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Organometallic polymer-functionalized Fe_3O_4 nanoparticles as a highly efficient and eco-friendly nanocatalyst for C–C bond formation

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Abstract

A magnetically recoverable biopolymer-based nanocatalyst was prepared through the covalent immobilization of a chitosan-bound 2-hydroxynaphthaldehyde Pd complex on the surface of superparamagnetic nanoparticles. The nanocatalyst was characterized by FTIR, X-ray powder diffraction and scanning electron microscopy, revealing an average particle size of 70 nm. The catalyst shows high thermostability by thermogravimetric analysis. Estimated Pd loading by inductively coupled plasma atomic emission analysis was found to be 0.348 mmol g^{-1}. The nanocatalyst exhibits excellent catalytic performance in Suzuki couplings of various aryl halides with phenylboronic acid, and Heck reactions of iodo- and bromoarenes with butylacrylate. The catalyst can be easily separated from the reaction mixture with an external magnet and reused consecutively four times without significant loss in activity.

Introduction

Palladium-catalyzed carbon–carbon cross-coupling reactions, especially Suzuki–Miyaura [1–4] and Heck–Mizoroki [5–8] coupling reactions, play a role key in the synthesis of pharmaceutical intermediates and agrochemicals, as well as in starting materials for conducting polymers and liquid crystalline materials. A variety of homogeneous and heterogeneous palladium catalytic systems have been developed to carry out these transformations under various reaction conditions. However, the homogenous Pd catalysts generally used in these reactions suffer a number of drawbacks such as tedious and time-consuming workup, difficulty in purification of the final products, problems in recycling of the catalysts, and contamination of the coupling products with palladium species, especially when they are used for the production of pharmaceutical products. In addition, most homogeneous palladium complexes are generally based on phosphine ligands [9, 10], which have associated problems like toxicity, air and moisture sensitivity, and high cost. Furthermore, heterogeneous catalysts, despite being easier to handle than their homogeneous counterparts, are often less effective and can also be difficult to separate from the reaction mixture.

In the last decades, the challenge of designing new catalysts that simultaneously provide the advantages of both homogeneous and heterogeneous catalysts has provided an important goal for the chemical community. With the significant advances in nanoscience, further attempts have been made to develop quasi-homogeneous and nanostructured catalysts which can act as a bridge between homogeneous and heterogeneous catalysts.

Magnetically recyclable nanocatalysts based on magnetite (Fe_3O_4) as a support have emerged as a promising area of study, as they not only present excellent catalytic activities and good chemical stability but also the magnetic nature of these catalysts facilitates their separation from the reaction media. Hence, in the present study, we have designed and prepared a novel heterogeneous palladium catalyst via functionalization of Fe_3O_4 nanoparticles with chitosan. Chitosan is a natural, biocompatible and biodegradable amino-polysaccharide, which, because of special properties including non-toxicity, biocompatibility, biodegradability, low immunogenicity and antibacterial properties, has shown applications in several fields. Functionalization of the free amine groups in chitosan with 2-hydroxynaphthaldehyde provides new active sites for grafting of Pd ions. The catalytic activity

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of this magnetically recyclable palladium catalyst was evaluated in Suzuki and Heck C–C cross-coupling reactions.

Experimental

All starting materials were of high purity as purchased from Merck and Aldrich. FTIR spectra were recorded on a VRTEX 70 model Bruker FTIR spectrophotometer in the range of 400–4000 cm^{-1} using KBr pellets. Thermogravimetric analysis (TGA) was carried out under air on a Shimadzu DTG-60 instrument. X-ray diffraction (XRD) data were collected on a Rigaku Dmax 2500 diffractometer with CuKα radiation ($\lambda = 1.54406$ Å). The morphology of the catalyst was observed with a Philips XL30 scanning electron microscope (SEM). Palladium content of the catalyst was measured by inductively coupled plasma atomic emission analysis (ICP-AES) VISTA-PRO. Known products were characterized by comparison of their spectral (^{1}HNMR, Bruker NMR Spectrometer FX 400Q) and physical data with those of authentic samples.

Preparation of the nanocatalyst

First, magnetic Fe_3O_4 nanoparticles were synthesized according to the chemical coprecipitation method [11]. $FeCl_36H_2O$ (2 mmol) and $FeCl_2{\cdot}4H_2O$ (1 mmol) were dissolved in deionized water (100 mL) at 70 °C, and the solution was stirred vigorously under a nitrogen atmosphere for 30 min. Concentrated ammonia solution (10 mL) was then added quickly to the mixture in one portion, and stirring was continued for another 30 min. The reaction mixture was then cooled; the magnetite precipitates were magnetically collected, washed several times with deionized water and dried overnight.

