

Pd immobilized on modified magnetic Fe₃O₄ nanoparticles: Magnetically recoverable and reusable Pd nanocatalyst for Suzuki-Miyaura coupling reactions and Ullmann-type *N*-arylation of indoles

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Abstract. The Pd supported on amidoxime (AO)-functionalized Fe₃O₄ (Fe₃O₄/AO/Pd) hybrid material was used as an effective and recyclable nanocatalyst in Suzuki-Miyaura coupling reactions. The catalyst was very effective for the Suzuki-Miyaura reaction of aryl halides (Ar-I, Ar-Br, Ar-Cl) with phenylboronic acid and conversion was excellent in most cases. The yields of the products were in the range from 7–98%. The catalyst showed good stability and could be recovered and reused for six reaction cycles without a significant loss in its catalytic activity. Also, a wide range of *N*-arylated indoles are selectively synthesized through intermolecular C(aryl)-N bond formation from the corresponding aryl iodides and indoles through Ullmann-type coupling reactions in the presence of the prepared catalyst.

Keywords. Fe₃O₄/AO/Pd; magnetic nanoparticles; heterogeneous catalyst; Pd nanoparticles; suzuki; ullmann.

1. Introduction

Catalyst plays a significant role in the production of chemicals today and nanomaterials have the potential for improving efficiency, selectivity, and yield of catalytic process. The higher surface to volume ratio means that many more catalysts are actively participating in the reaction. The potential for cost saving is tremendous from the perspective of material, equipment, labour and time. Higher selectivity means less waste and fewer impurities, which could lead to safer and reduced environmental impact. The study of application of metal nanoparticles in catalysis, particularly, on organic transformations, has become a frontier area of research in nanocatalysis.¹ Among the different metal nanocatalysts, palladium nanoparticles (PdNPs) have gained much reputation, because palladium is a versatile catalyst in modern organic synthesis and is widely used for a significant number of synthetic transformations^{2–4} such as, Heck, Suzuki, Stille, Sonogashira cross-coupling reactions and *N*-arylation of heterocycles.^{5–11}

Classically, the fixation of NPs on supports uses mostly the reduction of metal salts in the presence

of the support followed by an adequate thermal treatment.¹² Mesoporous supports (MCM-41, SBA) are frequently used supports of PdNPs-MNPs.^{13,14a–c} Other supports, such as polymer-coated MNPs^{14d–g} ionic-liquid-modified MNPs,^{14h} sulfonated graphene-decorated MNPs,¹⁴ⁱ are also employed for the stabilization of PdNPs.

The immobilization methods used to deposit palladium into heterogeneous solid beds have been studied extensively, and diverse supports on clay,¹⁵ carbon nanofiber,¹⁶ montmorillonite,¹⁷ magnetic mesoporous silica,¹⁸ zeolite,¹⁹ and metal oxides²⁰ have been investigated. A current challenge in this area is the development of efficient immobilized systems that could simultaneously fulfil the usual targets of achieving high TON values and facilitate recovering and reuse. Further, there is the need for obtaining Pd-free final products,^{21,22} complying with the strict purity specifications of the pharmaceutical industry.^{23,24} In particular, iron oxide magnetic nanoparticles (MNPs) have received considerable attention as they are biocompatible and can be recovered easily from reaction mixtures by using a simple external magnetic field.

Recently, we have reported modified single-walled carbon nanotubes and modified- mesoporous SBA-15

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as a support to stabilize palladium nanoparticles and its applications in Suzuki-Miyaura and Ullmann coupling reactions.²⁵ Also, very recently, we prepared a novel amidoxime-functionalized Fe_3O_4 nanoparticles for deposition of palladium nanoparticles ($\text{Fe}_3\text{O}_4/\text{AO}/\text{Pd}$) as an efficient and separable catalyst for Sonogashira coupling reaction.^{13f} In continuation of our interest on the synthesis of novel supported catalysts,²⁶ we decided to use amidoxime-functionalized Fe_3O_4 nanoparticles for stabilization of palladium nanoparticles (figure 1) and its application as a catalyst in Suzuki-Miyaura and Ullmann coupling reaction under mild and low palladium loading conditions.

