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ABSTRACT

In this study, magnetic nanoparticles (MNs) were functionalized using chlorodiphenylphosphine (CIPPh₂) and phosphine-functionalized magnetic nanoparticles (PFMN) as a recyclable phosphorus ligand was obtained. Also, palladium(II) complex of PFMN ligand (Pd-PFMN) was prepared and its catalytic activity was evaluated in the Heck reaction of chloroarenes. The results revealed that, this new catalyst showed high catalytic activity in the Heck reaction of chloroarenes and this can be attributed to the high reactivity of Pd complex involving phosphorus ligands and dispersible ability of MNs in solution as a high surface area support.

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1. Introduction

Transition metal-catalyzed protocols, especially palladium reactions, have become powerful tools in chemical synthesis of many materials [1–3]. In the context of Pd reactions, particularly C–C bond formations, preparation of high performance catalyst and the use of green reaction conditions have been considered [4,5]. Reactivity, stability and recycling of a catalyst system, are the most important factors to develop a new applicable Pd catalyst [6,7]. High performance Pd catalysts are considered, because they allow the use of aryl chlorides, which are less expensive than aryl bromides or iodides, providing both cost effective and more efficient reaction route. From the viewpoint of the reactivity, Pd complexes involving phosphorus ligands are one of the reactive classes of Pd catalysts [8]. However, phosphorus ligands as a precious ligand often suffer from some disadvantages, such as intrinsic toxicity, foul-smelling, easily oxidable during reaction process, difficulty of extraction and purification process and lack of recovery capability [9]. Supporting these ligands on a recyclable support is one of the most important approaches to improve their applicability in

organic reactions [10]. Fortunately, to make a recyclable catalyst, immobilization of ligands and homogeneous catalysts on different types of support materials has been extensively employed [11]. However, what is notable herein is that, the activity and selectivity of immobilized catalyst were decreased frequently, as result of the reduction in reactant diffusion rate to the surface of catalyst [12]. The latter problem can be resolved to some extent if support is selected in smallest possible size. Otherwise, the resulted reactivity due to homogeneous catalyst will not be fully effective in the reaction. It seems that, nanoparticles are a good support candidate because size of these materials is in the range of nanometre scale which allows the surface area to increase dramatically. Moreover nanoparticles are dispersible in solution, forming emulsion which further increases the diffusion rate [13]. In addition, reactants in solution have easy access to the active sites on the surface of nanoparticles. On the other hand, when the size of support is decreased in nanometre scale its recycleability using a simple filtration is a huge problem. As a solution, the efforts have been focused on magnetic recyclable supports such as magnetic nanoparticles (MNPs). Considered to the above mentioned points, when MNs are used as the support, both reactivity and reusability (catalyst can be separated from reaction condition using an external magnetic field) could be improved. So, if the hypothesis of phosphorus ligands on MNs directly (without any spacer) could be realized in practice, it would be possible to prepare a magnetic





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recyclable phosphorus ligands. This new improved phosphorus ligand can be used for preparation of transition metal complexes such as Pd, Pt, Ru and Rh for the specific applications in the related catalyzed reactions as catalyst.

However, to the best of our knowledge, up to now, there is no general study on preparation of phosphine-functionalised MNs in which magnetic reusable ligand has been described in this form. In the current study, we would like to report a new and easy access supported phosphine ligand on MNs (PFMN) for preparation of an efficient heterogeneous Pd catalyst for Heck reaction of chloroarenes.

In the current study, the Heck reaction was selected to evaluate the catalyst activity, because it is one of the most notable and widely used synthetic protocols for C–C bond formation [14]. In general, use of only reactive substrates, low yield, prolonged reaction time, tedious work-up processes, instability and lack of recovery capability of catalyst, are most important drawbacks linked to the application of this method [15]. Although the methodology for Heck reaction has been widely explored, but there is still widespread interest to develop a new Pd catalyst system to overcome these problems [16]. Herein, we report preparation, characterization and catalytic application of a Pd(II) complex of PFMN ligand (Pd-PFMN) in the Heck reaction of chloroarenes.

