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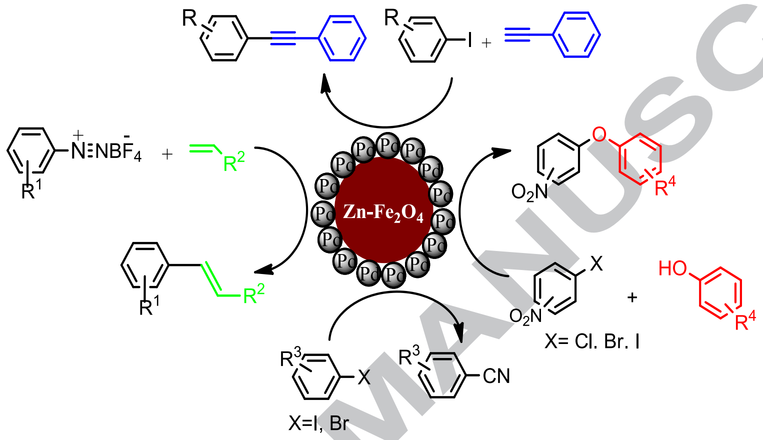

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Palladium supported on zinc ferrite: An efficient catalyst for ligand free C-C and C-O cross coupling reactions

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ABSTRACT

An efficient superparamagnetic Pd–$ZnFe_2O_4$ solid catalyst has been synthesized by loading Pd(0) species on zinc ferrite nanoparticles. Sonogashira cross couplings between terminal alkynes and aryl halides were achieved in the absence of any Cu co-catalyst. A Heck–Matsuda coupling reaction of structurally different aryldiazonium tetrafluoroborate substrates was preceded at 40°C in water. Cyanation of aryl halides was successfully done using $K_4[Fe(CN)_6]$ as the cyanide source over Pd–$ZnFe_2O_4$. The catalyst was also employed for Ullmann type cross coupling reactions. Excellent yield of the products, reusability and uncomplicated work-up make this catalyst efficient for C-C and C-O coupling reactions. Good yield of products, easy separation and negligible leaching of Pd from the catalyst surface confirm the true heterogeneity in these catalytic reactions.

Nowadays, magnetic nanomaterials as catalyst support have been efficiently employed in heterogeneous catalysis for various organic reactions.[1] In this context, Pd-catalyst supported on various magnetic nanoparticles has been widely used for different organic transformation reactions.[2-9] Metal nanoparticles anchored on the oxide surface work more efficiently as compared to bulk particles.[10]

The palladium catalyzed cross-coupling reactions are well known for generation of carbon-carbon bonds.[11-13] Sonogashira reaction, Heck reaction and cyanation reaction are excellent methods for the synthesis of organic compounds.[14-16] Sonogashira cross-coupling usually involves the coupling between aryl halide with aryl alkyne and many other terminal alkynes. This reaction was performed in an inert atmosphere using either an expensive gold(I) catalyst or phosphine containing Pd-catalyst along with CuI as co-catalyst.[17] However, in the presence of CuI as co-catalyst the dimerization of the alkyne as a byproduct takes place. Numerous modifications have been made using Zn, Sn, B, Al, AgOTf, Ag_2O, etc., instead of Cu, to enhance the yield of cross-coupling products.[18] Thus several attempts have been made to minimize the homo-coupling product by using bulky ligands in combination with palladium. The reaction proceeds well yielding considerable amounts of desired cross-coupling products by using Pd–$ZnFe_2O_4$ magnetic nanoparticles (MNPs) as a heterogeneous catalyst. The coupling of aryl halides with olefinic compounds known as Heck reaction, is an excellent method for the synthesis of organic compounds.[19] These products are widely present in pharmaceuticals and natural products.[20] Arenediazonium salts are a prospective alternative to aryl halides and are commonly used in Heck–Mizoroki reactions. This reaction has been performed in the presence of N-heterocyclic carbene ligands, palladacycle systems, ligand-free and heterogeneous conditions.[21] The palladium nanoparticles have also been widely used for such coupling reactions.[22] Herein we report a new catalytic application of palladium supported on zinc ferrite for the Heck–Matsuda coupling reactions using aryl diazonium salts. The nitrile compound and their derivatives are of considerable interest in organic chemistry as they are building blocks in the synthesis of agrochemicals, dyes, herbicides, pharmaceuticals and natural products.[23] Several synthetic strategies, and various ligands, have been developed to improve the synthesis of benzonitrile.[24] However, only a few catalytic systems in this context were able to accomplish by discarding the lethal cyanide source and minimizing production of heavy metal waste, together with good reusability. Here we explore the catalytic activity of Pd–$ZnFe_2O_4$ magnetic nanoparticles as efficient heterogeneous catalyst under mild reaction conditions.

