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COMMUNICATION



Magnetically recyclable palladium nanoparticles (Fe_3O_4 -Pd) for oxidative coupling between amides and olefins at room temperature

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Ashis Kumar Jena, Organic Synthesis and Nanocatalysis Laboratory, Department of Chemistry, North Orissa University, Baripada 757003, Odisha, India. Email: jenaashis016@gmail.com A convenient method for the synthesis of magnetically recyclable palladium nanoparticles (Fe₃O₄-Pd) is described. The catalytic application of the Fe₃O₄-Pd nanoparticles was explored for the first time in oxidative coupling between amides and olefins. *p*-Toluenesulfonic acid plays a significant role in the oxidative amidation reaction. The reaction proceeds at room temperature, resulting in (*Z*)-enamides under ambient air in the absence of co-catalyst and ligand. The superparamagnetic nature of Fe₃O₄-Pd facilitates easy, quantitative recovery of the catalyst from a reaction mixture, and it can be reused for up to three consecutive cycles with a slight decrease in catalytic activity.

KEYWORDS

Fe₃O₄-Pd nanoparticles, leaching redeposition, oxidative coupling, recyclable, (Z)-enamides

1 | INTRODUCTION

Over the past few years, transition-metal-catalysed oxidative coupling reactions have received much attention due to their being atom- and step-economic approaches for the preparation of complex molecules.^[1] In oxidative coupling reactions, two C—H and heteroatom—H bonds are directly coupled to form C-CC heteroatom bonds in the presence of oxidant and transition metal catalyst. Among the various transition metals employed in oxidative coupling, palladium has received considerable attention due to its excellent reactivity, high level of regio-, chemoand stereoselectivity, as well as good functional group tolerance.^[2] However, an expensive palladium catalyst needs to be recovered from the reaction mixture and also the product should be uncontaminated by metal species since in the pharmaceutical industry it is essential to remove all trace metal impurities.^[3] Magnetization of a metal catalyst, where the catalyst can be quantitatively isolated using an external magnet, is an ideal solution to this problem.^[4] Moreover, decreasing the size of a metal

catalyst to the nanometre scale enhances the reactivity of the catalyst. Therefore, the use of magnetically recyclable palladium nanoparticles in oxidative coupling reactions represents an efficient and eco-friendly method.

Enamide derivatives fall into a significant class of nitrogen-containing compounds and are versatile intermediates for the synthesis of bioactive molecules, heterocycles, amino acids and chiral amines.^[5] The enamide moiety also appears in a plethora of natural products such as altamide, lansiumamide A, lansiumamide B, salicyhalamide A, crocacin A, etc. (Figure 1).^[6]

Considering the importance of the enamide scaffold, several effective methods have been developed for its synthesis.^[7–12] Among them, transition-metal-catalysed oxidative coupling between amides and olefins would be a straight forward approach. Murahashi and co-workers reported the coupling of cyclic carbamates and amides with electron-deficient olefins using $PdCl_2(MeCN)_2$ as catalyst and cuprous chloride as co-catalyst.^[13] Later, Chang and co-workers developed a Pd/Cu co-catalysed method for the selective synthesis of (*Z*)-enamides from



acyclic amides.^[6] Liu and Hii reported a chloride-free Pd/Cu co-catalysed system for the oxidative coupling of electron-rich amides with olefins.^[14] Subsequently, Panda et al. reported the stereoselective synthesis of (Z)enamides by coupling amides with electron-deficient olefins employing 10 mol% palladium acetate as catalyst.^[15] However, use of homogeneous palladium catalysts in these enamide syntheses is associated with a number of disadvantages such as palladium metal contamination in the final product, use of co-catalyst as well as nonrecoverability of the catalyst. These difficulties could be overcome by employing a heterogeneous palladium nanocatalyst which has its own merits of easy recyclability and avoiding palladium contamination in products. To the best of our knowledge, compared to homogeneous counterparts, heterogeneous palladium catalysts in enamide synthesis have not been reported yet. In this context, we have synthesized palladium-decorated Fe₃O₄ nanoparticles $(Fe_3O_4-Pd)^{[16]}$ and employed them for the first time in oxidative coupling between amides and olefins. To our delight, the reaction resulted in thermodynamically disfavoured (Z)-enamides stereoselectively at room temperature in the absence of a co-catalyst.

