Chinese Journal of Catalysis 36 (2015) 1047–1053

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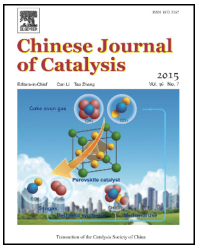

Article

Palladium particles from oxime-derived palladacycle supported on Fe_3O_4/oleic acid as a catalyst for the copper-free Sonogashira cross-coupling reaction

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ARTICLE INFO

Article history:
Received 7 January 2015
Accepted 4 March 2015
Published 20 July 2015

Keywords:
Oxime-derived palladacycle
Sonogashira cross-coupling reaction
Copper-free
Magnetite/oleic acid
Low Pd loading

ABSTRACT

An oxime-derived palladacycle was synthesized using 4-bromobenzoxime and pyridine in $CHCl_3$, and characterized by FT-IR and ^1H NMR spectroscopy. This Pd complex was supported on Fe_3O_4/oleic acid and shown to be an efficient catalyst for the copper-free Sonogashira cross-coupling reaction of various aryl halides with phenylacetylene in air and in ethanol or mixed aqueous medium. The oxime-derived palladacycle gave highly active palladium nanoparticles for the organic synthesis. The coupling products were obtained in high yields with low Pd loading and the heterogeneous catalyst can be separated by an external magnet and reused six times without loss of its activity. The characterization of the catalyst was carried out by XRD, SEM and TEM. Both TEM and XRD revealed that the palladium nanoparticles were well dispersed with diameters from 5 to 10 nm and average size 9.97 nm.

1. Introduction

As a class of organometallic compounds, palladacycles have been successfully applied in catalytic reactions [1–4]. Among these compounds, oxime-derived palladacycles have been investigated in Pd-catalyzed cross-coupling reactions. It has been demonstrated that oxime palladacycles are precatalysts that can provide a source of highly active Pd nanoparticles [5–8] that allowed the reaction to be performed under very mild reaction conditions, such as the use of aqueous solvents, the immobilization of the oxime-derived palladacycles on solid supports for increased efficiency, and the carrying out of the Sonogashira coupling reaction under copper-free conditions [9]. By immobilization of these compounds on solid supports, several advantages such as easy separation from reaction mixture, low waste, more active surface, high selectivity and low cost have been gained. In recent years different solid supports have been applied to immobilize the nanoparticles, such as silica [10], a magnetic material [11], polymers [12,13], dendrimer [14], carbon nanotube [15], metal oxides [16], and an ionic liquid [17].

One of the most efficient solid support is magnetite (Fe_3O_4), which has been employed for various reactions [18]. The magnetic Fe_3O_4 nanoparticles are very beneficial because of the increased contact area of the nanocatalyst with the reaction mixture, high chemical stability, and cost cient separation with an external magnet [18–30]. Therefore, the use of magnetite (Fe_3O_4) has been developed in the cross-coupling reactions, but the magnetic interaction between the particles has led to the agglomeration of Fe_3O_4 nanoparti-

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This work was supported by the Department of Chemistry, Isfahan University of Technology and the Iranian Nano Technology Initiative Council.
DOI: 10.1016/S1872-2067(15)60837-3 | http://www.sciencedirect.com/science/journal/18722067 | Chin. J. Catal., Vol. 36, No. 7, July 2015

cles. To prevent the agglomeration of the Fe_3O_4 nanoparticles, surface modification with functional groups is needed [31–34].

We have coated Fe_3O_4 nanoparticles with oleic acid because it is non-toxic and readily available. Then an oxime-derived palladacycle was supported on the Fe_3O_4/oleic acid support and its catalytic activity was examined in the copper-free Sonogashira cross-coupling reaction between phenylacetylene and various aryl halides. The Sonogashira cross-coupling reaction based on the reaction of terminal alkynes with aryl halides [35–39] is one of the most valuable methods for the synthesis of arylated alkynes. This reaction is usually carried out with catalytic amounts of a palladium complex and copper (I) iodide as co-catalyst. The use of CuI is harmful in large scale reactions because of the formation of insoluble copper-acetylides [40]. These byproducts are difficult to separate from the desired products. To solve this problem, we have carried out the reaction under copper-free conditions. For this purpose, we have investigated an oxime-derived palladacycle supported on Fe_3O_4/oleic acid as a heterogeneous catalyst in the copper-free Sonogashira cross-coupling reaction.

