



An incredible magnetic Pd/CuFe₂O₄ catalyst for low-temperature aqueous Suzuki-Miyaura coupling

Mira V. Parmekar · A. V. Salker

Received: 7 June 2019 / Accepted: 20 September 2019 / Published online: 26 October 2019
© Springer Nature B.V. 2019

Abstract In this investigation, a magnetic catalyst system based on CuFe₂O₄ was conveniently synthesised using citrate-gel method followed by wet impregnation. The synthesised compound was thoroughly characterised using XRD, XPS, IR, SEM-EDAX, TEM VSM and ICP-AES. It was then utilised for catalytic Suzuki-Miyaura coupling yielding excellent results. We thus report a remarkably efficient ligand-free magnetic Pd catalyst for Suzuki-Miyaura coupling in aqueous medium. Here the amount of Pd utilised is as low as 0.00047 mol% in terms of aryl iodide used. The catalyst showed unaltered activity for five consecutive cycles with an average yield of 89.6% with the model substrate.

Keywords Heterogeneous · Nanocatalysis · Magnetic support · Suzuki-Miyaura coupling · Aqueous · Biaryls · Nanostructures

Electronic supplementary material The online version of this article (<https://doi.org/10.1007/s11051-019-4667-2>) contains supplementary material, which is available to authorized users.

M. V. Parmekar (✉) · A. V. Salker (✉)
Department of Chemistry, Goa University, Taleigao-Goa 403504, India
e-mail: mira.parmekar@gmail.com
e-mail: sal_arun@rediffmail.com

Introduction

Using copper in organic transformations is not a novelty anymore, particularly in C–C coupling and C–hetero bond formation reactions. There has been tremendous research on this frontier with many noteworthy accomplishments (Liu et al. 2018; Shi et al. 2018; Zhou et al. 2019). The high melting point of this metal makes it ideal for high-temperature and pressure chemical reactions including continuous flow reactions, microwave-assisted reactions, vapour phase reactions and various organic transformations (Ranu et al. 2007; Reymond and Cossy 2008; Yoshida et al. 2010; Decan et al. 2014; Shaygan Nia et al. 2015; Gawande et al. 2016). Even on the electrochemical front, copper ferrites@rGO (reduced graphene oxide) is reported to be an improved anode material for advanced lithium storage for LIBs (Wang et al. 2017b). The magnetically retrievable property of copper ferrite makes it more an ideal candidate on the catalysis frontier classically for liquid phase reactions. To list a few of the reports, CuFe₂O₄ nanoparticles have been reported in the literature for the asymmetric hydrosilylation of ketones to chiral secondary alcohols in moderate to good yields and excellent enantiomeric excess at room temperature (Kantam et al. 2009). These nanoparticles are also known to carry out a simple one-pot three-component synthesis of spirooxindole-fused heterocycles between isatins, active cyanomethanes and cyclic 1,3-dicarbonyl derivatives in refluxing water (Bazgir et al. 2013). Nano copper ferrite is also described as a reusable catalyst, for the allylation

of acid chlorides in good to moderate yields (Murthy et al. 2012).

Among recipients of the shared Nobel Prize in Chemistry for the year 2010, the discovery by Akira Suzuki for carbon–carbon cross-coupling reaction is the most studied and widely used methodology for the synthesis of biaryl scaffolds (Colacot 2011; Johansson Seechurn et al. 2012; Rahman et al. 2019; Buchspies and Szostak 2019). Biaryls are at the heart of various natural products especially pharmaceuticals, and this protocol being the means to create them has become one of the most influential methods in synthetic organic chemistry (Matsushita et al. 2005; Hussain et al. 2016). Two of the several significant reasons for this impressive development are that the boronic acid substrates are stable molecules, readily available and sustainable in the first place and secondly, as the reaction conditions are quite mild, a variety of functional groups/substrates are tolerated proving highly cost-effective total synthesis of complex drug molecules (Polshettiwar et al. 2010; Gautam et al. 2016). This has led to tremendous popularity of this protocol in the pharmaceutical arena (Fihri et al. 2011).

The initial studies used a homogenous Pd-complex which was not recyclable and thus suffered due to the cost factor of Pd metal (Miyaura et al. 1979). Although researchers worldwide have been successful in lowering the amounts of precious Pd in the catalyst system, there are alternative methods too developed which uses greener and less expensive metals like Fe, Cu and Ni along with some high molecular weight ligands. This not only increases the steps in catalyst synthesis but also increases the overall cost, making the process tedious and expensive (Thathagar et al. 2002; Han 2013; Wang et al. 2017a). Not so in past, Pd–Cu-based nano-colloids were shown to catalyse the famous Suzuki coupling, thus somewhat hinting towards a more economical procedure for the Nobel-awarded reaction (Thathagar et al. 2002). On similar lines, with an even more reasonable approach of magnetic recovery and recyclability, the current research study highlights, a magnetic system based on CuFe_2O_4 designed and reported for the C–C Suzuki–Miyaura (SM) coupling reaction to yield a biaryl product as a greener alternative.

Our attempt to design a simple, ligand-free catalyst for this well-established cross-coupling led us to synthesise 2.5% Pd/ CuFe_2O_4 catalyst which uses only 0.00047 mole percent Pd per mole of aryl iodide to carry out the transformation. It is a highly efficient catalyst

yielding excellent to good yields for almost all the substrates we could study and yet recycle with no significant loss of activity and yielded an average of 89.6% yield for the model substrate over five cycles.

Experimental

Materials and methods

For all experimental procedures, doubly distilled water was used. All chemicals used for catalyst synthesis were obtained from Sigma Aldrich and used in the same form. AR-grade citric acid was obtained from Thomas Baker. The aryl halides and boronic acids used were of AR grade obtained from TCI chemicals. K_2CO_3 used was of commercially available reagent grade. The prepared catalyst sample was well characterised by IR spectroscopy recorded on Shimadzu IR prestige 21 spectrophotometer, and XRD pattern was recorded on a Rigaku diffractometer, using Cu $\text{K}\alpha$ radiation ($\lambda = 1.5418 \text{ \AA}$, filtered through Ni filter) to obtain its structure and phase. The XPS analysis was carried out to determine surface composition with PHI5000 Versa Probe II model. The morphology of catalysts was determined using Zeiss Avo18 scanning electron microscope (SEM). Particulate size confirmation and selected area electron diffraction (SAED) were carried out by transmission electron microscopy (TEM) using Philips CM 200 electron microscope (resolution = $2.4 \text{ \AA}$). Energy-dispersive X-ray spectroscopy (EDS) was recorded on an Oxford instrument. ICP-AES instrument used for the analysis is a ARCOS Simultaneous ICP spectrometer of SPECTRO Analytical Instruments (detection limit up to 0.01 ppm). As all samples analysed were solids, acid digestion was used for sample preparation. Reactions were monitored by thin-layer chromatography (TLC Silica gel 60 F254 purchased from Merck). All the ^1H NMR were recorded on a Bruker 400 instrument (400 MHz) using CDCl_3 as the solvent and TMS as an internal standard.