Apart from C-C coupling reaction, the C-O coupling reaction between aryl halides and phenols for the generation of diaryl ether derivatives is also very promising for the synthesis of medicinal and important natural products. Among the diaryl ethers the nitro substituted diphenyl ethers are important as bioactive compounds.[25] The traditional Ullmann-type coupling procedure requires stoichiometric amount of reagent and very

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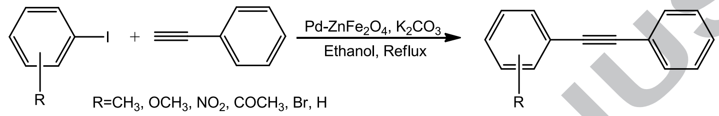
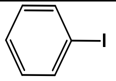
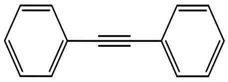
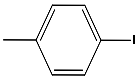
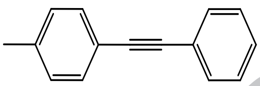
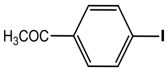
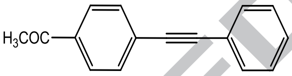
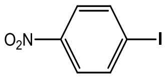
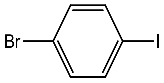
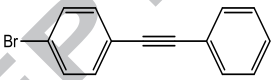
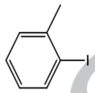
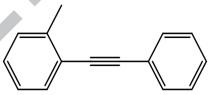
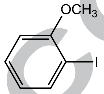
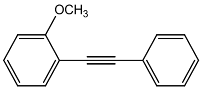
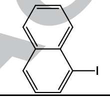
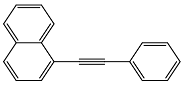
high temperatures.[26] In order to overcome these problems various ligands in combination with transition metals such as palladium and copper have been used.[27] Many of these methods suffer from the drawback of costly ligands and non recyclability of the catalyst. Recently we have reported palladium supported on zinc ferrite as a highly active, magnetically separable catalyst for ligand free Suzuki and Heck coupling.[28] Herein we report the application of our catalyst for C-C and C-O bond formation reactions as an environmentally benign, heterogeneous and recyclable catalyst. The catalyst was synthesized by loading Pd° species on zinc ferrite nanoparticles by ultrasound assisted co-precipitation in the absence of surface stabilizer or capping agents (Supplementary data).

We have carried several C–C and C-O cross-coupling reactions such as Sonogashira, Heck, cyanation and Ullmann using $ZnFe_2O_4$ magnetic nanoparticles catalyst.

Table 1

Sonogashira reaction of various aryl halides with alkynes catalyzed by Pd–$ZnFe_2O_4$ MNP[a]



Entry	Aryl halides	Products	Time (h)	Yield (%)[b]
1			12	90, 89[c], 89[c], 87[c]
2			13	82
3			13	85
4			12	93
5			12	70
6			13	84
7			14	82
8			12	88

[a] Reaction condition: 0.5 mmol of aryl halide, 0.75 mmol of terminal alkyne, 1.25 mmol of K_2CO_3, 10mg of Pd–$ZnFe_2O_4$ MNPs and 3 mL ethanol, reflux.

[b] Isolated yield by column chromatography.

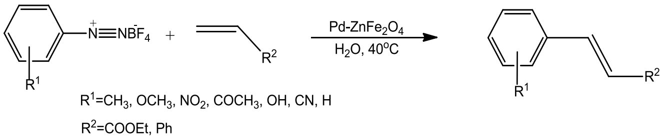
[c] The reaction was accomplished with reused catalyst.