2. Experimental

2.1. General

All reactants were purchased from Merck Chemical Company and Aldrich and used as received. Solvents were used without further purification or drying. Fourier transform infrared (FT-IR) spectra were obtained using KBr pellets with a Jasco FT/IR 680 Plus instrument. ^1H NMR spectra were measured on a Bruker spectrometer at 400.13 MHz. Scanning electron microscopy (SEM) studies were conducted on a Philips Model XL-30 instrument. Transmission electron micrographs (TEM) were recorded on a Philips Model CM30 instrument. Conversions were monitored using an Agilent Technology 6890N gas chromatograph equipped with a flame ionization detector (FID) and a HB-50$^+$ column (length = 30 m, inner diameter 320 μm, and film thickness = 0.25 μm). Products were identified by comparison with reference samples.

2.2. Procedure for the synthesis of the oxime-derived paladacycle

Initially 4-bromobenzoxime was synthesized from 4-bromobenzaldehyde and hydroxylamine hydrochloride according to a previous report [41]. Then 4-bromobenzoxime (1 mmol) and pyridine (2 mmol) were added to a solution of palladium acetate (1 mmol) in $CHCl_3$ (15 mL). This orange-red solution was refluxed for 3 h at 60 °C. Following the adding of water (10 mL) to the solution, the product was extracted with chloroform (3×15 mL). Evaporation of the solvent yielded a yellow oil which was dissolved in diethyl ether. Solvent evaporation led to the formation of yellow crystals (Fig. 1). ^1H NMR (400 MHz, $CDCl_3$, ppm): δ = 8.81 [1H, s, NCH], 8.72 [1H, d, NC_5H_5], 7.82 [3H, m, NC_5H_5], 7.71 [1H, s, OH], 7.51 [1H, d, NC_5H_5], 7.45 [1H, dd, Pd-C_6H_3BrC(CH)=NOH], 7.37 [1H, dd, Pd-C_6H_3BrC(CH)=NOH], 7.35 [1H, s, Pd-C_6H_3BrC(CH)=NOH], 1.72 [3H, s, CO_2CH_3].

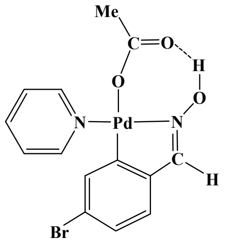


Fig. 1. The structure of Pd complex.

2.3. Procedure for the synthesis of the oleic acid Fe_3O_4-coated nanoparticles

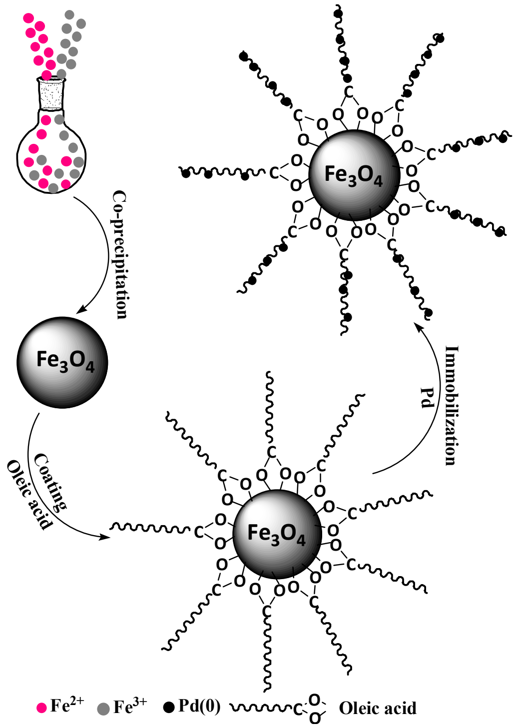
The oleic acid-coated Fe_3O_4 nanoparticles were prepared by the co-precipitation method according to a synthesis route described by Yang et al. [42]. Typically, $FeCl_2·4H_2O$ (0.86 g) and $FeCl_3·6H_2O$ (2.32 g) were dissolved in 70 mL deionized water. Then, the solution pH was adjusted to 11 with NH_4OH (25%, 20 mL) to form a black suspension. The resulting suspension was stirred for 5 min and then oleic acid (0.2 mL) was added to it. After mixing for 30 min, the nanoparticles obtained were separated from the aqueous solution by a magnet, washed several times with deionized water and dried in an oven overnight. The resulting powder was denoted as Fe_3O_4/oleic acid.