Preparation of CuFe_2O_4

Copper ferrite was prepared via earlier reported method changing the metal source (Parmekar and Salker 2016): in brief, 1:1.5 metal to fuel ratio of metal: citric acid was taken and dispersed in distilled water. This was allowed to mix well by continuous slow stirring at RT for some time. To this was then added adequate amount of citric acid and further homogenised. The mixture was later

subjected to heat to remove excess water until gel formation was seen. The formed gel was immediately subjected to combustion in a uniform heating furnace. The combusted gel was ground to fine powder and subjected to calcination at requisite temperature to remove any residual carbon. The obtained brick-red powder was the support material used in the study as CuFe_2O_4 .

Preparation of $\text{Pd/CuFe}_2\text{O}_4$

Pd was supported over the synthesised CuFe_2O_4 by wet impregnation method. For this, 0.5 g CuFe_2O_4 was dispersed in distilled water. To it, required amounts of Pd salt was weighed and added. The obtained mixture was stirred for a while prior to adding equivalent amounts of hydride in parts. Brief effervescence was observed turning the suspension colour black indicating Pd being reduced to its metallic state. The dark brown-coloured solid so obtained was rinsed a few times with ethanol and dried at 70 °C. Assigned as $\text{Pd/CuFe}_2\text{O}_4$ after thorough characterisation, it was then treated as the catalyst for SM cross-coupling reaction.

Experimental procedure for Suzuki cross-coupling reaction

To 0.5 mmol iodoarene was added 0.75 mmol aryl boronic acid along with 1 mmol K_2CO_3 . To this was added 1 mg catalyst followed by 3 mL 1:1 H_2O -EtOH. This was then introduced in an oil bath and subjected to reflux with constant stirring. The reaction was monitored by TLC initially and upon completion was allowed to cool and separated from the catalyst via external magnet. The obtained product crystals were recrystallised using hot water and characterised by IR and ^1H NMR. The used catalyst was washed with distilled water followed by acetone and dried at 70 °C before reuse.

Results and discussion

Catalyst characterisation

For the synthesis of support ferrite material, citrate-gel method was employed along with the nitrates of the metal salt. Figure S1 depicts the formation of the support ferrite CuFe_2O_4 using sol-gel combustion

technique using $\text{Fe}(\text{NO}_3)_3$ and $\text{Cu}(\text{NO}_3)_2$ as the metal source. As can be seen from the figure, the green line represents spectra for the metal-citrate complex obtained by evaporation of almost all the water from the mixture. It shows the typical broad $-\text{OH}$ stretching frequency ($\sim 3300\text{ cm}^{-1}$), the $-\text{C}-\text{H}$ stretching ($\sim 2900\text{ cm}^{-1}$) for $-\text{C}=\text{O}$ ($\sim 1750\text{ cm}^{-1}$) and other metal oxygen stretching like $\text{Fe}-\text{O}-\text{H}$ below 1000 cm^{-1} along with the characteristic $\text{Fe}-\text{O}$ stretching at $\sim 600\text{ cm}^{-1}$ and 400 cm^{-1} (Long et al. 2013; Shaabani et al. 2016). On combustion of the gel (the brown line), most of the bands arising due to organic moieties seem to disappear. Once calcined, the sample show characteristic stretching frequencies of ferrite at 576 cm^{-1} and 396 cm^{-1} confirming the formation of CuFe_2O_4 (Khalil 2015). Thus, the followed protocol of calcination yields the required ferrite. Figure S2 shows the IR spectra for CuFe_2O_4 and $\text{Pd/CuFe}_2\text{O}_4$. This again shows the characteristic tetrahedral and octahedral $\text{Fe}-\text{O}$ stretch at $\sim 398\text{ cm}^{-1}$ and $\sim 580\text{ cm}^{-1}$ respectively for both. No separate peaks arising due to $\text{Pd/Pd}-\text{O}$ are indicating the fact that Pd is well dispersed on the surface of CuFe_2O_4 support.

Figure 1 demonstrates the diffraction pattern obtained for CuFe_2O_4 and 2.5% Pd-loaded CuFe_2O_4 . The broadening of the peaks is indicative of the fact that the formed CuFe_2O_4 was of smaller particle size, which is confirmed from the crystallite sizes obtained from the XRD data as well as TEM analysis. The XRD data matches well with JCPDS data card 01-077-0010 and indexed to a cubic geometry (Yan et al. 2013). No extra peaks pertaining to Fe_2O_3 impurity were observed in any case. The obtained SEM images depicted in Fig. 2a, b clearly show the agglomerated nature of the sample resulting due to its magnetic property. The Pd-loaded sample in Fig. 2b shows smaller particles on the surface indicative of the fact that the precious metal is homogeneously covering it. The EDAX data also indicated the same and may be referred for further confirmation (ESI).

The data tabulated in Table S1 shows that the obtained value of elemental percentages by EDAX is a good match to the theoretically calculated values. As per the ICP-AES report, 2% of Pd is loaded on the ferrite support as compared with the intended 2.5%. Also the presence of excess oxygen (Table S1) hints towards formation of slight PdO in the system. This has been further confirmed by XPS results.

Fig. 1 Comparative XRD patterns of Fe_3O_4 , CuFe_2O_4 and 2.5% Pd-loaded CuFe_2O_4 . The graphs indicate the samples to be free of any Fe_2O_3 phase