2. Experimental

Chemicals were purchased from Fluka and Aldrich chemical companies and used without further purification. The known products were characterized by comparison of their spectral and physical data with those reported in the literature. ¹H (500 MHz) and ¹³C NMR (125 MHz) spectra were recorded on a Bruker Avance spectrometer in CDCl₃ solution with tetramethylsilane (TMS) as an internal standard. X-ray diffraction (XRD, D8, Advance, Bruker, axs) and FT-IR spectroscopy (Shimadzu FT-IR 8300 spectrophotometer) were employed for characterization of the Pd-PFMN catalyst and products. ICP analysis was determined using inductively coupled

plasma (ICP) analyzer (Varian, Vista-Pro). Transmission electron microscopy (TEM) analyses were performed on a Philips model CM 10 instrument. Melting points were determined in open capillary tubes in a Barnstead Electro-thermal 9100 BZ circulating oil melting point apparatus. The reaction monitoring was accomplished by TLC on silica gel PolyGram SILG/UV254 plates. Column chromatography was carried out on columns of silica gel 60 (70–230 mesh).

2.1. Preparation of Fe₃O₄ nanoparticles

Magnetic nanoparticles were prepared via co-precipitation of Fe(III) and Fe(II) ions in the presence of sodium hydroxide. In a canonical flask, a mixture of FeCl₂.2H₂O (16 mmol, 2.6 g) and FeCl₃.6H₂O (30 mmol, 8.1 g) was dissolved in 100 mL of deionized water. Then, the pH of this solution was increased to 11 by adding a 3 M solution of NaOH as drop wise (in a period of 5 min) at 40 °C. Subsequently, the temperature of mixture was enhanced to 80 °C and the solution was stirred for 20 min in this temperature. The magnetic nanoparticles as a dark solid were isolated from the solution by magnetic separation and washed with deionized water until pH 7 reached.

2.2. Preparation of Fe₃O₄@SiO₂ nanoparticles

 $Fe_3O_4@SiO_2$ nanoparticles were prepared based on the literature with some modification: to a mixture of 250 mL of cyclohexane, 50 mL of 1-hexanol, 80 mL of triton X-100, and 25 mL of water, 2 g of Fe_3O_4 was added. Then the mixture was stirred by mechanical stirrer under N_2 gas for 30 min. 20 mL of tetraethyl orthosilicate (TEOS) was added to the mixture next and then the solution was stirred for 12 h at 28 °C. After the specified time, 18 mL of ammonia was added and the solution was stirred continuously for another 12 h. The precipitation was washed with ethanol (3 \times 10) and collected by external magnetic field. The desired product was dried under vacuum overnight.



Scheme 1. Synthetic route for the preparation of PFMN ligand and Pd-PFMN catalyst. i) TEOS, N2, ii) ClPPh2, Et₃N, CH₂Cl₂, N2, iii) Pd (OAc)₂, CH₂Cl₂, N2.

2.3. Synthesis of phosphine-functionalized magnetic nanoparticles (Fe₃O₄@SiO₂@PPh₂, PFMN)

To a mechanically stirred vessel mixture of $Fe_3O_4@SiO_2$ (5.0 g) in dry CH₂Cl₂ (80 mL), ClPPh₂ (4.2 mmol, 0.76 mL) and triethyl amine (1.0 mL) were added and refluxed under nitrogen gas for 12 h. Then, the mixture was filtered and washed with dichloromethane (3 × 10 mL) and deionized water (3 × 10 mL). After drying in the oven at 100 °C for 2 h, PFMN ligand was obtained as dark powder.

2.4. Preparation of Pd-PFMN catalyst

To a mixture of phosphine-functionalized magnetic nanoparticles (5 g) in dry CH₂Cl₂ (50 mL), palladium acetate (0.112 g, 0.5 mmol) was added and stirred for 24 h at room temperature under nitrogen gas. Then, the mixture was filtered and washed with dichloromethane (3×15 mL) and diethyl ether (2×15). After drying in a vacuum oven at 100 °C for overnight the Pd-PFMN catalyst was obtained as a dark solid.