2.4. Procedure for the synthesis of Fe_3O_4/oleic acid/Pd nanocatalyst

In this step, the Fe_3O_4/oleic acid (0.5 g) and oxime-derived palladacycle (0.125 g) were dispersed in an ethanol solution (15 mL) and reflux for 10 h. Then the reaction mixture was cooled at room temperature and hydrazine hydrate solution (catalyst:hydrazine hydrate = 1:5) was slowly dropped into the mixture and it was refluxed further for 2 h. The resultant product was collected by an external magnet, washed several times with ethanol and deionized water and dried in a vacuum oven at 60 °C. The magnetic nanoparticles were denoted as Fe_3O_4/oleic acid/Pd. Thus Fe_3O_4/oleic acid/Pd was readily prepared by the two step procedure shown below in Scheme 1. Producing Fe_3O_4/oleic acid and reducing Pd(II) to Pd(0) by adding hydrazine hydrate in ethanolic solution (resulting in the trapping of Pd(0) within the oleic acid, as indicated by the colour change from dark brown to black).

2.5. General procedure for the Sonogashira cross-coupling reaction

An aryl halide (1 mmol) and phenylacetylene (1.5 mmol) were added to a mixture of Fe_3O_4/oleic acid/Pd catalyst (0.005 mmol) and K_2CO_3 (2 mmol) in ethanol (6 mL) as solvent in a glass flask under vigorous stirring. The mixture was refluxed at 75 °C for 6 h under aerobic conditions. The palladium catalyst was recovered by a simple magnet and reused for the next run. The solution was washed with ethanol and deionized water (10 mL) and dried in a vacuum oven at 60 °C.



Scheme 1. Schematic of the preparation of the Fe_3O_4/oleic acid/Pd nanocatalyst.

3. Results and discussion

3.1. Synthesis and characterization of the oxime-derived palladacycle

[Pd(OAc){C,N-(C_6H_3BrC(CH)=NOH)-2}(py)] (Fig. 1) was synthesized in one step by the reaction of [$Pd_3(OAc)_6$] with 4-bromobenzoxime and pyridine in $CHCl_3$ under reflux for 3 h at 60 °C. The complex was characterized by NMR and IR spectra. The IR spectrum of the complex (Fig. 2) showed a broad band at 3444 cm^{-1} for the OH stretching vibration. Two bands at 3077 and 2926 cm^{-1} were attributed to the stretching aromatic and aliphatic C-H bond, respectively. The peak at 1720 cm^{-1} was attributed to the C=O band in the acetate group. The peak at 1553 cm^{-1} was due to the C=C bands in aromatic rings. Also, two bands at 1605 and 1627 cm^{-1} were due to the C=N bond in pyridine and oxime, respectively. The ^{1}H NMR spectrum of the complex showed two well-separated sets of signals between $\delta = 7.51$–8.72 and 7.35–7.45, which corresponded to the phenyl groups in pyridine and oxime, respectively. The protons of the acetate and NCH were located at $\delta = 1.72$ and 8.81 as two singlet signals, respectively.

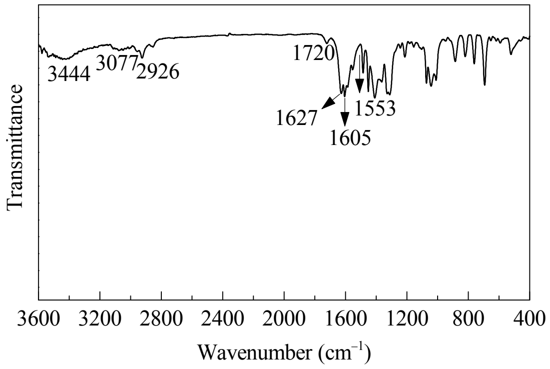


Fig. 2. FT-IR spectrum of [Pd(OAc){C,N-(C_6H_3BrC(CH)=NOH)-2}(py)].

3.2. Synthesis and characterization of Fe_3O_4/oleic acid/Pd

The Fe_3O_4/oleic acid nanoparticles were prepared by the addition of $FeCl_2·4H_2O$ and $FeCl_2·6H_2O$ to deionized water in the presence of NH_4OH. Then oleic acid was coated on the surface of the Fe_3O_4 particles. Finally the oxime-derived palladacycle was added to a mixture of Fe_3O_4/oleic acid and ethanol for the preparation of Fe_3O_4/oleic acid/Pd, and finally hydrazine hydrate was dropped onto the mixture. The mixture was filtered and dried under vacuum. The Fe_3O_4/oleic acid/Pd catalyst was characterized by FT-IR, XRD, SEM and TEM.