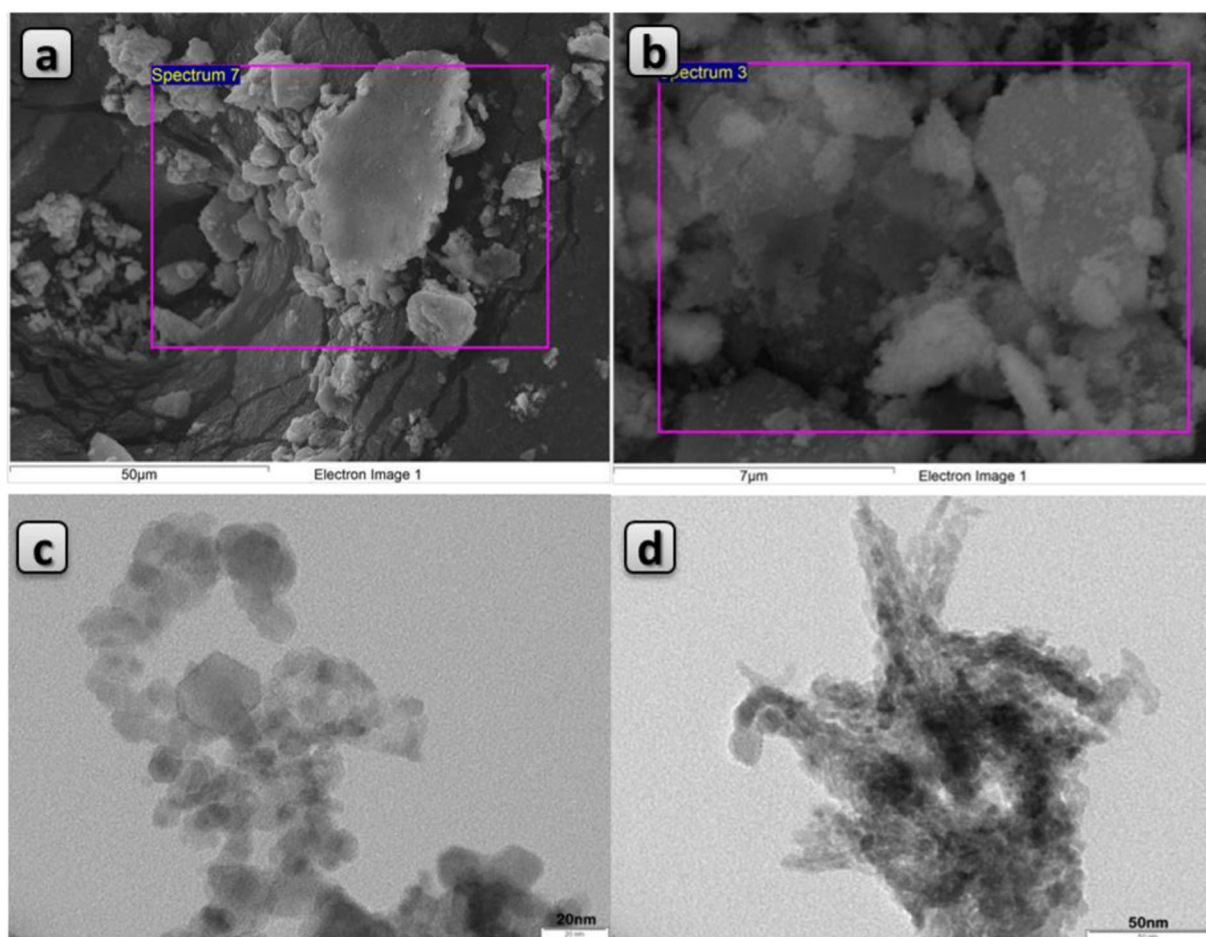
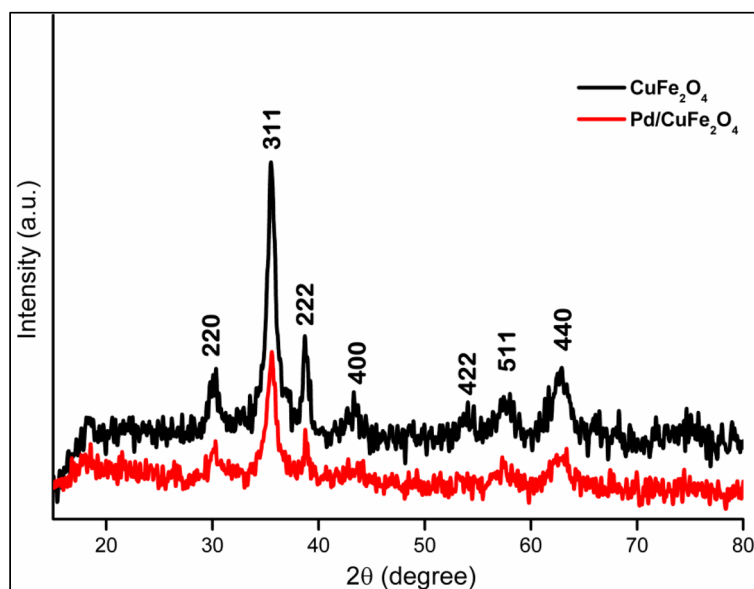


Fig. 2 SEM and TEM micrographs of CuFe_2O_4 (a, c) and 2.5% Pd/ CuFe_2O_4 (b, d)

TEM data supported the fact that the active metal is indeed homogeneously distributed. In here, the CuFe_2O_4 particles appeared quasi- spherical in nature (Fig. 2c). Agglomeration was observed for this magnetic ferrite as well. The SAED pattern shown in Fig. S3 represents *hkl* indexing for the sample matching with its obtained XRD data. A striking observation here was an axial growth of the Pd nanoparticles over the ferrite support. The Pd particles did not cover only the surface of CuFe_2O_4 support but also showed an axial growth in the outward direction as spikes (Fig. 2d). This might have resulted in an increased surface area of the sample making it highly efficient for catalysis. In addition, the micrographs also reveal the supported sample to be highly porous than the pristine. This factor again supports the obtained inference for its applicative studies that even the 1 mg sample could be easily recycled and reused for 5 cycles with no significant loss of activity as it is highly porous and facilitated the movement of reactants and products through, without any clogging of active sites.

The XPS was recorded of the Pd-loaded sample to determine the oxidation state of Pd along with confirming the proper stoichiometry of base copper ferrite. Figure S6 illustrates the survey scan of the sample confirming presence of all the compositional elements as well as indicating absence of any impurity in the sample. Here again, there are no extra elemental peaks besides the desired ones proving the purity of the sample. The elemental mapping data in ESI shows homogeneous distribution of the active metal Pd on the ferrite surface. Overall, it can be confirmed that the desired composition is formed.

Figure 3 shows the individual elemental scan of the sample. The Fe 2p scan (Fig. 3a) depicts the $2p_{1/2}$ peak at 724 eV and $2p_{3/2}$ peak at 710.9 eV with its satellite peak 8 eV higher which is characteristic of Fe in + 3 oxidation state (Nawale et al. 2011; Singh Yadav et al. 2015). The high-resolution spectrum of Cu 2p (Fig. 3b) shows two distinct peaks with a binding energy of 931.6 and 951.3 eV, which can be attributed to Cu $2p_{3/2}$ and Cu $2p_{1/2}$ respectively. Presence of strong satellite peak in cluster at B.E. $\sim$ 243 eV is characteristic of Cu in + 2 oxidation state. If compared with the previous sample, one can clearly note the difference in the intensity of the satellite peaks. Figure 3d displays the 3d scan for Pd clearly indicating peaks at 335.2 and 340.6 eV as well as 337 and 342.1 eV with a

characteristic difference of $\sim$ 5.26, which is distinctive of PdO and Pd metal.

Thus, in the synthesised compound, Pd exhibits both Pd^0 and Pd^{2+} oxidation state (Brun et al. 1999). The O 1s scan in Fig. 3c also shows prominent splitting of the peak into two, majority at 529.6 eV which can be assigned to the lattice oxygen of the ferrite with a comparative shoulder at 531.1 eV which could have very well originated due to some of the surface Pd existing in its oxide form PdO. Hence, the desired composition of 2.5% Pd loading on CuFe_2O_4 appears to have formed.

VSM studies were carried out at room temperature. A maximum field of 3 T was utilised for the measurement starting from zero. The obtained results indicated that the M_s values for both the Pd-loaded and base ferrite were quite close, the former being marginally less. This in fact is quite visible from the VSM plot in Fig. S7 as well. A value of 21.02 of saturation magnetisation was sufficient to prove the sample of interest is magnetic. The rest of the magnetic parameters are tabulated in Table S2. Not much change in the values of remanent magnetisation as well as coercivity is seen in both the samples indicating that Pd is well dispersed over the support. Overall, it could be established that magnetically retrievable samples were formed utilising the followed protocol which were later used for the catalytic applications.