Chitosan-functionalized Fe_3O_4 nanoparticles were prepared according to the reported procedure [12]. Freshly precipitated magnetite (1 g) was dispersed in a solution of chitosan (3 g) in 2% (v/v) acetic acid solution (300 mL). The resulting mixture was stirred at room temperature for 1 h and then neutralized with 10% (w/v) $NaHCO_3$ solution. The precipitate was magnetically separated, washed twice with deionized water and dried at 60 °C.

A portion of the freshly prepared chitosan-functionalized Fe_3O_4 nanoparticles (1 g) was dispersed in ethanol (40 mL) by sonication for 30 min. The resultant mixture was charged with a solution of 2-hydroxynaphthaldehyde (5 mmol) in ethanol (10), and the mixture was refluxed under nitrogen for 24 h and then cooled. The resulting nanoparticles were magnetically separated, washed several times with ethanol and then dried under vacuum.

Finally, palladium chloride (5 mmol) was added to a suspension of dispersed Fe_3O_4@chitosan-bound 2-hydroxynaphthaldehyde (1.0 g) in ethanol (60 mL). The resulting mixture was refluxed for 24 h under nitrogen. The magnetic nanocatalyst was collected by means of an external magnet, washed with ethanol and dried under vacuum.

General procedure for the Suzuki reaction

A mixture of aryl halide (1 mmol), phenylboronic acid (1.2 mmol), K_2CO_3 (1.5 mmol), nanocatalyst (25 mg) and PEG (4 mL) was placed in an overpressure screw-capped vial and stirred at 100 °C for the required reaction time. After completion of the reaction, as judged by TLC, the reaction mixture was cooled to room temperature. The catalyst was separated by magnetic decantation, washed with water and EtOH and dried for the next run. The decantate was diluted with H_2O (10 mL), and the organic phase was extracted with diethyl ether (3×20 mL). The organic extract was dried over Na_2SO_4, filtered and concentrated under reduced pressure to get the desired product. These crude products were purified by recrystallization.

4-Nitro-1,1′-biphenyl: ^{1}H NMR (400 MHz, $CDCl_3$) δ (ppm): 8.35–8.32 (m, 2H), 7.79–7.76 (m, 2H), 7.67–7.64 (m, 2H), 7.56–7.46 (m, 3H).

4-Methoxy-1,1′-biphenyl: ^{1}H NMR (400 MHz, $CDCl_3$) δ (ppm): 7.60–7.55 (m, 4H), 7.47–7.43 (m, 2H), 7.36–7.29 (m, 1H), 7.03–7.00 (d, $J = 8.8$ Hz, 2H), 3.89 (s, 3H).

[1,1′-Biphenyl]-4-carbonitrile: ^{1}H NMR (400 MHz, $CDCl_3$) δ (ppm): 7.77–7.70 (m, 4H), 7.64–7.61 (m, 2H), 7.54–7.44 (m, 2H).

General procedure for the Heck reaction

In a typical reaction, an overpressure screw-capped vial was charged with aryl halide (1 mmol), *n*-butyl acrylate (1.5 mmol), Et_3N (1.5 mmol), the catalyst (25 mg) and N,N-dimethylformamide (4 mL). The reaction mixture was stirred at 130 °C for the required time. After completion of the reaction as monitored by TLC, the mixture was cooled to room temperature; the catalyst was separated with a permanent magnet, washed with water and EtOH and dried for the next run. The decantate was diluted with H_2O (10 mL), followed by extraction with ethyl acetate (3×20 mL). The combined organic layers were dried over anhydrous Na_2SO_4, filtered, and concentrated to get the desired product. The crude products were purified by recrystallization.

(E)-*n*-Butyl cinnamate: ^{1}H NMR (400 MHz, $CDCl_3$) δ (ppm): 7.72 (d, 1H), 7.57–7.54 (m, 2H), 7.42–7.39 (m, 3H), 6.48 (d, 1H), 4.25 (t, 2H), 1.76–1.69 (m, 2H), 1.50–1.46 (m, 2H), 1.00 (t, 3H).

(E)-n-Butyl 3-(4-methylphenyl)acrylate: ^{1}H NMR (400 MHz, $CDCl_3$) δ (ppm): 7.69 (d, 1H), 7.45 (d, 2H), 7.22 (d, 2H), 6.43 (d, 1H), 4.23 (t, 2H), 2.40 (s, 3H), 1.75–1.68 (m, 2H), 1.50–1.44 (m, 2H), 1.00 (t, 3H).

(E)-*n*-Butyl 3-(4-nitrophenyl)acrylate: ^{1}HNMR (400 MHz, $CDCl_3$, δ): 7.65 (d, 1H), 7.49–7.46 (m, 2H), 7.40–7.37 (m, 2H), 6.43 (d, 1H), 4.25–4.22 (m, 2H), 2.35 (s, 3H), 1.62–1.70 (m, 2H), 1.75–1.68 (m, 2H), 1.49–1.43 (m, 2H), 0.99 (t, 3H).