2.5. General procedure for the "Heck reaction" in the presence of Pd-PFMN catalyst

In a typical experiment, to a mixture of aryl halide (1 mmol), acrylate/styrene (1.2 mmol), and K_2CO_3 (2 mmol) in 5 mL DMF, Pd-PFMN catalyst (0.05 g, 1 mol %) was added and heated in an oil bath at 120 °C, for the time specified in Table 2 (main text). The reaction was followed by TLC. After completion of the reaction, the mixture was cooled down to room temperature and the catalyst was magnetically separated from the reaction mixture and washed with diethyl ether (2 × 10 mL) followed by deionized and oxygen-free water (2 × 10 mL). The reused catalyst was dried for the next run.



Fig. 2. a) The XRD pattern of Pd-PFMN catalyst. b) The EDX spectrum of Pd-PFMN catalyst.

The aqueous phase was extracted with diethyl ether (2×10 mL) and the combined organic phases were dried over Na₂SO₄. The products were purified by column chromatography (hexane/ethyl acetate) to obtain the desired purity.

2.6. Preparation of Pd-MN catalyst

To a mixture of $Fe_3O_4@SiO_2$ (0.25 g) in dry CH_2Cl_2 (5 mL), palladium acetate (0.006, 0.025 mmol) was added and stirred for



Fig. 1. The TEM image of a) synthesized MNs, b) & c) two different positions of Pd-PFMN catalyst surface. d) The histogram of Pd-PFMN catalyst.



Fig. 3. A comparison between the FT-IR spectrum of the Pd-PFMN catalyst and Fe₃O₄@SiO₂.

24 h at room temperature under nitrogen gas. Then, the mixture was filtered and washed with dichloromethane (2 \times 5 mL) and diethyl ether (2 \times 5 mL). After drying in a vacuum oven at 100 °C for overnight a dark solid was obtained.

3. Results and discussion

3.1. Catalyst preparation and characterization

The preparation strategy for the Pd-PFMN catalyst is shown in Scheme 1.

In this study, MNs were prepared by co-deposition method using a procedure in the literature [17]. This method is one of the reliable and simple methods for the large-scale synthesis of MNs. The synthesized MNs, were coated by silica using a sol-gel process to obtain core-shell MNPs ($Fe_3O_4@SiO_2$) [18]. Based on this process by hydrolysis and then condensation of TEOS the silica layer is generated on MNs. The $Fe_3O_4@SiO_2$ nanoparticles are necessary for



Fig. 4. The comparison between TGA curves of ${\rm Fe_3O_4}$ nanoparticles, ${\rm Pd}({\rm OAc})_2$ and Pd-PFMN catalyst.

preparation of PFMN ligand, because when non core-shell MNs were used, PFMN ligand is not produced in ideal form. It seems that the silica shell not only prevents from the interactions and aggregation of MNs during the catalyst preparation process it also makes an easy access to connection of $-PPh_2$ species to the surface of MNs. After preparation of MNs, phosphine ligand is deposited on the MNs using an O-linker by a chemical process. Thus, ClPPh₂ was used as the reagent for this purpose. Subsequently, the synthesized MNs were reacted with ClPPh₂ and the obtained data were shown that under the mentioned condition (Scheme 1), the hydroxyl groups of MNs react with ClPPh₂ to produce the PFMN as a phosphine-modified ligand. It is noteworthy that, by use of this procedure the reaction of ClPPh₂ with the iron oxide particles was not resulted the immobilized phosphinate ligand (–POPh₂). Also, ClPPh₂ was not hydrolyzed during this process to form Ph₂POH and Ph₂POPPh₂ as byproducts. Finally, palladium acetate was complexed with this supported ligand to produce the Pd-PFMN catalyst.

