Stabilisation of Pd(0) on surface functionalised Fe_3O_4 nanoparticles: magnetically recoverable and stable recyclable catalyst for hydrogenation and Suzuki–Miyaura reactions†

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We describe here a methodology to immobilise/stabilise metallic Pd on surface-functionalised ferrite nanoparticles leading to a magnetically separable catalyst, which exhibits efficient catalytic activity in various hydrogenation and ligand-free Suzuki–Miyaura reactions. Importantly, the use of highly branched polyethylenimine to entrap Pd nanoparticles on the surface of Fe_3O_4 results in structurally stable catalytic sites, which makes them recyclable without any loss in activity.

Introduction

Interest in catalysis by metal nanoparticles (NPs) is increasing dramatically. The high surface area per volume renders metal nanoparticles ideal candidates for catalysis. Stabilized clusters and colloids of noble metals such as Pd with nanometre-scale dimensions are of particular interest as catalysts for organic and inorganic reactions.[1] However, its use is often complicated by issues surrounding the separation of the palladium from the desired product and its recyclability without loss of catalytic activity. It is here that nanoparticles amenable for magnetic separation have an edge.[2] Significantly, an increasing interest of surface-functionalised magnetic nanoparticles (MNPs) is paving the way to novel preparation methodologies in catalysis and also in biomedical applications. The strategy to use MNPs in catalysis requires development of simple and reliable protocols for the immobilisation of the catalytically active metal nanoparticles. A key challenge is to functionalise the MNPs surface such that it allows for the immobilisation of the catalytically active metal on its surface whilst preventing their agglomeration.[3] Recently, much attention has been focused on amine functionalisation,[3–5] since amines are well known to stabilise the nanoparticles against aggregation without disturbing the desired properties and also recognised to increase their catalytic activity. On the other hand, the aggregation behaviour of Pd species during the reaction greatly affects its reactivity. In conventional catalysts (Pd/zeolite and Pd/C), the Pd species are reported to aggregate forming less active metallic particles or clusters after Heck and Suzuki reactions.[6] Thus, the development of reusable heterogeneous Pd catalysts that preserve high Pd dispersion during the coupling reactions is as well desirable as its easy separability from the reaction mixture. Herein, we report on a new and versatile methodology to prepare Pd that is immobilised on Fe_3O_4 nanoparticles (Pd@Fe_3O_4). The catalyst is designed with an aim to combine the property of highly branched polyethylenimine (PEI) to effectively immobilise and stabilise Pd nanoparticles with the magnetic property of the Fe_3O_4 nanoparticles for easy catalyst separation. Our continuing interest in the utility of Pd under mild conditions led us to examine its catalytic potential in reductive reactions such as hydrogenation and Suzuki–Miyaura reactions with promising industrial applications.[5] The Suzuki–Miyaura coupling reaction is one of the most useful methods for selective C–C bond formation for the construction of biaryl skeletons, which are often included as partial structures in pharmaceuticals, natural products and functional materials.[7] Recent work has been focused on new catalyst systems that efficiently process challenging substrates such as aryl chlorides whilst still using relatively mild conditions and low catalyst loadings.[8] To our credit, our catalyst Pd@Fe_3O_4 is capable of taking care of the above-mentioned inadequacies as well as the common problems associated with dispersion and leaching of Pd.

Experimental

Materials

Sodium tetrachloropalladate, branched polyethylenimine (PEI) (average M_w ~750 000, 50 wt% in H_2O) and trisodium citrate were procured from Sigma–Aldrich and used as received. Ferrous oxalate was obtained from Fluka and ferric chloride from Qualigens, India. Sodium borohydride was purchased from Spectrochem, India. All the solutions were prepared using deionised water.

