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Introduction

NPs having a magnetic core can be easily separated from the reaction mixture by using an external magnet. This makes materials like Fe₃O₄ a promising support for nano-catalysts as easy separation improves their reusability.1 Nano-catalysts have a high specific surface area-to-volume ratio. Thus, more reactant molecules undergo association with the catalyst, enhancing the catalytic efficiency.² However, the high surface energy of a nano-catalyst can make it unstable and sometimes it causes agglomeration. On supporting the catalytic species on magnetic nanoparticles, agglomeration is prevented along with the significant advantage of recyclability, resulting from easy separation.^{3,4} Magnetically separable nano-catalysts have been designed successfully by the grafting methodology and used in metal-catalyzed organic reactions,5 organo-catalysis and enzymatic catalysis.⁶ Fe₃O₄ is a robust, low-cost, chemically stable, and readily available material of low toxicity. Therefore, it is suitable for designing magnetically retrievable NPs. The easy

Catalysis with magnetically retrievable and recyclable nanoparticles layered with Pd(0) for C–C/C–O coupling in water†

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Nanoparticles layered with palladium(0) were prepared from nano-sized magnetic Fe₃O₄ by coating it with silica and then reacting sequentially with phenylselenyl chloride under an N₂ atmosphere and palladium(II) chloride in water. The resulting Fe₃O₄@SiO₂@SePh@Pd(0) NPs are magnetically retrievable and the first example of NPs in which the outermost layer of Pd(0) is mainly held by selenium. The weight percentage of Pd in the NPs was found to be 1.96 by ICP-AES. The NPs were authenticated *via* TEM, SEM-EDX, XPS, and powder XRD and found to be efficient as catalysts for the C–O and C–C (Suzuki–Miyaura) coupling reactions of ArBr/Cl in water. The oxidation state of Pd in the NPs having size distribution from ~12 to 18 nm was inferred as zero by XPS. They can be recycled more than seven times. The main features of the proposed protocols are their mild reaction conditions, simplicity, and efficiency as the catalyst can be separated easily from the reaction mixture by an external magnet and reused for a new reaction cycle. The optimum loading (in mol% of Pd) was found to be 0.1–1.0 and 0.01–1.0 for *O*-arylation and Suzuki–Miyaura coupling, respectively. For ArCl, the required amount of NPs was more as compared to that needed for ArBr. The nature of catalysis is largely heterogeneous.

functionalization of Fe₃O₄ makes it a better alternative to other heterogeneous supports, viz., silica, graphene, and alumina. After completion of the reaction, the magnetic NPs can be easily removed from the mixture with the help of an external magnet.^{7,8} The functionalization of magnetic Fe₃O₄ with diverse functional groups, chemical entities, metal complexes, and NPs has led to efficient catalytic systems for a wide range of organic reactions.5,6,9 The metal complexes of organochalcogen ligands have emerged as promising single-source precursors for the synthesis of metal chalcogenide NPs and catalysts for various chemical transformations.¹⁰ Metal chalcogenide NPs supported on solids have been found to be efficient for catalyzing the organic reactions.11 Ru(OH)x NPs supported on selenium-silica coated Fe₃O₄ have been reported recently as efficient catalysts for amide synthesis.12 Encouraged by the catalytic potential of these metal chalcogenides, we have designed Fe₃O₄@SiO₂@-SePh@Pd(0) and investigated its catalytic activities for the C-C (Suzuki–Miyaura) and C–O coupling reactions. The NPs catalyze the reactions efficiently in water. The magnetic nanoparticles also often show a strong tendency to agglomerate as a result of self-interactions and hence, suitable protecting agents are used for stabilizing them. Therefore, Fe₃O₄ is coated with SiO₂ in the present case.13

Diaryl ether linkage is an important component of various polymers, agrochemicals, and pharmaceuticals.¹⁴ Several antibiotics and biologically active natural products like thyroxine (a mammalian hormone) have diaryl ether linkage.¹⁵ Palladium¹⁷ and copper¹⁶ are among the important metal catalysts for the *O*-