The Pd-PFMN catalyst was characterized using some different techniques such as, transmission electron microscopy (TEM), powder X-ray diffraction (XRD), energy dispersive X-ray spectra (EDX) and FT-IR spectroscopy.

TEM image of the Pd-PFMN catalyst (Fig. 1a-c) shows that, the functionalized magnetic nanoparticles possess almost spherical morphology with relatively good monodispersity. Comparison between MNs and Pd-PFMN catalyst is shown that the



Fig. 5. The XPS analysis of Pd-PFMN catalyst.

Table 1

Study of various conditions for "Heck reaction" between chlorobenzene and ethyl acrylate using Pd-PFMN catalyst.^a



Entry	Solvent	Base	Temp (°C)	Time (h)	Yield (%) ^b
1	DMF	K ₂ CO ₃	120	5	93
				12	94
2	DMSO	K ₂ CO ₃	120	5	78
3	CH₃CN	K ₂ CO ₃	Reflux	12	53
4	THF	K ₂ CO ₃	Reflux	12	57
5	DMF	Et ₃ N	120	5	72
6	DMF	Cs ₂ CO ₃	120	5	94
7	DMF	NaOH	120	5	79
8	DMF	K ₂ CO ₃	120	5	95 ^c
9	DMF	K ₂ CO ₃	120	12	58 ^d

^a Reaction condition: chlorobenzene (1 mmol), ethyl acrylate (1.2 mmol), catalyst (0.05 g, 1 mol%), base (1.5 mmol), solvent (5 mL).

^b Isolated yield.

^c 0.075 g (1.5 mol%) of catalyst was used.

^d 0.025 g (0.5 mol%) of catalyst was used.

monodispersity of catalyst is not changed significantly during preparation process. In this study, the average diameter of the Pd-PFMN catalyst was \sim 10 nm. The histogram revealed the size distributions of catalyst nanoparticles (Fig. 1d). The histogram was proposed according to the results obtained from the TEM image and revealed the size distributions of catalyst nanoparticles.

The XRD pattern of the Pd-PFMN catalyst also shows that we have Fe_3O_4 nanoparticles as substrate for catalyst (Fig. 2). The peaks are indexed as the (220), (311), (400), (422), (511) and (440) planes of the Fe_3O_4 nanoparticle [19].

Also, to confirm the Pd content of catalyst, it was treated with concentrated HCl and HNO_3 to digest the Pd species and then



Scheme 2. Products of Heck reaction between alkenes and aryl halides in the presence of Pd-PFMN catalyst. Reagents and conditions: alkene (1.2 mmol), aryl halide (1 mmol), K₂CO₃ (2 mmol), catalyst (0.05 g, 1 mol%), DMF (5 mL), and 120 °C. All yields are isolated yields.



Table 2

Entry [Ref.]	Catalyst	Reaction conditions	Х	Time (h)	Yield (%) ^a	$\mathrm{TOF}^{\mathrm{b}}\left(\mathrm{h}^{-1} ight)$
1 [This work]	Pd-PFMN	K ₂ CO ₃ , DMF, 120 °C, 1.0 mol% Pd	I	0.5	98	196
			Br	3	94	32
			Cl	6	93	15
2 [5b]	PNP-PSS	K ₂ CO ₃ , H ₂ O, reflux, 1.2 mol% Pd	Cl	8	64	7
			Br	5	92	15
3 [26]	Pd-PANI	n-Pr ₃ N, DMF, 130 °C, 5 mol% Pd	Ι	30	65	0.5
4 [27]	Pd-NPs-Chitosan	TBAB, TBAA, 130 °C, 0.35 mol% Pd	Cl	24	0	0
			Br	15 min	98	1120
5 [28]	[Pd]-NaY	NaOAc, DMAc, 140 °C, 0.1 mol% Pd	Br	20	85	42
6 [29]	Pd-PVP	K ₂ CO ₃ , DMF, 120 °C, 0.01 mol% Pd	Br	45 min	36	4800
7 [30]	Pd(OAc) ₂	Ligand: Dave-Phos (5 mol%), TBAE, Dioxane, 80 °C, 2 mol%	Cl	24	99	2
8 [31]	Palladaphosphacyclobutene	NaOAc, DMA, 140 °C, 1.0 mol% Pd	Cl	24	15	0.6
9 [32]	Palladacycle	K ₂ CO ₃ , NMP, 130 °C, 0.1 mol% Pd	Br	3 min	90	18,000
10 [33]	NHC-Pd	Cs ₂ CO ₃ , Dioxane, 80 °C, 1.0 mol% Pd	Br	15	90	6