Synthesis of citrate-capped ferrite nanoparticles

Ferrite nanoparticles were synthesized using the method described previously based on the co-precipitation of Fe^{2+} and Fe^{3+}.[9] Typically, under a nitrogen atmosphere, a concentrated

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† Electronic supplementary information (ESI) available: Magnetization curve of surface functionalised Fe_3O_4 and Pd@Fe_3O_4, IR spectra of citrate functionalised Fe_3O_4 and PEI crosslinked Fe_3O_4, TG-DTA profile of the Pd@Fe_3O_4, UV-Vis-diffuse reflectance spectra of Fe_3O_4 and Pd@Fe_3O_4, and literature references for the products of the Suzuki–Miyaura reaction. See DOI: 10.1039/b916261p

aqueous solution of 100 mL sodium hydroxide (10 M) was added in to a mixture of iron salts with Fe^{2+}/Fe^{3+} molar ratio of 1 : 2 forming an immediate dark brown/black solution. The solution was stirred for 1 h at room temperature and heated at 90 °C for 1 h, which resulted in the formation of a brown colloidal solution of ferrite. Then, 100 mL of trisodium citrate (0.3 M) was added and stirred for another 30 min. Subsequently, the thus obtained citrate-capped ferrite dispersion was cooled down to room temperature under continuous stirring, followed by the addition of an excess amount of acetone to precipitate the magnetic particles. The magnetic particles were washed 4–5 times with deionised water and collected with the help of a magnet. Finally, the magnetically collected nanoparticles were washed with ethyl acetate and dried at room temperature and stored for further studies.

Functionalisation of ferrite NPs with PEI

To a homogenous dispersion of citrate-capped ferrite NPs (300 mg) in 25 mL water maintained at pH = 4 by addition of 0.1 M HCl, 2 mL of PEI (100 mg mL^{-1}) aqueous solution was added drop by drop while stirring. The reaction mixture was refluxed for 6 h and then cooled to room temperature. The PEI functionalised NPs were magnetically separated and washed 4–5 times with an excess of deionised water. The magnetic NPs were collected with the help of a magnet and dried at room temperature.

Loading of Pd NPs on PEI functionalised ferrite NPs

Under a nitrogen atmosphere, PEI functionalised ferrite NPs (0.2 g) were dispersed in 20 mL of deionised water by sonication for 1 h followed by stirring at room temperature for 30 min. After adjusting the pH of the solution to 6, sodium tetrachloropalladate (5 mL, 0.056 M) was added dropwise whilst stirring and the solution was stirred further for 1 h. Whilst stirring the solution vigorously, 0.5 mL of freshly prepared sodium borohydride (1 mM) solution was added dropwise to reduce Pd^{2+} to Pd(0). The solution was kept closed for 1 h under stirring to ensure the complete reduction of Pd^{2+} ions. The Pd NP immobilised on PEI functionalised ferrite NPs ($Pd@Fe_3O_4$) were collected by an external magnet and washed with excess of deionised water for 3–4 times and finally with ethyl acetate and dried at room temperature. The catalyst preparation can be scaled up simply by taking higher amount of the PEI functionalised ferrite particles to load with Pd nanoparticles. We could synthesise the catalyst in ~1.0 g scale in a single batch to use in our experiments.

$Pd@Fe_3O_4$ catalyst for hydrogenation and Suzuki–Miyaura coupling reactions

In a typical reaction to demonstrate the catalytic activity of $Pd@Fe_3O_4$ for hydrogenation of nitroarenes and unsaturated compounds, 2 mmol of the reactant was dissolved in 5 mL of ethanol with 50 mg of catalyst under 1 atm of hydrogen pressure. The reaction progress was monitored by thin layer chromatography (TLC) and conversion was estimated by gas chromatography (GC) after separating the catalyst from the reaction mixture with a magnet. The catalyst was then washed several times with chloroform and dried at room temperature for its reuse. To compare the activity of $Pd@Fe_3O_4$, commercial Pd/C (Aldrich, 10 wt% of Pd) was also used as catalyst under similar reaction conditions.

In the Suzuki–Miyaura coupling reactions, 0.5 mmol of the aryl chloride was taken in 5 mL of methanol. To this solution, 0.6 mmol of phenyl boric acid and 1.5 mmol of K_3PO_4 were added. The amount of catalyst used in each reaction was 50 mg, and the reaction mixture was refluxed at 60 °C. Completion of the reaction was monitored by thin layer chromatography (TLC). The same procedure was used for the bromo and iodo derivatives except with temperatures maintained at 50 and 45 °C, respectively. After completion of the reaction an excess amount of diethyl ether was added to the reaction mixture, and then a magnet was used to separate the catalyst from the reaction mixture. The pure product was isolated by column chromatography and confirmed with ^1H NMR studies. The separated catalyst was washed several times with chloroform and dried at room temperature for use in the next run.