Figure 3 shows the FT-IR spectra of Fe_3O_4/oleic acid and Fe_3O_4/oleic acid/Pd. The broad band at 3436 cm^{-1} in Fig. 3(1) was the OH stretching vibration. Two peaks at 2926 and 2853 cm^{-1} were attributed to the asymmetric and symmetric stretching of the CH_2 groups in oleic acid, respectively. The presence of the C=C stretching vibration was observed by the peak at 1628 cm^{-1}. In Fig. 3(1), it can be seen that the stretching vibration of C=O in oleic acid was absent at 1710 cm^{-1}. In addition, the absorption peaks at 1402 and 1515 cm^{-1} were due to the asymmetric and symmetric stretching of COO^-, respectively. From these results, it was clear that oleic acid was chemically adsorbed on the surface of the Fe_3O_4 nanoparticles, and it can be concluded that the interaction between the oxygen atoms in COO^- and the Fe atoms was the bridging bidentate form [42]. The strong absorption bands at 628 cm^{-1} in Fig. 3(1) and 598 cm^{-1} in Fig. 3(2), corresponding to the Fe–O vibrations, proved the presence of Fe_3O_4 nanoparticles in the samples. From the above results, it can be concluded that Fe_3O_4/oleic acid/Pd nanoparticles were obtained. This synthesis procedure was based on the physical adsorption of Pd by the Fe_3O_4/oleic acid support, as well as on the electronic interaction between the electron from the C=C band of the oleic acid-based Fe_3O_4 and the vacant orbitals of the catalyst. Finally, Fig. 3(2) showed that the coordination mode of oleic acid to Fe_3O_4 did not change

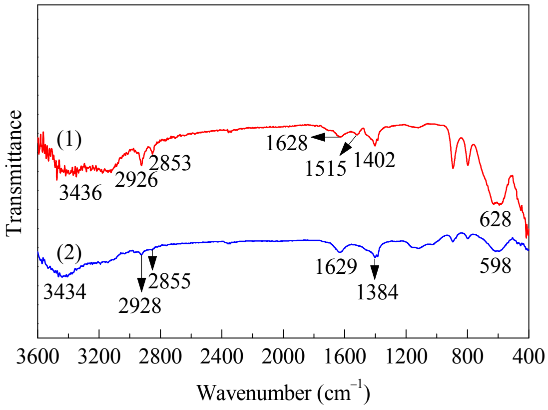


Fig. 3. The FT-IR spetra of Fe_3O_4/oleic acid (1) and Fe_3O_4/oleic acid/Pd (2).

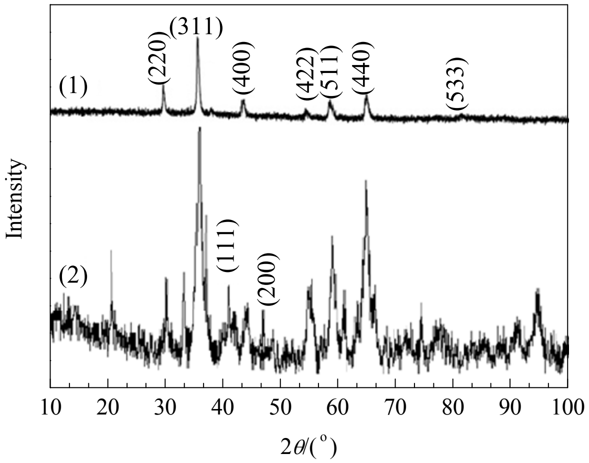


Fig. 4. XRD pattern of Fe_3O_4/oleic acid (1) and Fe_3O_4/oleic acid/Pd (2).

after the immobilization of palladium.

The XRD pattern of Fe_3O_4/oleic acid and Fe_3O_4/oleic acid/Pd are shown in Fig. 4. Figure 4(1) shows characteristic peaks at 2θ = of 30°, 35°, 43°, 53°, 57° and 63° due to the diffraction of the (220), (311), (400), (422), (511) and (440) planes of Fe_3O_4, which agreed with the previous work by Zhao et al. [43]. The result confirmed that nanoparticles have been synthesized and the structure of Fe_3O_4 was not damaged during catalyst production. Moreover, the characteristic peaks of Pd at 2θ = 40° and 46° (Fig. 4(2)) corresponding to the diffraction of the (111) and (200) planes were observed, indicating that Pd existed in the form of Pd(0). The peak of Pd(0) at 2θ = 68° was associated with the metal phase due to the low Pd loading.

Figure 5 shows the SEM image of the Fe_3O_4/oleic acid/Pd nanocatalyst. It can be seen that the magnetic interaction between the particles led to the aggregation of particles since they were almost spherical. The TEM image in Fig. 6 showed the morphology of the Fe_3O_4/oleic acid/Pd nanocatalyst. The Pd nanoparticles were completely dispersed on the surface of the Fe_3O_4/oleic acid nanoparticles. The histogram of Fe_3O_4/oleic acid/Pd in Fig. 7 showed that the particle diameters were about 10 nm and they have a uniform size.