After completion of these reactions, the catalyst was separated simply by using an external magnet and the reaction mixture was subjected to further work-up for collection of alkynes, arylated styrene or acrylate, benzonitriles and nitro substituted diphenyl ethers. Under the optimized reaction conditions, various substituted aryl iodides were subjected to couple with aromatic terminal alkynes to obtain di-substituted alkynes. The above catalytic system does not require any inert atmosphere and Cu(I) salt which leads to the formation of undesirable homocoupling products. The reaction of iodobenzene with phenylacetylene was chosen as a model reaction for which 90% yield of cross-coupling product was obtained.[29] Good to excellent yields were obtained for various substituted halides which are studied and the results are depicted in (Table 1). The catalyst show excellent chemoselectivity (iodine vs. bromine) and lack of steric hindrance (Table 1, entries 5-6).

The scope of the catalyst was further extended to Heck–Matsuda coupling reaction, using aryl diazonium tetrafluoroborate and alkenes. Initially the reaction of 4-methylphenyl diazonium tetrafluoroborate with ethyl acrylate was chosen as a model reaction.[30] The reaction conditions were optimized for model reaction, where 0.5mmol of aryl diazonium tetrafluoroborate was treated with 0.75mmol of styrene or acrylate at 40 °C using water as solvent and under base free condition. The reaction in the absence of catalyst under optimized condition did not proceed at all. Various substituted aryl diazonium tetrafluoroborate were studied and good to excellent yield of the arylated styrene or acrylate products were obtained. The results are presented in Table 2.

Table 2

Reaction of diazonium tetrafluoroborates with styrene and ethyl acrylate in the presence of the catalyst in water[a]



Entry	R_1	R_2	Yield (%)[b]
1	H	COOEt	81
2	4-CH_3	COOEt	85
3	4-NO_2	COOEt	87
4	4-OCH_3	Ph	82
5	4-NO_2	Ph	86
6	4-OH	Ph	81
7	4-OH	COOEt	85
8	4-$COCH_3$	Ph	84
9	4-CN	Ph	85
10	4-CH_3	Ph	80

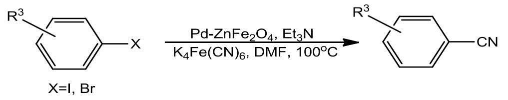
[a] Reaction condition: 0.5 mmol of aryldiazonium tetrafluoroborate, 0.75 mmol of alkene, 10mg of Pd–$ZnFe_2O_4$ MNPs and 3 mL water, 40°C, reaction time 4 h.

[b] Isolated yield by column chromatography.

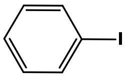
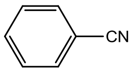
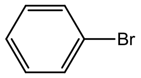
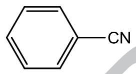
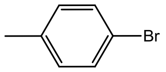
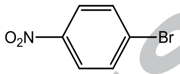
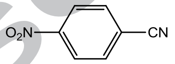
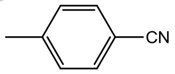
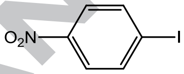
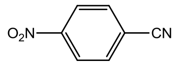
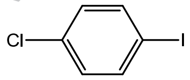
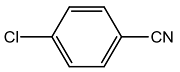
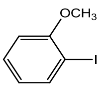
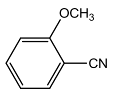
The catalytic activity of the catalyst was also explored for the cyanation reactions of aryl halides to form corresponding benzonitriles. The reaction proceeds very efficiently for aryl iodides and aryl bromides in the presence of non-toxic potassium ferrocyanide.[31] The various substituted benzonitrile derivatives were obtained in moderate to good yield. However these C-C coupling reaction failed in the absence of catalyst indicating the importance of palladium in the reaction. Various aryl halides with electron donating and withdrawing groups were studied for the reaction and the results are shown in Table 3. The catalyst works efficiently for iodo and bromo derivatives, however it failed to catalyze the less reactive chloro substituent (Table 3, entry 7).

