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A new magnetically recoverable heterogeneous palladium catalyst for phosphonation reactions in aqueous micellar solution

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A new heterogeneous palladium complex of 2-aminothiophenol supported on nanomagnetic γ -Fe₂O₃ was synthesized and characterized using various methods. The catalyst was used as a magnetically recoverable heterogeneous palladium catalyst for phosphonation reactions via C–P bond formation. Using this method, a wide range of electrophilic benzenes was coupled successfully with phosphite esters (triethyl/tri-isopropyl/triphenylphosphite and diethyl/di-isopropyl/diphenylphosphite) in aqueous micellar solution to generate the corresponding arylphosphonates in good to high yields. The catalyst was separated using an external magnet and reused for six consecutive cycles without any significant loss of its reactivity. Copyright © 2015 John Wiley & Sons, Ltd.

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Introduction

In the past few decades, much attention has been paid to research dedicated to the development of environmentally compatible processes.^[1] The major drive towards this initiative is avoiding waste formation by using heterogeneous catalysts. Heterogenization of homogeneous catalysts by their immobilization on various insoluble supports would simplify catalyst removal and minimize the amount of waste formed.^[2] Among these solid supports, magnetic nanoparticles (MNPs) are some of the best supporting material because of their magnetic nature, which allows facile recovery and recycling of the catalyst without use of the traditional filtration method.^[3] Moreover, MNPs have unique physical properties including high surface area, surface modification ability and excellent thermal and chemical stability.^[4] Another approach to an environmentally benign and economical process is the replacement of volatile organic solvents by 'green' reaction media.^[5] In this regard, water is the most preferred solvent^[6] because it is considerably safe, readily available, non-toxic, non-flammable, sustainable and cheap. Apart from the economic and environmental benefits, water also exhibits unique physical and chemical activity that leads to unique selectivity compared with organic solvents. However, many reaction substrates have poor solubility in water, while solubility is generally considered as a prerequisite for reactivity.^[7] One approach to deal with this problem is to add inexpensive surfactants into aqueous media to form micelles, burying water-insoluble organic substrates within hydrophobic cores. In recent years, many methods have been developed for various chemical reactions in aqueous micelles.^[8]

Transition metal-catalysed C–P bond-forming reactions are powerful and reliable tools for the synthesis of various types of phosphorus compounds such as phosphonates, phosphine oxides and phosphines. Some of these compounds have wide biological activities and material science applications, and some have been

considered as versatile ligands in catalytic reactions or building blocks in polymer sciences.^[9] In comparison with the phosphorus compounds containing N-P, S-P or O-P linkages, organophosphonates, which have C-P bonds, are synthetically more important due to the high resistance of their C-P linkage to chemical hydrolysis, thermal decomposition and photolysis.^[10] The first powerful approach to C-P bond formation involved the direct cross-coupling of aryl halides with dialkylphosphites catalysed by palladium (Hirao reaction).^[11] After the pioneering work of Hirao et al. in 1980, significant progress has been achieved on improvements and modifications of the reaction conditions such as using different substrates as coupling partners,^[12] ligands^[13] and metals.^[14] However, despite of all of these improvements, C-P couplings still have a limitation due to the problems associated with the separation and recovery of the homogeneous catalyst, which might result in undesirable metal contamination of the products. Therefore, the immobilization of a homogeneous catalyst on a suitable supporting material to enable efficient recovery and recycling of the catalyst could be the subject of intense research in this area.

As part of our efforts directed towards the development of new heterogeneous catalysts for organic reactions,^[15] we have recently introduced a palladium complex of bisiminopyridine (BIP) supported on γ -Fe₂O₃@SiO₂ nanoparticles (Pd-BIP- γ -Fe₂O₃@SiO₂) as the first magnetic heterogeneous catalyst for the synthesis of arylphosphonates.^[16] In this connection, herein we report the synthesis of a new palladium complex of 2-aminothiophenol (2-ATP) supported on γ -Fe₂O₃ (Pd-2-ATP- γ -Fe₂O₃). This newly synthesized catalyst was characterized using various methods such as scanning

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electron microscopy (SEM), transmission electron microscopy (TEM), Fourier transform infrared (FT-IR) spectroscopy, thermogravimetric analysis (TGA), inductively coupled plasma (ICP) analysis, X-ray diffraction (XRD), X-ray photoelectron spectroscopy (XPS), vibrating sample magnetometry (VSM) and elemental analysis, and was used as a magnetically recoverable heterogeneous palladium catalyst for the phosphonation reactions of aryl halides with triethyl/tri-isopropyl/triphenylphosphites and diethyl/di-isopropyl/ diphenylphosphites in aqueous micellar solution.