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arylation reaction. The research groups of Hartwig and Buchwald have contributed immensely in this area.¹⁸ In most of the cases, a ligand is used with a metal salt to catalyze the reaction. There is also a report on a ligand-free catalytic system.¹⁹ However, recyclable catalytic systems applicable under mild reaction conditions in water are rarely reported.¹³

Suzuki-Miyaura coupling is an important C-C coupling reaction,²⁰ affording biaryls, building blocks of natural products,²¹ agrochemicals, and pharmaceutical ingredients. The palladium complexes of phosphines,^{22,23} carbenes,²⁴ palladacycles,25 and organochalcogen ligands26 are reported as efficient homogeneous catalysts for this coupling. Several of the catalytic systems known for this coupling reaction are air- and moisturesensitive and for a good yield, an inert atmosphere is a necessity.27 Heterogeneous catalytic systems are also known28-30 for the coupling reactions as well as other organic transformations. Among them, some are air- and moisture-sensitive and require an inert atmosphere.29b Furthermore, with most of the catalysts reported for coupling and other organic reactions, an organic solvent is necessary to achieve a good yield.^{29e,30} Water, being environment-friendly, economical, non-toxic, non-flammable, cheap, and readily available,31 is of enormous interest as a solvent for catalytic reactions. Many reactions in an aqueous medium reported in the literature were performed at a high temperature and/or in the presence of a co-solvent to get a good yield of the product.30g-k Herein, we report the Fe₃O₄@SiO₂@-SePh@Pd(0) nanoparticle (NP)-catalyzed Suzuki-Miyaura coupling and O-arylation of phenol in pure water at a moderate temperature of 80 °C.

Results and discussion

The preparation of Fe₃O₄@SiO₂@SePh@Pd(0) NPs is summarized in Scheme 1. Fe₃O₄ prepared using a recently reported protocol¹² was coated with silica and treated in an aqueous medium under an N₂ atmosphere with phenylselenyl chloride and PdCl₂ successively. Magnetic Fe₃O₄@SiO₂@SePh@Pd(0) NPs were separated using an external magnet, washed with water followed by Et₂O, and dried *in vacuo* at 60 °C for 2 h. Neither Fe₃O₄@SiO₂@SePh@Pd(0) NPs nor their precursor was found to be soluble in water or the organic solvent. The weight percentage of Pd in Fe₃O₄@SiO₂@SePh@Pd(0) NPs was determined to be 1.96% with ICP-AES. TEM, SEM-EDX, and powder X-ray diffraction (PXRD) (Fig. 1) were used to authenticate the NPs as Fe₃O₄@SiO₂@SePh@Pd(0). They appeared to have irregular cubic morphology.

Powder XRD and XPS of Fe₃O₄@SiO₂@SePh@Pd(0) NPs

The PXRD pattern¹² of Fe₃O₄ exhibits peaks (*hkl*) at 220, 311, 333, and 440. They can be well indexed to the cubic phase of Fe₃O₄ and are in good agreement with the literature results (JCPDS 82-1533). The silica-coated NPs (Fe₃O₄@SiO₂) show a broader PXRD pattern¹² at $2\theta = 20$ to 29° (JCPDS 83-2470) due to their non-crystalline nature. Their peaks (*hkl*) at 220, 311, 333, and 440 correspond to the Fe₃O₄ core. After the immobilization of selenium-containing species (SePh) onto



Scheme 1 The synthesis of Fe₃O₄@SiO₂@SePh@Pd(0) NPs.

Fe₃O₄@SiO₂, additional peaks due to Se appear in the PXRD pattern of Fe₃O₄@SiO₂@SePh along with the peaks of Fe₃-O₄@SiO₂.¹² On layering Fe₃O₄@SiO₂@SePh with Pd, the dispersity of Se increases as it becomes a part of the metal's coordination sphere. Thus, peaks corresponding to Se were not detected in the PXRD pattern of Fe₃O₄@SiO₂@SePh@Pd(0) (Fig. 1). Palladium coordinated with Se and the binding of Pd with selenium donor sites was expected to be strong. The PXRD pattern of Fe₃O₄@SiO₂@SePh@Pd(0) exhibits peaks (*hkl*) at 111, 200, and 220, corresponding to Pd(0) NPs (JCPDS 87-0643). No peak indicating any impurity was noticed, thereby authenticating the purity of Fe₃O₄@SiO₂@SePh@Pd(0) NPs.