2 | RESULTS AND DISCUSSION

The magnetic Fe_3O_4 -Pd was synthesized using a two-step process. Fe_3O_4 nanoparticles were synthesized by a chemical co-precipitation method. In the second step palladium metal was deposited on the surface of Fe_3O_4 by a wet impregnation method. The synthesized Fe_3O_4 -Pd was characterized using several techniques such as powder X-ray diffraction (XRD), field emission scanning electron microscopy (FESEM), transmission electron microscopy (TEM), energy-dispersive X-ray spectroscopy (EDS), X-ray photoelectron spectroscopy (XPS) and vibrating sample magnetometry (VSM).

The crystal structure and the phase purity of Fe_3O_4 and Fe_3O_4 -Pd were determined using powder XRD (Figure 2). The diffraction peaks of Fe_3O_4 can be easily indexed to a crystalline cubic spinel structure of Fe_3O_4

FIGURE 1 Enamide-containing natural products



FIGURE 2 XRD patterns of Fe₃O₄ and Fe₃O₄-Pd

(JCPDS no. 82-1533). No other impurity peaks were detected. For Fe_3O_4 -Pd, all the peaks correspond to cubic spinel Fe_3O_4 . The absence of reflection peaks corresponding to Pd metal deposited on Fe_3O_4 was probably due to very low content of Pd or a low level of crystallization. This observation regarding crystal structure is consistent with that for Fe_3O_4 -CeO nanocatalyst prepared by Gawande *et al.*^[17]

The loading of Pd on the nanomaterial was determined using atomic absorption spectroscopy (AAS) as 2.4 wt%, corresponding to the expected value. The morphology and size distribution of Fe₃O₄-Pd were obtained from FESEM and TEM analyses. The FESEM image (Figure 3a) clearly reveals that the particles are spherical and have a narrow size distribution of 30-45 nm. EDS analysis confirms the presence of Fe and Pd in Fe₃O₄-Pd (Figure 3c). The TEM image of Fe₃O₄-Pd (Figure 3b) shows the formation of magnetic nanoparticles having somewhat spherical morphology with a size range of 20-28 nm. It is observed that particles are slightly agglomerated. The agglomeration observed using TEM might occur during TEM sample preparation and drying effect in addition to magnetic interaction under a highenergy electron beam. The appearance of dark dot-like



FIGURE 3 (a) FESEM image of Fe₃O₄-Pd at 500 nm. (b) TEM image of Fe₃O₄-Pd at 20 nm. (c) EDS profile of Fe₃O₄-Pd

structures on the surface of Fe_3O_4 nanoparticles clearly indicates the deposition of PdO.

To further examine the presence of Pd on the surface of Fe_3O_4 , XPS measurements were carried out. In a typical survey spectrum (Figure 4a) of the nanoparticles, the peaks at 57, 330-345, 530-538 and 705-730 eV correspond to the binding energy of Fe 3p, Pd 3d, O 1s and Fe 2p regions, respectively. The binding energies at 710 and 723 eV corresponding to Fe $2p_{3/2}$ and Fe $2p_{1/2}$ are consistent with the Fe 2p binding energy of magnetite nanoparticles (Figure 4b). The O 1s spectrum (Figure 4d) can be deconvoluted into two peaks at 528.8 and 530.9 eV, which correspond to M-O and O-H respectively. The highresolution spectrum of Pd (Figure 4c) clearly indicates the presence of Pd $3d_{5/2}$ (336.1 eV) and Pd $3d_{3/2}$ (341.3 eV), corresponding to Pd in oxidation state of +2. The +2 oxidation state of Pd indicates the presence of both PdO and Pd(OH)₂, which may be formed during the hydrolysis of PdCl₂ under basic conditions.^[16]