Catalytic studies

Suzuki-Miyaura (SM) coupling reaction was investigated on some of designed catalysts of which Pd/ CuFe_2O_4 was found to be the best (Table S3). After screening different solvent systems for the reaction, it was concluded that 1:1 H_2O -EtOH system worked best in the employed reaction conditions. The solvent mixture refluxes around 80 °C, and the reaction for most substrates worked well within an hour making the process highly efficient and comparatively quicker to previously reported Pd-catalyst systems (Nehlig et al. 2015). In addition, every reaction used roughly 25 μg of the active metal (0.00047 mol% Pd), which is one among the lowest reported Pd concentrations active for the reaction.

To test the catalytic activity of the synthesised catalyst, SM coupling reaction was performed over it. For trial, 4 mg catalyst was utilised for 0.5 mmol iodobenzene which yielded the desired solid product

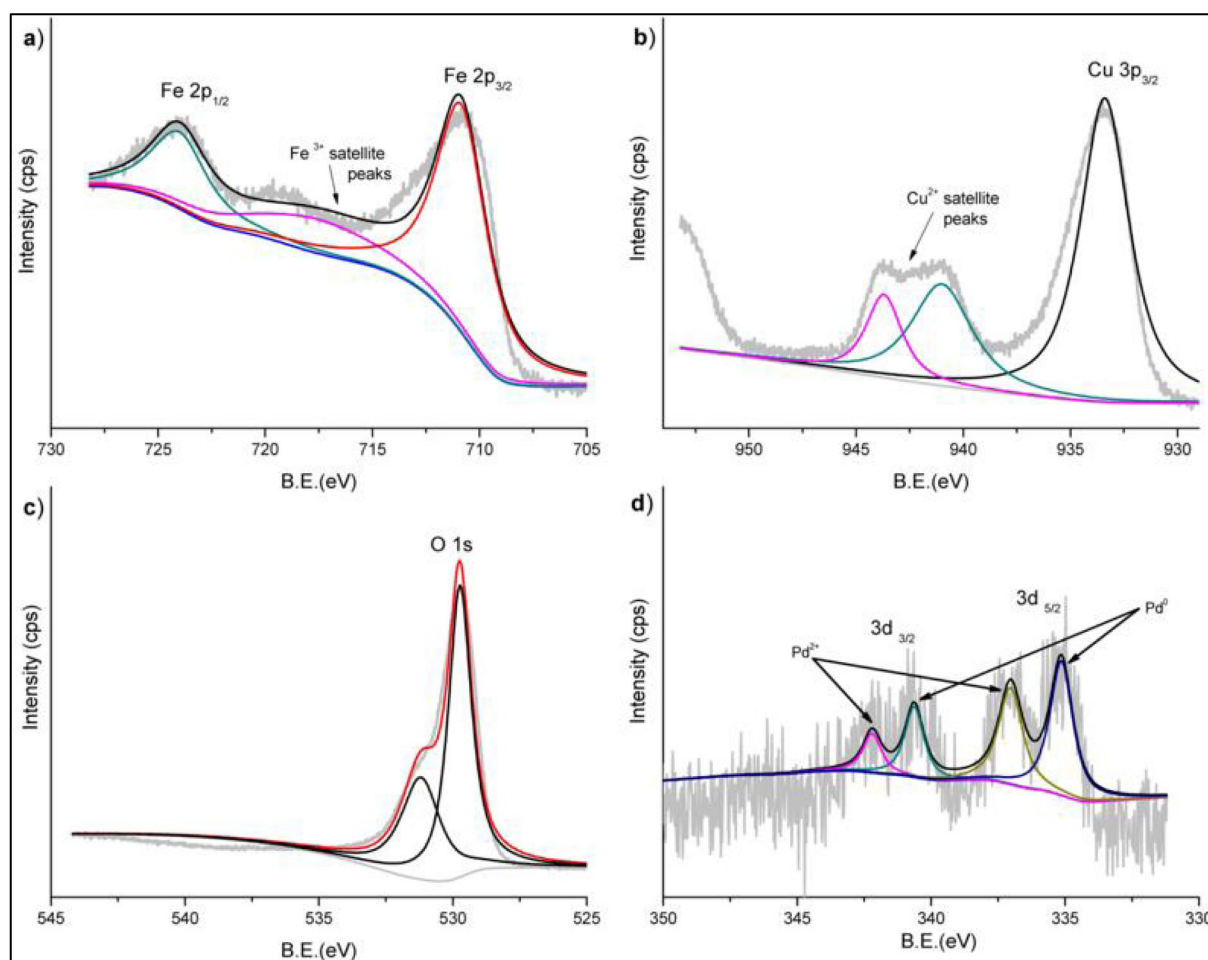
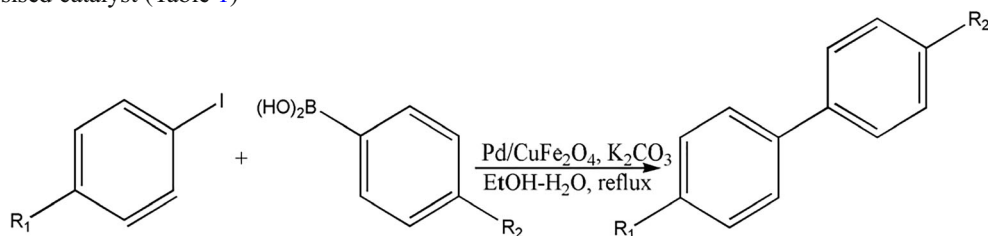


Fig. 3 Individual elemental scan for the Pd/CuFe₂O₄ sample

within 45 min as monitored by TLC. The catalyst amount was then gradually reduced and the reaction repeated to optimise the conditions. This ensured 1 mg of the catalyst to be ideal for the reaction if carried out at reflux in 1:1 H₂O-EtOH mixture when used along with a slight excess of the boronic acid (0.75 mmol) and 1 mmol of a mild base. This yielded the corresponding biphenyl in 92% yield characterised by matching its IR (Fig. S8 and ¹H NMR). A series of substrates were tried over the catalyst for SM coupling yielding excellent to good yields. Once the reaction conditions were optimised, SM coupling reaction over the catalyst was studied using different substituted iodobenzenes as well as substituted boronic acids. All derivatives with electron-donating groups like -CH₃, -OCH₃ and -CH₂OH and electron-withdrawing groups like -NO₂, -Cl, -Br and -COOH at *para* position were

found to smoothly react within the stipulated time to yield the biaryl product. As reported elsewhere, we also did not find a trend in yields and electronic nature of the substrates (Wang et al. 2017a). However, reaction between some of the boronic acids with an electron-withdrawing group in the *para* position seemed sluggish yielding low yields (entries 24–26). For comparison, we tested Pd on three different magnetic supports Fe₃O₄, NiFe₂O₄ and CuFe₂O₄. The results tabulated in Table S3 clearly show that Pd when supported on CuFe₂O₄ showed the best results under operated reaction conditions. The exact reason for which cannot be pinpointed and further studies are under progress. Cu as such in the absence of Pd failed to show a positive SM coupling indicating that Cu only synergistically supports the activity of Pd and by itself is not active for the reaction alone.

