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Anchored complexes of Ni, Pt, and Pd on Fe₃O₄ nanoparticles as new and eco-friendly nanocatalysts in Suzuki and Heck coupling reactions

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Three recoverable nanocatalysts were developed by immobilizing Ni, Pt, and Pd Schiff-base complexes on the magnetite nanoparticles. Successful preparation of the nanocatalysts was evidenced by Fourier transform infrared (FT-IR) and energy dispersive X-ray (EDX) spectroscopy. Nano-sized spherical structure of the nanocatalysts was indicated by scanning electron microscopy (SEM). X-ray powder diffraction (XRD) determined that the crystalline cubic spinel structure of Fe₃O₄ remained constant through the synthesis of three complexes on Fe₃O₄ nanoparticles. Magnetic properties of the nanocatalysts were analyzed by the vibration sample magnetometer (VSM). Thermostability of the nanocatalysts was studied by thermogravimetric analysis (TGA). Metal loading of these nanocatalysts was evidenced by inductively coupled plasma atomic emission (ICP-AES).

Investigating the catalytic activity of these nanocatalysts in Suzuki and Heck reactions implicated that in the presence of Pd nanocatalyst coupling reactions proceeded efficiently. For Pt nanocatalyst, Suzuki reaction took place in longer time with moderate to good yield. For the Heck reaction, the desired products were achieved only for aryl iodide and some aryl bromides. The Ni nanocatalyst could just catalyze the Suzuki reaction.

Relying on the magnetic characteristic, these nanocatalysts could be simply recovered and reused several cycles without significant loss in catalytic activity.

Keywords: Magnetically-reusable nanocatalyst; Eco-friendly nanocatalyst; Fe₃O₄-Supported complex; Suzuki-Miyaura reaction; Mizoroki-Heck reaction

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1. Introduction

Since catalysts have the potential for a wide range of applications in medicinal, chemical, food and textile industries, growing attention has been paid to the development of catalytic systems with high performance, ecologically greener processes and economical proficiency. Homogeneous catalysts, despite having high catalytic activity and good selectivity, do not have widespread applications due to difficulty involved in separation and recovery of expensive active catalysts from the final products of reactions. In heterogeneous catalysts the problem of isolation is resolved, but their activity and selectivity are lower.

Extensive efforts to fabricate catalysts that have high activity and selectivity coupled with ease of catalyst separation and recovery have led to the development of nanocatalysts [1-6]. In nano-sized catalysts, the surface area of the active components of catalysts increase, thereby enhancing contact between reactants and catalysts similar to behavior of homogeneous catalysts. Although, their insolubility in reaction mixture like heterogeneous catalysts affords separation and the product isolation stage effortless, isolation of these nanocatalysts from the reaction mixture due to the nano size of these catalysts is not so easy and conventional filtration is not efficient. To overcome this limitation, synthesis of catalysts over magnetic nano-supports has developed as one of the best solutions [7-12]. To date, numerous magnetic-based catalytic systems have been reported for various organic transformations such as reduction, oxidation, Knoevenagel condensation, N-arylation of amines and carbon-carbon cross-coupling reactions [13-19].

C-C coupling reactions, especially Suzuki (which affords substituted biaryls from reactions of aryl halides and phenylboronic acid) and Heck (which includes arylation of olefins by aryl halides) coupling reactions, have been applied to many areas such as bioactive compounds [20], organic materials synthesis [21], and advanced electronic and photonic materials [22]. Therefore, effort has been devoted to these reactions and development of heterogeneous catalysts, which proceed efficiently and can be easily separated from the reaction systems.

In the present study, we report the synthesis of fully characterized Schiff base complexes of Pd, Pt and Ni-functionalized magnetite nanoparticles and efficient application of these magnetic nanocatalysts in Suzuki and Heck coupling reactions.

2. Experimental

All starting materials in high purity were purchased from Merck and Aldrich. FT-IR spectra were recorded on a Perkin Elmer Spectrum 100 FT-IR spectrophotometer using KBr pellets. TGA was carried out under air on a Shimadzu DTG-60 instrument. XRD data were collected on an X' Pert Pro Panalytical with Cu K α radiation ($\lambda = 1.54406$ Å). The morphology of the catalyst was obtained using a SIGMA VP-500 ZEISS SEM. The metal content of the catalyst was measured by ICP-AES Optima 7300DV Perkin Elmer. The known products were characterized by physical data from authentic samples.