Experimental

Chemicals were purchased from Merck Chemical Company. NMR spectra were recorded in CDCl₃ with a Bruker Avance DPX-400 instrument using tetramethylsilane as internal standard. The purity of the products and the progress of the reactions were monitored using TLC on silica-gel Polygram SILG/UV254 plates. FT-IR spectra were recorded with a JASCO FT-IR 460 plus spectrophotometer. TEM analysis was performed using a Philips CM30 microscope. The morphology of the products was determined using a SEM instrument (model s4160, Hitachi, Japan) at an accelerating voltage of 15 kV. TGA was performed using a Shimadzu thermogravimetric analyser (TG-50). Elemental analysis was carried out with a Costech 4010 CHN elemental analyser. Power XRD was performed using an X'Pert Pro MPD diffractometer with Cu K_{α} (λ = 0.154 nm) radiation. Surface analysis spectroscopy of the catalyst was performed with an ESCA/AES system. This system was equipped with a concentric hemispherical (CHA) electron energy analyser (Specs model EA10 plus) suitable for XPS. Room temperature magnetization isotherms were obtained using VSM (Lake Shore 7400). The content of palladium in the catalyst was determined with an OPTIMA 7300DV ICP analyser.

Synthesis of chloro-functionalized γ -Fe₂O₃

The synthesized γ -Fe₂O₃ (2 g)^[16] was sonicated in dry toluene (25 ml) for 30 min. 3-Chloropropyltrimethoxysilane (11 mmol, 2 ml) and triethylamine (1.4 mmol, 0.2 ml) were added to the γ -Fe₂O₃ dispersed in toluene. The mixture was slowly heated to 105°C and stirred at this temperature for 48 h. The resulting chloro-functionalized γ -Fe₂O₃ was separated using an external magnet and washed sequentially with toluene, deionized water and ethanol (3 × 20 ml), and dried in an oven at 90°C under vacuum.

Synthesis of 2-ATP- γ -Fe₂O₃

Chloro-functionalized γ -Fe₂O₃ (2 g) was sonicated in dry dimethylformamide (DMF; 20 ml) for 30 min. A solution of 2-ATP (30 mmol, 3.2 ml) in DMF (20 ml) and NaOH (30 mmol, 1.2 g) was added dropwise to the chloro-functionalized γ -Fe₂O₃ dispersed in DMF and was refluxed for 48 h under argon atmosphere. The resulting light-brown solid was separated using an external magnet, repeatedly washed with DMF, ethanol and methanol (3 × 20 ml) and finally dried in an oven at 90°C under vacuum.

Synthesis of Pd-2-ATP- γ -Fe₂O₃

 $2-ATP-\gamma-Fe_2O_3$ (2 g) was sonicated in methanol (30 ml) for 30 min. A solution of Pd(OAc)₂ (0.6 mmol, 0.134 g) in methanol (10 ml) was added to the $2-ATP-\gamma-Fe_2O_3$ dispersed in methanol and stirred under reflux for 10 h. The reaction mixture was cooled to room

temperature. The solid was separated using an external magnet, washed several times with methanol (3 \times 20 ml) and dried in an oven at 80°C overnight under vacuum.

General procedure for phosphonation of aryl halides with phosphite esters

Pd-2-ATP-γ-Fe₂O₃ (3.5 mg, 0.001 mmol, 0.1 mol%) was added to a stirred mixture of aryl halide (1 mmol), phosphite ester (1.5 mmol) and Et₃N (2 mmol) in aqueous micellar solution of sodium dodecylsulfate (SDS; 5 ml, 1 CMC, 8.1 × 10⁻³ M) and heated at 100°C. The reaction was monitored using TLC. After an appropriate time, the reaction mixture was cooled to room temperature. The catalyst was separated using an external magnet from the reaction mixture, washed with water and EtOAc, dried for 30 min at 100°C and reused for a subsequent run under the same reaction conditions. The organic compound was extracted with ethyl acetate (3 × 10 ml) from aqueous layer and dried over anhydrous Na₂SO₄, filtered and concentrated in vacuum. The crude organic mixture was then purified using silica gel column chromatography with *n*-hexane–ethyl acetate (3:1) as eluent to afford the desired product.