Characterization

Powder X-ray diffraction (PXRD) measurements were performed on a Seimens (Cheshire, UK) D5000 X-ray diffractometer using CuKα ($\lambda = 1.5406$ Å) radiation at 40 kV and 30 mA with a standard monochromator using a Ni filter. Transmission electron microscope (TEM) (Philips Tecnai G^2 FEI F12, operating at 80–100 kV) was used to investigate morphology and size of the particles. For higher magnification TEM analysis, the samples were characterised using a JEOL TEM 2010 microscope operating at 200 kV. The samples for TEM were prepared by dispersing the material in water and drop-drying onto a Formvar resin coated copper grid. FT-IR spectra were recorded on a Nicolet Nexus 670 spectrometer equipped with a DTGS KBr detector over a range of 4000–400 cm^{-1}. The UV-DRS (ultraviolet diffuse reflectance spectroscopy) analysis was done on a GBC UV-Vis Cintra 10/20/40 spectrometer using KBr diluted pellets of solid samples and pure KBr used as the reference. For elemental analysis, a Perkin Elmer Analyst 300 atomic absorption spectrometer was used. Thermogravimetric analysis was done with Mettler Toledo star TG analyzer under an N_2 atmosphere, with a heating rate of 10 °C min^{-1} from 25–1000 °C. Magnetic properties of the powder samples were evaluated using a ADE-EV9 vibrating sample magnetometer. GC analysis of the reaction mixtures was performed using Shimadzu GC-1010 using a ZB–5 capillary column. ^1H NMR spectra were recorded on a Varian Gemini 200 MHz and Avance 300 MHz spectrometers. Chemical shifts (δ) are reported in parts per million (ppm) using TMS as an internal standard.

Results and discussions

The TEM image in Fig. 1a shows that the synthesized citrate functionalised Fe_3O_4 nanoparticles are of nearly spherical shape with an average size of 10 ± 0.5 nm. The XRD pattern (Fig. 2a) confirms that the nanoparticles are magnetite (Fe_3O_4) and the average crystallite sizes estimated using Scherrer's equation is ~8.7 nm. The crystallite size nearly matches with the average particle size seen in the TEM analysis indicating that the particles are mostly constituted of a single crystalline domain. The

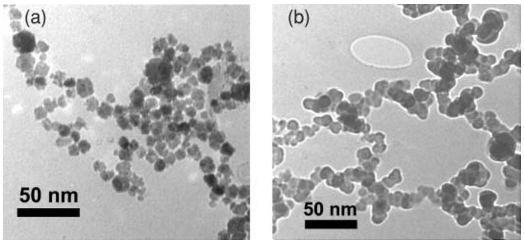


Fig. 1 TEM images of (a) citrate functionalised ferrite; (b) PEI-citrate functionalised ferrite.

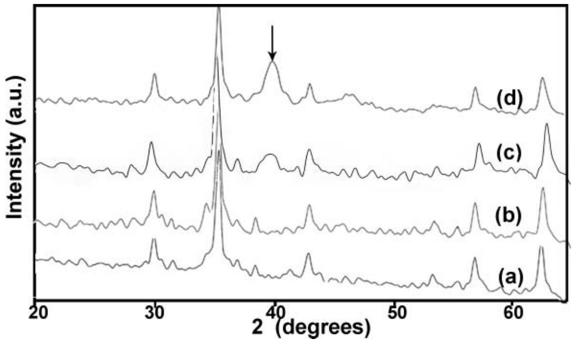


Fig. 2 XRD patterns of (a) citrate functionalised ferrite; (b) PEI-citrate functionalised ferrite; (c and d) Pd@Fe_3O_4 with 8.68 and 12.56 wt% of Pd loadings, respectively. The arrow mark indicates the (100) diffraction peak due to metallic Pd.