2. Experimental

2.1 Preparation of the magnetic Fe_3O_4 nanoparticles (MNPs)

Naked Fe_3O_4 nanoparticles were prepared according to the literature method.^{13c}

2.2 Preparation of the $\text{Fe}_3\text{O}_4/\text{AO}$

The obtained MNPs powder (500 mg) was dispersed in 50 mL toluene solution by sonication for 20 min, and then triethoxyethylcyanide (3 mmol) was added

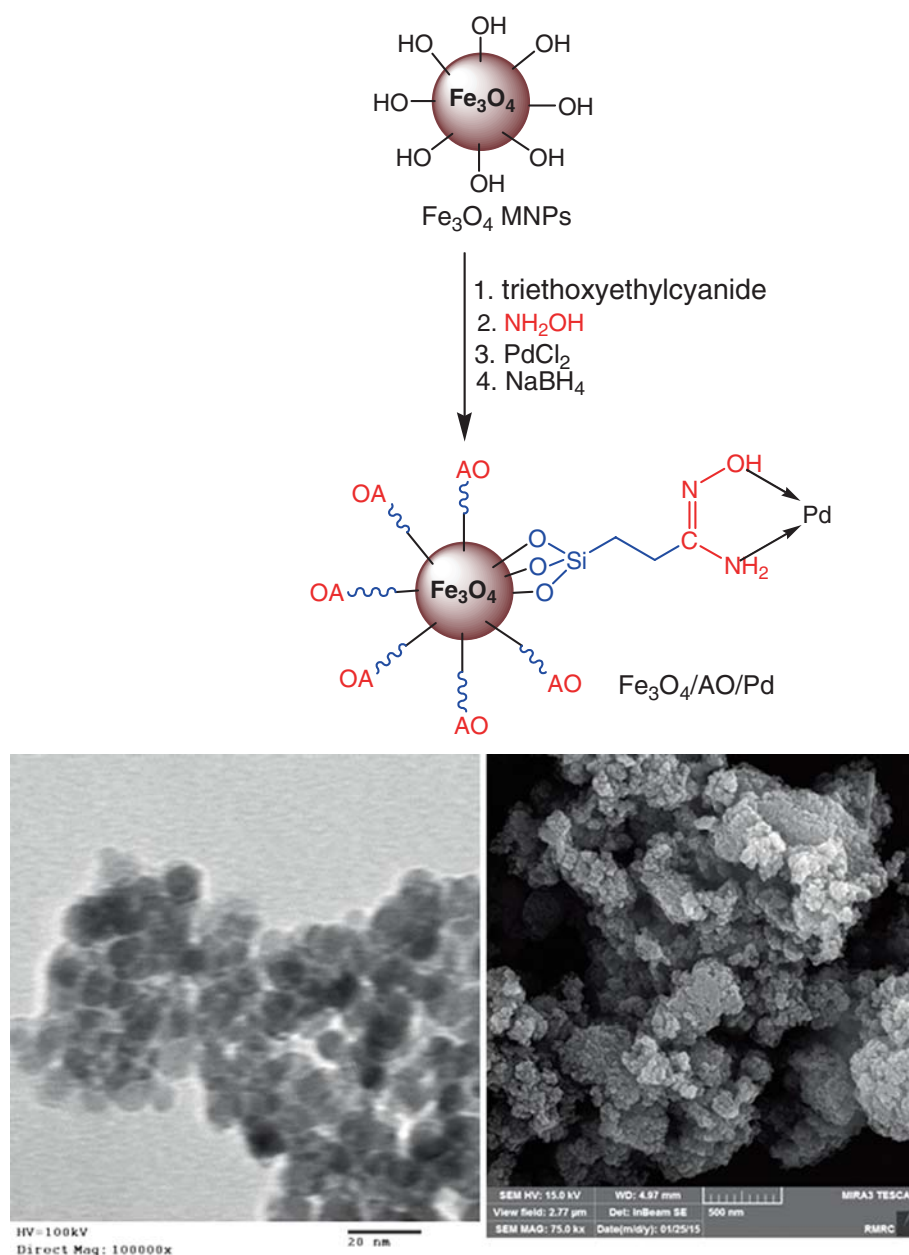


Figure 1. Preparation of $\text{Fe}_3\text{O}_4/\text{AO}/\text{Pd}$ and its SEM and TEM images.

to the mixture. The mixture was refluxed under argon atmosphere at 100°C for 48 h. The product was separated by filtration, washed with ethanol, and dried under vacuum for 24 h at 50°C. The precipitated product (Fe₃O₄/Ethyl-CN) was dried at room temperature under vacuum. Then, the [2-cyanoethyl]-functionalized MNPs (1 g) were immersed in NH₂OH aqueous solution (50 mL, 50%) at 65°C for 5 h (figure 1). The amidoxime groups in MNPs (Fe₃O₄/AO) were filtrated off, washed with distilled water for several times and dried.