Comparison of the results of the synthesis of 1,2-diphenylethene, using Pd-PFMN-catalyzed Heck reaction of halobenzenes (Ph-X, X = Cl, Br, I) and styrene (PhCH=CH2).

^a Isolated yield.

^b TOF = (mol product/mol cat) h^{-1} .

analyzed by ICP analysis. The Pd content was determined to be 22.1 ppm (22.1 mg/L) which was equal to 2.21% w/w.

In accordance with the FT-IR spectra, which are shown in Fig. 3, the peaks positioned at ~1575 and ~467 cm⁻¹ are related to the formation of Fe₃O₄ nanoparticles [20].

The FT-IR shows three bands at around 1648, 789 and 463 cm⁻¹, which are presumably due to asymmetric stretching (ν_{as}), symmetric stretching (ν_s), and bending modes of Si–O–Si, respectively [21]. These peaks demonstrated that SiO₂ shell is properly generated around Fe₃O₄ nanoparticles cores. The peaks at ~1650 and 1406 cm⁻¹ are to confirm the presence of acetate ligand in the structure of Pd-PFMN catalyst [22]. Also, the peaks positioned at 1045 cm⁻¹ related to the formation of P–O bond [23]. Consequently, PPh₂ groups were connected to the magnetic support by an O-linker. Any peak at around 1210–1140 cm⁻¹ which is related to P=O bond is not observed [24]. This is confirmed that, the phosphine ligand during the preparation process is not oxidized.

The TGA curve of Pd-PFMN catalyst was shown two main weight losses (Fig. 4).

The first one was occurred at ~230 °C which is related to decomposition of palladium acetate from the $Fe_3O_4@SiO_2@PPh_2$ substrate. This part of the thermogram reveals the amounts of palladium acetate on magnetic nanoparticle support which is estimated to ~7.8%, (W/W). Finally, the reduction in the weight percentage of the catalyst at temperatures to ~285 °C is related to

decomposition of phosphine species. So, the elevated temperature for phosphine removal indicates the high thermal stability for PFMN substrate, because phosphine is covalently bonded to the MNs.

The chemical oxidation state of the Pd in Pd-PFMN catalyst was also analyzed using XPS. The XPS spectrum of catalyst reveals that there is only Pd(II) on the structure of Pd-PFMN catalyst (Fig. 5) [25].

3.2. Heck reaction of chloroarenes

The Pd-PFMN catalyst was applied in the Heck reaction to evaluate the catalytic performance. To evaluate the catalytic reactivity of the Pd-PFMN catalyst, the Heck reaction between chlorobenzene (**1a**) and ethyl acrylate (**2a**) was selected as simple model substrate and optimization condition is shown in Table 1.

According to the data which were obtained from optimizing study (Table 1), the Heck reaction properly carried out at 120 °C in the presence of Pd-PFMN (1 mol%), using K_2CO_3 as base, without addition of free ligand or any promoting additives in DMF solvent. It is noteworthy that, Pd-PFMN catalyst is ferromagnetic and can easily separated from the reaction mixture by simple magnetic attraction (Fig. 6b & c).