room-temperature magnetization curve for these nanoparticles, as measured by a vibrating sample magnetometer is shown in the ESI (Fig. S1).† The absence of remanence magnetization and coercivity reveals the superparamagnetic nature of the nanoparticles. The presence of citrate groups on the surface of ferrite NPs is characterized by FTIR spectroscopy (ESI, Fig. S2a).† For functionalisation with amine groups, branched polyethylenimine is reacted with citrate to form amide linkages. FTIR analysis (ESI, Fig. S2b)† shows that the amide linkage is accompanied with a shift in the carbonyl stretching frequency from 1622 cm^{-1} in citrate functionalised ferrite NPs to 1538 cm^{-1} for the amide bond in the PEI functionalised ferrite NPs.[10] The broad band at 3356 cm^{-1} is assigned to the surface-adsorbed water and the N–H stretching of the free amine groups and the band at 2924 cm^{-1} is assigned to the C–H stretching vibrations in PEI and citrate attached on the ferrite surface. The vibration at 1331 cm^{-1} is due to C–N stretching of amine groups, whereas the sharp peak at 578 cm^{-1} corresponds to the Fe–O stretching frequency for ferrite particles.[11] As estimated from the XRD (Fig. 2b), the average crystallite sizes of PEI functionalised Ferrite NPs remains unaffected during the functionalisation process. The TEM studies (Fig. 1b) reveal that after functionalisation the particles are interconnected to form a network-like structure.

From the thermal studies (ESI, Fig. S3)† we estimated an organic content of 12.51 wt% corresponding to citrate and PEI present on the ferrite NPs surface. The free amines on the ferrite NPs surface are then utilized to entrap $PdCl_4^-$ ions, which first bind with the positively charged ammonium groups in PEI at pH = 6. The bound ions are then reduced by sodium borohydride producing Pd(0)@Fe_3O_4. We monitored this reduction process by UV-vis spectroscopy (ESI, Fig. S4).† The disappearance of absorbance due to Pd(II) was obscured by the absorbance from the ferrite NPs and hence it was not helpful in ascertaining the reduction. However, the presence of a broad plasmon absorbance with shift in its baseline indicated the formation of Pd(0). The weight percentage of Pd in the material as determined by atomic absorption spectroscopic (AAS) analysis was 8.68 wt%. The as-synthesised Pd@Fe_3O_4 can be dispersed in various polar solvents, namely, water, ethanol, DMF, methanol *etc.*

In Fig. 2c the XRD results could not establish the formation of metallic Pd because of the lower Pd content. When the Pd loading was increased to 12.56 wt%, we could see the appearance of a diffraction peak at 39.86° due to Pd in metallic state (Fig. 2d). Moreover, there were no Bragg reflections due to any crystalline PdO within the detection limit. Furthermore, to ascertain the oxidation state of Pd, the material was characterized by X-ray photoelectron spectroscopy. In Fig. 3 the deconvoluted spectrum shows a doublet typically seen in Pd(0) containing catalysts.[12] The Pd $3d_{5/2}$ binding energy (BE) at 335.3 eV is assigned to the presence of metallic Pd similar to that seen in Pd/C or Pd powder having BE = 334.5 eV and 335.6 eV, respectively.[12,13] It is known that electron withdrawing groups around the Pd can increase the BE of Pd,[14] while an increase in BE up to 1.6 eV can be due to a decrease in size to form smaller particles of <10 nm.[15] These previous studies prompted us to interpret that Pd exists as Pd(0) in Pd@Fe_3O_4 and there are two types of such species. The first one being larger Pd nanoparticles >10 nm has a binding energy of 335.3 eV[13] and the second one corresponds to smaller Pd particles with a binding energy of 336.7 eV. The higher binding energy at 336.7 eV (Pd $3d_{5/2}$) for the Pd(0) in smaller sized Pd nanoparticles (5–7 nm) has been attributed to a relatively compact ligand environment, which reduces the extent of atomic relaxation during the charge generated by the core-electron loss.[12] More importantly these smaller Pd sites in Pd(0) containing catalysts are the ones responsible for higher catalytic activity in Suzuki–Miyaura reactions.[12]