Table 3

KCN free cyanation of aryl halides with $K_4Fe[(CN)_6]$ over Pd-$ZnFe_2O_4$ MNP[a]



R^3=CH_3, OCH_3, NO_2, Cl

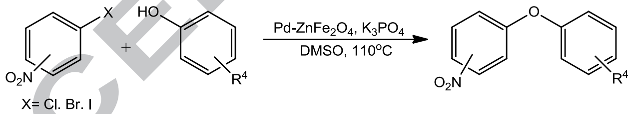
Entry	Substrate	Product	Time (h)	Yield(%)[b]
1			10	90
2			12	81
3			13	83
4			12	85
5			11	85
6			10	91
7			10	86
8			12	75

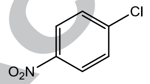
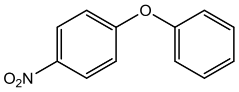
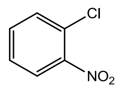
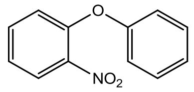
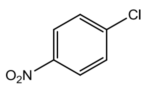
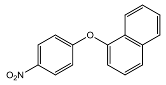
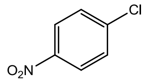
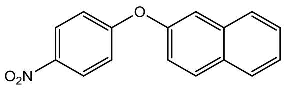
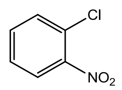
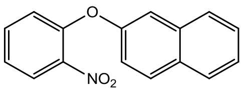
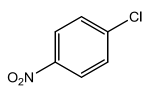
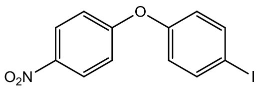
[a] Reaction condition: 0.5 mmol of aryl halide, 0.35 mmol of potassium ferrocyanide, 0.6 mmol of triethylamine, 10mg of Pd–$ZnFe_2O_4$ MNPs and 3 mL DMF, 100°C

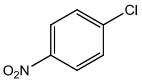
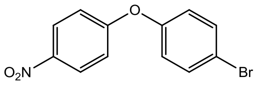
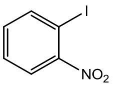
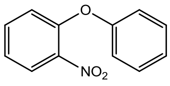
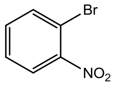
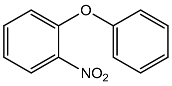
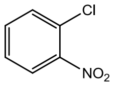
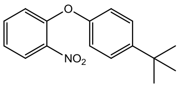
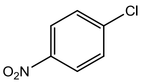
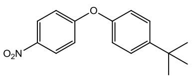
[b] Isolated yield by column chromatography.

Table 4

Pd–$ZnFe_2O_4$ MNP catalyzed C–O cross coupling reaction[a]



Entry	Substrate	Product	Time (h)	Yield(%)[b]
1			4	89, 88[c], 86[c], 84[c]
2			3.5	91
3			4	88
4			4	86
5			3.5	92
6			5	85

7			5	81
8			4	84
9			4	88
10			3.5	90
11			4	86

[a] Reaction condition: 0.5 mmol of aryl halide, 0.65 mmol of phenol, (1.0 mmol) of K_2CO_3 10mg of Pd–$ZnFe_2O_4$ MNPs and 2 mL DMSO, 100°C.

[b] Isolated yield by column chromatography

[c] The reaction was accomplished with reused catalyst.

After C-C coupling the catalyst activity was further explored for C-O coupling reaction. Nitro substituted aryl halides act as important precursors for amino compounds as well as intermediates for several bioactive molecules. Hence the development of methodology for the synthesis of these nitro substituted compounds through coupling reaction is highly desirable. The reaction of 4-chloronitrobenzene with phenol was chosen as a model reaction and the reaction afforded product with 88% yield.[32] The reaction of 1 and 2-napthol with 4-chloronitrobenzene and 2-chloronitrobenzene gave considerable yield of the desired products (Table 4, entries 3–5). The electron rich phenols also afforded the corresponding diarylethers in good yields. Reasonable yields were obtained for electron deficient phenols (Table 4, entries 6–7). The reaction of 4-substituted chloronitro benzenes with 4-bromo and iodo substituted phenols under similar conditions provided chemoselective cross coupled products (Table 4, entries 6–7). The ortho substituted iodo and bromo nitrobenzenes under identical conditions gave good yields of the desired products (Table 4, entries 8–9). The reaction of 2-chloronitrobenzene and 4-chloronitrobenzene with electron rich phenols afforded the corresponding diarylethers in good yield (Table 4, entries 10–11).

The recyclability of the catalyst was studied for the Sonogashira and Ullmann cross coupling reactions. The reaction mixture was cooled to room temperature after completion and the catalyst (MNP) was separated using an external magnet. The catalyst was then washed with ethanol, dried at 100°C for 3h and preserved for next run. The TEM image of the catalyst was studied for before and after three recycles runs (Supplementary data). The image of recycled catalyst shows that there was no significant change in the morphology and dispersion of the catalyst particles.