2.1. Preparation of the nanocatalysts

Magnetic Fe_3O_4 nanoparticles were synthesized according to a modified method [23]. In a typical procedure, 2 mmol of $FeCl_3 \cdot 6H_2O$ and 1 mmol of $FeCl_2 \cdot 4H_2O$ were dissolved in 100 ml of deionized water. The resulting solution was degassed by nitrogen bubbling at 70 °C with vigorous stirring. After being stirred for 30 min, 10 mL of concentrated ammonia solution was added quickly to the mixture and stirring was continued for another 30 min. The precipitate was magnetically collected, washed several times with deionized water and left to be dried overnight.

In order to synthesize amine-functionalized Fe_3O_4 nanoparticles, 1 g of precipitated Fe_3O_4 nanoparticles was left to be ultrasonically dispersed in 100 ml ethanol. Next, 1 mL of 3-aminopropyl (triethoxy) silane (APTES) was added to the solution and the resulting mixture was stirred at 60 °C for 24 h. The obtained precipitate was magnetically separated, washed several times with ethanol, and dried under vacuum.

Afterward, 1 g of amine-functionalized Fe_3O_4 nanoparticles was dispersed in ethanol (40 mL). 5 mmol of 2-hydroxynaphataldehyde was added to the mixture and refluxed for 24 h. The mixture was cooled and the resulting precipitate was magnetically separated, washed with ethanol, and dried in an oven.

Finally, 5 mmol of metal salt (K_2PdCl_4 or K_2PtCl_4 or NiCl_2) was added to the solution of dispersed Fe₃O₄@Schiff base nanoparticles (1.0 g) in 60 mL ethanol and the resulting mixture was refluxed for 24 h. The magnetic nanocatalysts were collected by an external magnet, washed with ethanol, and dried.

2.2. General procedure for the Suzuki reaction

A mixture of arylhalides (1 mmol), phenylboronic acid (1.2 mmol), base and PEG (4 mL) was placed in an overpressure screw-capped vial. An appropriate amount of the catalyst was added to the mixture and the mixture was stirred at the appropriate temperature. The progress of the reaction was monitored by thin layer chromatography (TLC) until complete consumption of the aryl halide. The catalyst was separated by magnetic decantation, washed with water and EtOH, and stored for the next run. The residual mixture was diluted with H_2O and the organic phase was extracted with diethyl ether (4×15 mL). The extracted organic layers were dried over Na_2SO_4 , filtered and concentrated under reduced pressure to get the desired product. These crude products were purified by recrystallization.

2.3. General procedure for the Heck reaction

In a typical reaction, a screw-capped glass vial was charged with arylhalides (1 mmol), n-butyl acrylate (1.5 mmol), base, catalyst and PEG (4 mL). The mixture was stirred at the appropriate temperature and reaction progress was monitored by TLC. After completion of the reaction, it was cooled to room temperature. The catalyst was magnetically separated and then washed with water and EtOH to recover the catalyst for the next run. The residual mixture was diluted with H_2O , followed by extraction with ethyl acetate (4×15 mL). The combined organic layers were dried over anhydrous Na_2SO_4 , filtered and concentrated to get the desired product. These crude products were purified by recrystallization.

3. Results and discussion

3.1. Catalyst characterization

The Schiff base complex-supported magnetic nanoparticles were synthesized following the procedure shown in scheme 1. The magnetic nanosupport was prepared via the co-precipitation method and subsequently coated with APTES as the functionalizing agent. The obtained nanoparticles were reacted with 2-hydroxynaphthaldehyde and further metallated with metal salts of Pd, Pt and Ni to achieve the final complexes grafted on magnetically recoverable nanoparticles.



Scheme 1. A schematic illustration of preparation method for Fe_3O_4 nanoparticle-supported Pd, Pt and Ni complexes.

The SEM images of Fe_3O_4 -supported Schiff-base complexes (figure 1) confirm that the catalysts were made up of uniform nanometer size with nearly spherical shapes.

The elemental composition of the Pd, Pt and Ni complexes-supported on Fe_3O_4 was determined by EDX analysis. The presented results in figure 2 indicate that the as-prepared products contain the successful functionalization. The loading of Pd, Pt and Ni was also calculated by ICP-AES. It was found that the loading amount of Pd, Pt and Ni ions in the nanocatalysts was 0.476, 0.734 and 0.238 mmol g⁻¹, respectively.