The zero oxidation state of Pd in Fe₃O₄@SiO₂@SePh@Pd(0) was established by the X-ray photoelectron spectra, as shown in Fig. 2. The binding energies of the $3d_{5/2}$ and $3d_{3/2}$ states of Pd were found to be 335.8 and 341.2 eV, respectively, which were consistent with its zero oxidation state, thereby indicating the complete reduction of Pd(π) to Pd(0).³²

TEM and SEM-EDX of Fe₃O₄@SiO₂@SePh@Pd(0) NPs

The transmission electron microscopy (TEM) images of Fe₃-O₄@SiO₂@SePh@Pd(0) NPs are shown in Fig. 3. The SEM-EDX spectrum (Fig. S2 in the ESI⁺) supports the presence of iron,



Fig. 1 PXRD of Fe₃O₄@SiO₂@SePh@Pd(0) NPs.



Fig. 2 The XPS spectra of Fe₃O₄@SiO₂@SePh@Pd(0) NPs.

oxygen, silicon, selenium, carbon, and palladium in Fe₃O₄(a)-SiO₂@SePh@Pd(0) NPs. The size distribution of these NPs was found to be approximately ~12-18 nm (Fig. S1 in ESI[†]).

Catalytic applications

O-Arylation of phenol. The Fe₃O₄@SiO₂@SePh@Pd(0) NPs were explored to catalyze the C-O coupling reaction of phenol with several aryl halides in water. The conditions for the coupling reaction were optimized for the reaction of 4-bromobenzaldehyde with phenol (Table 1). In the absence of the catalyst as well as a base, the conversion to the coupled product was negligible (Table 1, entries 7 and 8). The reaction was investigated with different quantities of the catalyst (0.01 to 0.5 mol%). The best results were achieved with 0.1 mol% catalyst loading. On increasing the quantity of the catalyst, significant improvement was not observed in the yield of the product. However, on lowering the catalyst amount to 0.01 mol%, the yield of the product decreased (Table 1, entry 9). Among the bases tested, namely, K2CO3, CS2CO3, Et3N, K3PO4, and NaOH, optimum results were obtained with NaOH (Table 1, entry 5). The performance of a range of solvents, viz., DMF, EtOH, DMSO, and toluene was tested and compared to that of water. All these alternatives to water did not show better results (Table 1, entries 10-13).

The scope of the present protocol was explored using a range of aryl halides. The results (Table 2) showed that the present catalyst was capable of coupling aryl chlorides, bromides, and iodides with phenol. The yield was good even in the case of less



Fig. 3 The TEM images of Fe₃O₄@SiO₂@SePh@Pd(0) NPs at 20 nm scale bar.

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Table 1 Screening of reaction conditions for O-arylation ^a								
Entry no.	Catalyst (mol%)	Base	Solvent	Time (h)	Yield ^b (%)			
1	0.5	K ₂ CO ₃	Water	3	83			
2	0.5	Cs_2CO_3	Water	3	78			
3	0.5	Et ₃ N	Water	3	10			
4	0.5	K_3PO_4	Water	3	45			
5	0.5	NaOH	Water	3	94			
6	0.1	NaOH	Water	3	93			
7	0.5	_	Water	12	_			
8	_	NaOH	Water	12				
9	0.01	NaOH	Water	3	76			
10	0.1	NaOH	DMF	3	79			
11	0.1	NaOH	EtOH	3	92			
12	0.1	NaOH	DMSO	3	88			
13	0.1	NaOH	Toluene	3	46			

^a Reaction conditions: 4-bromobenzaldehyde (1 mmol), phenol (1.1 mmol), solvent (5 mL), base (1.5 mmol), bath temp. (80 °C). ^b Isolated yield.