Results and discussion

The synthesis of the Pd complex of functionalized chitosan supported on Fe_3O_4 nanoparticles is illustrated in Scheme 1. First, the magnetite Fe_3O_4 nanoparticles were prepared by the conventional coprecipitation of Fe(III) and Fe(II) in basic solution. The Fe_3O_4 nanoparticles were then functionalized with chitosan, followed by treatment of the chitosan amino groups with 2-hydroxynaphthaldehyde in ethanol under reflux for 24 h. Finally, reaction of the as-synthesized nanoparticles with $PdCl_2$ led to the corresponding Pd complex of chitosan supported on the nanoparticles.

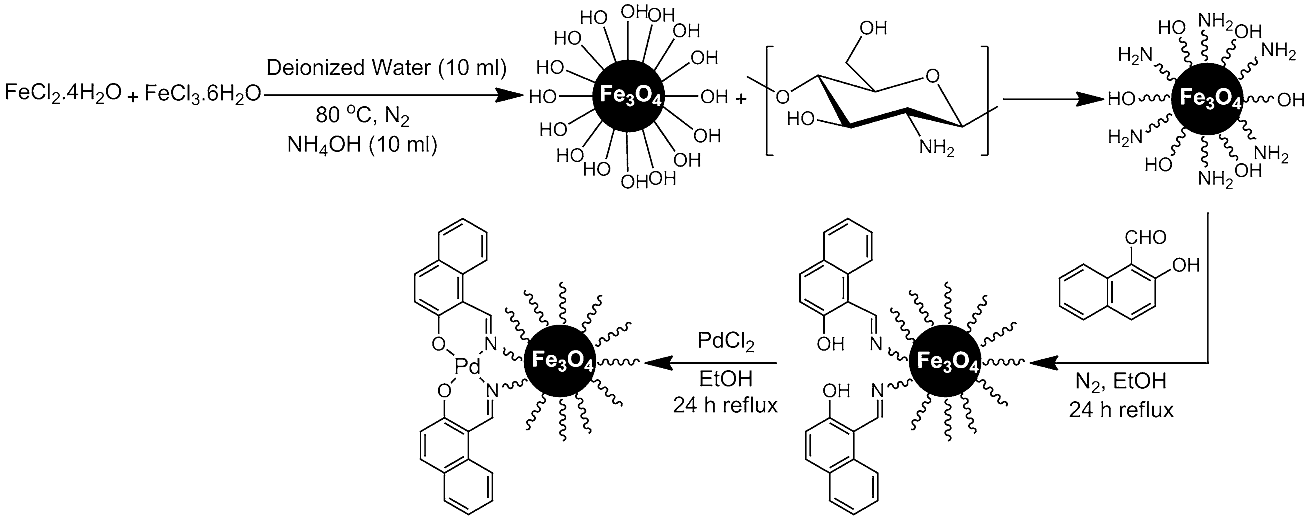
Catalyst characterization

The nanocatalyst was characterized using a variety of different techniques. The FTIR spectrum of the nanocatalyst is shown in Fig. 1. The characteristic peak around 580 cm^{-1} is due to the vibrations of the Fe–O bonds (Fig. 1a). A broadband at 3399 cm^{-1} and a band at 1625 cm^{-1} are assigned to the stretching and bending vibrations of the surface OH groups. In the spectrum of the chitosan-functionalized Fe_3O_4 nanoparticles (Fig. 1b), additional peaks at 2924 and 2854 cm^{-1} and a band at 1624 cm^{-1} are attributed to the aliphatic C–H and N–H stretching vibrations, respectively. Successful reaction of Fe_3O_4@chitosan with 2-hydroxynaphthaldehyde can be inferred from the appearance of a characteristic sharp band at 1623 cm^{-1} in Fig. 1c, assigned to the imine group (C=N). On the complexation with palladium chloride, the C=N peak is shifted to lower wave number at 1612 cm^{-1} (Fig. 1d), indicative of a metal–ligand interaction.

The size and morphology of the Fe_3O_4@chitosan-bound 2-hydroxynaphthaldehyde Pd complex were investigated by SEM. As shown in Fig. 2, the average diameter of the nanoparticles is estimated to be less than 70 nm, with nearly spherical shape.