To examine the magnetic properties of the synthesized Fe_3O_4 -Pd, magnetization curves were measured using VSM with the magnetic field cycling between -9000

and +9000 Oe at 300 K (Figure 5a). The saturation magnetization (M_s) value for Fe₃O₄-Pd was found to be 45 emu g⁻¹. Fe₃O₄-Pd shows a superparamagnetic nature. The superparamagnetic nature and high M_s make Fe₃O₄-Pd an efficient and reusable catalyst for oxidative coupling of amides with olefins. The complete magnetic separation of the Fe₃O₄-Pd nanocatalyst using an external magnetic field (Figure 5b) demonstrates the strong magnetic sensitivity of the catalyst.

The nitrogen adsorption/desorption isotherm of the synthesized Fe₃O₄-Pd is of type IV with H3 hysteresis (Figure 6a). This indicates the formation of aggregates of plate-like particles giving rise to slit-shaped pores. The Brunauer–Emmett–Teller surface area was found to be 91.144 m² g⁻¹, which is much higher than that reported in the literature.^[16] The high surface area favours catalytic activity of the synthesized nanoparticles. Furthermore, the corresponding Barrett–Joyner–Halenda analyses indicate that the average pore size was 3.95 nm. Most of the pores ranged from 3 to 22 nm (Figure 6b).

To investigate the catalytic efficiency of Fe_3O_4 -Pd for enamide synthesis, we commenced our investigation



FIGURE 4 XPS survey spectrum (a) and high-resolution scans of Fe_3O_4 -Pd corresponding to Fe 2p (b), Pd 3d (c) and O 1s (d)



FIGURE 5 (a) Room temperature magnetic hysteresis curve of Fe_3O_4 -Pd and (b) photograph showing separation of catalyst

using benzamide (1a) and methyl acrylate (2a) as model substrates. The results of the oxidative amidation are

summarized in Table 1. The reaction of **1a** (0.826 mmol) with **2a** (2.478 mmol) was carried out in the presence of Fe₃O₄-Pd (30 mg, 2.3 wt% Pd), *p*-toluenesulfonic acid (PTSA) (1.652 mmol) and *tert*-butyl hydroperoxide (TBHP) (1.156 mmol) as oxidant under ambient air at room temperature for 14 h using toluene as the solvent, resulting in **3a** in 72% yield (Table 1, entry 1). The formation of (*Z*)-enamide was proved from the ¹H NMR spectrum (Supporting information). The appearance of doublet at 11.49 ppm (for N—H) and 5.28 ppm (vinylic proton) with coupling constant of 8.8 Hz confirmed the synthesis of (*Z*)-enamide.^[6] We investigated the optimization reaction with both polar and non-polar solvents. Polar solvents such as dimethylformamide (DMF), dimethylsulfoxide (DMSO)



FIGURE 6 (a) Nitrogen adsorption/desorption isotherm and (b) pore size distribution of Fe₃O₄-Pd