The amounts of Pd leaching into solution for the Sonogashira and Ullmann type coupling reactions were determined through ICP-AES. In Sonogashira cross coupling reaction, no deactivation of catalyst was found for three consecutive cycles. Similarly the catalyst was found to be highly active in recyclable study of Ullmann coupling reactions. Hot filtration test of Sonogashira and Ullmann cross coupling reactions were determined. No increase in the product yield was observed even after 24 h which suggests the negligible palladium leaching and heterogeneity of the catalyst. The ICP-AES elemental analysis of the filtered solution after magnetic separation shows the palladium concentration of 10 ppb for Sonogashira reaction and 21 ppb for Ullmann reaction. This loss in Pd content explains the decrease in yield with increase in the number of recycle runs.

In summary, we have synthesized efficient superparamagnetic Pd–$ZnFe_2O_4$ nanoparticles which have been applied as an efficient heterogeneous catalyst for C–C and C-O cross-coupling reactions. The reactions are carried out in an environmentally benign condition, giving moderate to good yields for the respective coupling products. The reusability of the catalyst was tested up to three recycle runs. Copper-free Sonogashira couplings in ethanol, Heck–Matsuda reaction of diazonium salt in water, cyanide-free cyanations of aryl halides and Ullmann type coupling of phenols gave respective coupling products with the Pd–$ZnFe_2O_4$ catalyst. Hence the catalyst offers a mild and efficient protocol over existing methods under ligand free conditions.

Acknowledgments

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29. Sonogashira cross coupling: In a typical procedure, the Sonogashira coupling reactions consist of aryl halide (0.5 mmol) in 3mL of pure ethanol, phenyl acetylene (0.75 mmol), K_2CO_3 (1 mmol) and 10 mg of the Pd–$ZnFe_2O_4$ catalyst (0.000764mmol of Pd or 0.153 mol% of Pd). The reaction was carried out under reflux condition for 11-14 h and was monitored by Gas chromatography (GC). After completion, the reaction mixture was cooled to room temperature and the catalyst (MNPs) was separated using an external magnet. The catalyst was then washed with ethanol, dried at 100 °C for 3h and preserved for next cycle. The pure product was obtained using silica gel column chromatography using n-hexane-EtOAc as mobile phase.
30. Heck–Matsuda coupling: Aryldiazonium tetrafluoroborate (0.5 mmol) and (0.75 mmol) of alkene were added to a flask containing 10mg of the Pd–$ZnFe_2O_4$ catalyst and water (3 ml) at 40 °C. The resulting mixture was heated in air for 4 h. The reaction mixture was then cooled to room temperature and washed with Et_2O (3 x 5 ml) to extract the desired product. Further purification was performed using silica gel column chromatography eluted with n-(hexane–EtOAc :: 95:5) to yield the desired aryl alkene products in high yield.
31. Cyanation: In a typical procedure, a mixture of aryl iodide (0.5 mmol), $K_4[Fe(CN)_6]$ (0.35 mmol), catalyst Pd–$ZnFe_2O_4$ (10mg), triethylamine (0.6 mmol) and DMF (3 ml) was added in a round bottom flask and stirred under reflux at 120°C under atmospheric conditions. The progress of the reaction was monitored by GC. After the reaction was over, the catalyst was removed using external magnet and the solution was quenched by water. This solution was extracted thrice with ethyl acetate and washed with brine repeatedly. The organic layer was dried in anhydrous sodium sulphate and then removed by rotary evaporation to produce the pure product, which was further purified using silica gel column chromatography (hexane/EtOAc :: 90:10)..
32. Ullmann Coupling: A mixture of 4-nitrochlorobenzene (0.5 mmol), phenol (0.65 mmol), catalyst Pd–$ZnFe_2O_4$ (10 mg), and K_2CO_3 (1.0 mmol) in DMSO (2 ml) was placed in a round bottomed flask. The reaction mixture was then heated at 100 °C under magnetic stirring for 4 h. The completion of reaction was monitored by GC. After cooling to room temperature, the catalyst was separated. The reaction mixture was diluted with water, and extracted with ethyl acetate three times (3 x 10 ml). The combined organic layer was concentrated to yield the crude product, which was purified by column chromatography on silica gel (hexane/EtOAc :: 99:1).