General reaction for the SM C–C cross-coupling using the synthesised catalyst (Table 1)



The products formed were well characterised by their melting points, IR and ^1H NMR data. The characterisation data is given below. Some of the product NMR spectra are available in the supporting information

Entry 1: shiny white solid; IR (KBr, cm^{-1}) 2950, 1610, 1500, 1295, 1250, 1040, 810, 500; ^1H NMR (400 MHz, CDCl_3): δ = 2.38 (s, 3H), 3.85 (s, 3H), 6.96 (d, J = 8.8 Hz, 2H), 7.22 (d, J = 8.0 Hz, 2H), 7.44 (d, J = 8.0 Hz, 2H), 7.50 (d, J = 8.8 Hz, 2H); melting point 111 $^\circ\text{C}$

Entry 2: dark yellow solid; IR (KBr, cm^{-1}) 3050, 2825, 1600, 1550, 1350, 850; ^1H NMR (400 MHz, CDCl_3): δ = 7.79 (d, J = 8.8 Hz, 4H), 8.37 (d, J = 8.8 Hz, 4H); melting point 239 $^\circ\text{C}$

Entry 3: white flaky solid; IR (KBr, cm^{-1}) 3100, 2900, 2850, 1600, 1500, 1280, 1060, 860; ^1H NMR (400 MHz, CDCl_3): δ = 3.86 (3H, s), 6.97 (d, J = 7.2 Hz, 2H), 7.30 (m, 1H), 7.41 (t, J = 8.0 Hz, 2H), 7.55 (t, J = 8.0 Hz, 4H); melting point 89 $^\circ\text{C}$

Entry 4: crimson solid; IR (KBr, cm^{-1}) 3500, 2985, 1600, 1485, 1400, 1000; ^1H NMR (400 MHz, DMSO): δ = 7.33 (t, J = 7.2 Hz, 3H), 7.44 (t, J = 8.0 Hz, 1H), 7.52 (d, J = 8.4 Hz, 2H), 7.65 (d, J = 7.6 Hz, 2H), 7.88 (d, J = 8.4 Hz, 1H); melting point 221 $^\circ\text{C}$

Entry 5: white solid; IR (KBr, cm^{-1}) 2950, 2820, 1610, 1490, 1300, 1060, 820; ^1H NMR (400 MHz, CDCl_3): δ = 3.85 (s, 3H), 6.97 (d, J = 8.8 Hz, 2H), 7.37 (t, J = 8.4 Hz, 2H), 7.49 (m, 4H); melting point 110 $^\circ\text{C}$

Entry 6: pale yellow solid; IR (KBr, cm^{-1}) 3100, 2830, 2450, 1600, 1520, 1350, 820; ^1H NMR (400 MHz, CDCl_3): δ = 7.49 (d, J = 8.4 Hz, 2H), 7.63 (d, J = 8.4 Hz, 2H), 7.71 (d, J = 8.0 Hz, 2H), 8.31 (d, J = 8.8 Hz, 2H); melting point 170 $^\circ\text{C}$

Entry 8: shiny white flaky solid; IR (KBr, cm^{-1}) 3100, 1500, 1450, 765, 720; ^1H NMR (400 MHz, CDCl_3): δ = 7.36 (t, J = 8.4 Hz, 2H), 7.45 (t, J = 7.6 Hz, 4H), 7.60 (dd, J = 4.2 Hz, J = 1.2, 4H); melting point 70 $^\circ\text{C}$

Entry 10: yellow solid; IR (KBr, cm^{-1}) 3140, 2850, 1600, 1550, 1350, 1100, 880, 740; ^1H NMR (400 MHz, CDCl_3): δ = 7.49 (m, 3H), 7.64 (d, J = 8.8 Hz, 2H), 7.74

Table 1 Substrate scope for SM coupling over the designed catalyst

Entry	R ₁	R ₂	Time (h)	% Yield
1	CH ₃	OCH ₃	1	99
2	NO ₂	NO ₂	1	98
3	OCH ₃	H	1	98
4	H	COOH	1	97
5	OCH ₃	Cl	1	95
6	NO ₂	Br	1	94
7	CH ₂ OH	OCH ₃	1	93
8	H	H	1	92
9	CH ₂ OH	Cl	1	91
10	NO ₂	H	1	91
11	OCH ₃	Br	1	90
12	CH ₂ OH	H	1	87
13	NO ₂	OCH ₃	1	87
14	CH ₂ OH	NO ₂	1	83
15	H	OCH ₃	1	82
16	OCH ₃	OCH ₃	1	80
17	OCH ₃	NO ₂	1	78
18	CH ₃	H	1	77
19	H	Cl	1	74
20	CH ₂ OH	Br	1	72
21	H	NO ₂	1	71
22	NO ₂	Cl	1	71
23	H	Br	1	64
24	CH ₃	Cl	1	58
25	CH ₃	NO ₂	1	56
26	CH ₃	Br	1	41

*Reaction conditions: 0.5 mmol aryl iodide, 0.75 mmol aryl boronic acid, 1 mg catalyst (25 μg Pd), 1 mmol K_2CO_3 in 3 mL of 1:1 H_2O -EtOH refluxing at approximately 75 $^\circ\text{C}$

(d, $J = 8.8$ Hz, 2H), 8.30 (d, $J = 8.8$ Hz, 2H); melting point 112 °C

Entry 11: white solid; IR (KBr, cm^{-1}) 2895, 1605, 1495, 1300, 1265, 1060, 810; ^1H NMR (400 MHz, CDCl_3): $\delta = 3.85$ (s, 3H), 6.97 (d, $J = 8.0$ Hz, 2H), 7.41 (d, $J = 8.4$ Hz, 2H), 7.54 (m, 4H); melting point 141 °C

Entry 12: white flaky solid; IR (KBr, cm^{-1}) 3250, 2900, 1550, 1400, 1060, 760; ^1H NMR (400 MHz, CDCl_3): $\delta = 1.69$ (t, $J = 6.0$ Hz, 1H), 4.75 (s, $J = 6.0$ Hz, 2H), 7.36 (1H, d), 7.44 (4H, d), 7.6 (4H, d); melting point 100 °C

Entry 13: shiny yellow solid; IR (KBr, cm^{-1}) 3100, 2900, 2880, 2810, 1600, 1500, 1350, 1240, 835; ^1H NMR (400 MHz, CDCl_3): $\delta = 3.88$ (s, 3H), 7.01 (dd, $J = 8.8$ Hz, $J = 2.0$ Hz, 2H), 7.58 (dd, $J = 8.8$ Hz, $J = 2.0$ Hz, 2H), 7.70 (dd, $J = 8.8$ Hz, $J = 2.0$ Hz, 2H), 8.28 (dd, $J = 8.8$ Hz, $J = 2.0$ Hz, 2H); melting point 106 °C

Entry 14: yellow solid; IR (KBr, cm^{-1}) 3550, 2860, 1600, 1500, 1350, 830; ^1H NMR (400 MHz, CDCl_3): $\delta = 4.79$ (d, $J = 5.6$ Hz, 2H), 7.52 (d, $J = 8.0$ Hz, 2H), 7.63 (d, $J = 8.0$ Hz, 2H), 7.74 (d, $J = 8.8$ Hz, 2H), 8.30 (d, $J = 8.8$ Hz, 2H); melting point 160 °C