2.3 Preparation of the Fe₃O₄/AO/Pd(0)^{13c}

The Fe₃O₄/AO (500 mg) were dispersed in CH₃CN (30 mL) by ultrasonic bath for 30 min. Subsequently, a yellow solution of PdCl₂ (30 mg) in 30 mL acetonitrile was added to dispersion of Fe₃O₄/AO and the mixture was stirred for 10 h at 20–25°C. Then, the Fe₃O₄/AO/Pd(II) was separated by magnetic decantation and washed by CH₃CN, H₂O and acetone, respectively, to remove the unattached substrates.

The reduction of Fe₃O₄/AO/Pd(II) by hydrazine hydrate was performed as follows: 50 mg of Fe₃O₄/AO/Pd(II) was dispersed in 60 mL of water, and then 100 µL of hydrazine hydrate (80%) was added. The pH of the mixture was adjusted to 10 with 25% ammonium hydroxide and the reaction was carried out at 95°C for 2 h. The final product Fe₃O₄/AO/Pd(0) was washed with water and dried in vacuum at 40°C. Figure 1 depicted the synthetic procedure of Fe₃O₄/AO/Pd. The concentration of palladium in Fe₃O₄/AO/Pd was 1.83 wt% (0.17 mmol/g), which was determined by ICP-AES and EDS.

2.4 Suzuki-Miyaura coupling reaction^{13c}

In a typical reaction, 7 mg of the Fe₃O₄/AO/Pd (10 mg = 0.0017 mmol Pd) was placed in a 25 mL Schlenk tube, 1 mmol of the aryl halide in 5 mL of water/ethanol (1:1) was added 0.134 g (1.1 mmol) of phenyl boronic acid, 0.276 mg of K₂CO₃ (2 mmol). The mixture was then stirred for the desired time at room temperature. The reaction was monitored by thin layer chromatography (TLC). After completion of the reaction, 5 mL ethanol was added, and the catalyst was removed by external magnet. Further purification was achieved by column chromatography. All the products were identified by melting point and NMR spectroscopy.

2.5 Ullmann-type N-Arylation of indoles

In a typical reaction, 10 mg of the catalyst (10 mg catalyst = 0.0017 mmol Pd, 0.1 mol%) was placed in a

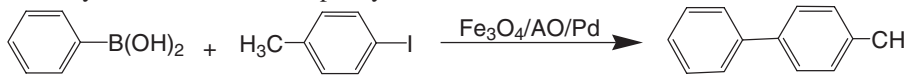
25 mL balloon, 1.1 mmol of the aryl iodides in 3 mL of DMF was added 1 mmol of indoles and 2 mmol of Et₃N. The mixture was then refluxed for 2 h at 110°C. After completion of reaction monitored by TLC (*n*-Hexane/acetone, 4:1), the reaction mixture was cooled to room temperature (the catalyst was recovered by magnet) and was extracted with diethyl ether three times (3 × 10 mL). The combined organic layers were washed with brine solution and dried over anhydrous Na₂SO₄ and concentrated *in vacuo*. The crude product was purified by column chromatography on silica gel (60–120 mesh) to provide the *N*-aryl indoles.

3. Results and discussion

As a part of our ongoing research program to develop new synthetic methodologies, after successful fabrication of the catalyst,^{13f} we have again investigated the morphology surface by FESEM and TEM images (figure 1). The FESEM image (right) of the synthesized Fe₃O₄/AO/Pd confirmed that the catalyst was made up of uniform nanometer-sized particles. The TEM image of the Fe₃O₄/AO/Pd catalyst (left) revealed that the Pd nanoparticles with nearly spherical morphology were formed on the surface of the modified Fe₃O₄ nanoparticles. In the transmission electron microscopy images, iron oxide nanoparticles of 10–15 nm in diameter and palladium nanoparticles of ~3 nm, entrapped in iron oxide are observed. Also, the TEM image of the Fe₃O₄/AO/Pd catalyst shows that the functionalized magnetic nanoparticles possess almost spherical morphology with nearly monodispersity.

The catalytic activity of prepared catalyst (Fe₃O₄/AO/Pd) was evaluated in Suzuki coupling reaction. In order to find the optimized reaction conditions, the reaction between 4-methyl-iodobenzene and phenylboronic acid was chosen as model reaction (table 1). The effect of different factors such as solvents, bases and amount of the catalyst were studied at room temperature (table 1). Results indicated that using K₂CO₃ as a base, H₂O/EtOH (1:1) as a solvent, and 0.1 mol% catalyst at 25°C afforded highest yield of the product (table 1, Entry 5).