Results and discussion

Synthesis and characterization of Pd-2-ATP- γ -Fe₂O₃

The chemistry of nitrogen-sulfur chelating ligands has witnessed a great deal of interest because of their stability, chemical and electrochemical activities and biological relevance.^[17] It is also well known that chelating nitrogen-sulfur donors can stabilize metal ions in unusual oxidation states and uncommon coordination numbers in complexes.^[18] In the work reported in this paper, supported 2-ATP was used as a nitrogen-sulfur chelating ligand to synthesize a new heterogeneous palladium complex (Pd-2-ATP-y-Fe₂O₃). The synthetic procedure is described in Scheme 1. This is the first report of the use of 2-ATP as a chelating ligand for a palladium catalyst. First, chloro-functionalized γ-Fe₂O₃ was synthesized by the reaction of γ -Fe₂O₃ MNPs with 3-chloropropyltrimethoxysilane in refluxing dry toluene. Pd-2-ATP-7-Fe2O3 was obtained by the reaction of chloro-functionalized γ-Fe₂O₃ with 2-ATP followed by complex formation with Pd(OAc)₂. The synthesized Pd-2-ATP- γ -Fe₂O₃ was fully characterized using SEM, TEM, FT-IR spectroscopy, TGA, ICP, XRD, XPS, VSM and elemental analysis.

The morphology of Pd-2-ATP- γ -Fe₂O₃ was studied using SEM and TEM (Fig. 1). SEM and TEM images indicate that Pd-2-ATP- γ -Fe₂O₃ has uniform and spherical morphology. The particle size distribution of Pd-2-ATP- γ -Fe₂O₃ was also evaluated using TEM, the average diameter of the particles being 8.2 nm.



Scheme 1. Synthesis of Pd-2-ATP-γ-Fe₂O₃.



Figure 1. (a, b) SEM images, (c, d) TEM images and (e) particle size distribution histogram for Pd-2-ATP- γ -Fe₂O₃.

FT-IR spectra of chloro-functionalized γ -Fe₂O₃, 2-ATP- γ -Fe₂O₃ and Pd-2-ATP- γ -Fe₂O₃ are shown in Fig. 2. The bands at around 576–624 and 2913 cm⁻¹ are assigned to the stretching vibrations of Fe–O and CH₂ bonds, respectively. In the FT-IR spectra of 2-ATP- γ -Fe₂O₃ and Pd-2-ATP- γ -Fe₂O₃, the bands observed at 1509, 1590 and 1408–1436 cm⁻¹ can be attributed to C=C stretching vibrations. Strong broad peaks at about 1030–1110 cm⁻¹ are assigned to the stretching vibrations of Si–O bond. The bands at around 3328 and 3446 cm⁻¹ are due to the N–H vibration. In the spectrum of Pd-2-



The thermal behaviour of 2-ATP- γ -Fe₂O₃ is shown in Fig. 3. A significant decrease in the weight percentage at around 100°C is related to the desorption of water molecules from the catalyst surface. This is evaluated to be *ca* 0.3% according to the TGA. The organic parts decompose completely at around 829°C. The amount of 2-ATP functionalized on γ -Fe₂O₃ is calculated to be 0.3 mmol g⁻¹ according to the elemental analysis (N = 0.43% and C = 3.26%). These results are in agreement with those obtained from TGA of 2-ATP- γ -Fe₂O₃.

ICP analysis of Pd-2-ATP- $\gamma\text{-}Fe_2O_3$ shows that 0.28 mmol of Pd is loaded on 1 g of the catalyst.