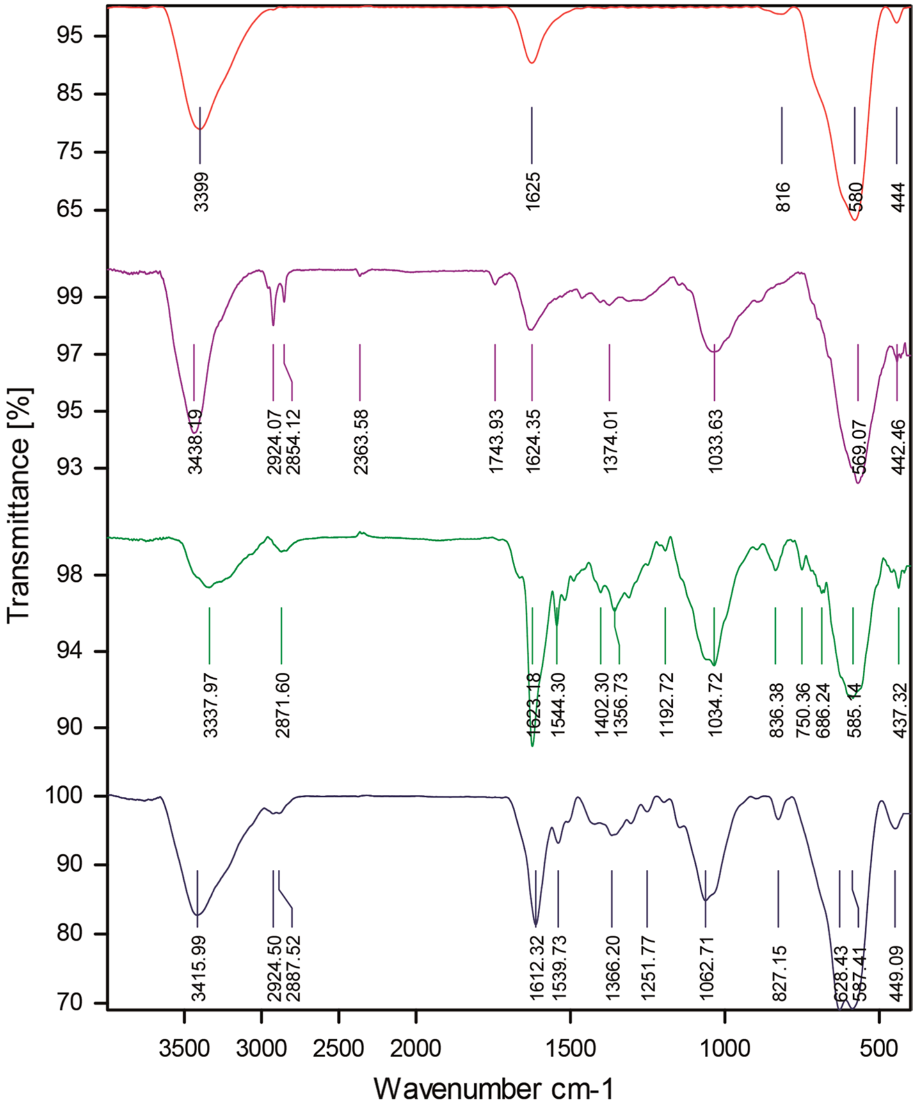
The crystalline structures of the Fe_3O_4 nanoparticles and Fe_3O_4@chitosan-bound 2-hydroxynaphthaldehyde Pd catalyst were investigated by XRD (Fig. 3). The XRD patterns of the Fe_3O_4 nanoparticles include peaks at $2\theta = 30.14°$, 35.72°, 43.42°, 54.12°, 57.97° and 63.96°, which are, respectively, attributed to the (2 2 0), (3 1 1), (4 0 0), (4 2 2), (5 1 1), and (4 4 0) phases of Fe_3O_4, indexed to the crystalline cubic spinel structure of standard Fe_3O_4 nanoparticles. The observed diffraction peaks appearing in the XRD of the synthesized nanocatalyst, which are also comparable with standard magnetite XRD patterns, indicate retention of crystallinity during the immobilization process. New peaks at $2\theta = 40.18°$, 44.28° and 67.16° are attributed to the Pd species.

The thermal stability and organic content of the Fe_3O_4@chitosan-bound 2-hydroxynaphthaldehyde Pd complex were measured by TGA (Fig. 4). The observed weight loss for the nanocatalyst below 150 °C is ascribed to the loss of adsorbed water or solvent. Around 150–770 °C, a large weight reduction occurred, which can be attributed to decomposition of the chitosan-bound 2-hydroxynaphthaldehyde Pd complex. From the observed weight loss, it was estimated that the organic content in the catalyst is about 40 wt%. The palladium content was found to be 0.348 mmol per gram of the catalyst, based on the ICP-AES chemical analysis.



Scheme 1 Schematic illustration for the synthesis of Fe_3O_4@chitosan-bound 2-hydroxynaphthaldehyde Pd complex

Fig. 1 FTIR spectra of **a** Fe_3O_4 nanoparticles, **b** Fe_3O_4@chitosan, **c** Fe_3O_4@chitosan-bound 2-hydroxynaphthaldehyde and **d** Fe_3O_4@chitosan-bound 2-hydroxynaphthaldehyde Pd complex