3.3. Catalytic activity of Fe_3O_4/oleic acid/Pd in the Sonogashira cross-coupling reaction

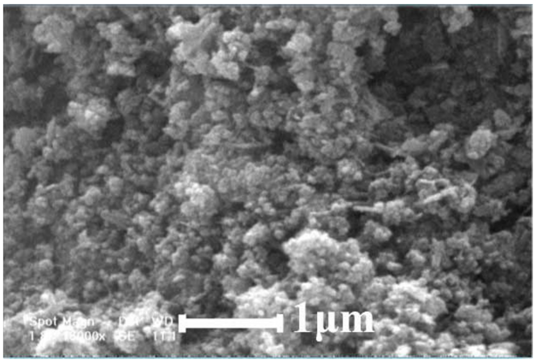


Fig. 5. SEM image of Fe_3O_4/oleic acid/Pd.

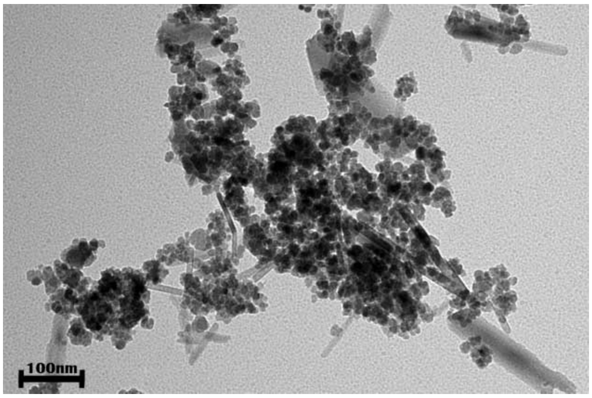


Fig. 6. TEM image of Fe_3O_4/oleic acid/Pd.

To evaluate the catalytic activity of Fe_3O_4/oleic acid/Pd and to optimize the reaction conditions, the copper-free Sonogashira cross-coupling reactions between phenylacetylene and various aryl halides were used. In the first step, various solvents were examined to optimize the reaction of iodobenzene with phenylacetylene at different temperatures. The results are summarized in Table 1. EtOH as a green solvent was found to be the best choice at 75 °C (Table 1, entry 6). Also, using DMF:H_2O (1:1) as an aqueous solvent gave a good result at 100 °C (Table 1, entry 12). Since EtOH is a more environmentally benign solvent, it was selected for the reaction of aryl iodides with phenylacetylene. Also, DMF:H_2O (1:1) was selected for the less reactive aryl bromides and chlorides because using EtOH did not give good results. Then different bases such as Na_2CO_3, CH_3COONa, $K_3PO_4\cdot 3H_2O$, NaN_3, and K_2CO_3 were examined of which K_2CO_3 was the best candidate for investigating the efficiency of the heterogeneous catalyst (Table 1, entry 10).

In addition, a small amount of Pd catalyst (0.0005 mmol) was used in the reactions and it was observed that when the amount of Pd catalyst was increased from 0.0005 to 0.001 mmol, the conversion decreased slightly from 100% to 92% and from 93% to 75% (Table 1, entry 11 and 13). From these results, the optimum amount of catalyst was 0.0005 mmol for the Sonogashira cross-coupling reaction. These observations showed that a small amount of Fe_3O_4/oleic acid/Pd (0.0005

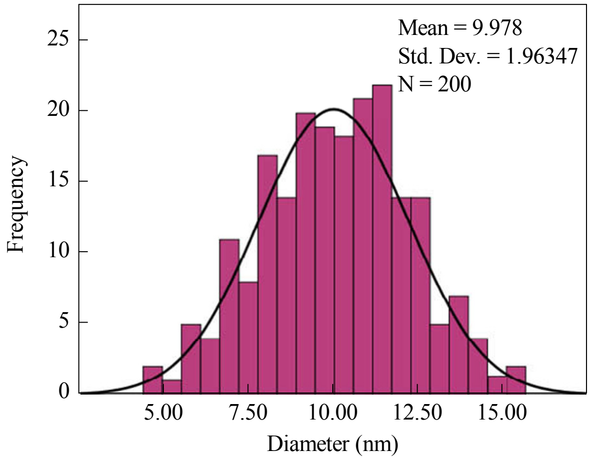
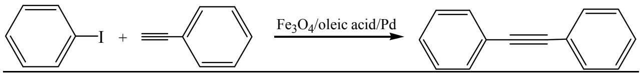


Fig. 7. Histogram of Fe_3O_4/oleic acid/Pd size.

Table 1
Optimization of the reaction conditions for the Sonogashira cross-coupling reaction of iodobenzene with phenylacetylene.