As presented in Fig. 4, the reflection planes of (2 2 0), (3 1 1), (4 0 0), (4 2 2), (5 1 1) and (4 4 0) at $2\theta = 30.3^{\circ}$, 35.7° , 43.4° , 53.8° , 57.4° and 63.0° are readily recognized from the XRD pattern of Pd-2-ATP- γ -Fe₂O₃. The observed diffraction peaks indicate that γ -Fe₂O₃ MNPs mostly exist in face-centred cubic structure. A weak peak appears at $2\theta = 39.9^{\circ}$ corresponding to (1 1 1) reflection of the supported Pd (Fig. 4(b)).

XPS was carried out to establish the oxidation state of Pd in the catalyst (Fig. 5). The peaks at binding energies of 337.4 and 342.5 eV corresponding to Pd $3d_{5/2}$ and Pd $3d_{3/2}$, respectively, confirm the presence of Pd(II) in the catalyst.^[19]

The magnetic properties of the samples containing a magnetite component were studied using VSM at 300 K. Figure 6 shows the absence of a hysteresis phenomenon and indicates that Pd-2-ATP- γ -Fe₂O₃ shows superparamagnetism at room temperature. The saturation magnetization values for γ -Fe₂O₃ and Pd-2-ATP- γ -Fe₂O₃ are 68.9 and 65.2 emu g⁻¹, respectively. The slight decrease of the saturation magnetization of Pd-2-ATP- γ -Fe₂O₃ is due to the immobilization of Pd complex of 2-ATP on the surface of γ -Fe₂O₃ MNPs.

Catalytic activity of Pd-2-ATP- γ -Fe_2O_3 in phosphonation of electrophilic benzenes with phosphite esters in water

In order to optimize the reaction conditions, the phosphonation of iodobenzene with triethylphosphite (1.5 equiv.) in the



Figure 2. FT-IR spectra of (a) chloro-functionalized γ -Fe₂O₃, (b) 2-ATP- γ -Fe₂O₃ and (c) Pd-2-ATP- γ -Fe₂O₃.



Figure 3. TGA diagram of Pd-2-ATP-γ-Fe₂O₃.



Figure 4. XRD patterns of (a) γ -Fe₂O₃ and (b) Pd-2-ATP- γ -Fe₂O₃.



Figure 5. XPS spectrum of Pd-2-ATP- γ -Fe₂O₃.

presence of Pd-2-ATP- γ -Fe₂O₃ (1 mol%) and Et₃N in water at 100°C was chosen as a model reaction (Table 1). In the initial study, the effect of various types of surfactants was evaluated. As evident from Table 1, surfactants cetyltrimethylammonium bromide (CTAB) as a cationic micelle and Triton X-100 as a neutral micelle at their critical micellar concentration (CMC) in water produce the desired product in 80 and 82% yields, respectively (entries 1 and 2). The yield of the product is enhanced when



Figure 6. Magnetization curves of γ -Fe₂O₃ and Pd-2-ATP- γ -Fe₂O₃.

Table 1. Phosphonation of idobenzene with triethylphosphitecatalysed by Pd-2-ATP- γ -Fe ₂ O ₃ under various conditions							
$ P(OEt)_3 \xrightarrow{Pd-2-ATP-\gamma-Fe_2O_3, H_2O} P(OEt)_2 $							
Entry	Base	Surfactant	Time (h)	Isolated yield (%) ^a			
1	Et₃N	СТАВ	1.5	80			
2	Et_3N	Triton X-100	1.5	82			
3	Et ₃ N	Sodium stearate	2	95			
4	Et_3N	SDS	1.5	97			
5	Et_3N	—	4 (24)	75 (75)			
6	(<i>n-</i> Pr)₃N	SDS	3	92			
7	(i-Pr) ₂ NH	SDS	2.5	87			
8	KOH	SDS	3	75			
9	K ₂ CO ₃	SDS	3	82			
10	NaOAc	SDS	3	70			
11 ^b	Et₃N	SDS	1.5	97			
12 ^c	Et_3N	SDS	1.5	97			
13 ^d	Et_3N	SDS	2	92			
14 ^e	Et_3N	SDS	2	83			
15 ^f	Et_3N	SDS	2.5	95			
16 ^g	Et_3N	SDS	1.5	97			
17 ^h	Et₃N	SDS	24	Trace			
^a Reaction conditions: iodobenzene (1 mmol), triethylphosphite (1.5 mmol, except for entries 15, 16), base (2 mmol), Pd-2-ATP- γ -Fe ₂ O ₃ (1 mol%, except for entries 11–13, 17), 100°C (except for entry 14), H ₂ O (5 ml). ^b Pd-2-ATP- γ -Fe ₂ O ₃ (0.5 mol%). ^c Pd-2-ATP- γ -Fe ₂ O ₃ (0.1 mol%). ^d Pd-2-ATP- γ -Fe ₂ O ₃ (0.08 mol%). ^e Temperature = 80°C. ^f Triethylphosphite (1 mmol). ^g Triethylphosphite (2 mmol). ^h No catalyst.							