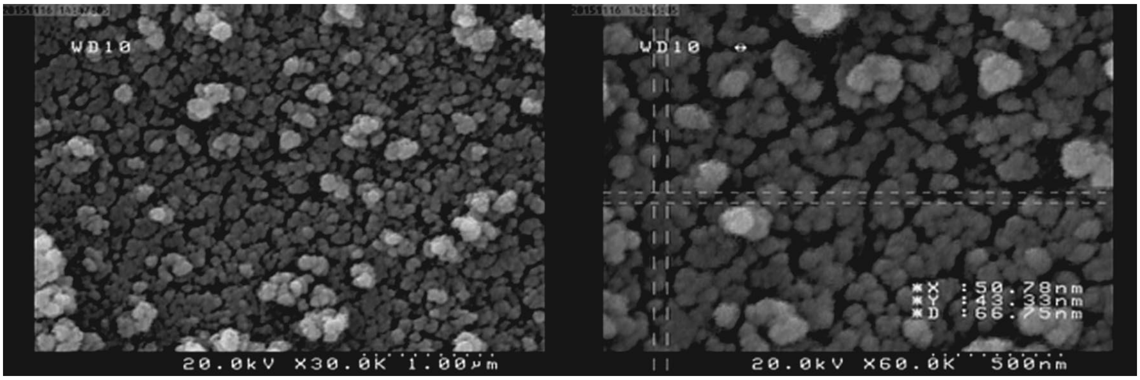


Fig. 2 SEM images of Fe_3O_4@chitosan-bound 2-hydroxynaphthaldehyde Pd complex

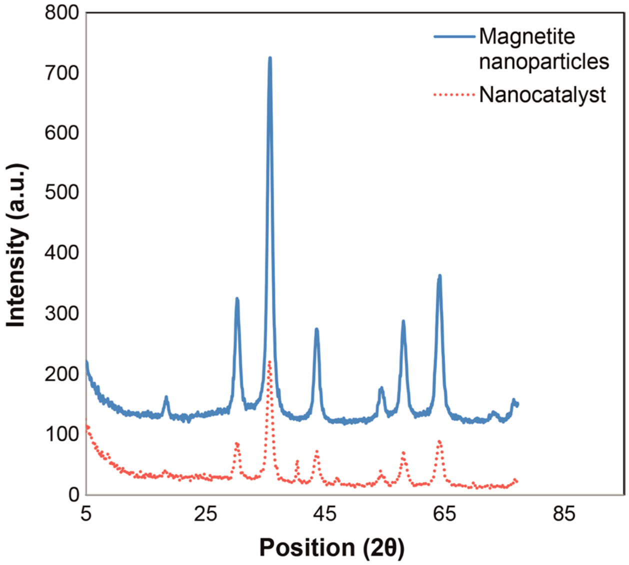


Fig. 3 XRD patterns of Fe_3O_4@chitosan-bound 2-hydroxynaphthaldehyde Pd complex

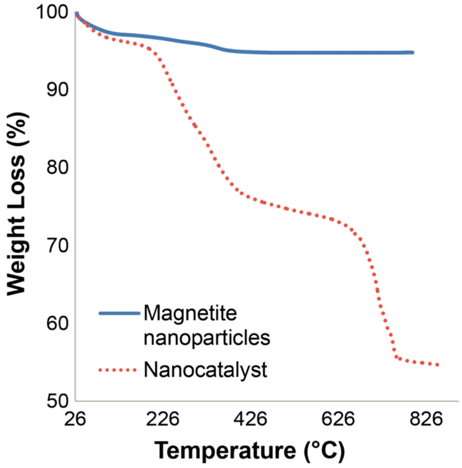
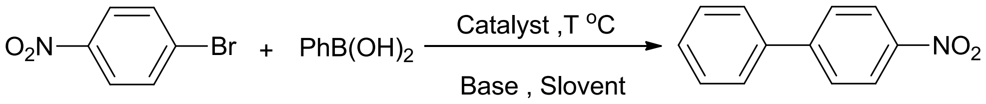


Fig. 4 TGA curves for Fe_3O_4 nanoparticles and Fe_3O_4@chitosan-bound 2-hydroxynaphthaldehyde Pd complex

Catalytic activity in Suzuki and Heck reactions

The catalytic efficacy of the nanocatalyst was initially explored in Suzuki–Miyaura coupling reactions. In order to optimize the reaction parameters, the reaction of 4-nitrobromobenzene with phenylboronic acid was chosen as a model reaction (Scheme 2) in order to study the influence of catalyst loading, base, solvent and temperature (Table 1).

As listed in Table 1, the nanocatalyst played a significant role in the C–C coupling reaction. When the model reaction was carried out in the absence of the catalyst, no product was obtained. On testing different amounts of the catalyst, 25 mg was found to be optimal; higher amount of catalyst did not have any significant impact on the progress of the reaction.