The crystalline structures of Pd, Pt and Ni complex-functionalized Fe₃O₄ nanoparticles were analyzed by XRD. As displayed in figure 3, same set of diffraction peaks at 20 of 30.1°, 35.7° , 43.2° , 53.2° , 57.0° and 62.7° corresponding to (220), (311), (400), (422), (511) and (440) faces are indexed to the crystalline cubic spinel structure of Fe₃O₄ [24], indicating retention of the crystalline phase during the immobilization process. The appearance of other peaks at XRD pattern was attributed to the Pd and Pt species.

The magnetic property of Pd, Pt and Ni complexes-supported on Fe₃O₄ was investigated with VSM at room temperature (figure 4). It can be seen that the saturation magnetization (*Ms*) value for Pd, Pt and Ni nanocatalysts are 49.1, 39.9 and 55.1 emu g⁻¹, respectively. As can be seen from figure 4, the *Ms* of the nanocatalysts are considerably less than that of the Fe₃O₄

nanoparticles that are attributed to the fact that the Fe_3O_4 nanoparticles were coated by Pd, Pt and Ni complexes.

FT-IR technique was employed to characterize the magnetic nanoparticles and successful functionalization on moving from Fe₃O₄ to the nanocatalysts. Figure 5a illustrates the characteristic bands at 580 cm⁻¹ and the broad band around 3384 cm⁻¹ which are caused by vibrations of the Fe–O bond of the iron oxide core and O–H stretching vibrations of adsorbed water. The introduction of APTES to the surface of Fe₃O₄ nanoparticles was confirmed by the bands at 1006 cm⁻¹ and 2918 cm⁻¹, which were ascribed to the Fe–O–Si and aliphatic C–H stretching vibrations (figure 5b). After the Schiff base condensation reaction, the characteristic band of the imine group appeared at 1632 cm⁻¹ (figure 5c) that on metallation this absorption was shifted to a lower frequency of 1617 cm⁻¹, 1618 cm⁻¹ and 1621 cm⁻¹ for Pd, Pt and Ni, respectively.

Thermal stability of the nanocatalysts was investigated by TGA (figure 6). The weight loss for all samples, which occurred below 200 °C, was due to removal of the adsorbed solvent or trapped water on the surface. In comparison with Fe_3O_4 , the TGA curves of the nanocatalysts demonstrated significant decomposition around 250 to 420 °C representing the surface grafting of the Fe₃O₄ nanoparticles by complexes of Pd, Pt and Ni.

3.2. Catalytic performance

The catalytic activities of the as-prepared nanocatalysts of Pd, Pt and Ni have been explored in both Suzuki and Heck cross-coupling, which are the most investigated synthesis protocols in modern chemistry and in industrial applications.

First, the reaction conditions for the Suzuki reaction were screened by performing a model reaction between 4-iodotoluene and phenylboronic acid in the presence of Pd, Pt and Ni nanocatalysts. The results are summarized in tables 1, 2 and 3.

After screening a range of solvents in the three catalytic systems, the highest yields were achieved when the model reaction was carried out in PEG, which supports solvation of organic substrates and inorganic bases. Besides the nature of the solvent, the effect of the base for Suzuki coupling reaction was considered and it was found that in the presence of Pd-catalyst, NaOH was the most suitable base for the reaction. Meanwhile for Pt and Ni-catalysts, Na₂CO₃ and NaHCO₃ were most effective. The best result for Pd-catalyst was obtained in 6 mg amount of the catalyst

at 80 °C; however, in the case of Pt and Ni, more catalyst loading (up to 16 mg) and higher temperatures (120 °C) were needed.

With optimized reaction conditions for the nanocatalysts, the generality and efficacy of the nanocatalyst coupling reactions of a variety of substituted aryl halides with phenylboronic acid were investigated under the optimized reaction conditions, and the results are summarized in table 4.

In the presence of Pd-catalyst, the reaction of substituted bromobenzenes, as well as substituted iodobenzenes, provided satisfactory yields in appropriate times. For Pt-catalyst, the desired products were obtained in good to excellent yields albeit relatively longer reaction times were required. In the case of Ni-catalyst, the results of substituted iodobenzenes were satisfactory. However for substituted bromobenzenes, all our attempts to enhance yields of the reaction failed.

