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PAPER

Magnetically recyclable magnetite-palladium (Nanocat-Fe-Pd) nanocatalyst for the Buchwald-Hartwig reaction

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Abstract

The immobilization of Pd on magnetite surface afforded (Nanocat-Fe-Pd) using inexpensive precursors and its catalytic role in the Buchwald-Hartwig reaction for arylation of amines and amides was investigated; C-N bond formation was achieved in moderate to excellent yields and the catalyst could be separated and recycled up to five cycles by magnetic decantation without significant loss in yield.

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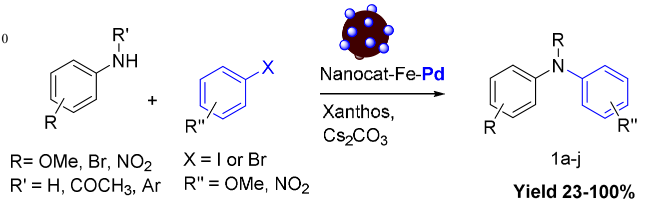
Introduction

Reagents and complexes containing transition metals are fundamental in modern organic synthesis because they allow apparently impossible reactions to occur. The palladium-catalyzed cross-coupling of (hetero)aryl (pseudo)halides and amines including amides, imides, or sulfonamides, known as the Buchwald–Hartwig cross-coupling reaction, has emerged as a highly effective C–N bond-forming protocol that is employed on industrial scales in a diverse array of products, such as pharmaceuticals and agrochemicals.[1] Being a metal catalyzed process, the recovery of the costly noble metal species is essential and also the production of arylamines uncontaminated by metal species need to be certified since metal contamination is strictly regulated by the pharmaceutical industry.[2] The advantages of homogeneous catalysts such as high selectivity, better yield, and easy optimization of the catalytic systems can’t overcome the difficulty of catalyst separation from the final product which involves cumbersome work-up thus reducing their scope. Heterogeneous catalysis is well suited to address this problem as it has the advantage of a straightforward recovery and reuse of the catalyst from the reaction mixture by simple filtration or decantation; recent developments to separate such catalysts magnetically by applying an external magnet identifies the use of magnetic nanoparticles (MNPs) as ideal solution.

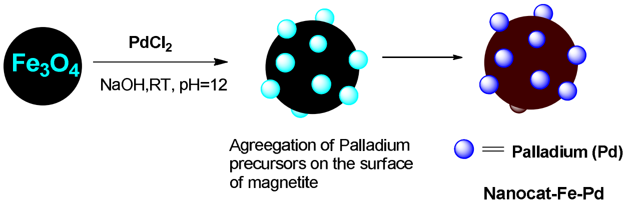
Palladium immobilization on solid supports has been applied mainly for catalytic hydrogenations and for C-C cross coupling type reactions,[3] the typical solid supports being carbon, metal oxides,[4b,5] molecular sieves,[6] carbon mesoporous material[7], and polymeric materials.[8] Heterogeneous palladium catalyst systems based on silica supports, are among the most widely used due to the excellent stability (chemical and thermal), good accessibility and porosity, and efficient anchorage of organic functionalities.[9] Nevertheless, the Buchwald–Hartwig reactions using silica-supported Pd have only rarely been explored and without success.[10] Yet, Uozumi and co-workers[11] achieved a Buchwald–Hartwig amination in water under heterogeneous conditions by using an immobilized palladium complex, coordinated with an amphiphilic PS-PEG resin–supported di(*tert*-butyl)phosphine ligand. Although higher yields of triarylamines were obtained the protocol involves very harsh conditions, such as refluxing in a KOH (20M) solution. The immobilization of metals and organic ligands over the surface of magnetic nanoparticles is a popular substitute to bridge the gap between heterogeneous and homogeneous catalysis and has emerged as an environmentally benign chemical alternative to conventional methodologies.[12] The major advantages are the combination of well-known procedures for catalyst heterogenization with techniques for magnetic separation. A variety of catalytic systems involving metal and organic ligands supported MNPs have been devised and employed in synthetic organic reactions such as nano-magnetite dopa supported-Pd,[13] magnetite-cysteine,[14] magnetite-nickel,[15] magnetite-molybdenum[16] and related catalytic systems.[17] Recently, magnetic Fe_3O_4 NPs coated with APTES free NH_2 were effective in binding the *in situ* formed Pd nanoparticles;[18] the catalyst showed high catalytic activity in the reduction of nitroaromatic compounds. A newer magnetic composite catalyst has been prepared by immobilizing a Pd(0) complex, onto Mg–Al-layered double hydroxide shell supported on a magnetite core.[19] Both catalysts displayed excellent performance for Suzuki and Heck coupling reactions under ligand-free conditions. In continuation of our efforts to develop greener protocols using nanocatalysis,[20-22] we have developed a new, simple, and efficient protocol for functionalization of magnetite with Pd and its application for the Buchwald-Hartwig C-N cross coupling reaction allowing the preparation of di- and tri-phenylamines (**1a-j**) (Scheme 1). This protocol avoids several multistep processes of post synthetic functionalization and use of linkers between the metal and ferrites thus rendering the present protocol cost effective.