TABLE 1 Optimization of reaction conditions

0 NH ₂ +	OMe O	Fe ₃ O₄-Pd-nano catalyst Oxidant, Additives, Solvent, rt, 14 h			
Entry	Catalyst	Solvent	Oxidant	Additive	Yield (%) ^a
1	Fe ₃ O ₄ -Pd	Toluene	TBHP	PTSA	72
2	Fe ₃ O ₄ -Pd	Dioxane	TBHP	PTSA	35
3	Fe ₃ O ₄ -Pd	DCE	TBHP	PTSA	15
4	Fe ₃ O ₄ -Pd	DMF	TBHP	PTSA	< 5
5	Fe ₃ O ₄ -Pd	DMSO	TBHP	PTSA	< 5
6	Fe ₃ O ₄ -Pd	NMP	TBHP	PTSA	< 5
7	Fe ₃ O ₄ -Pd	Hexane	TBHP	PTSA	15
8	Fe ₃ O ₄ -Pd	Benzene	TBHP	PTSA	16
9	Fe ₃ O ₄ -Pd	Xylene	TBHP	PTSA	18
10	Fe ₃ O ₄ -Pd	—	TBHP	PTSA	n.r.
10	Fe ₃ O ₄ -Pd	Toluene	BQ	PTSA	12
11	Fe ₃ O ₄ -Pd	Toluene	Cu(OAc) ₂	PTSA	15
12	Fe ₃ O ₄ -Pd	Toluene	AgOAc	PTSA	n.r.
13	Fe ₃ O ₄ -Pd	Toluene	DTBP	PTSA	< 5
14	Fe ₃ O ₄ -Pd	Toluene	DDQ	PTSA	n.r.
15	Fe ₃ O ₄ -Pd	Toluene	$K_2S_2O_8$	PTSA	30
16	Fe ₃ O ₄ -Pd	Toluene	NaIO ₄	PTSA	< 5
17	Fe ₃ O ₄ -Pd	Toluene	TBHP	AcOH	n.r.
18	Fe ₃ O ₄ -Pd	Toluene	TBHP	PhCOOH	n.r.
19	Fe ₃ O ₄ -Pd	Toluene	—	PTSA	Trace
20	—	Toluene	TBHP	PTSA	n.r.
21	Fe ₃ O ₄ -Pd	Toluene	TBHP	—	n.r
22	Fe ₃ O ₄ -Pd	Toluene	TBHP	PivOH	10
23	Fe ₃ O ₄ -Pd	Toluene	TBHP	PTSA	40 ^b
24	Fe ₃ O ₄ -Pd	Toluene	TBHP	PTSA	50 ^c
25	Fe ₃ O ₄	Toluene	TBHP	PTSA	n.r.

^aReaction conditions: benzamide (0.826 mmol), methyl acrylate (2.478 mmol), Fe_3O_4 -Pd (30 mg, 2.3 wt% Pd, 5.5 mol% Pd), oxidant (1.156 mmol), additive (1.652 mmol), 4 ml of solvent, 14 h in air; n.r., no reaction.

^bAdditive (0.826 mmol).

^cTBHP (2.065 mmol).

and *N*-methylpyrrolidone (NMP) resulted in very low yield of the product. With non-polar solvent, moderate to good yields of (*Z*)-enamide were obtained. In the absence of solvent, the reaction failed to proceed (Table 1, entry 10). Next, we investigated several oxidants such as benzoquinone (BQ), 2,3-dichloro-5,6-dicyanoquinone (DDQ), TBHP, di-*tert*-butyl perbenzoate (DTBP), sodium periodate (NaIO₄), copper acetate (Cu(OAc)₂) and silver acetate (AgOAc). Among the oxidants tested, TBHP was found to be highly effective for promoting the reaction (Table 1, entry 1). Also various additives such as PTSA, acetic acid (AcOH) and pivallic acid (PivOH) were examined. The optimization results revealed that 2.0 eqiv. of PTSA was necessary to maintain the efficacy of the reaction (Table 1, entry 1). Decreasing the additive concentration to 1 equiv. decreased the yield of the reaction (Table 1, entry 23). This is due to the strong coordination of benzamide with metal catalyst leading to deactivation of the catalyst. However, with excess PTSA (2.0 equiv.) the competitive binding of amide with nanocatalyst may