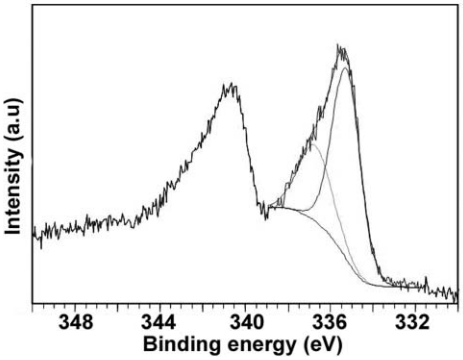


Fig. 3 XPS spectrum of the Pd@Fe_3O_4 showing Pd $3d_{5/2}$ and Pd $3d_{3/2}$ binding energies.

The TEM images of Pd@Fe_3O_4 are shown in Fig. 4. There is no apparent change in the morphology of the magnetic particles after Pd loading. As seen in the high magnification TEM image (Fig. 4b), the Pd nanoparticles are clearly distinguishable with the difference in their contrast. There are Pd particles of 2–6 nm and some have agglomerated into bigger particles of >10 nm. This observation further supports the XPS results that

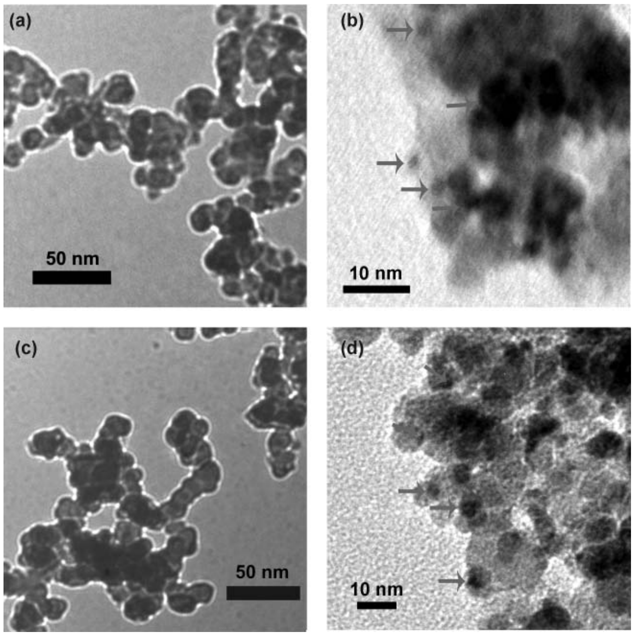
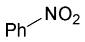
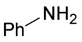
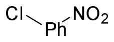
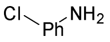
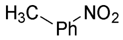
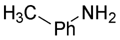
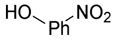
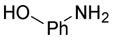
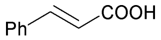
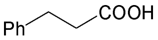
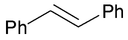
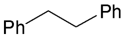
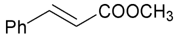
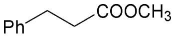
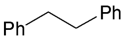
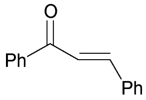
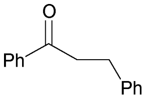
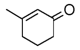
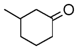


Fig. 4 TEM images of the catalyst Pd@Fe_3O_4; (a and b) low and high-magnification TEM images of the fresh catalyst, respectively; (c and d) low and high-magnification TEM images of the catalyst after five cycles of Suzuki–Miyaura reactions, respectively. The arrows indicate some of the Pd nanoparticles.

Table 1 Hydrogenation of various substrates using Pd@Fe_3O_4 as catalyst[a]

Entry	Reactant	Product	Conversion (%)	t/min
1			>99	60
			>99[b]	60[b]
			>99[c]	180[c]
2			>99	60
3			>99	60
4			>99	60
5			>99	60
6			98	60
7			93	60
8			>99	60
9			>99	60
10			>99	60

[a] Reaction conditions: catalyst = 50 mg (Pd, 0.203 mol%); H_2 = 1 atm; substrate = 2 mmol; solvent = ethanol. [b] Conversion after 10 runs. [c] With Pd/C (Aldrich, 10 wt% Pd).

there are Pd nanoparticles of two different size distributions in Pd@Fe_3O_4.