Scheme 1. Buchwald-Hartwig C-N cross coupling reaction using Nanocat-Fe-Pd.

Results and Discussion

Nanocat-Fe-Pd MNPs were prepared by the simple wet impregnation method using $PdCl_2$ as the palladium source, followed by chemical reduction (Scheme 2). We believe that due to the weak Van der Wall forces and hydrogen bonding the Pd species are strongly attached to the surface of magnetite. The as synthesized nanocatalysts is well characterized by X-ray diffraction (XRD), inductive coupled plasma-atomic emission spectroscopy (ICP-AES), transmission electron microscopy (TEM), secondary ion mass spectrometry (SIMS), field-emission gun scanning electron microscope and electron dispersive spectrometry (FEG-SEM-EDS), and X-ray photoelectron spectroscopy (XPS).



Scheme 2. Synthesis of Nanocat-Fe-Pd MNPs

Although the sample's weight percentage of Pd was determined to be 9.89% by ICP-AES analysis, there are no traces of a crystalline Pd phase in the XRD spectrum of Nanocat-Fe-Pd (See SI) presumably due to the very small size of Pd clusters deposited on magnetite[23] and/or its amorphous nature. Comparison between unmodified Fe_3O_4 and synthetized Pd-enriched MNPs clearly shows overlapping of both spectra in the frame of the experimental error, with all XRD line being attributed to Fe_3O_4. The high crystallinity is evidenced by the observed peaks' sharpness. The crystallite size of the Nanocat-Fe-Pd MNPs determined by Debye Scherrer equation, on the basis of the 311 line, was found to be 29.1 nm, in agreement with the result obtained from the TEM which shows a size distribution between 30-40 nm.In the XPS survey spectrum of the Nanocat-Fe-Pd the main lines of oxygen, iron and palladium are clearly visible. XPS spectrum of Pd 3d line is shown in Figure 1. Since the shape of Pd $3d_{5/2}$ and Pd $3d_{3/2}$ lines clearly indicate presence of at least two different chemical phases, each line of the Pd 3d doublet was fitted to two contributions (peaks A and B for Pd $3d_{5/2}$, peaks C and D for Pd $3d_{3/2}$). Peaks A and C are assumed to correspond to the 1st chemical phase, while the peaks B and D correspond to the 2nd phase. Appropriate constraints for the peak intensities, characteristic for d lines, were adopted: S_A:S_C = S_B:S_D = 3:2. Additionally, we consider the peak widths corresponding to the same line to be equal. Pseudo-Voigt profile GL (30) was used for all peaks and the background was assumed to be of a Shirley type.

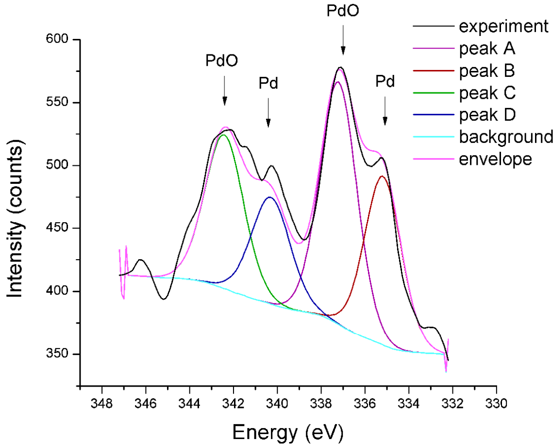


Figure 1. XPS spectrum of Pd 3d line. The expected line positions in the case of metallic Pd and PdO are marked by arrows.