Using these optimized reaction conditions, the efficiency of this catalyst was studied for Suzuki reaction of various aryl halides and the results are summarized in table 2. Aryl iodide (entries 1–6) and aryl bromide (entries 7–13) with different functional groups efficiently reacted with phenylboronic acid to produce biaryl products in good to excellent yields (table 2). This catalytic system was also applied for the aryl chlorides (table 2, entries 13–16). It is clear from table 2

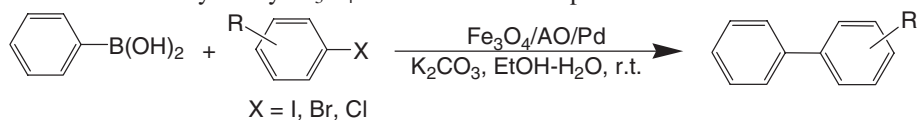
Table 1. Optimization of the conditions for the Suzuki-Miyaura reaction of 4-methyl-iodobenzene with phenylboronic acid.^a


Entry	Solvent	Pd (mol%)	Base	Time (min)	Yield (%) ^b
1	DMF	0.1	K ₂ CO ₃	90	82
2	toluene	0.1	K ₂ CO ₃	90	60
3	EtOH	0.1	K ₂ CO ₃	80	75
4	H ₂ O	0.1	K ₂ CO ₃	180	50
5	EtOH/H ₂ O ^c	0.1	K ₂ CO ₃	60	96
6	EtOH/H ₂ O ^c	0.1	NaOAc	60	60
7	EtOH/H ₂ O ^c	0.1	Et ₃ N	60	70
8	EtOH/H ₂ O ^c	0.05	K ₂ CO ₃	60	75
9	EtOH/H ₂ O ^c	0.2	K ₂ CO ₃	60	96
10	EtOH/H ₂ O ^c	0.1	No base	90	Trace

^aReaction conditions: 4-methyl-iodobenzene (1 mmol), PhB(OH)₂ (1.1 mmol), Fe₃O₄/AO/Pd, solvent (3 mL).

^bIsolated yield.

^cEtOH/ H₂O = 1:1.

Table 2. Heterogeneous Suzuki-Miyaura reaction of aryl halides with phenylboronic acid catalyzed by Fe₃O₄/AO/Pd at room temperature.^a

Entry	R	X	Time (h)	Yield (%) ^b	M.p. (°C)	M.p. (°C) ^{ref}
1	H	I	1	96	68-70	69-70 ²⁷
2	4-CH ₃ O	I	1	96	88-90	89-90 ²⁷
3	4-CH ₃	I	1	95	47-49	45-49 ²⁷
4	2-CH ₃ O	I	2	85	Oil	Oil ²⁸
5	4-F	I	2	95	73-75	73-74 ²⁸
6	4-NO ₂	I	2	90	114-115	114-115 ²⁸
7	H	Br	2	96	68-70	69-70 ²⁷
8	4-CH ₃ O	Br	4	90	88-90	89-90 ²⁷
9	4-CH ₃	Br	4	90	47-49	45-49 ²⁷
10	2-CH ₃ O	Br	6	85	Oil	Oil ²⁸
11	4-F	Br	4	90	73-75	73-74 ²⁸
12	4-NO ₂	Br	6	88	114-115	114-115 ²⁸
13	4-COCH ₃	Br	5	96	120-122	120-121 ²⁸
14	H	Cl	15	70	68-70	69-70 ²⁷
15	4-CH ₃	Cl	24	65	47-49	45-49 ²⁷
16	4-CH ₃ O	Cl	24	60	88-90	89-90 ²⁷

^aReaction conditions: Arylhalide (1 mmol), phenylboronic acid (1.2 mmol), K₂CO₃ (2 mmol), H₂O/EtOH (1:1) (3 mL), catalyst (0.1 mol%) and 25°C.

^bIsolated yield.

that aryl chlorides coupled with phenylboronic acid in moderate yields within 15–24 h reaction times.