Furthermore, the efficiency of the nanocatalysts was evaluated in Heck coupling reactions. In order to indicate optimal reaction conditions, the coupling reaction of iodobenzene with n-butyl acrylate was chosen as the model reaction. It was observed for Pd-catalyst, the model reaction proceeded effectively by using 6 mg of the catalyst, Et_3N as base, PEG as solvent and at 100 °C (table 5, entry 10). While for Pt-catalyst, the optimum best result was obtained using 16 mg of the catalyst, CH_3COONa as a base, PEG as a solvent, and at 120 °C (table 6, entry 6). For Ni-catalyst, catalysis was not observed.

With identified optimal conditions, coupling reactions of a variety of aryl halides with n-butyl acrylate in the presence of Pd and Pt-catalysts were then explored. As shown in table 7, for Pd-catalyst, the coupling reaction of n-butyl acrylate with aryl iodides and bromides, which contained electron-donating and electron-withdrawing groups, proceeded to afford the corresponding products. The ortho-substituted aryl halide, because of steric effects, generated the corresponding product in lower yield for a longer time. As expected for Pt-catalyst, the corresponding products were obtained in lower yield even when higher Pt loading was applied and reaction time was prolonged.

Based on economic and environmental preference for recyclable catalysts, the reusability of these nanocatalysts was investigated in the Suzuki and Heck model reactions under determined optimized reaction conditions. The magnetic property of these nanocatalysts causes simply separation of these catalysts without noticeable loss in catalytic activity (Table 8). As clearly shown in table 9, the catalytic efficiency of Pd complex supported on Fe_3O_4 nanoparticles is considered remarkable in terms of the mild reaction conditions, short reaction time, high reaction yield, and easy recovery in catalyzing Suzuki and Heck coupling reactions compared with some other published works.

4. Conclusion

Regarding the increasing importance of magnetic nanocatalysts from the point of view of green chemistry and industry, we developed efficient and reusable nanocatalysts by supporting complexes of Pd, Pt and Ni onto Fe₃O₄ magnetic nanoparticles. Pd and Pt nanocatalysts presented remarkable catalytic capacity for the Suzuki and Heck reactions while Ni nanocatalyst affected just the Suzuki reaction. As the Crystal Field Stabilization Energy (CFSE) of platinum group is in accordance to the order of Pt>Pd>Ni, thus their should be reversed as Ni>Pd>Pt. Moreover, in basic media of the Heck reaction, Ni²⁺ converts to Ni(OOH) (Ni² \rightarrow Ni³⁺). Accordingliy, Ni²⁺ is not able to do Heck reaction and the reactivity of Ni, Pd and Pt in the Heck reaction is Pd>Pt>Ni. However, in the Suzuki reaction, one of components involved in coupling reaction is boronic acid, which prevents the conversion of Ni²⁺ to Ni³⁺. Here, Ni²⁺ has the opportunity to reduce to Ni(0) by oxidizing the PEG but as there is a base also in the reaction media it does not occur. This result is true also for Pd and Pt. Therefore, reactivity order of this group in the Suzuki reaction is Pd>Pt>Ni.

These magnetic nanocatalysts were simply recovered from the reaction mixture by an external permanent magnet and reused for consecutive runs without significant loss of their catalytic activities.

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Figure 1. SEM images of Fe_3O_4 -supported complexes of (a) Pd, (b) Pt and (c) Ni.





Figure 2. EDX analysis of Fe₃O₄-supported complexes of (a) Pd, (b) Pt and (c) Ni.



Figure 3. XRD patterns of Fe₃O₄-supported complexes of (a) Pd, (b) Pt and (c) Ni.

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Figure 4. VSM curves of Fe_3O_4 -supported complexes of (a) Pd, (b) Pt and (c) Ni.

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Figure 5. FT-IR spectra of (a) Fe_3O_4 nanoparticles, (b) amine-functionalized Fe_3O_4 nanoparticles, (c) Schiff base-functionalized Fe_3O_4 nanoparticles, (d) Pd, (e) Pt and (f) Ni complex-functionalized Fe_3O_4 nanoparticles.



Figure 6. TGA curves of Fe₃O₄-supported complexes of (a) Pd, (b) Pt and (c) Ni.