The catalytic activity of Pd@Fe_3O_4 was tested for various hydrogenation reactions (Table 1). We observed an efficient catalytic activity for the catalyst in hydrogenation of nitroarenes to aniline carried out with 1 atm pressure of H_2 at room temperature. As the amine groups are known to enhance the catalytic activity of Pd,[3–5] the PEI on the ferrite surface provides the ideal environment for better conversions when compared with the commercial Pd/C catalyst. The commercial Pd/C catalyst takes three hours for the completion of the reaction, whereas the Pd@Fe_3O_4 completes the reaction in one hour with relatively low Pd loading under similar experimental conditions. The Pd@Fe_3O_4 catalyst exhibits a TOF = 48.5 h^{-1} ($mol_{converted}$ $mol^{-1}{}_{Pd}$ h^{-1}) in contrast to 14.04 h^{-1} for the Pd/C catalyst. The Pd@Fe_3O_4 catalyst is also active in reducing substrates with various functional groups with similar efficiency (Table 1).

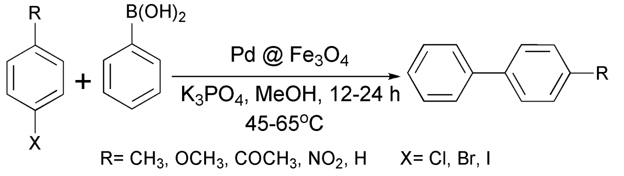
After the reaction was complete, the used catalyst was easily recovered from the reaction mixture with an external magnet. The superparamagnetic property of ferrite nanoparticles facilitated the magnetic separation of the catalyst while ensuring redispersion of the particles in the solvent for further use. The recovered Pd@Fe_3O_4 catalyst showed the same Pd content indicating the Pd leaching was insignificant. With Pd/C, the separation of the catalyst from the reaction mixture is tedious and Pd leaching is also not controllable. The filtrate of the reaction system containing 10 wt% Pd/C was brown in colour, owing to almost 90% leaching of the Pd after just one run.[16] The recovered Pd@Fe_3O_4 catalyst was tested for activity and recyclability. As shown in Table 1, the catalytic activity in hydrogenation of nitrobenzene to aniline remained unaffected for 10 runs with an accumulated TON = 485 and TOF = 48.5 h^{-1}. The estimated Pd content (8.6 wt%) remained just about the same as the fresh catalyst. The recyclability of the catalyst can be attributed to the efficient stabilisation of the active Pd metal by the highly branched PEI present on the ferrite surface. Furthermore, the versatility of the catalyst was demonstrated for other hydrogenation reactions involving reduction of various unsaturated compounds with equal effectiveness. The presence of bulkier substituents did not affect the reactivity indicating that the Pd sites are easily accessible to the reactants.

The efficiency and stability of Pd@Fe_3O_4 prompted us to use the catalyst for the commercially important Suzuki–Miyaura coupling reactions.[16] The chemical conditions for performing Suzuki–Miyaura coupling reactions generally employs the use of phosphine ligands along with Pd. However, Pd-catalysed Suzuki coupling under phosphine-free conditions is a topic of considerable interest because of both economic and environmental reasons. Another limitation of Suzuki–Miyaura coupling is that more economical aryl chlorides are less reactive than aryl bromides and iodides. To verify the effectiveness of the Pd@Fe_3O_4 catalyst, we investigated the reactions of aryl halides with phenyl boric acid (Scheme 1). The yields were 75–95% for aryl chlorides bearing a variety of substituents (Table 2). It is interesting to note that the activity is comparable with those for bromo and iodo derivatives. On the other hand, the Pd/C catalyst showed lower activity. Based on the most accepted Suzuki–Miyaura reaction mechanism, Pd is active only

Table 2 Suzuki–Miyaura coupling reactions involving aryl chlorides, bromides and iodides with phenyl boric acid[a]