The expected positions of Pd $3d_{5/2}$ line for a Pd metal[24], and PdO[25] respectively, are marked by arrows. Apparently, Pd is present at the surface of the nanocatalyst in two main phases i.e. as PdO and in its metallic form (oxidation state of Pd(0)). However, since the expected Pd $3d_{5/2}$ line position for $Pd(OH)_2$ differs for only 0.1 eV with respect to that of PdO,[26] presence of palladium hydroxide cannot be excluded. Both, PdO or $Pd(OH)_2$ may have been generated independently in the hydrolysis of $PdCl_2$ under basic conditions used. As a matter of fact, it is suggested[23a] that palladium is initially deposited from a basic solution in the form of $Pd(OH)_2$ colloids, which are then transformed into PdO upon drying. In any case, from the relative intensities of the corresponding contributions Pd 3d line, 60 % of all Pd is bound as PdO (and/or $Pd(OH)_2$), while the rest (i.e. 40 %) is in zero-valent state, Pd(0).

The analysis by SIMS shows the characteristic peaks of Fe^+ (with isotope patterns in the range of *m/z* 54-58), FeO^+, FeH^+ and FeH_2^+. The near-surface regions of the sample exhibited the presence of hydrogen, carbon and hydrocarbons, and some common electro-positive contaminants like Na^+, K^+ and Ca^+. The intensities of these ions were found to be rather great, however it should be taken into account that the positive secondary ion yield of alkaline and alkaline-earth metals are very high as compared to other elements. Ga^+ peaks are due to analytic primary ions implanted into the samples during analysis, and some small content of In^+ ions originates from the substrate onto which the nanocatalyst was supported. Chlorine, a very electro-negative element, was detected which is related to the production process. Figure 2 shows the surface mass spectrum, and Figure 3 displays the mass spectrum after 30 s of sputtering by defocusing Ga^+ beam, i.e. after removal of a few surface layers. Using computer code DECO[27] for identification and decomposition of these data, we estimated that the intensity of Pd has decreased 3 times after the sputtering (with normalization to Fe) with approximate calculation for the concentration of Pd on the surface (Fig. 3) using the relative sensitivity factors. According to Wilson,[28] the sensitivity of SIMS analysis to Fe is bigger than the sensitivity to Pd in 5-6 times.

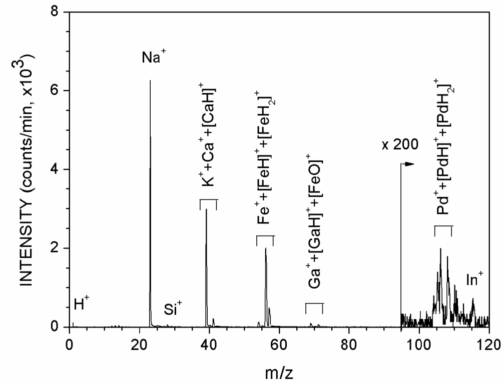


Figure 2. TOF-SIMS spectra of Nanocat-Fe-Pd MNPs (surface)

It is interesting that the normalized intensity of Fe_2^+ ions increased 6 fold after sputtering.

The TEM and SEM images of Fe_3O_4 and Nanocat-Fe-Pd MNPs are depicted in Fig. 4a–e; particles are observed in the nano range sizes (20–35 nm). The clustering tendencies formerly observed (Fig. 4 a, b) notwithstanding, small groups of equiaxial particles are visible, almost entirely detached from each other. The coresponding EDS profile exhibits a weak Pd peak, which is consistent with the ICP-AES results.