In order to prove the heterogeneous nature of the catalyst, heterogeneity test was performed, in which two separate experiments were performed with 4-methyl-iodobenzene and phenylboronic acid. In the first

experiment, the reaction was terminated after 30 min; at this temperature, the catalyst was separated from the reaction mixture by an external magnet and the reaction was continued with the filtrate for an additional 60 min. In the second experiment, the reaction was terminated after 30 min. In both cases, the desired product was

obtained in the same yield (55%). The results indicate that the nature of reaction process was heterogeneous and there was no reaction in the homogeneous phase.

One of the main advantages of magnetite-NPs-supported catalysts is the easy separation and recycling of the catalyst. To study the recycling properties of this catalyst, the reaction of 4-methyl-iodobenzene with phenylboronic acid under same conditions was selected. The results showed that the catalyst is recyclable in six consecutive runs just by decantation with a magnetic bar without any significant loss of catalytic activity (figure 2). Palladium leaching of the catalyst was studied before and after the reaction by ICP-AES analysis. The Pd content was found to be 1.80 wt% and 1.70 wt% before and after the six reaction series, respectively, which implied insignificant Pd leaching.

After its successful application of the prepared catalyst in the Suzuki coupling reaction, its catalytic activity was investigated for Ullmann type *N*-arylation

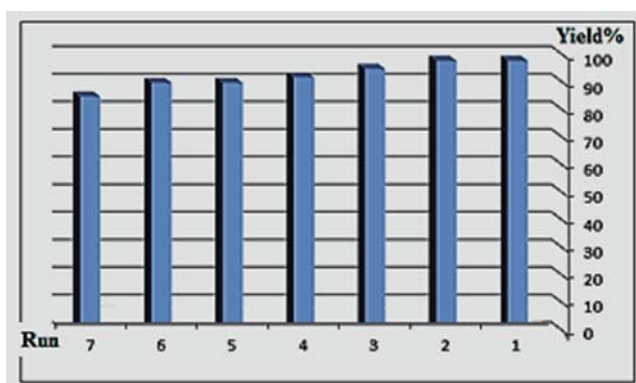


Figure 2. The recycling of the Fe₃O₄/AO/Pd for the Suzuki coupling reaction under similar conditions.

of indoles. To find the best conditions, the reaction between iodobenzene and indole was chosen as model reaction. Influences of different parameters were examined to obtain the best possible combination. The parameters included solvent, reaction temperature, base, catalyst concentration without the protection by an inert gas. Observation indicated that the best conditions for the *N*-arylation of indole with iodobenzene involve the use of 0.1 mol% of Pd catalyst, 2 equiv. of Et₃N in DMF at 110°C for 2 h. So, based on the optimized conditions, the scope and generality of the developed protocol with respect to various aryl iodides were investigated using our catalyst. The results are summarized in table 3. When indole was coupled with aryl iodides containing both electron-donating and electron-withdrawing groups, the corresponding products were obtained in excellent yields (table 3, entries 1–6). It is very important to mention that the reaction is very selective to give only *N*-arylated product and in none of these cases *C*-arylation of indole was observed. To ensure that there was no *C*-arylation in the reaction, the reaction was carried out with 1-methyl indole and it was found that no product was formed (table 3, Entry 7). This shows the high selectivity of Fe₃O₄/AO/Pd as catalyst in the *N*-arylation of indole by aryl iodides.

4. Conclusions

In conclusion, we have prepared and characterized novel Fe₃O₄ nanoparticles supported palladium nanoparticles. The catalyst showed high activity in Suzuki coupling reaction of aryl halides (X = I, Br, Cl). The catalyst showed good stability and was recycled for

Table 3. Synthesis of *N*-aryl-indoles catalyzed by Fe₃O₄/AO/Pd.^a

Entry	R ₁	R ₂	Time (h)	Yield (%) ^b
1	H	H	2	96
2	H	4-OCH ₃	2	96
3	H	2-OCH ₃	4	90
4	H	4-CH ₃	2	85
5	H	4-Cl	2	95
6	H	4-NO ₂	2	90
7	CH ₃	H	10	0.0

^aReactions were carried out under aerobic conditions in 3 mL of DMF, 1.1 mmol aryl iodide, 1.0 mmol indole and 2 mmol Et₃N in the presence of Pd catalyst (0.010 g, 0.1 mol% Pd) and 110°C for 2–4 h.

^bIsolated yield.

several times with small decrease in its catalytic activity. These advantages make the process highly valuable from the synthetic and environmental points of view. Also, we have developed a novel and practical method for the synthesis of *N*-arylindoles through the reaction of indoles with aryl iodides by using Fe₃O₄/AO/Pd catalyst under mild reaction conditions.

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