After optimizing reaction conditions using chlorobenzene and ethyl acrylate and in view of the fact that Pd-PFMN catalyst was an



Fig. 6. a) Reaction conditions: Pd-PFMN (0.05 g, 1 mol%), chlorobenzene (1.0 mmol), ethyl acrylate (1.2 mmol) and DMF (5 mL). Reaction time is 5 h. b) Reactants containing Pd-PFMN catalyst, c) Recycled Pd-PFMN catalyst from reaction mixture.

Table 3

Catalytic activity and recyclability of Pd-MN catalyst.



Entry	Catalyst (g)	Time (h)	Yield (%)
Fresh	0.05	12	55
Fresh	0.075	12	64
Fresh	0.1	12	68
Cycle 1	0.98	12	48
Cycle 2	0.97	12	31

efficient and reusable catalyst for Heck reaction of chloroarenes, the catalyst was used to other substrates (Scheme 2).

As shown in Scheme 2, the Heck reaction of both electron-rich and electron-deficient aryl chlorides also proceeded smoothly to furnish the desired products with good to excellent yields. Evidences show that, our environmentally benign catalyst system is comparable with the classic homogeneous catalysts in efficiency. In order to show the merit and the reactivity of Pd-PFMN catalyst related to other catalysts, a comparison with some other reported homogeneous and heterogeneous palladium catalysts for Heck reaction of chloroarenes is presented in Table 2. As shown in Table 2, our catalyst is superior to some of the previously reported catalysts in terms of reaction condition, reaction time and yield.

3.3. The catalyst recyclability and heterogeneity tests

For practical applications of this heterogeneous catalyst, the level of reusability was also evaluated. The recycled catalyst could be reused for at least four times without any treatment (Fig. 6a).

The ICP analysis of the catalyst after five cycle of reusability was shown that, only a very small amount (less than 1%) of the Pd metal (in 0.1 g of catalyst) removed from the magnetic nanoparticle substrate.

To confirm that the high activity of Pd-PFMN catalyst is resulted from the supported palladium and not from the leached Pd, after completion of the reaction between chlorobenzene and ethyl acrylate under optimized condition, the catalyst was separated from the reaction mixture and the obtained aqueous solution from the hot filtration was applied for next operation. When the purification processes were done, the obtained product was less than 3%. The results confirmed that the supported palladium magnetic nanoparticles provide the high catalytic activity without leach of the significant quantity of Pd.

To establish the function of phosphine ligand in the stabilization of Pd species on the surface of magnetic support, we examined the following experiments. According to the procedure for synthesis of Pd-PFMN catalyst we used from $Fe_3O_4@SiO_2$ instead of $Fe_3O_4@-SiO_2@PPh_2$ and as a result Pd on MNs (Pd-MNs) was obtained. The catalytic usefulness of Pd-MNs was explored in the reaction between chlorobenzene and ethyl acrylate and results of this study are summarized in Table 3.

As shown in Table 3, the catalytic activity and heterogeneity of Pd-PFMN catalyst are not comparable with Pd-MNs in practice. Obviously, Pd-PFMN is more active than Pd-MNs and its heterogeneity is superior. Accordingly, these experiments confirmed the role of phosphine ligand in the stabilization of Pd species on the MNs surface.

4. Conclusion

In conclusion, the phosphine-functionalized magnetic nanoparticles as a new supported ligand were synthesized and used for complexation of palladium in order to prepare Pd-PFMN catalyst. In PFMN ligand, P-atom is directly linked to the magnetic nanoparticle via a surface O atom. We also reported preparation, characterization and utilization of a new and high performance catalyst system for Heck reaction of chloroarenes. This new catalyst can be well dispersed in solution to produce a pseudo-homogeneous catalyst system to generate a highly reactive catalyst sites. Reusability and easy workup (using external magnetic attraction) were two other advantages of this catalyst system. Also PFMN ligand and Pd-PFMN catalyst provide great promise towards further useful applications in other transition metal complexes and palladium transformations in future, respectively.

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Appendix A. Supplementary material

Supplementary material associated with this article can be found, in the online version, at http://dx.doi.org/10.1016/j. jorganchem.2013.05.013.

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