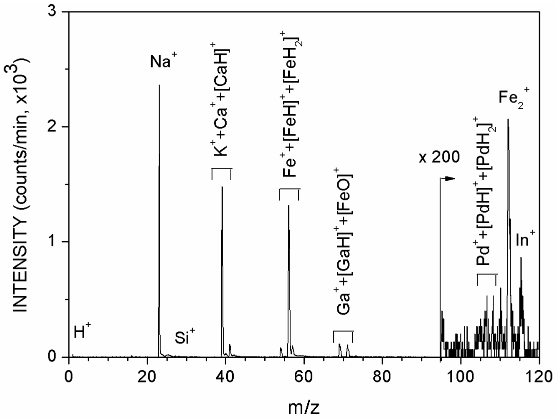


Figure 3. TOF-SIMS spectra of Nanocat-Fe-Pd MNPs (after 30 s of sputtering)

The as synthesized and well-characterized Nanocat-Fe-Pd catalyst was explored for the coupling reaction of iodobenzene with aniline using Xantphos as ligand and cesium carbonate as base. The ideal reaction conditions were found using 25 mg of Fe_3O_4-Pd MNPs (0.023 mmoles of Pd or 8.5 mol% in relation to aniline) to 0.27 mmol of aniline, 0.54 mmol of iodobenzene, 0.54 mmol of base and 0.0134 mmmol (4.9 mol%) of Xantphos. The reaction proceeded cleanly in dioxane during 24h providing the coupling product, diphenylamine (**1a**) in 98% yield (Table 1, entry 1). When the reaction was performed with PPh_3 as ligand the yield decreased slightly and the time of reaction increased substantially (entry 2). No reaction was observed in the absence of Xantphos which means that a ligand is essential to stabilize the Pd species over the surface of magnetite; literature documents that Xantphos is the most suitable ligand for Buchwald-Hartwig reaction.[29] After optimization of the reaction conditions, the catalytic activity of Fe_3O_4-Pd MNPs was explored with other amine/amide substrates (Table 1).

As expected, iodobenzene gave a better result (3 fold better than bromobenzene, Table 1, entry 1 vs 4) which reflects the ease of oxidative addition of the Pd(0) complex[30] to the C-I bond. With bromobenzene the yield of the reaction could only be improved with a different amine to aryl halide ratio, 1:1 instead of 1:2 (Table 1, entry 5 vs 4). Exceptional result was obtained with more electron deficient halides such as *p*-nitrobromobenzene that allowed the synthesis of *p*-nitro-*N*-phenylaniline (**1b**) (entry 6) in quantitative yield. Electron donating substituents on the amine substrate gave a better result than when present as substituents in the aryl halide (entry 8 vs 7); *p*-methoxy-*N*-phenylaniline (**1c**) was obtained in 78% *vs* 23% yield. Predictably, electron withdrawing groups on the amine substrate lowered the yield of the reaction product (entry 10 vs 8); *p*-nitro-*N*-phenylaniline (**1b**) was obtained only in 45% yield.

A moderate yield was obtained for *p*-bromo-*N*-phenylaniline (**1e**) (66%) ascribable to the formation of lateral products (not identified) probably arising from other parallel reactions due to the reactivity of the C-Br bond in the presence of a Pd catalyst. The method proved to be of general applicability as primary amides, acetamide, gave acetanilide (**1f**) in almost quantitative yield (entry 12). However, for the arylation of secondary amides, acetanilide, only highly reactive substrates such as *p*-nitrobromobenzene (entry 15 vs 13) were able to perform the arylation to *p*-(4-nitrophenyl)-*N*-phenylacetamide (**1g**) in very good yield (96%). This excellent result could only be obtained in the presence of dry dioxane. At the reaction temperature, only small amout of water is enough to hydrolyse the amide and only **1b** was observed in moderated yield (entry 14 vs 15). Less reactive amides such as *p*-toluenosulfonamide afforded no product either with iodobenzene or *p*-nitrobromobenzene. (entries 16 and 17).