the reaction is performed in anionic micellar solutions (entries 3 and 4). The product is obtained in a shorter reaction time in SDS in comparison with sodium stearate. The model reaction was examined in the absence of a surfactant, the product being obtained in 75% yield after 4 h. The yield of the product in the absence of any surfactant does not increase even after 24 h

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(entry 5). Therefore, to push the reaction forward, using a surfactant in water is necessary. Some other reaction conditions such as base, molar ratio of catalyst and temperature were also optimized using the model reaction in aqueous micellar solution of SDS (entries 6–14). The best result is obtained using Et₃N as a base in the presence of 0.5 and 0.1 mol% of the catalyst at 100°C (entries 11 and 12). The lower amount of catalyst was chosen as the optimized amount of Pd-2-ATP- γ -Fe₂O₃ (entry 12). Similar reaction in the presence of lower amount of triethylphosphite proceeds in a longer reaction time (entry 15). Increasing the amount of phosphite ester to 2 equiv. does not have any effect on the yield of the product (entry 16). To show the role of the catalyst in this reaction, the model reaction was examined in the absence of the catalyst, with a trace amount of product being obtained after 24 h (entry 17).

To explore the scope of this method, the phosphonation of various electrophilic benzenes with a variety of phosphite esters was studied under the optimized reaction conditions (Table 1, entry 12). The results of these studies are summarized in Table 2.

Table 2. Phosphonation of electrophilic benzenes with various phosphite esters catalysed by Pd-2-ATP- γ -Fe2O3							
$ \begin{array}{c} X \\ P(OR^{2})_{3} \\ e^{-1} \\ R^{1} \\ R^{1} \\ \hline R$							
Entry	X	К	К	Time (n)	Isolated yield (%)	TON	
1 ^[21]	I	_	Et	1.5	97	970	
2 ^[21]	I	_	ⁱ Pr	2	94	940	
3 ^[21]	I	_	Ph	2	91	910	
4 ^[21]	I	_	Et	3	89	890	
5 ^[21]	I	_	ⁱ Pr	3	87	870	
6 ^[21]	I	_	Ph	3	81	810	
7 ^[21]	I	4-Cl	Et	2.5	93	930	
8 ^[21]	I	4-OMe	Et	2	94	940	
9 ^[21]	Br	_	Et	2.5	92	920	
10 ^[21]	Br	4-Cl	Et	3	90	900	
11 ^[21]	Br	4-OMe	Et	2	93	930	
12 ^[21]	Br	4-Me	Et	2	90	900	
13 ^[21]	Br	4-NO ₂	Et	5	65	650	
14 ^[21]	Br	4-CN	Et	3	93	930	
15 ^[21]	Cl	_	Et	4	91	910	
16 ^[21]	Cl	4-Me	Et	3	89	890	
17 ^[21]	Cl	2-Me	Et	4	82	820	
18 ^[21]	Cl	4-NO ₂	Et	6	68	680	
19 ^[21]	Cl	4-CN	Et	4	92	920	
20 ^[11]	Cl	4-COMe	Et	8	54	540	
21 ^[21]	OTs	_	Et	6	71	710	
22 ^[21]	B(OH) ₂	_	Et	7	75	750	
23 ^[22]	I	4-I	Et	2.5	92	920	
24 ^[11]	I	4-I	Et	10	73 ^c	730	
25 ^[21]	Br	4-Br	Et	4.5	91	910	
26 ^[11]	Br	4-Br	Ft	15	48 ^c	480	

^aAll products are known compounds.