Entry 15: dense white solid; IR (KBr, cm^{-1}) 3100, 2950, 1600, 1525, 1280, 1180, 1060, 850, 725; ^1H NMR (400 MHz, CDCl_3): $\delta = 3.85$ (s, 3H), 6.98 (dd, $J = 8.8$ Hz, 2.0 Hz, 2H), 7.31 (m, 1H), 7.41 (m, 2H), 7.54 (m, 4H); melting point 88 °C

Entry 16: shiny white flaky solid; IR (KBr, cm^{-1}) 2890, 2810, 1610, 1500, 1280, 1190, 1060, 830; ^1H NMR (400 MHz, CDCl_3): $\delta = 3.85$ (s, 6H), 6.95 (d, $J = 8.8$ Hz, 4H), 7.44 (d, $J = 8.4$ Hz, 4H); melting point 165 °C (sublimes)

Entry 18: white solid; IR (KBr, cm^{-1}) 3150, 2900, 1900, 1690, 1500, 1150, 820, 760; ^1H NMR (400 MHz, CDCl_3): $\delta = 2.40$ (s, 3H), 7.33 (d, $J = 7.2$ Hz, 2H), 7.42 (t, $J = 7.6$ Hz, 3H), 7.49 (d, $J = 8.0$ Hz, 2H), 7.58 (d, $J = 8.4$ Hz, 2H); melting point 48 °C

Entry 19: white solid; IR (KBr, cm^{-1}) 3100, 1900, 1740, 1600, 1490, 1400, 1100, 850, 760, 700; ^1H NMR (400 MHz, CDCl_3): $\delta = 7.44$ (m, 5H), 7.55 (m, 4H); melting point 77 °C

Entry 20: white solid; IR (KBr, cm^{-1}) 3300, 2920, 1480, 1390, 1000, 805; ^1H NMR (400 MHz, CDCl_3): $\delta = 1.70$ (t, 1H), 4.75 (d, $J = 6.0$ Hz, 2H), 7.46–7.57 (6H, m), 7.65 (t, $J = 8.8$ Hz, 2H); melting point 217 °C

Entry 22: buff-coloured solid; IR (KBr, cm^{-1}) 3100, 1590, 1510, 1350, 1100, 880, 820, 700; ^1H NMR (400 MHz, CDCl_3): $\delta = 7.47$ (d, $J = 8.4$ Hz, 2H), 7.56 (d, $J =$

8.4 Hz, 2H), 7.71 (d, $J = 8.8$ Hz, 2H), 8.30 (d, $J = 8.8$ Hz, 2H); melting point 110 °C

Entry 24: white solid; IR (KBr, cm^{-1}) 3100, 2900, 1525, 1100, 1000, 815, 500; ^1H NMR (400 MHz, CDCl_3): $\delta = 2.39$ (s, 3H), 7.25 (d, $J = 8.0$ Hz, 2H), 7.38 (d, $J = 8.8$ Hz, 2H), 7.45 (d, $J = 8.4$ Hz, 2H), 7.50 (d, $J = 8.4$ Hz, 2H); melting point 121 °C

Entry 25: brownish yellow solid; IR (KBr, cm^{-1}) 3100, 1600, 1550, 1350, 1100, 825; ^1H NMR (400 MHz, CDCl_3): $\delta = 2.43$ (s, 3H), 7.30 (d, $J = 8.0$ Hz, 2H), 7.53 (d, $J = 8.0$ Hz, 2H), 7.72 (d, $J = 8.8$ Hz, 2H), 8.28 (d, $J = 8.8$ Hz, 2H); melting point 125 °C

Entry 26: white solid; IR (KBr, cm^{-1}) 3380, 3050, 2900, 1480, 1000, 805; ^1H NMR (400 MHz, CDCl_3): $\delta = 2.17$ (s, 3H), 7.55 (m, 8H); melting point 120 °C

Recyclability and leaching studies

Recyclability is an important factor where heterogeneous catalysis is concerned from an economic as well as green chemistry prospective (Parmekar and Salker 2019). For this reason, it was mandatory to know the principle of working of the active catalyst, whether it is operating homogeneously or heterogeneously. To test this the reaction was carried out on a 5 times scaled-up amount in a 100-mL round bottom flask. After 30 min of reaction time, half of the mixture was separated and filtered and the other half was continued to reflux in the presence of the catalyst. The filtrate was subjected to the same reaction condition, i.e. reflux in a separate 50-mL round bottom flask but in absence of the catalyst and monitored via TLC. The reaction did not proceed any further and both the reactant and product

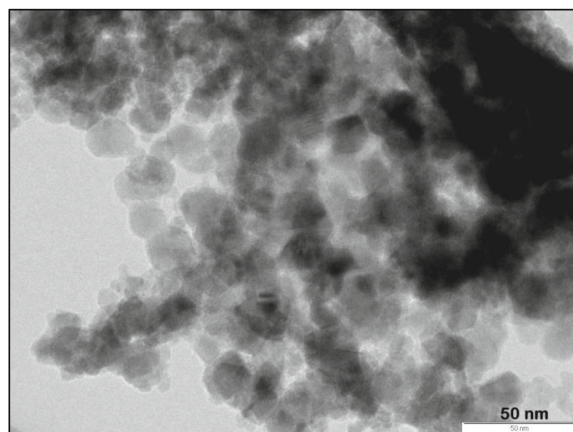


Fig. 4 TEM image of the recovered sample after five cycles

spots remained intact up till 4 h of reaction time. Whereas the first half continued with the reaction in the presence of the catalyst showed complete product formation within 50-min time. This proved the mode of working of the catalyst to be a heterogeneous one. In addition, on the optimised scale of 0.5 mmol of the substrate with 1 mg of the catalyst, the reaction was carried out for five consecutive cycles. After every cycle the catalyst was recovered using a magnet, washed with acetone and dried at 70 °C before reuse. The obtained results are tabulated in Table S4 and Fig. S9 indicating the average yield of the five cycles to be 89.6%.

The recovered catalyst from the five consecutive recycles was subjected to ICP-AES analysis, which showed no loss of the active Pd from the surface of the catalyst. The surface morphology too was seen to be intact in the TEM study of the five times used sample (Fig. 4). Thus, this proved the recyclability as well as heterogeneous nature of the catalyst and confirmed the fact no leached metal is responsible for the said activity.

Conclusion

In all, the highlight of this work is the loading of Pd over the catalyst, which is just 2.5 weight percent over the support. Each coupling reaction used only 1 mg of this catalyst, which in terms of Pd comes to just 0.00047 mol% with respect to amount of substrate used. This is one of the lowest active amounts of Pd reported for this reaction. Also the fact that it could be recycled five times with average yield of 89.6 % is quite noteworthy. Owing to the synergistic effect of copper substitution in the magnetic core, the Pd/ CuFe₂O₄ catalyst showed much better performances for the Suzuki-Miyaura coupling reaction in an aqueous medium with remarkable stability. The magnetic recovery and recyclability of this catalyst further is an additional high point of this work. We thus propose an excellent, highly efficient, magnetically separable and recyclable heterogeneous catalyst for the Nobel-winning Suzuki coupling reaction which would be highly cost-effective to be run on industrial scale and also a greener and less-toxic alternative to the conventional one.