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Н ₃ С—	I + P	$hB(OH)_2 \frac{Cat}{Bas}$	alyst ,T °C			—CH ₃	
Entry	Base	Solvent	Т	Catalyst	Time	Yield ^b	
5			(°C)	(mg)	(min)	(%)	
1	-	PEG	80	6	10 h	-	
2	Na ₂ CO ₃	PEG	80	6	240	40	
3	KOH	PEG	80	6	20	98	
4	NaOH	PEG	80	6	10	98	
5	NaHCO ₃	PEG	80	6	180	60	
6	NaOAc	PEG	80	6	180	25	
7	Et ₃ N	PEG	80	6	180	5	
8	NaOH	H_2O	80	6	120	30	
9	NaOH	DMF	80	6	120	40	
10	NaOH	DMSO	80	6	120	25	
11	NaOH	CH ₃ CN	80	6	120	10	
12	NaOH	PEG	40	6	4 h	60	
13	NaOH	PEG	60	6	90	80	
14	NaOH	PEG	100	6	10	98	
15	NaOH	PEG	80	8	8	98	

Table 1. Optimization of reaction parameters for Suzuki reaction of 4-iodotoluene with phenylboronic acid catalyzed by $Fe_3O_4@Pd$ -based complex.^a

^a Reaction conditions: 4-iodotoluene (1 mmol), phenylboronic acid (1.2 mmol), base (2 mmol) and solvent (2 ml).

	H ₃ C	—I + PhB(C	$(\text{DH})_2 \frac{\text{Cataly}}{\text{Base}},$	st ,T °C			-CH ₃
Fntry	Base	Solven	Base	Т	Catalyst	Time	Yield ^b
Lifti y	Duse	t	(mmol)	(°C)	(mg)	(min)	(%)
1	-	PEG	-	80	6	10 h	-
2	Et ₃ N	PEG	2	80	6	180	
3	Na ₂ CO ₃	PEG	2	80	6	180	50
4	NaOH	PEG	2	80	6	180	50
5	NaHCO ₃	PEG	2	80	6	180	42
6	CH ₃ COONa	PEG	2	80	6	180	31
7	K_2CO_3	PEG	2	80	6	180	48
8	KOH	PEG	2	80	6	180	42
9	NaOH	PEG	3	80	6	180	50
10	Na ₂ CO ₃	PEG	2	100	6	180	64
11	Na ₂ CO ₃	PEG	2	120	6	180	80
12	NaOH	PEG	2	100	6	180	62
13	NaOH	PEG	2	120	6	180	76
14	Na ₂ CO ₃	PEG	2	120	10	180	80
15	Na ₂ CO ₃	PEG	2	120	16	180	95
16	Na ₂ CO ₃	PEG	2	120	20	180	95
17	Na ₂ CO ₃	PEG	2	120	24	180	95
18	Na ₂ CO ₃	DMSO	2	120	16	180	23
19	Na ₂ CO ₃	DMF	2	120	16	180	34

Table 2. Optimization of reaction parameters for Suzuki reaction of 4-iodotoluene with phenylboronic acid catalyzed by $Fe_3O_4@Pt$ -based complex.^a

^a Reaction conditions: 4-iodotoluene (1 mmol), phenylboronic acid (1.2 mmol), base and solvent (2 ml).

	H ₃ C	–I + PhB(OF	$I)_2 \frac{Catalyst}{Base, S}$,T °C			·CH ₃
Entry	Base	Solvent	Base	Т	Catalyst	Time	Yield ^b
Litti y	Dase	Solvent	(mmol)	(°C)	(mg)	(min)	(%)
1	-	PEG	3	120	16	10 h	×
2	Et ₃ N	PEG	3	120	16	180	\mathbf{O}
3	Na ₂ CO ₃	PEG	3	120	16	180	87
4	NaOH	PEG	3	120	16	180	85
5	NaHCO ₃	PEG	3	120	16	180	94
6	CH ₃ COONa	PEG	3	120	16	180	53
7	K ₂ CO ₃	PEG	3	120	16	180	61
8	КОН	PEG	3	120	16	180	70
9	NaHCO ₃	PEG	1	120	16	180	82
10	NaHCO ₃	PEG	2	120	16	180	93
11	NaHCO ₃	PEG	2	100	16	180	84
12	NaHCO ₃	PEG	2	80	16	180	72
13	NaOH	PEG	2	80	16	180	61
14	NaOH	PEG	2	100	16	180	70
15	NaOH	PEG	2	120	16	180	90
16	NaHCO ₃	PEG	2	120	10	180	91
17	NaHCO ₃	PEG	2	120	28	180	94
18	NaHCO ₃	DMSO	2	120	16	180	15
19	NaHCO ₃	DMF	2	120	16	180	22

Table 3. Optimization of reaction parameters for Suzuki reaction of 4-iodotoluene with phenylboronic acid catalyzed by $Fe_3O_4@Ni$ -based complex.^a

^a Reaction conditions: 4-iodotoluene (1 mmol), phenylboronic acid (1.2 mmol), base and solvent (2 ml).