Entry	R	X	Yield[b] (%)	TON ($mol_{product}\ mol^{-1}{}_{Pd}$)	TOF ($mol_{product}\ mol^{-1}{}_{Pd}\ h^{-1}$)	t/h
1	H	Cl	94	11.5	0.48	24
			92[d]	57.0[e]	0.48[e]	24
2	NO_2	Cl	95	11.6	0.49	24
			49[c]	5.2[c]	0.22[c]	24
3	CH_3	Cl	85	10.4	0.43	24
4	$COCH_3$	Cl	89	10.9	0.46	24
5	OCH_3	Cl	75	9.2	0.38	24
6	H	Br	95	11.6	0.65	18
			93[d]	57.6[e]	0.64[e]	18
7	NO_2	Br	96	11.8	0.65	18
			60[c]	6.4[c]	0.35[c]	18
8	CH_3	Br	90	11.0	0.61	18
9	$COCH_3$	Br	92	11.3	0.63	18
10	OCH_3	Br	89	10.9	0.61	18
11	NO_2	I	95	11.6	0.97	12
			84[c]	8.9[c]	0.74[c]	12
12	CH_3	I	91	11.2	0.93	12
13	$COCH_3$	I	93	11.4	0.95	12
14	OCH_3	I	90	11.0	0.92	12

[a] Reaction conditions: catalyst = 50 mg (Pd, 0.816 mol%); aryl halide = 0.5 mmol; phenyl boric acid = 0.6 mmol; K_3PO_4 = 1.5 mmol; solvent = methanol. [b] Isolated yield. [c] With Pd/C (Aldrich, 10 wt% Pd). [d] Yield in 5th run with Pd@Fe_3O_4. [e] Accumulated TON and TOF after 5 runs.



Scheme 1 Schematic illustration of Suzuki–Miyaura coupling reactions.

in the Pd(0) oxidation state[17] and the smaller Pd nanoparticles with a relatively higher BE of 336.7 eV are expected to be the reasons for the high catalytic activity of the catalyst Pd@Fe_3O_4 in comparison with Pd/C. The catalyst could be collected from the reaction medium by a magnet for reuse. As shown in Table 2, the recovered catalyst retains its activity over 5 consecutive runs. The accumulated TON and TOF are 57.01 and 0.48 h^{-1}, respectively, for the reaction of chloro benzene with phenyl boric acid. AAS results also showed that Pd leaching is negligible (Pd wt% ~8.65). Thus, the reusability can be ascribed to effective stabilization of Pd in the catalyst, which prevents leaching or aggregation of the active metal. Furthermore, the TEM images in Fig. 4c–d reveal that the morphology of Pd@Fe_3O_4 does not go any drastic change and the size of the Pd nanoparticles (2-6 nm) remains almost similar before and after the reaction.

To confirm that the catalytic activity originated from the supported palladium and not from temporarily leached Pd, a controlled experiment was performed by carrying out the reaction of iodo nitrobenzene with phenyl boric acid in presence of the filtrate, which was obtained after removal of the solid catalyst at the same reaction temperature. After 12 h of reaction, only a trace amount of the corresponding product could be identified. This result confirms the heterogeneous nature of catalysis by the supported palladium on magnetic nanoparticles.

Conclusion

In summary, we have demonstrated here a methodology to use suitably surface functionalised ferrite nanoparticles as magnetic catalyst support. The amine groups of branched PEI on the ferrite surface stabilise Pd(0) and prevents metal leaching during the reaction. The superparamagnetic nature of Pd@Fe_3O_4 allows for easy separation and redispersion of the catalyst for its reuse. Moreover, the environment provided by the amine groups immobilising Pd(0) in Pd@Fe_3O_4 results in excellent catalytic activity for a host of substrates in hydrogenation and Suzuki–Miyaura reactions. The catalyst does not require activation or any toxic ligand. Importantly, the structural stability of the Pd metal particles was the key for achieving such a stable recyclable heterogeneous catalyst for these reactions. All these advantages make Pd@Fe_3O_4 a competitive catalyst and thus can be a clean and convenient alternative for other industrially important reactions.

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