Acknowledgements We gracefully thank SAIF IIT Bombay, IIT Kanpur, Birla Furukawa, Verna and CSIR-NIO, Dona Paula, for instrumental analysis.

Funding information Authors thank UGC-New Delhi for BSR fellowship to MVP.

Compliance with ethical standards

Conflict of interest The authors declare that they have no conflict of interest.

References

- Bazgir A, Hosseini G, Ghahremanzadeh R (2013) Copper ferrite nanoparticles: an efficient and reusable nanocatalyst for a green one-pot, three-component synthesis of spirooxindoles in water. *ACS Comb Sci* 15:530–534. <https://doi.org/10.1021/co400057h>
- Brun M, Berthet A, Bertolini J (1999) XPS, AES and Auger parameter of Pd and PdO. *J Electron Spectros Relat Phenomena* 104:55–60. [https://doi.org/10.1016/S0368-2048\(98\)00312-0](https://doi.org/10.1016/S0368-2048(98)00312-0)
- Buchspies J, Szostak M (2019) Recent advances in acyl Suzuki cross-coupling. *Catalysts* 9:53. <https://doi.org/10.3390/catal9010053>
- Colacot TJ (2011) The 2010 Nobel Prize in Chemistry: palladium-catalysed cross-coupling. *Platin Met Rev* 55:84–90. <https://doi.org/10.1595/147106711X558301>
- Decan MR, Impellizzeri S, Marin ML, Scaiano JC (2014) Copper nanoparticle heterogeneous catalytic ‘click’ cycloaddition confirmed by single-molecule spectroscopy. *Nat Commun* 5:1–8. <https://doi.org/10.1038/ncomms5612>
- Fihri A, Bouhrara M, Nekoueishahraki B et al (2011) Nanocatalysts for Suzuki cross-coupling reactions. *Chem Soc Rev* 40:5181–5203. <https://doi.org/10.1039/c1cs15079k>
- Gautam P, Dhiman M, Polshettiwar V, Bhanage BM (2016) KCC-1 supported palladium nanoparticles as an efficient and sustainable nanocatalyst for carbonylative Suzuki–Miyaura cross-coupling. *Green Chem* 18:5890–5899. <https://doi.org/10.1039/C6GC02012G>
- Gawande MB, Goswami A, Felpin F-X et al (2016) Cu and Cu-based nanoparticles: synthesis and applications in catalysis. *Chem Rev* 116:3722–3811. <https://doi.org/10.1021/acs.chemrev.5b00482>
- Han F-S (2013) Transition-metal-catalyzed Suzuki–Miyaura cross-coupling reactions: a remarkable advance from palladium to nickel catalysts. *Chem Soc Rev* 42:5270. <https://doi.org/10.1039/c3cs35521g>
- Hussain I, Capricho J, Yawer MA (2016) Synthesis of biaryls via ligand-free Suzuki–Miyaura cross-coupling reactions: a review of homogeneous and heterogeneous catalytic developments. *Adv Synth Catal* 358:3320–3349. <https://doi.org/10.1002/adsc.201600354>
- Seechurn J, Kitching MO, Colacot TJ, Snieckus V (2012) Palladium-catalyzed cross-coupling: a historical contextual perspective to the 2010 Nobel Prize. *Angew Chem Int Ed* 51: 5062–5085