The arylation of diphenylamine with iodobenzene lead to the triphenylamine (**1h**) in 46% (entry 20). Using *p*-nitrobromobenzene, the yield of *p*-nitro-*N*,*N*-diphenylaniline (**1i**) was also low in 47% yield (entry 21). All the attempts to improve the yield using excess of aryl halide or increasing the temperature by changing the solvent were unsuccessful (entry 22). Less nucleophilic and basic substrates such as imidazole or phenol were unreactive under these reaction conditions (entries 18 and 19); the adsorption of phenol at the surface of magnetite cannot be ruled out. Aliphatic amines such as cyclohexylamine and tert-butylamine gave no reaction product (entries 23 and 24); after 24h, iodobenzene was still present but no amine was observed. We cannot exclude here the fact that basic amines are good ligands for palladium and consequently being trapped in the catalyst rendering it inactive.

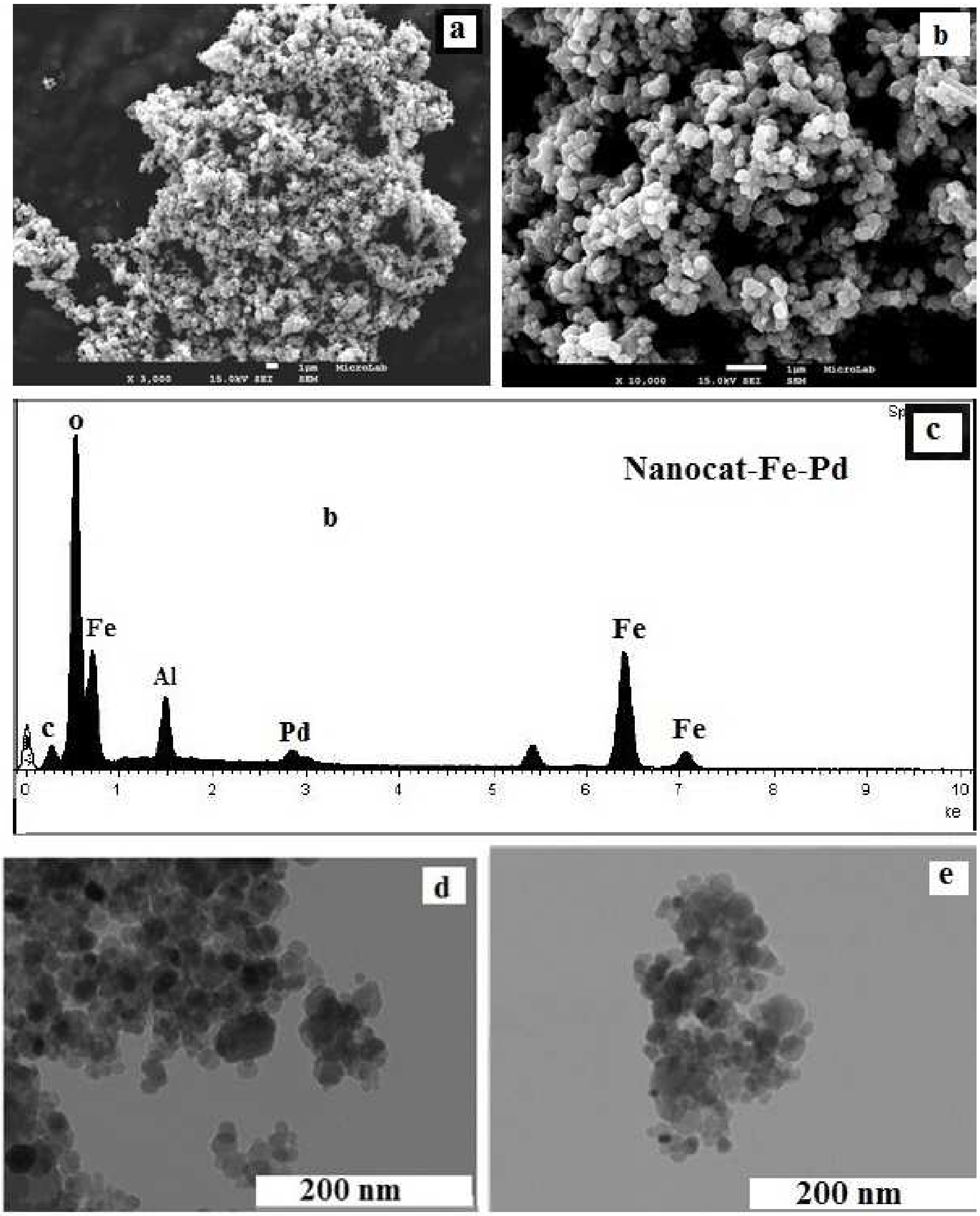


Figure 4. SEM images of Nanocat-Fe-Pd a and b; c) EDS profile of Nanocat-Fe-Pd d) TEM image of Fe_3O_4 and e) TEM image of Nanocat-Fe-Pd