Entry	Solvent	Base	T/ (°C)	Time (h)	Conversion (%)
1	DMF	Na_2CO_3	100	7	28
2	$DMF{:}H_2O$	Na_2CO_3	100	5	78
3	CH_3CN	Na_2CO_3	80	5	<5
4	$CHCl_3$	Na_2CO_3	100	6	<5
5	Toluene	Na_2CO_3	100	6	<5
6	EtOH	Na_2CO_3	75	6	80
7	EtOH	CH_3COONa	75	5	<5
8	EtOH	$K_3PO_4\cdot 3H_2O$	75	5	84
9	EtOH	NaN_3	75	5	<5
10	EtOH	K_2CO_3	75	6	100
11	EtOH	K_2CO_3	75	6	92 [a]
12	$DMF\text{-}H_2O$	K_2CO_3	100	5	93
13	$DMF\text{-}H_2O$	K_2CO_3	100	5	75 [a]
14	EtOH	K_2CO_3	75	6	0 [b]

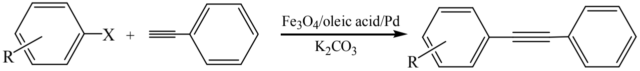
Reaction conditions: aryl halide (1 mmol), phenylacetylene (1.5 mmol), K_2CO_3 (2 mmol), EtOH (6 mL), Pd catalyst (0.05 mol%).
[a] Pd catalyst (0. 1 mol%).
[b] In the presence of Fe_3O_4/oleic acid.

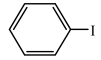
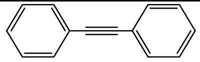
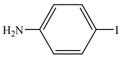
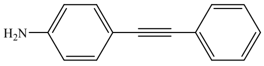
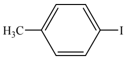
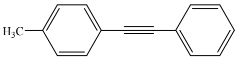
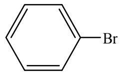
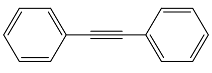
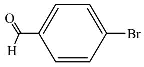
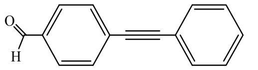
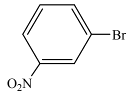
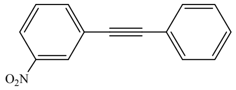
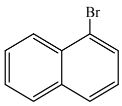
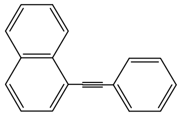
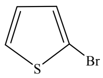
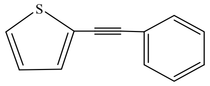
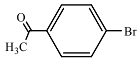
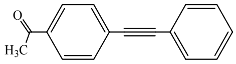
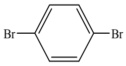
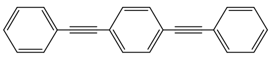
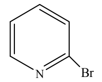
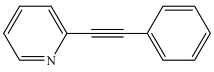
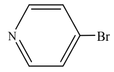
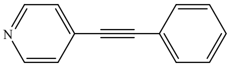
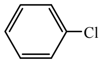
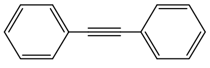
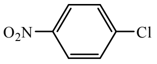
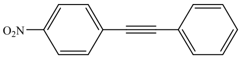
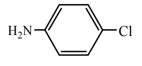
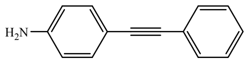
mmol) in the presence of K_2CO_3 as the base and either EtOH or $DMF{:}H_2O$ (1:1) as solvent were the best catalytic system. Also, in the presence of Fe_3O_4/oleic acid as catalyst, the reaction did not occur (Table 1, entry 14).

This optimized catalytic system was applied to examine various aryl halides with electron-donating or electron-withdrawing groups (Table 2). In most cases, electron-withdrawing groups showed high efficiency in the cross-coupling reactions. In the case of aryl iodides, both groups were reactive. As shown in Table 2 by entry 1, 2 and 3, the coupling products between aryl iodides and phenylacetylene were obtained with good conversion. This was due to that the weak strength of the C–I bond increased the rate of Sonogashira cross-coupling reaction.

Also in the case of aryl bromides, the electronic effect of the substrate was considerable. In fact, aryl bromides containing electron-withdrawing groups in the *para* situation gave higher conversion and shorter reaction time. This indicated the rate determining step of the Sonogashira cross-coupling reaction was the oxidative addition (Table 2, entry 5). Also, aryl bromides containing electron-withdrawing groups in the *meta* situation were less reactive (Table 2, entry 6). The reaction of 4-bromoacetophenone was slower than that of bromobenzene (Table 2, entry 9). The reason for this was not clear. Aryl bromides with an *ortho* substitution are weak substrates because of steric hindrance. This pattern was seen in the case of 1-bromonaphthalene which did not show significant conversion even after long reaction time (Table 2, entry 7). In addition, induction withdrawing of the *p*-Br group overcomes the resonance donating of it, thus the conversion was increased with bromobenzene (Table 2, entry 10).