	R	-X + Pl	$hB(OH)_2 \frac{C}{H}$	atalyst , T °C Base , PEG				
		Pd cata	lyst ^a	Pt cat	alyst ^b	Ni ca	talyst ^c	Mn(°C)
Entry	Aryl halide	Time	Yield	Time	Yield	Time	Yield	$= \operatorname{IRef.}^{\operatorname{IRef.}}$
		(min)	$(\%)^d$	(min)	$(\%)^d$	(min)	(%) ^d	[1001.]
1		5	98	240	95	200	98	68–70 [25]
2	H ₂ N I	30	95	450	51	220	40	49-51 [26]
3	H ₃ C	10	98	180	95	180	82	45-48 [27]
4	CH ₃	15	98	180	90	200	94	Light yellow liquid [28]
5	H ₃ CO	15	98	180	71	200	75	88-90 [29]
6	OCH3	30	60	200	50	220	70	Colorless oil [30]
7	Br	15	96	120	98	200	20	68–70 [25]
8	H ₃ C Br	20	96	180	95	180	10	45-47 [27]
9	H ₃ CO-Br	15	90	180	20	180	10	86-89 [29]

Table 4. Suzuki coupling of aryl halides with phenylboronic acid catalyzed by $Fe_3O_4@$ Schiff base- Pd, Pt and Ni complex.



^a Reaction conditions: aryl halides (1 mmol), phenylboronic acid (1.2 mmol), NaOH (2 mmol), Pd-catalyst (6 mg) and PEG (2 ml).

^b Reaction conditions: aryl halides (1 mmol), phenylboronic acid (1.2 mmol), Na₂CO₃ (2 mmol), Pt-catalyst (for iodo (16 mg) and bromo aryl halides (28 mg)) and PEG (2 ml).

^c Reaction conditions: aryl halides (1 mmol), phenylboronic acid (1.2 mmol), NaHCO₃ (2 mmol), Ni-catalyst (for iodo (16 mg) and bromo aryl halides (24 mg)) and PEG (2 ml).

^d Yields refer to those of pure isolated products.

Accepted

	▶ I + ▶	O OC ₄ H ₉	Catalyst ,T °C Base , Sloven	t		°OC ₄ H ₉
Entry	Base	Solvent	T (°C)	Catalyst	Time	Yield
			< - /	(mg)	(min)	(%) ^b
1	Et ₃ N	H ₂ O	100	6	20	10
2	Et ₃ N	DMF	100	6	20	30
3	Et ₃ N	DMSO	100	6	20	25
4	Et ₃ N	CH ₃ CN	100	6	20	10
5	Et ₃ N	EtOH	100	6	20	50
6	Et ₃ N	PEG	80	6	40	80
7	-	PEG	100	6	24 h	-
8	NaOAc	PEG	100	6	30	-
9	K ₂ CO ₃	PEG	100	6	120	45
10	Et ₃ N	PEG	100	6	20	98
11	Na ₂ CO ₃	PEG	100	6	60	80
12	Et ₃ N	PEG	RT	6	120	-
13	Et ₃ N	PEG	120	6	15	98
14	Et ₃ N	PEG	100	10	20	98

Table 5. Optimization of reaction parameters for Heck reaction of iodobenzene with n-butyl acrylate catalyzed by $Fe_3O_4@Schiff$ base-Pd complex.^a

^a Reaction conditions: iodobenzene (1 mmol), n-butyl acrylate (1.2 mmol), base (2 mmol) and solvent (2 ml), 100 °C.