To prove that the reaction is heterogeneous, a standard leaching experiment was conducted by the hot filtration method. The reaction between aniline and iodobenzene allowed to proceed for 20 minutes in the presence of Fe_3O_4-Pd, Xantphos and Cs_2CO_3 at reflux in dioxane (standard conditions Table 1). After decanting the solution, the hot filtered reaction mixture was then stirred without catalyst for 24 h; no formation of diphenylamine was observed, even after 24 h, which indicates that no homogeneous catalysis was involved. To rule out any ambiguity due to shorter time duration (20 minutes), the same hot filtration test was repeated for 24 h under the same conditions. After decanting the solution, the hot filtered reaction mixture was then submitted to ICP analysis. The Pd content found was negligible (0.00054 mmoles), of the total amount of palladium present. Independent homogeneous reactions performed with exactly this small amount of palladium, using $PdCl_2$ were unsuccessful. No formation of diphenlamine (**1a**) was observed which means that no homogeneous catalyst could be involved. Also, the reusability of the catalyst was tested on the reaction for the preparation of diphenylamine (**1a**) starting with aniline and iodobenzene; after five consecutive cycles only a slight loss of activity was observed as the yields from all the experiments were above 90%.

Table 1. Results of C-N coupling reactions between arylhalides and nitrogenated substrates over Nanocat-Fe-Pd.[a]

Entry	Amine (1)	Aryl halide	Time (h)	Product (2)	Yield (%)
1	PhNH$_2$	PhI	24	PhNHPh (**1a**)	98
2	PhNH$_2$	PhI	68	PhNHPh (**1a**)	74[b]
3	PhNH$_2$	PhI	24		No reaction [c]
4	PhNH$_2$	PhBr	268	PhNHPh (**1a**)	30
5	PhNH$_2$	PhBr	96	PhNHPh (**1a**)	74[d]
6	PhNH$_2$	*p*NO$_2$C$_6$H$_4$Br	24	PhNHC$_6$H$_4$-NO$_2^p$ (**1b**)	100
7	PhNH$_2$	*p*MeOC$_6$H$_4$I	144	PhNHC$_6$H$_4$-OMe^p (**1c**)	23
8	*p*MeOC$_6$H$_4$NH$_2$	PhI	48	PhNHC$_6$H$_4$-OMe^p (**1c**)	78
9	*m*NO$_2$C$_6$H$_4$NH$_2$	PhI	120	PhNHC$_6$H$_4$-NO$_2^m$ (**1d**)	56
10	*p*NO$_2$C$_6$H$_4$NH$_2$	PhI	120	PhNHC$_6$H$_4$-NO$_2^p$ (**1b**)	45
11	*p*BrC$_6$Hr$_4$NH$_2$	PhI	21	PhNHC$_6$H$_4$-Br (**1e**)	66
12	CH$_3$CONH$_2$	PhI	49	CH$_3$CONHPh (**1f**)	97
13	PhNHCOCH$_3$	PhI	168		No reaction
14	PhNHCOCH$_3$	*p*NO$_2$C$_6$H$_4$Br	24	PhNHC$_6$H$_4$-NO$_2^p$ (**1b**)	43
15	PhNHCOCH$_3$	*p*NO$_2$C$_6$H$_4$Br	24	PhNCOCH$_3$C$_6$H$_4$-NO$_2^p$ (**1g**) [e]	96
16	TsSO$_2$NH$_2$	PhI		No reaction	No reaction
17	TsSO$_2$NH$_2$	*p*NO$_2$C$_6$H$_4$Br		No reaction	No reaction
18	imidazole	PhI		No reaction	No reaction
19	phenol	PhI		No reaction	No reaction
20	Ph$_2$NH	PhI	144	Ph$_3$N (**1h**)	46
21	Ph$_2$NH	*p*NO$_2$C$_6$H$_4$Br	144	Ph$_2$NC$_6$H$_4$-NO$_2^p$(**1i**)	47
22	Ph$_2$NH	PhI	93	Ph$_3$N (**1h**)	39[f]
23	*tert*-butylamine	PhI	24	No reaction	No reaction
24	cyclohexylamine	PhI	24	No reaction	No reaction