Table 2
Sonogashira cross-coupling reactions of various aryl halides with phenylacetylene.



Entry	Aryl halide	Product	Time (h)	Conversion (%)
1			6	100 (97) [b]
2			7	86
3			6	100
4			8	84 [a](82) [b]
5			7	87 [a]
6			6	50
7			9	71 [a]
8			7	70 [a]
9			8	23 [a]
10			6	95 [a]
11			7	41 [a]
12			6	83 [a]
13			7	26 [a](23) [b]
14			7	31 [a]
15			6	22 [a]

Reaction conditions: aryl halide (1 mmol), phenylacetylene (1.5 mmol), K_2CO_3 (2 mmol), EtOH (6 mL), Pd catalyst (0.05 mol%), 75 °C.
[a] Solvent $DMF{:}H_2O$ (1:1), 100 °C.
[b] Isolated yields after column chromatography.

In aryl chlorides, the high strength of the C–Cl bond led to less reactivity than with the other aryl halides. Here the reaction of 1-chloro-4-nitrobenzene was more efficiency than chlorobenzene and the reaction of 4-chloroaniline showed lower conversion than chlorobenzene (Table 2, entries 14 and 15).

After the reaction was complete, the reaction mixture was cooled to room temperature and diluted with H_2O and EtOAc. Then the organic phase was dried with $MgSO_4$, filtered, and concentrated under reduced pressure using a rotary evaporator. The product was purified by silica gel column chromatography.

Table 3
Performance of different heterogeneous Pd catalysts for the reaction of iodobenzene with phenylacetylene.

Entry	Pd catalyst (mol%)	Time(h)/Temp (°C)	Solvent	Base	Yield [a] (%)	TOF [b] (h^{-1})	[Ref.]
1	Fe_3O_4/oleic acid/Pd (0.05)	6/75	EtOH	K_2CO_3	97	323	This work
2	MCM-41-2P-Pd (0) (0.5)+CuI (5 mol%)	2/r.t	piperidine	piperidine	98	98	[44]
3	PS-ppdot-Pd(II)(1)	3/r.t	Solvent free	Et_3N	97	32	[45]
4	trans-(NHC)$PdCl_2$ (pyridine)(3)	1/100	DMF:H_2O (3:1)	Cs_2CO_3	96	32	[46]
5	Pd–Fe–H (2)+CuI (0.3 mol%)	9/80	H_2O	K_2CO_3	97	5	[47]
6	diatomit-supported Pd(II) salophen complex(0.3)	5/r.t	Solvent free	Et_3N	97	64	[48]

[a] isolated yield.
[b] TOF was difined as the product (mmol) per unit time (h) per catalyst (mmol).

In order to evaluate the efficiency of the Fe_3O_4/oleic acid/Pd nanocatalyst, the catalytic system was compared with some other catalysts. As shown in Table 3, for the reaction of iodobenzene with phenylacetylene, Fe_3O_4/oleic acid/Pd was the most efficient catalyst with the highest turnover frequency (TOF) of 323 h^{-1} (Table 3, entry 1). Compared to other catalysts, a very small amount of Fe_3O_4/oleic acid/Pd catalyst (0.0005 mmol) was used in an ethanolic solution as a green solvent for the Sonogashira cross-coupling reaction der copper-free conditions.

The reaction kinetics of the Sonogashira reaction of iodobenzene with phenylacetylene with Fe_3O_4/oleic acid/Pd (0.0005 mmol) as catalyst was investigated. The result is shown in Fig. 8(1). The yield of product increased quickly with reaction time until it reached 97% at 6 h. For further investigation, a comparison reaction was carried out and the catalyst was removed after 2 h from the reaction mixture. The resulting filtrate was monitored for an additional reaction time but no coupling product was observed after the removal of the catalyst (Fig. 8(2)). This result suggested the high efficiency of Fe_3O_4/oleic acid/Pd and confirmed the heterogeneous character of the catalytically active species. This showed that this catalytic system defines an efficient method for the Sonogashira cross-coupling reaction of aryl halides in a green solvent. Also, this system requires a very small amount of the catalyst and runs under copper-free conditions as well as providing a source of highly active palladium nanoparticles for the Sonogashira cross-coupling reaction.

