. In case of aryl bromides, the reaction takes a longer time compared to that for aryl iodides. However, for aryl chloride the reaction does not work well, showing only a trace amount of the coupling products.

Reusability of the catalyst was tested for the reaction of iodobenzene and phenylacetylene. To reuse, the catalyst was separated by magnetic decantation after completion of the reaction, dried at 100 °C for 6 h, and kept in a desiccator overnight before reuse. The reaction was performed under the same conditions that were used for the fresh experiment. It was observed that the catalyst could be reused for five catalytic cycles without an appreciable loss in activity (Fig. 6).

Conclusions

In conclusion, we have developed a green process for Sonogashira coupling reaction using Pd^0-doped $CoFe_2O_4$ MNP as a catalyst. The catalyst was found to be very effective in ethanol at 70 °C under ligand- and Cu-free conditions. Both aliphatic and aromatic alkynes could be coupled with aryl iodides and aryl bromides using our catalytic route. The catalyst could be recycled up to five catalytic cycles with sustained catalytic activity. Easy recovery of the catalyst with the help of a magnet makes it highly important for green and sustainable chemistry.

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