	→_I + →	$Cata Cata OC_4H_9$ Bas	llyst ,T °C e , Slovent	\bigcirc		C ₄ H ₉	
Fntry	Base	Solvent	$T(^{\circ}C)$	Catalyst	Time	Yield	X
Lifti y	Dase	Solvent	1(0)	(mg)	(min)	(%) ^b	
1	-	PEG	120	16	24 h	<-	K
2	Et ₃ N	PEG	120	16	120	52	Ť
3	Na ₂ CO ₃	PEG	120	16	120	10	
4	NaOH	PEG	120	16	120	-	
5	NaHCO ₃	PEG	120	16	120	52	
6	CH ₃ COONa	PEG	120	16	120	72	
7	K_2CO_3	PEG	120	16	120	10	
8	KOH	PEG	120	16	120	-	
9	CH ₃ COONa	PEG	100	16	150	10	
10	CH ₃ COONa	PEG	80	16	150	10	
11	CH ₃ COONa	PEG	120	12	120	51	
12	CH ₃ COONa	PEG	120	28	120	72	
13	CH ₃ COONa	DMSO	120	16	120	11	
14	CH ₃ COONa	DMF	120	16	120	17	

Table 6. Optimization of reaction parameters for Heck reaction of iodobenzene with n-butyl acrylate catalyzed by $Fe_3O_4@Schiff$ base-Pt complex.^a

^a Reaction conditions: iodobenzene (1 mmol), n-butyl acrylate (1.2 mmol), base (2 mmol) and solvent (2 ml), 120 °C.

R	$X + OC_4 H$	Catalyst , ^I 9 NEt ₃ , F	$\xrightarrow{100 °C}$			C ₄ H ₉
		Pd cat	alyst ^a	Pt cat	alyst ^b	Mn (°C)
Entry	Aryl halide	Time	Yield	Time	Yield	[Ref.]
		(min)	(%) ^c	(min)	(%) ^c	
1	Γ_I	20	98	120	72	Pale yellow liquid [34]
2	H ₃ CO-	90	95	120	26	Pale yellow liquid [34]
3	H ₃ C	40	95	240	57	Pale yellow liquid [34]
4		100	98	370	52	Pale yellow liquid [34]
5	H ₂ N-	90	93	240	54	Pale yellow liquid
6	OCH ₃	30	40	120	21	Pale yellow liquid [34]
7	Br	200	90	-	-	Pale yellow liquid [34]
8	H ₃ C-Br	180	72	-	-	Pale yellow liquid [34]
9	H ₃ CO Br	140	45	-	-	Pale yellow liquid [34]

Table 7. Heck coupling of aryl iodides/bromides with n-butyl acrylate catalyzed by $Fe_3O_4@Schiff$ base- Pd and Pt complexes.^a



^a Reaction conditions: aryl halides (1 mmol), n-butyl acrylate (1.2 mmol), Et_3N (2 mmol), $Fe_3O_4@Schiff$ base- Pd complex (6 mg) and PEG (2 ml), 100 °C. ^b Reaction conditions: aryl halides (1 mmol), n-butyl acrylate (1.2 mmol), CH_3COONa (2 mmol), $Fe_3O_4@Schiff$ base- Pt complex (16 mg) and PEG (2 ml), 120 °C. ^c Yields refer to those of pure isolated products.

Received

			Suzuki r	eaction			Heck reaction				
Run	Pd car	talyst ^a	Pt cat	alyst ^b	Ni ca	talyst ^c	Pd cata	alyst ^d	Pt cat	alyst ^e	
	Time	Yield	Time	Yield	Time	Yield	Time	Yield	Time	Yield	
	(min)	$(\%)^{1}$	(min)	$(\%)^{1}$	(min)	$(\%)^{1}$	(min)	$(\%)^{1}$	(min)	$(\%)^{1}$	
1	10	98	180	95	180	82	20	98	120	72	
2	10	98	180	93	180	80	20	98	120	68	
3	10	95	180	88	180	71	20	94	120	45	
4	10	90	180	73	180	45	20	90	X	-	

Table 8. Recyclability of the synthesized nanocatalysts in Suzuki and Heck model reaction.

^a Reaction conditions: 4-iodotoluene (1 mmol), phenylboronic acid (1.2 mmol), NaOH (2 mmol), Pd-catalyst (6 mg) and PEG (2 ml).

^b Reaction conditions: 4-iodotoluene (1 mmol), phenylboronic acid (1.2 mmol), Na₂CO₃ (2 mmol), Pt-catalyst (16 mg) and PEG (2 ml).

^c Reaction conditions: 4-iodotoluene (1 mmol), phenylboronic acid (1.2 mmol), NaHCO₃ (2 mmol), Ni-catalyst (16 mg) and PEG (2 ml).

 d Reaction conditions: iodobenzene (1 mmol), n-butyl acrylate (1.2 mmol), Et_3N (2 mmol), Fe_3O_4@Schiff base- Pd complex (6 mg) and PEG (2 ml), 100 °C.