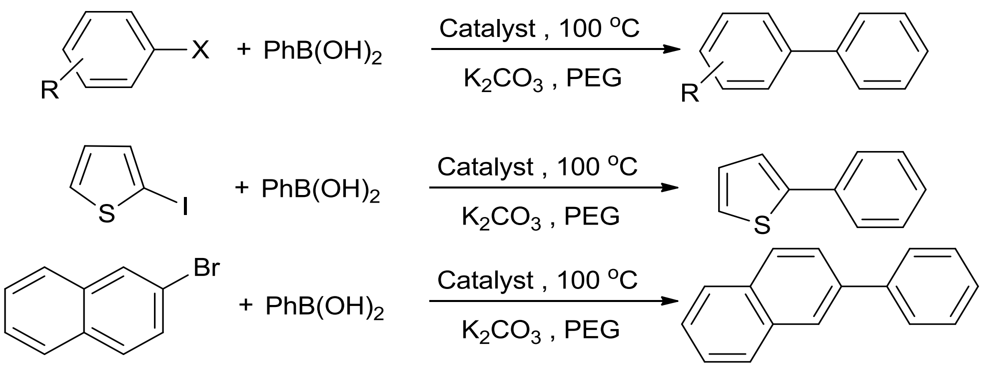
Scheme 2 Suzuki coupling of 4-nitrobromobenzene with phenyl boronic acid catalayzed by Fe_3O_4@chitosan-bound 2-hydroxynaphthaldehyde Pd complex

Table 1 Optimization of parameters for the Suzuki reaction of 4-nitrobromobenzene with phenyl boronic acid

Entry	Base	Solvent	*T* (°C)	Catalyst (mg)	Time (min)	Yield[a] (%)
1	–	PEG	80	20	10 h	–
2	K_2CO_3	PEG	80	–	24 h	–
3	K_2CO_3	PEG	80	20	65	65
4	$NaHCO_3$	PEG	80	20	60	45
5	NaOAc	PEG	80	20	70	30
6	Et_3N	PEG	80	20	100	5
7	K_2CO_3	H_2O	80	20	100	35
8	K_2CO_3	DMF	80	20	70	45
9	K_2CO_3	DMSO	60	20	70	50
10	K_2CO_3	PEG	100	20	50	80
11	K_2CO_3	PEG	110	20	50	82
12	K_2CO_3	PEG	100	25	50	93
13	K_2CO_3	PEG	100	30	45	94

Reaction conditions: nitrobromobenzene (1 mmol), phenyl boronic acid (1.2 mmol), base (1.5 mmol) and solvent (2 mL)

[a] Yields refer to those of pure isolated products



Scheme 3 Suzuki coupling of aryl halides, 2-iodothiophene and 2-bromonaphthalene with phenyl boronic acid catalyzed by Fe_3O_4@chitosan-bound 2-hydroxynaphthaldehyde Pd complex

Next, the model reaction was carried out in the presence of various organic and inorganic bases. Comparison of the results shows that the reaction in the presence of K_2CO_3 afforded the product in the highest yield.

Next, the solvent screening demonstrated that polyethylene glycol (PEG) was the most appropriate choice. Further experiments carried out at different temperatures showed that model reaction gave best results at 100 °C.

Next, in order to demonstrate the versatility of the nanocatalyst, a series of aryl halides (including both electron-donating and electron-withdrawing substituents) were subjected to the Suzuki reaction under the optimal conditions (Scheme 3). As listed in Table 2, the couplings between aryl iodides and bromides with various electron-donating and electron-withdrawing substituents and phenyl boronic acid proceeded effectively to afford the corresponding products in good-to-excellent conversions. Ortho-substituted aryl iodides and bromides required longer reaction times than para-substituted, because of steric effects. Encouragingly, the nanocatalyst exhibited good activity toward chlorobenzene.

Table 2 Suzuki coupling of aryl halides with phenyl boronic acid catalyzed by Fe_3O_4@chitosan-bound 2-hydroxynaphthaldehyde Pd complex

Entry	R	X	Time (min)	Yield (%)[a]	Mp (°C) [References]
1	H	I	15	94	68–70 [13]
2	*p*-NH_2	I	55	92	49–51 [14]
3	*p*-Me	I	35	96	46–48 [15]
4	*o*-Me	I	74	90	Light yellow liquid [16]
5	*p*-MeO	I	32	92	88–90 [17]
6	*o*-MeO	I	48	96	Colorless oil [19]
7	*o*-CO_2H	I	30	94	110–112
8	H	I	40	95	68–70 [13]
9	*p*-Me	Br	32	94	46–48 [15]
10	*p*-MeO	Br	45	82	87–89 [17]
11	*p*-NH_2	Br	65	90	49–50 [14]
12	*p*-CN	Br	35	93	84–87 [19]
13	*p*-CHO	Br	50	90	56–59 [20]
14	*m*-CHO	Br	90	91	51–53 [18]
15	*m*-CF_3	Br	27	96	Viscous liquid [21]
16	*p*-NO_2	Br	43	92	112–114 [15]
17	*p*-Cl	Br	50	90	78–79 [22]
18	H	Cl	80	92	69–71 [13]
19	C_4H_3SI		30	94	38–40 [23]
20	$C_{10}H_7Br$		24 h	38	96–98 [24]