[a] Reaction conditions: Aniline (0.27 mmol), Xantphos (0.0134 mmmol; 4.9 mol%), Cs$_2$CO$_3$ (0.54 mmol), Aryl halide (0.54 mmol), Fe$_3$O$_4$-Pd (25 mg; 0.023 mmoles of Pd or 8.5 mol% in relation to aniline), Dioxane (2.5mL), reflux; [b] PPh$_3$ (0.0134 mmmol) as ligand; [c] no Xantphos; [d] Aniline (0.54 mmol); [e] dry dioxane; [f] PhI (3 equivalentes) and DMF at reflux.The physical data obtained for all the products fully agree with those reported in literature.[31]

This result is further supported by the XPS analysis of the recovered catalyst. From XPS data (SI), no changes in the palladium species were observed. The percentage of Pd(0) and PdO (Pd(OH)$_2$) was almost the same, and no change in the oxidation state of Pd species was discernible. This clearly indicates that after recyclability study catalyst integrity remained structurally intact.

Conclusions

In summary, we have developed an efficient and viable heterogeneous magnetically separable Nanocat-Fe-Pd nanocatalyst for the Buschwald-Hartwig reaction which could be prepared from inexpensive precursors, and without resorting to cumbersome linkers or ligands; various amines and amides are converted to corresponding products in good to excellent yield. Due to sturdy interaction between Pd and ferrite MNPs, the catalyst could be reused and recycled without any significant loss in catalytic activity and the negligible Pd leaching observed was not responsible for the results. The salient feature of the catalyst is its robustness and magnetically recoverable nature which avoids the necessity for a traditional filtration process.

Experimental

Preparation of Fe_3O_4 MNPs [32]

$FeCl_3.6H_2O$ (5.4 g) and urea (3.6 g) were dissolved in water (200 mL) at 85 to 90°C for 2 h. The solution turned brown. To the resultant reaction mixture, cooled to room temperature, was added $FeSO_4.7H_2O$ (2.8 g) and then 0.1 M NaOH until pH 10. The molar ratio Fe(III) to Fe(II) in the above system was nearly 2.0. The obtained hydroxides were treated by ultrasound in the sealed flask at 30 to 35 °C for 30 min. After ageing for 5 h, the obtained black powder (Fe_3O_4) was washed, and dried under vacuum.

Preparation of Nanocat-Fe-Pd

Magnetite nanoparticles Fe_3O_4 (2 g), palladium chloride (to get 10 wt % of Pd on magnetite) and KCl (0. 5 gm) were stirred at room temperature in aqueous solution (50 mL) for 1 h. After impregnation, the suspension was adjusted to pH 12 by adding sodium hydroxide (1.0 M) and further stirred for 20 h. The solid was washed by distilled water (5 x 10 mL). The resulting Nanocat-Fe-Pd particles were sonicated for 10 min., washed with distilled water and subsequently with ethanol, and dried under vacuum at 60 °C for 24 h. The Pd content was determined by ICP-AES and it was found to be 9.89%.

Experimental procedure for Buschwald-Hartwig reaction catalyzed by Nanocat-Fe-Pd

Amine (0.27 mmol), Xantphos (0.0134 mmol, 4.9 mol% in relation to aniline), Cs_2CO_3 (0.54 mmol), aryl halide (0.54 mmol), Fe_3O_4-Pd (25 mg; 0.023 mmoles of Pd or 8.5 mol% in relation to aniline) were stirred in dioxane at reflux in appriopriated time After completion of the reaction (followed by thin layer chromatography), the catalyst was separated magnetically, washed with ethyl acetate and the organic extracts evaporated in vacuum. The crude product was purified by column chromatography on silica gel using n-hexane and ethyl acetate as the eluent.

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