activated substrates in a short time (2-6 h) compared to many literature results.^{29a-29f} The present NPs also showed good catalytic activity for heteroaryl halides. The electronwithdrawing and releasing substituents on haloarene had a significant effect on the yield of the coupled product (Table 2). The reaction of deactivated aryl halides with phenol gave a good yield, but it was less in comparison to those of activated aryl halides. The position of a substituent on the ring of aromatic halide also affected the yield of the coupled product; the substituent at a position ortho to the halo group gave a lower



^a Reaction conditions: aryl halide (1 mmol), phenol (1.1 mmol), catalyst (0.1 mol%), time 3 h, water (5 mL), NaOH (1.5 mmol), and bath temp. 80 °C. ^b Isolated yield. ^c Catalyst 1 mol% and reaction time 6 h. ^d Catalyst 0.01 mol% and reaction time 2 h.

 Table 3
 Screening of reaction conditions for Suzuki–Miyaura reaction^a

Entry no.	Catalyst (mol%)	Base	Solvent	Time (h)	$\operatorname{Yield}^{b}(\%)$
1	0.5	K_2CO_3	Water	3	95
2	0.1	K_2CO_3	Water	3	94
3	0.1	Cs_2CO_3	Water	3	90
4	0.5	Et ₃ N	Water	3	34
5	0.5	K_3PO_4	Water	3	86
6	0.5	NaOH	Water	3	68
7	0.5	_	Water	12	_
8	_	K_2CO_3	Water	12	_
9	0.01	K_2CO_3	Water	3	81
10	0.1	NaOH	DMF	3	77
11	0.1	NaOH	DMF + water	3	92
12	0.1	NaOH	EtOH	3	91
13	0.1	NaOH	EtOH + water	3	94
14	0.1	NaOH	DMSO	3	74
15	0.1	NaOH	Toluene	3	36

^a Reaction conditions: 4-bromobenzaldehyde (1 mmol), phenylboronic acid (1.2 mmol), solvent (5 mL), and base (1.5 mmol), bath temp. (80 °C). ^b Isolated yield.

yield in comparison to that for the substrates having a substituent at the *para* position (Table 2, entries 1, 4–6).

Some of the previously reported heterogeneous catalytic systems reported for the O-arylation of phenol, viz, (i) Fe₃O₄(a)-SiO₂@PPh₂@Pd(0) (ref. 29a) (ii) maghemite-copper nanocomposites (ref. 29b) (iii) NiFe2O4 (ref. 29c) (iv) CNT@a-



^a Reaction conditions: aryl halide (1 mmol), phenylboronic acid (1.2 mmol), catalyst (0.1 mol%), time 3 h, water (5 mL), K₂CO₃ (1.5 mmol), and bath temp. (80 °C). ^b Isolated yield. ^c Catalyst 1 mol% and reaction time 6 h. d Catalyst 0.01 mol% and reaction time 2 h.

Fe₂O₃@CuO (ref. 29d) (v) Pd-ZnFe₂O₄ (ref. 29e) and (vi) CuFe₂O₃ (ref. 29f) were compared with the present catalyst (Table S1 (ESI[†])). The comparison revealed that the present protocol with Fe₃O₄@SiO₂@SePh@Pd(0) NPs was better in efficiency than those reported earlier. The medium of the reaction was water (a major advantage), with the scope and the reaction time being comparable (Table 2).

Suzuki-Miyaura coupling. The magnetically retrievable catalyst was also explored for the Suzuki-Miyaura coupling of aryl halides. The reaction of 4-bromobenzaldehyde with phenylboronic acid was chosen as the model reaction. In the absence of the catalyst and a base, no conversion was observed. K₂CO₃ as a base and water as a solvent were found to give the best combination for the reaction (Table 3). Under the optimized conditions (3 h, 0.1 mol% of the catalyst, 80 °C), nearly quantitative conversion of 4-bromobenzaldehyde to the coupled product was observed (isolated yield: 94%). On lowering the



Fig. 4 Time profiles of Suzuki-Miyaura and C-O coupling of 4-bromobenzaldehyde (1 mmol); catalyst, (0.1 mol%); phenyl boronic acid (for SMC), phenol (for C-O coupling), (1.2 mmol); K₂CO₃ (for SMC), NaOH (for C-O coupling) (1.5 mmol); water 5 mL; bath temperature, 80 °C; isolated yield in %.