- Kantam ML, Yadav J, Laha S et al (2009) Asymmetric hydrosilylation of ketones catalyzed by magnetically recoverable and reusable copper ferrite nanoparticles. *J Organomet Chem* 74:4608–4611. <https://doi.org/10.1021/jo9002823>
- Khalil MI (2015) Co-precipitation in aqueous solution synthesis of magnetite nanoparticles using iron(III) salts as precursors. *Arab J Chem* 8:279–284. <https://doi.org/10.1016/j.arabjc.2015.02.008>
- Liu C, Li G, Shi S et al (2018) Acyl- and decarbonylative Suzuki coupling of N-acetyl amides: electronic-tuning of twisted, acyclic amides in catalytic carbon–nitrogen bond cleavage acyl- and decarbonylative Suzuki coupling of N-acetyl amides: electronic-tuning of twisted, acyclic. *ACS Catal* 8:9131–9139. <https://doi.org/10.1021/acscatal.8b02815>
- Long Y, Xie M, Niu J et al (2013) Preparation of acid–base bifunctional core–shell structured Fe₃O₄@SiO₂ nanoparticles and their cooperative catalytic activity. *Appl Surf Sci* 277:288–292. <https://doi.org/10.1016/j.apsusc.2013.04.050>
- Matsushita M, Kamata K, Yamaguchi K, Mizuno N (2005) Heterogeneously catalyzed aerobic oxidative biaryl coupling of 2-naphthols and substituted phenols in water. *J Am Chem Soc* 127:6632–6640. <https://doi.org/10.1021/ja050436k>
- Miyaura N, Yamada K, Suzuki A (1979) A new stereospecific cross-coupling by the palladium-catalyzed reaction of 1-alkenylboranes with 1-alkenyl or 1-alkynyl halides. *Tetrahedron Lett* 20:3437–3440. [https://doi.org/10.1016/S0040-4039\(01\)95429-2](https://doi.org/10.1016/S0040-4039(01)95429-2)
- Murthy YLN, Diwakar BS, Govindh B et al (2012) Nano copper ferrite: a reusable catalyst for the synthesis of β , γ -unsaturated ketones. *J Chem Sci Indian Acad Sci* 124:639–645. <https://doi.org/10.1007/s12039-012-0258-9>
- Nawale AB, Kanhe NS, Patil KR et al (2011) Magnetic properties of thermal plasma synthesized nanocrystalline nickel ferrite (NiFe₂O₄). *J Alloys Compd* 509:4404–4413. <https://doi.org/10.1016/j.jallcom.2011.01.057>
- Nehlig E, Waggeh B, Millot N et al (2015) Immobilized Pd on magnetic nanoparticles bearing proline as a highly efficient and retrievable Suzuki–Miyaura catalyst in aqueous media. *Dalton Trans* 44:501–505. <https://doi.org/10.1039/C4DT02899F>
- Parmekar MV, Salker AV (2016) Room temperature complete reduction of nitroarenes over a novel Cu/SiO₂@NiFe₂O₄ nano-catalyst in an aqueous medium – a kinetic and mechanistic study. *RSC Adv* 6:108458–108467. <https://doi.org/10.1039/C6RA21942J>
- Parmekar M V, Salker A V (2019) Highly tuned cobalt-doped MnO₂ nanozyme as remarkably efficient uricase mimic. *Appl Nanosci* 9. <https://doi.org/10.1007/s13204-019-01118-x>
- Polshettiwar V, Decottignies A, Len C, Fihri A (2010) Suzuki–Miyaura cross-coupling reactions in aqueous media: green and sustainable syntheses of biaryls. *ChemSusChem* 3:502–522. <https://doi.org/10.1002/cssc.200900221>
- Rahman MM, Buchspies J, Szostak M (2019) N-acylphthalimides: efficient acyl coupling reagents in suzuki-miyaura cross-coupling by N–C cleavage catalyzed by Pd-PEPPSI precatalysts. *Catalysts* 9:129. <https://doi.org/10.3390/catal9020129>
- Ranu BC, Saha A, Jana R (2007) Microwave-assisted simple and efficient ligand free copper nanoparticle catalyzed aryl-sulfur bond formation. *Adv Synth Catal* 349:2690–2696. <https://doi.org/10.1002/adsc.200700289>
- Reymond S, Cossy J (2008) Copper-catalyzed Diels–Alder reactions. *Chem Rev* 108:5359–5406. <https://doi.org/10.1021/cr078346g>
- Shaabani A, Sepahvand H, Hooshmand SE, Borjian Boroujeni M (2016) Design, preparation and characterization of Cu/GA/Fe₃O₄@SiO₂ nanoparticles as a catalyst for the synthesis of benzodiazepines and imidazoles. *Appl Organomet Chem* 30:414–421. <https://doi.org/10.1002/aoc.3448>
- Shaygan Nia A, Rana S, Döhler D et al (2015) Carbon-supported copper nanomaterials: recyclable catalysts for Huisgen [3+2] cycloaddition reactions. *Chem - A Eur J* 21:10763–10770. <https://doi.org/10.1002/chem.201501217>
- Shi S, Nolan SP, Szostak M (2018) Well-defined palladium(II)–NHC precatalysts for cross-coupling reactions of amides and esters by selective N–C/O–C cleavage. *Acc Chem Res* 51:2589–2599. <https://doi.org/10.1021/acs.accounts.8b00410>
- Singh Yadav R, Havlica J, Masilko J et al (2015) Effects of annealing temperature variation on the evolution of structural and magnetic properties of NiFe₂O₄ nanoparticles synthesized by starch-assisted sol–gel auto-combustion method. *J Magn Magn Mater* 394:439–447. <https://doi.org/10.1016/j.jmmm.2015.07.012>
- Thathagar MB, Beckers J, Rothenberg G (2002) Copper-catalyzed Suzuki cross-coupling using mixed nanocluster catalysts. *J Am Chem Soc* 124:11858–11859. <https://doi.org/10.1021/ja027716>
- Wang C, Salmon L, Ciganda R et al (2017a) An efficient parts-per-million α -Fe₂O₃ nanocluster/graphene oxide catalyst for Suzuki–Miyaura coupling reactions and 4-nitrophenol reduction in aqueous solution. *Chem Commun* 53:644–646. <https://doi.org/10.1039/C6CC08401J>
- Wang J, Deng Q, Li M, Jiang K, Zhang J, Hu Z, Chu J (2017b) Copper ferrites@reduced graphene oxide anode materials for advanced lithium storage applications. *Sci Rep* 7:1–12. <https://doi.org/10.1038/s41598-017-09214-0>
- Yan K, Wu X, An X, Xie X (2013) Facile synthesis and catalytic property of spinel ferrites by a template method. *J Alloys Compd* 552:405–408. <https://doi.org/10.1016/j.jallcom.2012.11.054>
- Yoshida K, Gonzalez-Arellano C, Luque R, Gai PL (2010) Efficient hydrogenation of carbonyl compounds using low-loaded supported copper nanoparticles under microwave irradiation. *Appl Catal A Gen* 379:38–44. <https://doi.org/10.1016/j.apcata.2010.02.028>
- Zhou T, Li G, Nolan SP, Szostak M (2019) [Pd(NHC)(acac)Cl]: Well-defined, air-stable, and readily available precatalysts for Suzuki and Buchwald–Hartwig cross-coupling (transamidation) of amides and esters by N–C/O–C activation. *Org Lett* 21:3304–3309. <https://doi.org/10.1021/acs.orglett.9b01053>

Publisher's note Springer Nature remains neutral with regard to jurisdictional claims in published maps and institutional affiliations.

Terms and Conditions

Springer Nature journal content, brought to you courtesy of Springer Nature Customer Service Center GmbH (“Springer Nature”). Springer Nature supports a reasonable amount of sharing of research papers by authors, subscribers and authorised users (“Users”), for small-scale personal, non-commercial use provided that all copyright, trade and service marks and other proprietary notices are maintained. By accessing, sharing, receiving or otherwise using the Springer Nature journal content you agree to these terms of use (“Terms”). For these purposes, Springer Nature considers academic use (by researchers and students) to be non-commercial.

These Terms are supplementary and will apply in addition to any applicable website terms and conditions, a relevant site licence or a personal subscription. These Terms will prevail over any conflict or ambiguity with regards to the relevant terms, a site licence or a personal subscription (to the extent of the conflict or ambiguity only). For Creative Commons-licensed articles, the terms of the Creative Commons license used will apply.

We collect and use personal data to provide access to the Springer Nature journal content. We may also use these personal data internally within ResearchGate and Springer Nature and as agreed share it, in an anonymised way, for purposes of tracking, analysis and reporting. We will not otherwise disclose your personal data outside the ResearchGate or the Springer Nature group of companies unless we have your permission as detailed in the Privacy Policy.

While Users may use the Springer Nature journal content for small scale, personal non-commercial use, it is important to note that Users may not:

1. use such content for the purpose of providing other users with access on a regular or large scale basis or as a means to circumvent access control;
2. use such content where to do so would be considered a criminal or statutory offence in any jurisdiction, or gives rise to civil liability, or is otherwise unlawful;
3. falsely or misleadingly imply or suggest endorsement, approval, sponsorship, or association unless explicitly agreed to by Springer Nature in writing;
4. use bots or other automated methods to access the content or redirect messages
5. override any security feature or exclusionary protocol; or
6. share the content in order to create substitute for Springer Nature products or services or a systematic database of Springer Nature journal content.

In line with the restriction against commercial use, Springer Nature does not permit the creation of a product or service that creates revenue, royalties, rent or income from our content or its inclusion as part of a paid for service or for other commercial gain. Springer Nature journal content cannot be used for inter-library loans and librarians may not upload Springer Nature journal content on a large scale into their, or any other, institutional repository.

These terms of use are reviewed regularly and may be amended at any time. Springer Nature is not obligated to publish any information or content on this website and may remove it or features or functionality at our sole discretion, at any time with or without notice. Springer Nature may revoke this licence to you at any time and remove access to any copies of the Springer Nature journal content which have been saved.

To the fullest extent permitted by law, Springer Nature makes no warranties, representations or guarantees to Users, either express or implied with respect to the Springer nature journal content and all parties disclaim and waive any implied warranties or warranties imposed by law, including merchantability or fitness for any particular purpose.

Please note that these rights do not automatically extend to content, data or other material published by Springer Nature that may be licensed from third parties.

If you would like to use or distribute our Springer Nature journal content to a wider audience or on a regular basis or in any other manner not expressly permitted by these Terms, please contact Springer Nature at

onlineservice@springernature.com