Reaction conditions: aryl halide (1 mmol), phenyl boronic acid (1.2 mmol), K_2CO_3 (1.5 mmol), polymer-based nanocatalyst (25 mg) and PEG (2 mL)

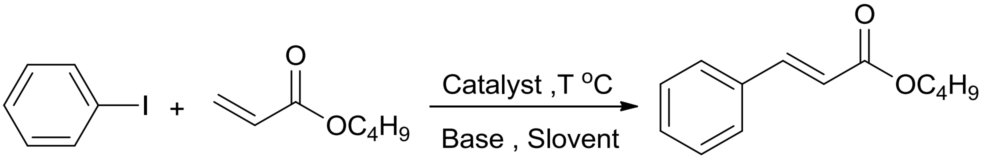
[a] Yields refer to those of pure isolated products

The catalytic performance of the nanocatalyst was further investigated in Heck reactions of iodo- and bromobenzene with n-butyl acrylate. In order to determine the optimum reaction conditions, the reaction of iodobenzene with n-butyl acrylate was taken as a model (Scheme 4). Table 3 presents optimization data for the catalyst loading, base, solvent and temperature. Based on these results, it was found that 25 mg of the catalyst can effectively catalyze the model reaction using K_2CO_3 as base in DMF at 130 °C.

In order to explore the general applicability of the catalyst, coupling reactions of different aryl iodides and bromides containing electron-withdrawing or electron-donating substituents were evaluated (Scheme 5). The results are listed in Table 4. As expected, for aryl iodides and electron-poor aryl bromides, the yields were generally good. For electron-rich bromobenzenes, and the yields were moderate, and in the case of chlorobenzenes, no activity was detected.

Finally, the reusability of the catalyst was evaluated by using the Suzuki coupling of 4-nitrobromobenzene with phenylboronic acid and the Heck coupling of iodobenzene with n-butyl acrylate under the optimized condition as the model reactions. The recycling results for the catalyst are presented in Table 5. As shown, satisfactory yields were still observed after four cycles in both Suzuki and Heck coupling reactions. Also, ICP analysis of the recovered catalyst after consecutive runs indicated no significant change in the Pd content of the catalyst.

In order to evaluate the efficiency of the present catalytic system, it was compared with other reported Pd catalysts. As Table 6 shows, the present nanocatalyst gave comparable



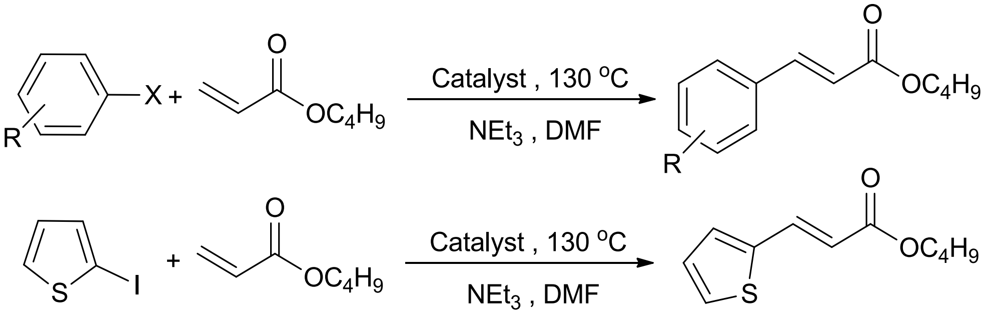
Scheme 4 Heck coupling of iodobenzene with n-butyl acrylate catalyzed by Fe_3O_4@chitosan-bound 2-hydroxynaphthaldehyde Pd complex

Table 3 Optimization of reaction parameters for Heck reaction of iodobenzene with n-butyl acrylate

Entry	Base	Solvent	*T* (°C)	Catalyst (mg)	Time (min)	Yield (%)[a]
1	Et_3N	H_2O	120	20	140	20
2	Et_3N	DMF	120	20	80	85
3	Et_3N	DMSO	120	20	90	65
4	Et_3N	PEG	120	20	100	60
5	–	DMF	120	20	5 h	–
6	$NaHCO_3$	DMF	120	20	95	73
7	NaOAc	DMF	120	20	90	78
8	K_2CO_3	DMF	120	20	120	45
9	Et_3N	DMF	120	–	24	–
10	Et_3N	DMF	120	25	65	93
11	Et_3N	DMF	120	30	60	94
12	Et_3N	DMF	130	25	45	94
13	Et_3N	DMF	140	25	47	96

Reaction conditions: iodobenzene (1 mmol), *n*-butyl acrylate (1.2 mmol), base (1.5 mmol) and solvent (2 mL)

[a] Yields refer to those of pure isolated products



Scheme 5 Heck coupling of aryl iodides/bromides and 2-iodothiophene with n-butyl acrylate catalyzed by Fe_3O_4@chitosan-bound 2-hydroxynaphthaldehyde Pd complex

results to the best of the well-known systems from the literature.