Table

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Entry	Catalyst	Time (h)	Yield ^{d} % (for C–O)	Yield ^d % (for SMC)
1	Fe ₃ O ₄	6	0	0
2	Fe_3O_4 (a) SiO_2	6	0	0
3	Fe ₃ O ₄ @SiO ₂ @SePh	6	0	0
4^b	PdCl ₂	3	18	27
5	Fe ₃ O ₄ @SiO ₂ @SePh@Pd(0) NPs	3	93	94
6 ^{<i>c</i>}	Fe ₃ O ₄ @SiO ₂ @SePh@Pd(0) NPs	3	93	94

Reaction conditions: 4-bromobenzaldehyde (1 mmol); catalyst, (30 mg); phenyl boronic acid (for SMC), phenol (for C–O coupling), (1.2 mmol); K₂CO₃ (for SMC), NaOH (for C-O coupling) (1.5 mmol); water, 5 mL; temperature, 80 °C. ^b 1 mol%. ^c 100 °C. ^d Isolated yield.

loading of the catalyst to 0.01 mol%, the yield of the product decreased (Table 3, entry 9). Similar to the O-arylation of phenol, the catalyst Fe_3O_4 (a)SiO_2 (a)SePh (a)Pd(0) successfully converted several aryl halides to biaryls with very good yields in 1.5-6 h (Table 4).

The effect on the yield of the coupled product due to the nature and position of the substituent present on the benzene ring of aryl halides may be inferred from Table 4. The presence of electron-withdrawing groups gave a somewhat better yield than the electron-donating ones. The aryl halides having a substituent at the para position gave a better yield of the coupled product compared to ortho-substituted derivatives (Table 4, entries 1, 4-6). The coupling of heteroaromatic halides was also efficiently catalyzed by Fe₃O₄@SiO₂@SePh@Pd(0).

In summary, the magnetically separable Fe₃O₄(a)SiO₂(a)-SePh@Pd(0) NPs result in good catalytic conversion with low catalyst loading (0.01-1 mol%) in an aqueous medium without any co-solvent/additive. The comparison of the present catalyst for Suzuki-Miyaura coupling with the previously reported ones, viz., (i) HMMS (hollow magnetic mesoporous spheres)-NH₂-Pd,^{30a} (ii) Pd@Mag-MSN,^{30b} (iii) Pd-CoFe₂O₄ MNPs,^{30c} (iv) silicasupported palladium catalyst,30d (v) iron oxide-supported palladium NHC complex, 30e (vi) NiFe2O4-(dopamine)-Pd, 30f (vii) Pd/C-cetyltrimethylammonium bromide (CTAB),^{30g} (viii) layered double hydroxide (LDH)-supported nanopalladium,^{30h} (ix) Pd-polyoxomatalate nanoparticles,³⁰ⁱ (x) Pd/C^{30j} (xi) mercaptopropyl-modified mesoporous silica-supported palladium catalyst^{30k} (xii) Pd-PPh₂-SiO₂@Fe₃O₄,^{30l} (xiii) magnetic nanoparticle-supported (β-oxoiminato)-(phosphanyl) palladium complex,^{30m} and (xiv) Pd-Fe₃O₄ heterodimer nanocrystals³⁰ⁿ

made in Table S2 (ESI[†]) reveals that its catalytic efficiency is better than that of most of the related heterogeneous Pd-based catalysts.

The time profiles of both C-O and Suzuki-Miyaura coupling reactions of 4-bromobenzaldehyde (1 mmol) shown in Fig. 4 indicate that on increasing the reaction time from 3 to 5 h, there is almost no increment in the yield of the coupled product, and 78-82% of the reaction is completed in 2 h. The catalysis of both the coupling reactions with nano-sized Fe₃O₄, Fe₃O₄(a)SiO₂, and Fe₃O₄@SiO₂@SePh was attempted. No coupled product was formed even after 6 h (Table 5, entries 1-3). When the C-O coupling and SMC reactions were carried out using PdCl₂ as the catalyst under the present optimum conditions, the resulting yields were 18 and 27%, respectively (Table 5, entry 4). The yield was maximum for both the coupling reactions (Table 5, entry 5) when Fe₃O₄@SiO₂@SePh@Pd(0) NPs were used as the catalyst.