^e Reaction conditions: iodobenzene (1 mmol), n-butyl acrylate (1.2 mmol), CH₃COONa (2 mmol), Fe₃O₄@Schiff base- Pt complex (16 mg) and PEG (2 ml), 120 °C.

AcceR

O	P_2N Br + Ph	$B(OH)_2 \frac{Catalyst, T \circ C}{Base, solvent}$	-		N	O ₂
Entry	Catalytic system	Solvent/Base	$T(^{\circ}C)$	TON	TOF	Ref.
1	Diaminomaleonitrile- based Schiff-base Pd complex	Toluene/K ₂ CO ₃	70	45.5	9.1	36
2	Salicylideneimine-based Pd complex	DMAc-H ₂ O- EtOH/K ₂ CO ₃	100	98	8.16	37
3	NC Palladacycles	Methanol/Na ₂ CO ₃	85	48	48	38
4	SMNPs-Salen Pd(II)	DMF-H ₂ O/K ₂ CO ₃	100	192	64	39
5	Fe ₃ O ₄ @Pd complex	PEG/NaOH	80	340	2037	This work
	H_3CO $Br +$	$ \begin{array}{c} O\\ OC_4H_9\\ \end{array} $ $ \begin{array}{c} Catalyst , T \circ C\\ Base , Slovent\\ H \end{array} $	H ₃ CO		O OC ₄ H	9
Entry	H ₃ CO Br + Catalytic system	O OC ₄ H ₉ Catalyst ,T °C Base , Slovent H Solvent/Base	H ₃ CO T (°C)	TON	O OC ₄ H TOF	9 Ref.
Entry 1	H ₃ CO-Br + Catalytic system NHC-Pd	O OC ₄ H ₉ Catalyst ,T °C Base , Slovent H Solvent/Base DMF/K ₂ CO ₃	H ₃ CO T (°C) 100	TON 900		9 Ref. 40
Entry 1 2	H ₃ CO-Br + Catalytic system NHC-Pd Cyclopalladated complexes	O OC ₄ H ₉ Catalyst ,T °C Base , Slovent H Solvent/Base DMF/K ₂ CO ₃ DMAc/NaOAc	н ₃ со Т (°С) 100 140	TON 900 87	о ОС ₄ н ТОF 150 1.8	9 Ref. 40 41
Entry 1 2 3	H ₃ CO-Br + Catalytic system NHC-Pd Cyclopalladated complexes Carbene–palladacycles	O OC ₄ H ₉ Catalyst ,T °C OC ₄ H ₉ Base , Slovent H Solvent/Base DMF/K ₂ CO ₃ DMAc/NaOAc DMAc/NaOAc	T (°C) 100 140 140	TON 900 87 190	$ \begin{array}{c} 0\\ \hline 0C_4H\\ \hline TOF\\ \hline 150\\ \hline 1.8\\ \hline 15.8\\ \end{array} $	9 Ref. 40 41 42
Entry 1 2 3 4	H ₃ CO-Br + Catalytic system NHC-Pd Cyclopalladated complexes Carbene–palladacycles Pd ⁰ -NHC complex	O OC ₄ H ₉ Catalyst ,T °C OC ₄ H ₉ Base , Slovent Base DMF/K ₂ CO ₃ DMAc/NaOAc DMAc/NaOAc DMAc/NaOAc DMAc/Na2CO ₃	T (°C) 100 140 140 140	TON 900 87 190 800	O OC ₄ H TOF 150 1.8 15.8 45	⁹ Ref. 40 41 42 43
Entry 1 2 3 4 5	H ₃ CO-Br + Catalytic system NHC-Pd Cyclopalladated complexes Carbene–palladacycles Pd ⁰ -NHC complex CNC pincer type Pd(II) complex	O Catalyst, T °C OC ₄ H ₉ Base, Slovent Base Slovent/Base DMF/K ₂ CO ₃ DMAc/NaOAc DMAc/NaOAc DMAc/NaOAc DMAc/NaOAc DMAc/NaOAc DMAc/NaOAc	T (°C) 100 140 140 140 140 110	TON 900 87 190 800 21	$ \begin{array}{c} $	 ⁹ Ref. 40 41 42 43 44

Table 9. Comparison of the activity of various catalysts in coupling reaction.

TON: (turnover number, yield of product/per mol of Pd)

TOF: (turn over frequency, TON/time of reaction)