Conclusions

In conclusion, a magnetically separable nanocatalyst has been prepared from a chitosan-based Pd complex on Fe_3O_4 nanoparticles.

As a phosphine-free catalyst, the stability of the catalyst against air, moisture and temperature is high. Also, the catalyst offers advantages such as short reaction times and excellent yields for Suzuki and Heck reactions. Furthermore, the catalyst can easily be separated with an external magnet and reused for four consecutive runs without any significant loss of activity. These promising characteristics suggest that the catalyst would be suitable for industrial applications.

Table 4 Heck coupling of aryl iodides/bromides with *n*-butyl acrylate catalyzed by Fe_3O_4@chitosan-bound 2-hydroxynaphthaldehyde Pd complex

Entry	R	X	Time (min)	Yield (%)[a]	Mp (°C) [Ref]
1	H	I	45	94	Pale yellow liquid [25]
2	*p*-MeO	I	60	92	Pale yellow liquid [25]
3	*p*-Me	I	53	92	Pale yellow liquid [25]
4	*o*-Me	I	85	90	Pale yellow liquid [25]
5	*o*-MeO	I	110	90	Pale yellow liquid [25]
6	H	Br	4 h	45	Pale yellow liquid [25]
7	*p*-Me	Br	120	45	Pale yellow liquid [25]
8	*p*-MeO	Br	130	40	Pale yellow liquid [25]
9	*p*-CN	Br	100	91	43–45 [26]
10	*m*-CF_3	Br	120	70	Colorless oil [22]
11	*p*-NO_2	Br	140	95	60–63 [26]
12	C_4H_3SI		80	50	Brown oil [27]

Reaction conditions: aryl halide (1 mmol), n-butyl acrylate (1.2 mmol), Et_3N (1.5 mmol), polymer-based nanocatalyst (20 mg) and DMF (2 mL)

[a] Yields refer to those of pure isolated products

Table 5 Reusability of the catalyst in Suzuki–Miyaura and Heck–Mizoroki model reactions

Run	Suzuki reaction[a]		Heck reaction[b]	
	Yield (%)[c]	Time (min)	Yield (%)[c]	Time (min)
1	43	92	45	94
2	43	92	45	93
3	45	90	45	93
4	45	90	47	90

[a] Reaction conditions: nitrobromobenzene (1 mmol), phenyl boronic acid (1.2 mmol), K_2CO_3 (1.5 mmol), polymer-based nanocatalyst (25 mg) and PEG (2 mL)

[b] Reaction conditions: iodobenzene (1 mmol), *n*-butyl acrylate (1.2 mmol), Et_3N (1.5 mmol), polymer-based nanocatalyst (20 mg) and DMF (2 mL)

[c] Yields refer to those of pure isolated products

Table 6 Comparison of the activity of various catalysts in coupling reactions

Entry	Yield (%)	Time	*T* (°C)	Solvent/base	Catalytic system	References
Suzuki–Miyaura coupling of *p*-$NO_2C_6H_4Br$ with $PhB(OH)_2$						
1	Fe_3O_4@Pd	$MeOH/K_3PO_4$	45–65	18 h	96	[28]
2	MCM-41-Pd Schiff base complex	DMF/KF	100	3.5 h	95	[29]
3	Biopolymer–metal complex wool–Pd	H_2O/K_2CO_3	75	16 h	90	[30]
4	SMNPs-Salen Pd (II)	DMF-H_2O/K_2CO_3	100	3 h	96	[31]
5	HMMS–salpr–Pd	EtOH-H_2O/K_2CO_3	70	1.5 h	97	[32]
6	Pd nanoparticles	H_2O/KOH	100	12 h	91	[33]
7	Fe_3O_4/P(GMA-AA-MMA)–Schiff base–Pd	DMF-H_2O/K_2CO_3	80	1 h	99	[34]
8	Fe_3O_4@Pd complex	PEG/K_2CO_3	100	43 min	92	This work
Heck–Mizoroki coupling of PhI with $CH_2{=}CHC(O)C_4H_9$						
1	HMMS-NH_2-Pd	NMP/K_2CO_3	130	8 h	98	[35]
2	Pd@MIL-101	DMF/K_2CO_3:TBAB	120	120	97	[36]
3	Bio-Pd(0)	DMF/Na_2CO_3	80	12 h	97	[37]
4	SBA-16 supported Pd complex	DMA:H_2O/Na_2CO_3	125	240	95	[38]
5	PDVB-IL-Pd	Solvent free/Et_3N	120	6 h	95	[39]
6	Si–PNHC–Pd	NMP/K_2CO_3	120	2 h	95	[40]
7	CB [6] –Pd NPs	DMF/Na_2CO_3	140	24 h	99	[41]
8	Fe_3O_4@Pd complex	DMF/Et_3N	130	45 min	95	This work

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