The recyclability of the catalyst was studied by carrying out the reaction between 4-bromobenzaldehyde and phenol/ phenylboronic under optimum conditions, as described in the experimental section; the results are shown in Fig. 5.

Thus, the present catalyst is reusable for at least more than 7 times but with a small loss in the yield.

The catalyst was re-analyzed with TEM, SEM-EDX, and ICP-AES after the recycling experiment. The TEM image (Fig. 6) indicates some agglomeration in the nanoparticles, which is probably responsible for the decrease in the catalytic activity with the decrease in its surface area. The SEM-EDX (Fig. S3 in ESI[†]) result revealed that the catalyst composition remained almost the same after the catalytic reaction. The palladium

O-Arylation 94% 93% 91% 95 SMC 90% 90 Yield(%) 84% 85 81% 80 75 70 Cycle 1 Cycle 2 Cycle 3 Cycle 4 Cycle 5 Cycle 6

Fig. 5 Recycling experiments.



Fig. 6 The TEM image of recycled Fe₃O₄@SiO₂@SePh@Pd(0) NPs at 100 nm scale bar.

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content of the catalyst was determined with ICP-AES before and after the seven reaction cycles; it was found to be 1.96% in the beginning and 1.91% after the seventh reaction cycle. The small amount of leaching is due to the strong binding of Pd with selenium and indicates the good stability of the present catalyst. A hot filtration test was conducted for *O*-arylation as well as SMC carried out under optimum conditions to establish the role of Pd leaching, if any, on the catalytic reaction. Both the reactions did not proceed after the removal of the catalyst as the yield remained at the same level, indicating its heterogeneous nature.²⁸

Conclusions

A magnetically retrievable palladium nano-catalyst $[Fe_3O_4@-SiO_2@SePh@Pd(0)]$ was designed and authenticated with PXRD, SEM-EDX, ICP-AES, XPS, and TEM. It catalyzed the *O*-arylation of phenol with aryl halides and Suzuki–Miyaura coupling under mild reaction conditions in water. The optimum loading (in mol% of Pd) was found to be 0.1–1.0 and 0.01–1.0 for arylation and SMC, respectively. For ArCl, the required amount of NPs was more as compared to that needed for ArBr. The nature of catalysis was heterogeneous, as revealed by hot filtration. The recyclability of the catalyst was good. The comparison with other relevant catalytic systems indicated that it was superior to them.

Experimental

Physical measurement

 1H and $^{13}\mathrm{C}\{^1H\}$ NMR spectra were recorded using a Bruker Spectrospin DPX 300 NMR spectrometer at 300.13 and 75.47 MHz, respectively. The chemical shifts were reported in ppm relative to the internal standard (tetramethylsilane) for the ¹H and ¹³C¹H NMR spectra. All the reactions were carried out in glassware dried in an oven. Powder X-ray diffraction (PXRD) studies were carried out using a Bruker D8 Advance diffractometer using Ni-filtered Cu-Ka radiation at a scan speed of 1 s and a scan step of 0.05°. Transmission electron microscopy (TEM) studies were carried out using a JEOL JEM 200CX TEM instrument operated at 200 kV. The specimens for these studies were prepared by dispersing the powdered sample in ethanol by ultrasonic treatment. A few drops of the resulting homogenized slurry were put on a porous carbon film supported on a copper grid and dried in air. The elemental composition of the NPs was studied with a Carl ZEISS EVO5O scanning electron microscope (SEM) and the associated EDX system Model QuanTax 200, which is based on the SDD technology and provides an energy resolution of 127 eV under Mn-Ka radiation. The sample was mounted on a circular metallic sample holder with a sticky carbon tape. X-ray photoelectron spectroscopic (XPS) studies were carried out on Specs instrument equipped with an Mg Kradiation source (E = 1253.60 eV) and hemispherical analyzer. The estimation of palladium in the nanoparticles was carried out using ICP-AES (DRE, PS-3000UV, Leeman Labs, Inc. USA).