Applied Organometallic– Chemistry

Wiley

6 of 9 WILEY Organometallic-Chemistry

TABLE 2 Oxidative coupling between amides and olefins^a

$\begin{array}{c} O \\ Ar \\ H \end{array}^{R} + X \\ Ar, R = Aryl, alkyl \\ CN, CONH_{2} \end{array} \qquad $									
Entry	Substrate	Product	Time (h)	Yield (%) ^b					
1	NH ₂		14	72					
2	NH ₂		15	70					
3	O ₂ N 1b	O ₂ N 4a O OMe	48	42					
4	O ₂ N 1b	O ₂ N 4b OBu	48	35					
5	CI 1c		35	41					
6	1c O NH ₂		35	37					
7	$F_{3}C$ 1d NH_{2}	F ₃ C N H O OBu	48	0					
8	O NH Me	O O N Me 7	48	15					
9	CI If	CI N Me 8	48	<5					
10	O ₂ N Ig	O O O O O O O O O O O O O O O O O O O	48	0					
11	NH ₂ NO ₂	$ \begin{array}{c} $	48	26					

(Continues)

TABLE 2 (Continued)

Ar, R = Aryl, alkyl Entry Substra	$ \begin{array}{c} $	$3O_4$ -Pd HP, PTSA Jene, rt Time (h) % Yield ^b		
Entry	Substrate	Product	Time (h)	Yield (%) ^b
12	NH ₂ 1i		24	52
13		BuO O H 12	24	43
14	NH ₂		48	0
15	NH ₂		48	0
16	MeO 1k	MeO H OEt	36	38
17	CI NH2	CI H OEt	36	40
18			24	32
19	NH ₂		15	62

^aReaction conditions: amide (0.826 mmol), olefin (2.478 mmol), Fe₃O₄-Pd (30 mg, 2.3 wt% Pd, 5.5 mol% Pd), PTSA (1.652 mmol), TBHP (1.156 mmol) toluene (4 ml), r.t.

^bIsolated yield.

decrease and hence deactivation of the nanocatalyst is prevented, so higher yield was obtained.^[18] In the absence of the Fe_3O_4 -Pd nanocatalyst, no reaction proceeds, highlighting the important role of the nanocatalyst in the coupling reaction (Table 1, entry 20). Performing the coupling reaction in the absence of Pd with Fe_3O_4 failed to afford the desired enamide (Table 1, entry 25). Increasing the catalyst loading did not enhance the yield of the reaction, perhaps due to possible polymerization. Furthermore, when the reaction was conducted under nitrogen atmosphere, a very low yield of the product was obtained, indicating the crucial role played by molecular oxygen in the air.

With the optimized conditions in hand, the scope of the reaction was investigated by coupling various amides with olefins. The results of the reactions are summarized in Table 2. Interestingly, moderate to good yields with high level of (Z)-selectivity were observed in almost all cases. Under the standard reaction conditions, functional groups such as chloro, nitro and methoxy were well tolerated on the phenyl ring of amide. Reactions of *p*-nitrobenzamide with methyl acrylate and butyl acrylate resulted the corresponding (Z)-enamide in 42 and 35% yield, respectively (Table 2, entries 3 and 4). However, with *o*-nitrobenzamide, a low yield of the product was observed (Table 2, entry 11). This may be due to the steric hindrance by *ortho* substituent.

Applied Organometallic-Chemistry

Wiley

7 of 9



2

71

Yield (%)^a ^aIsolated yield.

Cycle

We also examined the coupling of trifluoroacetamide with butyl acrylate (Table 2, entry 7) and failed to observe any expected product. It is important to mention that sterically demanding secondary amides also reacted with methyl acrylate and butyl acrylate, affording the product (E)enamides in low yield (Table 2, entries 8 and 9). The absence of formation of hydrogen bonding results the synthesis of (E)-enamide. In addition, low yield of the product may be due to the partial deactivation of the nanocatalyst by secondary amides. Heterocyclic amides such as furan-2carboxamide coupled with methyl acrylate and butyl acrylate to afford the corresponding (Z)-enamide in 52 and 43% yield (Table 2, entries 12 and 13). Also thiophene-2carboxamide reacted with butyl acrylate, affording the product (15) in 43% yield (Table 2, entry 18). Electronically deficient alkenes such as acrylamide and acrylonitrile were found unsuitable for oxidative amidation reaction (Table 2, entries 14 and 15). This may be due to the possible coordination of nitrogen atom of these olefinic substrates with the nanocatalyst, leading to catalyst deactivation.