^bReaction conditions: electrophilic benzene (1 mmol), trialkylphosphite (1.5 mmol, except for entries 4–6, 24 and 26), dialkylphosphite (1.5 mmol, entries 4–6) Et₃N (2 mmol), Pd-2-ATP-γ-Fe₂O₃ (0.1 mol%), SDS (1 CMC), H₂O (5 ml), 100°C. ^cTriethlphosphite (3 mmol).

As is evident from Table 2, the catalytic reactions of iodobenzene with triethyl-, tri-isopropyl- and triphenylphosphite proceed well and the desired products are isolated in 97, 94 and 91% yields, respectively (entries 1-3). The possibility of using dialkylphosphites instead of trialkylphosphites for the phosphonation of iodobenzene in micellar solution of SDS was also studied. The results show that the present method is applicable for the phosphonation of iodobenzene with diethyl-, di-isopropyl and diphenylphosphite as phosphite esters without using any additive (entries 4-6). It is worth noting that dialkylphosphites are unstable in water and reversibly produce phosphorous acid and their corresponding alcohols. In previous reports addition of a suitable alcohol to the reaction mixture to avoid the side reaction in water was necessary.^[20] Phosphonation reactions of aryl halides (iodides, bromides and chlorides) bearing either electron-withdrawing or electron-donating groups with triethylphosphite proceed well and the corresponding products are generated in 54-94% yields (entries 7-20). In addition to halobenzenes, some other electrophilic benzenes such as aryl tosylate and `benzeneboronic acid were also examined to carry out the reaction with triethylphosphite (entries 21 and 22). The results show that the desired product is obtained in 71 and 75% yields, respectively. Under the present reaction conditions, the coupling reaction of dihalobenzenes with triethylphosphite proceeds well and halophenylphosphonate is obtained in high yields (entries 23 and 25). Both halogens in dihalobenzenes are replaced by twice the amount of phosphite ester under the present reaction conditions (entries 24 and 26).

To investigate the catalytic effect of SDS aqueous micellar solution in the phosphonation reaction, we performed two experiments to make a comparison of conversion versus time in pure water and SDS aqueous micellar solution (1 CMC) (Fig. 7(a)). In both pure water and SDS aqueous micellar solution, the reaction proceeds quickly at first and then slows down over the time in pure water. This would imply that the reaction rate is predominantly based on the concentration of the substrates. It can also be concluded that the reaction takes place in the proximity of the head group of the surfactants, where the polarity is very similar to that of water. Meanwhile, due to the very large interfacial area, the reaction takes place more easily in a micelle droplet with respect to its functioning as a micro- or nanoreactor.^[23]

According to the results, a tentative mechanism of the phosphonation reaction in aqueous micelles is illustrated in Fig. 7(b). At first the Pd catalyst is inserted into the aryl halide bond via an oxidative addition in the oil–water interface and the reaction continues in the hydrophobic core of the micelle droplets. Then, triethylphosphite reacts with the produced palladium halide. The corresponding arylphosphonates are produced after ethyl halide elimination by an Arbuzov-type reaction and reductive elimination. The products are left in the hydrophobic core and the regenerated Pd catalyst returns to the hydrophilic environment.

The recovery and reusability of Pd-2-ATP- γ -Fe₂O₃ were investigated in the reaction of iodobenzene with triethylphospite under the present reaction conditions. After the reaction was completed and allowed to cool, the catalyst was separated using an external magnet from the reaction mixture (Fig. 8(b)), washed with water and EtOAc, dried for 30 min at 100°C and reused for a subsequent run under the same reaction conditions.

The average isolated yield of the product for six consecutive runs is 95.3%, which clearly demonstrates the practical reusability of this catalyst (Fig. 9). It is worth mentioning that Pd-2-ATP- γ -Fe₂O₃



Figure 7. (a) Comparison of conversion versus time in pure water and SDS aqueous micellar solution. (b) Tentative mechanism of the phosphonation reaction in aqueous micelles catalysed by Pd-2-ATP- γ -Fe₂O₃.



Figure 8. (a) Reaction mixture. (b) Separation of Pd-2-ATP- γ -Fe₂O₃ from the reaction mixture using a magnetic bar.

is also reusable in sequential condensations by the addition of new samples of iodobenzene and triethylphosphite to the reaction mixture.