Chemicals and reagents

FeCl₃·6H₂O, urea, FeSO₄·7H₂O, tetraethylorthosilicate (TEOS), PdCl₂, phenylselenyl chloride, phenol, aryl halides, phenyl boronic acid, KOH, and K₂CO₃ obtained from Sigma-Aldrich (USA) were used as received. The solvents (toluene, acetone, ethyl acetate, and ethanol) of AR grade were dried and distilled before use according to standard procedures.³³ Fe₃O₄@SiO₂@-SePh was synthesized according to a previously reported method.¹²

Synthesis of Fe₃O₄@SiO₂@SePh@Pd(0) NPs³⁴

An aqueous solution of $PdCl_2$ (1 mmol in 60 mL H₂O) was added to Fe_3O_4 @SiO₂@SePh NPs (2 g) dispersed in water, and the mixture was stirred for 30 min. The aqueous solution of sodium hydroxide (1 M) was added dropwise to the mixture until its pH reached ~12. The resulting mixture was stirred for 20 h with refluxing. The product was separated magnetically, washed 5–6 times with water followed by ethanol, and dried *in vacuo* for 2 h. The weight percentage of Pd in the catalyst was found to be 1.96% with ICP-AES.

Procedure for Suzuki-Miyaura coupling (SMC)

A round bottom flask of 50 mL was charged with aryl halide (1 mmol), phenylboronic acid (1.2 mmol), K_2CO_3 (1.5 mmol) catalyst (0.01–1.0 mol%), and deionized water (5 mL). The mixture was stirred at 80 °C. The reaction was monitored with TLC. When the conversion of aryl halide reached maximum, the reaction mixture was cooled to room temperature and extracted with diethyl ether (20 mL). The extract was dried over anhydrous Na_2SO_4 . Its solvent was evaporated with a rotary evaporator, and the residue was purified through a column of silica gel with CHCl₃/hexane as an eluent. All coupling products were analyzed with ¹H NMR spectroscopy.

Procedure for C-O coupling

Aryl halide (1 mmol), phenol (1.1 mmol), NaOH (1.5 mmol), catalyst (0.01–1.0 mol%), and deionized water (5 mL) were mixed in a round bottom flask of 50 mL and stirred at 80 °C. The reaction was monitored with TLC. On approaching the completion of the reaction, the mixture was cooled to room temperature. It was extracted with ethyl acetate (20 mL). The extract was dried with anhydrous Na₂SO₄. The solvent of the extract was evaporated with a rotary evaporator, and the residue was purified through a column of silica gel with ethyl acetate/ hexane as the eluent. All coupling products were analysed with ¹H NMR spectroscopy.

Recyclability

4-Bromobenzaldehyde was used to check recyclability. 4-Bromobenzaldehyde (1 mmol), catalyst (0.1 mol%), phenol (1.1 mmol), NaOH (1.5 mmol) [for C–O coupling]/phenylboronic acid (1.2 mmol), K_2CO_3 (1.5 mmol) [for SMC], and deionized water (5 mL) were mixed in a round bottom flask of 50 mL and stirred at 80 °C. The reaction was monitored with TLC. After completion of the C–C/C–O coupling reaction, the catalyst $(Fe_3O_4@SiO_2@SePh@Pd(0) NPs)$ was separated with an external magnet. It was washed with H₂O, dried *in vacuo* and reused for a new reaction cycle of 4-bromobenzaldehyde.

Hot filtration experiment

4-Bromobenzaldehyde (1 mmol), phenol/phenylboronic acid (1.2 mmol), NaOH/K₂CO₃ (1.5 mmol), and catalyst (0.1 mol%) were mixed with deionized water (5 mL). The mixture was stirred at 80 °C. The reaction was stopped after 1 h, and the catalyst was separated using an external magnet. The clear reaction mixture was divided into two equal parts and each part was taken separately in a 50 mL round bottom flask. The separated NPs were added to one of them. Thereafter, the reactions in both the flasks were allowed to proceed for another 3 h, and the product/conversion was analyzed with ¹H NMR spectroscopy.

Conflicts of interest

There are no conflicts to declare.

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