1

72

2.1 | Mechanism

To investigate the mechanism of the reaction, a radical trapping reagent, 2,2,6,6-tetramethylpiperidin-1-yloxy (TEMPO), was added to the reaction in the optimized condition (Scheme 1). No desired product (**3a**) was formed, indicating that a radical process was most likely involved. However, the exact mechanism of the reaction is unclear and requires further investigation.

2.2 | Reusability study

The stability and catalytic activity of the Fe_3O_4 -Pd nanocatalyst were investigated in recycling experiments using the model reaction between benzamide and methyl

acrylate under the optimized conditions (Table 1, entry 1). After completion of the reaction, the catalyst was separated magnetically, washed with water and dichloromethane (thrice), dried in a hot-air oven at 50°C for 2 h and reused for the next cycle. The yields of the reaction versus the number of cycles are presented in Table 3. The catalyst could be reused without loss of activity up to the second cycle. In the third reuse, the yield was decreased (53%).

3

53

We were interested to investigate further as to whether the reaction took place on the surface of the catalyst or the active species were present in the reaction solution. We conducted a hot filtration test using the standard conditions to determine the exact nature of catalysis. The crude reaction mixture was filtered through celite after 40 min at 32% conversion and the reaction continued further for 14 h. The yield of the reaction was increased to 71%. AAS analysis after 32% conversion indicated Pd in solution.^[19]

Surprisingly, the Pd abundance in solution after reaction does not seem to correlate with the observed results of reusability. After the second cycle there is a small decrease in catalytic activity. This may be due to the adsorption of by-products on the surface of the catalyst, small loss of Pd metal and insufficient redeposition of Pd on magnetite.^[16] The change in Pd content in solution indicates that soluble catalytically active species may be formed and redeposited on the magnetite.^[19] Reusability study and hot filtration test hint at the occurrence of a boomerang phenomenon.^[20]

3 | CONCLUSIONS

We have demonstrated for the first time the application of Fe_3O_4 -Pd nanocatalyst for oxidative coupling of amides with olefins. This method allows the stereoselective synthesis of (*Z*)-enamides at room temperature in the absence of co-catalyst and ligands. The magnetic nature of the Fe₃O₄-Pd nanocatalyst is particularly advantageous

for easy and quantitative separation of the catalyst for reuse. Further applicability of this catalyst for C–C and C–heteroatom oxidative coupling reactions is under investigation in our laboratory.

4 | GENERAL PROCEDURE FOR OXIDATIVE COUPLING BETWEEN AMIDES AND OLEFINS

A 15 ml screw-cap tube was charged with a mixture of amide (0.826 mmol), olefin (2.478 mmol), 70% aqueous solution of TBHP (1.156 mmol), PTSA (1.652 mmol) and Fe₃O₄-Pd nanocatalyst (30 mg, 2.3 wt% Pd, 5.5 mol% Pd), and stirred in toluene at room temperature under ambient air. The progress of the reaction was monitored by TLC; upon completion, dichloromethane was added to the reaction mixture. The nanocatalyst was separated using an external magnet. The organic layer was washed repeatedly with water, dried over Na_2SO_4 and concentrated using a rotary vacuum evaporator. The crude product was then purified by silica gel column chromatography (eluent: ethyl acetate-petroleum ether) to afford the corresponding enamides.

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CONFLICT OF INTEREST

The authors declare no conflict of interest.

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SUPPORTING INFORMATION

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