Figure 9. Reusability of Pd-2-ATP- γ -Fe₂O₃ as a magnetically recyclable catalyst.

The amount of Pd leached after six runs was measured using ICP. It is observed that only a very small amount (less than 1%) of Pd is leached. CHN analysis of Pd-BIP- γ -Fe₂O₃@SiO₂ was carried out after six times of reuse and any ligand leaching is not detected. A slight agglomeration is observed from TEM images of the catalyst after six times of reuse (Fig. 10).

To check whether Pd is leached out from the solid catalyst during coupling reaction or whether the catalyst is stable, phosphonation of iodobenzene with triethylphosphite was investigated. After completion of 30% of the coupling reaction at 100°C, the catalyst was separated using a magnet and the remaining solution was stirred for 10 h. In the absence of the catalyst, no increase in the conversion value is detected. These results suggest that the catalyst is stable and can tolerate the present reaction conditions without leaching of a significant quantity of Pd.

A comparison of the catalytic activity of Pd-2-ATP- γ -Fe₂O₃ with that of our recently reported catalyst (Pd-BIP- γ -Fe₂O₃@SiO₂) shows that Pd-2-ATP- γ -Fe₂O₃ is more efficient (turnover number (TON) = 540–970) than Pd-BIP- γ -Fe₂O₃@SiO₂ (TON = 33–47.5)^[16] for the synthesis of arylphosphonates. Furthermore, in order to compare the catalytic activity of Pd-2-ATP- γ -Fe₂O₃ with that of Pd-BIP- γ -Fe₂-O₃@SiO₂ under our present reaction conditions, the coupling of iodobenzene with triethylphosphite catalysed by Pd-BIP- γ -Fe₂-O₃@SiO₂ (0.1 mol%) in micellar solution of SDS (1 CMC) at 100°C was performed. Under these conditions, the reaction leads to the formation of the desired product in 10 and 49% yields after 1.5 and 24 h, respectively. These results show that Pd-BIP- γ -Fe₂O₃@SiO₂ (TON = 490) is not as effective as Pd-2-ATP- γ -Fe₂O₃ (TON = 970) for the phosphonation of iodobenzene under the same reaction conditions.

The catalytic activity of Pd-2-ATP- γ -Fe₂O₃ was also compared with that of various reported Pd catalysts in the phosphonation reaction (Table 3). From Table 3 it is apparent that Pd-2-ATP- γ -Fe₂O₃



Figure 10. TEM images of Pd-2-ATP- γ -Fe₂O₃ after six times of reuse.