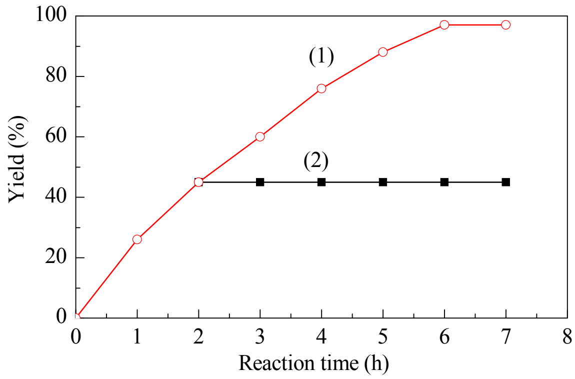


Fig. 8. Kinetic plot of the Sonogashira reaction of iodobenzene with phenylacetylene. (1) Normal reaction kinetics; (2) The catalyst was removed after reaction for 2 h. Reaction condition: 1 mmol iodobenzene, 1.5 mmol phenylacetylene, 2 mmol K_2CO_3, 6 mL EtOH, 0.05% Fe_3O_4/oleic acid/Pd, 75 °C.

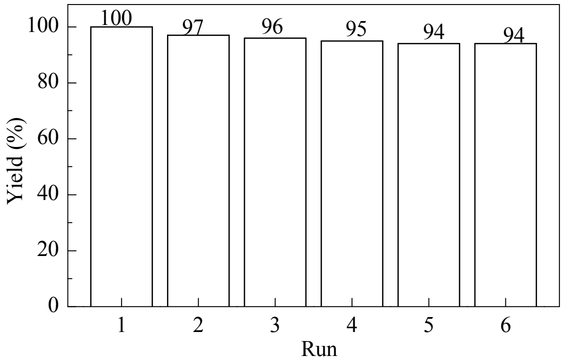


Fig. 9. Reusability of Fe_3O_4/oleic acid/Pd in the model reaction after 6 h.

3.4. *Reusability of the catalyst*

The investigation of the reusability of the catalyst is particularly important in heterogeneous reactions. For this purpose, the reusability of the catalyst was carried out using the Sonogashira cross-coupling reaction between iodobenzene and phenylacetylene over Fe_3O_4/oleic acid/Pd in ethanol. The Fe_3O_4/oleic acid/Pd catalyst was used for the reaction and easily recovered after reaction completion by an external magnet and then was washed with deionized water and ethanol. This recovering method prevents loss of the catalyst due to its simple separation from the reaction mixture. The catalyst was used for 6 cycles and its catalytic activity did not change in these repeated cycles (Fig. 9). This showed that this new heterogeneous catalyst is an efficient magnetic catalyst for Pd-catalyzed reactions.

4. Conclusions

An oxime-derived palladacycle immobilized on a highly active Fe_3O_4/oleic acid solid support as a heterogeneous catalyst for the copper-free Sonogashira cross-coupling reaction was reported. By the immobilization of this complex on a Fe_3O_4/oleic acid solid support, it was possible to perform the Sonogashira cross-coupling reaction in ethanol and water-organic solvent mixtures, and the catalyst can be recovered and reused without loss of activity or leaching of Pd from the solid to the liquid phase. With a very small amount of this catalyst, the copper-free Sonogashira cross-coupling reaction was successfully carried out.

Graphical Abstract

Chin. J. Catal., 2015, 36: 1047–1053 doi: 10.1016/S1872-2067(15)60837-3

Palladium particles from oxime-derived palladacycle supported on Fe_3O_4/oleic acid as a catalyst for the copper-free Sonogashira cross-coupling reaction

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Isfahan University of Technology, Iran;
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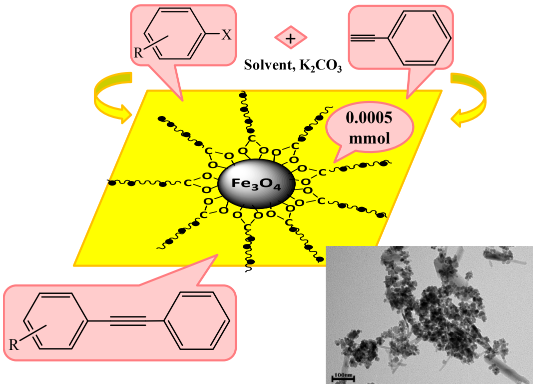

This review presents a Pd catalyst on the surface of Fe_3O_4/oleic acid for copper-free Sonogashira cross-coupling. Very small amounts of the catalyst catalyzed the Sonogashira reaction in ethanol and water-organic solvent mixtures.

Acknowledgments

The authors thank the Department of Chemistry, Isfahan University of Technology for the support in this work. Also we gratefully acknowledge the funding support received for this project from the Iranian Nano Technology Initiative Council. P. Hervés acknowledges financial support from Spanish MINECO (MAT 2013-45168-R).

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