Table 3. Catalytic activity of Pd-2-ATP- γ -Fe ₂ O ₃ compared with some other catalysts reported for the phosphonation reaction								
$ \begin{array}{c} & & P(R)_3 \\ & & & or \\ & & HP(O)(R)_2 \end{array} \end{array} \xrightarrow{O}_{HP(R)_2} P(R)_2 $								
Entry	Phosphite ester	Х	Catalyst (mol%)	Conditions	Time (h)	Yield (%)	TON ^a	
1	P(OEt) ₃ P(O-iPr) ₃	l, Br, Cl	PdCl ₂ (4.4)	H₂O, TBAB, <i>n</i> -Pr₃N, 100°C	1.5–6	65–99 ^[21]	14.7–22.5	
2 3	$HP(O)(O-iPr)_2$ $HP(O)Ph_2$	l, Br, Cl l, Br, Cl	Palladacycle (1) Pd/C (1)	H ₂ O, TBAB, KF, reflux, iPrOH, N ₂ H ₂ O, K ₂ CO ₃ , MW, 180°C	16 1	53–99 ^[20] 18–86 ^[24]	53–99 18–86	
4	HP(O)(OEt) ₂	l, Br, OTf	Pd(OAc) ₂ /dppf ^b (10)	THF, Et₃N, KOAc, 68°C	1.5–32	63-98 ^[25]	6.3–9.8	
5	$HP(O)(OEt)_2$ $HP(O)(OMe)_2$ $HP(O)(O-iPr)_2$	Br	Pd(pph ₃) ₄ (5)	THF, Cs ₂ CO ₃ or Et ₃ N, MW, 120°C	0.17	72–96 ^[26]	14.4–19.2	
6	HP(O)(OEt) ₂ HP(O)Ph ₂	l, Br	Pd(OAc) ₂ (5 or 10)	Solvent free, Et ₃ N, MW, 150–200°C	0.03–0.25	27–93 ^[27]	3–18.6	
7	PhP(O)(OEt)(Oct) HP(O)(OEt) ₂	I, Br, Cl, OTf	Pd/Xantphos (2)	Toluene/EG ^c , iPr ₃ N, 110°C	24	50-86 ^[28]	25–43	
8	$HP(O)(Et)_{2}$ $HP(O)(Me)_{2}$ $HP(O)(Ph)_{2}$ $HP(O)(Cy)(Bn)$	I	Pd ₂ (dba) ₃ ^d /Xantphos (0.5)	1,4-Dioxane, Et₃N, 24°C	2	34–97 ^[29]	68–194	
9	HP(O)(OEt) ₂	B(OH) ₂	Pd(OAc) ₂ /dmphen ^e (2)	DMF, P-BQ ^f , MW, 100°C	0.5	51–90 ^[30]	25.5–45	
10	HP(O)(iPr) ₂	l, Br, OTf	Pd(OAc) ₂ /dppf (1)	DMF, 110°C or MeCN, reflux, (iPr) ₂ NEt	24	27–92 ^[31]	27–92	
11	HPO(OEt) ₂	Br	Pd(OAc) ₂ /PPh ₃ (2)	EtOH, (cyclohexyl) ₂ MeN, reflux	16	80–93 ^[32]	40-46.5	
12	$\begin{array}{l} HP(O)(OEt)_2\\ HP(O)(OBu)_2\\ HP(O)Ph_2 \end{array}$	Br	Pd(OAc) ₂ (5 or 10)	Solvent free, Et ₃ N, MW, 150–200°C	0.08–0.25	41–95 ^[33]	5.5–18.2	
13	$\begin{array}{l} P(OEt)_{3} \\ P(OPh)_{3} \\ HP(O)(OEt)_{2} \\ HP(O)(OPh)_{2} \\ HP(O)(O-iPr)_{2} \\ HP(O)(O-iPr)_{2} \end{array}$	I, Br, CI OTs B(OH) ₂	Pd-2-ATP-γ-Fe ₂ O ₃ (0.1)	H₂O, SDS, 100°C	1.5–8	51–97 (This work)	510-970	
^a TON = mol of product/mol of catalyst. ^b 1,1'-Bis(diphenylphosphino)ferrocene. ^c Ethylene glycol. ^d Tris(dibenzylideneacetone). ^e 2,9-Dimethyl-1,10-phenanthroline. ^f <i>p</i> -Benzoquinone.								

provides significant advantages in terms of TON compared with the other catalytic systems. More importantly, our catalyst is a magnetic heterogeneous catalyst and can be easily separated from the reaction mixture using an external magnet. It is worth noting that although there are many reports of using various heterogeneous Pd catalyst for C–C bond coupling reactions, the synthesis of arylphosphonates catalysed by heterogeneous Pd catalyst is rare in the literature (Table 3, entry 3).^[24] Pd-2-ATP- γ -Fe₂O₃ is the first magnetically recoverable Pd catalyst which is used for efficient C–P bond formation reactions in aqueous micellar solution.

Conclusions

In summary, a new heterogeneous Pd complex of 2-ATPsupported on γ -Fe₂O₃ was synthesized and characterized using various methods such as SEM, TEM, FT-IR spectroscopy, TGA, ICP, XRD, XPS, VSM and elemental analysis. The catalyst was successfully (TON = 540–970) used as the first magnetically recoverable heterogeneous Pd catalyst for C–P bond formation of a wide range of electrophilic benzenes with phosphite esters (triethyl/tri-isopropyl/ triphenylphosphite and diethyl/di-isopropyl/diphenylphosphite) in aqueous micellar solution. Efficient and simple reusability of the catalyst and the use of water as an eco-friendly solvent make this protocol an environmentally compatible process for the synthesis of arylphosphonates in good to high yields.

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