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Palladium Nanoparticles Supported on Modified Hollow-Fe₃O₄@TiO₂: Catalytic Activity in Heck and Sonogashira Cross Coupling Reactions

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Palladium nanostructures have been extensively employed as versatile catalysts for a variety of transformations, such as the hydrogenation of alkenes and alkynes,^{1,2} carbon-fluorine bond formation³ and a number of C-C cross-coupling transformations including Suzuki, Negishi, Kumada, Hiyama and Stille reactions.^{4–15} The importance of the coupling reactions is reflected by the fact that one of the inventors, Akira Suzuki, was awarded with the Nobel Prize in chemistry in 2010.¹⁶ Moreover, the resultant biaryl compounds occur in a wide range of natural products.¹⁷

The high material cost of palladium naturally restricts its applications, so many approaches that enable one to maximize its catalytic performance and thus reduce the required palladium loading in the catalyst have received a great deal of research attention. Key challenges for the commercial development and practical use of any homogeneous Pd catalyst is the recovery, recyclability and re-use of the catalyst.¹⁸ To address these problems, the immobilization of Pd nano-particles on solid supports has received a lot of interest owing to potential applications in catalysis.¹⁹

Nano-particles have higher dispersion than many conventional macro-sized particles, leading to the improved catalytic activity of the heterogeneous catalysts. Recently, a variety of heterogeneous catalysts anchoring Pd nano-particles for easy separation and recovery have been synthesized and applied to a range of chemical reactions.^{20–29}

As is well known, the incorporation of magnetic nano-particles (NPs) in the support makes separation fast and cost-effective. This makes NPs ideal candidates for practical uses in catalysis processes.^{30–32} The desirable features include low density, high surface area, easy recovery, self supporting capacity, cost reduction and surface permeability. Hollow-Fe₃O₄ particles, may be promising candidates for many applications.^{33–36}

In continuation of our work on metal-mediated transformations,^{37–41} and as part of our continuing interest in the synthesis of magnetic nano-catalysts,^{42,43} we wish to report the synthesis and full characterization of a new Pd catalyst based on hollow-Fe₃O₄@TiO₂ particles. The hollow-Fe₃O₄ has been conveniently prepared through the solvothermal method⁴⁴ and coated with a layer of TiO₂ in order to avoid the aggregation of nanoparticles to a cluster and to protect the hollow magnetite from abrasion under harsh shaking condition⁴⁵ After that it was functionalized with (3-aminopropyl)triethoxysilane (APTES).⁴⁶

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Finally Pd nano-particles were immobilized on this shell system with reduction reaction (*Scheme 1*). We performed ligand-free cross coupling transformations, such as Heck and Sonogashira reactions with this new nano-catalyst to test its activity. The ease of preparation, recovery and reusability of the catalyst, stability toward air and compatibility with a variety of substrates make it ideal for the above mentioned coupling reactions.



Scheme 1

The hollow-Fe₃O₄@TiO₂-NH₂/Pd was fabricated *via* a 4-step synthetic procedure which is given in the experimental section. The composite was characterized using X-ray powder diffraction (XRD), Fourier transform infrared spectroscopy (FT-IR), field emission scanning electron microscopy (FE-SEM), energy-dispersive X-ray spectroscopy (EDX), transmission electron microscopy (TEM), thermogravimetric analysis (TGA) and vibrating sample magnetometer (VSM) analysis and the process for the preparation of it is graphically summarized in *Scheme 1*.

Having synthesized and characterized the h-Fe₃O₄@TiO₂-NH₂/Pd magnetic composite, its catalytic activity was tested in the Sonogashira coupling reaction of iodobenzene and phenyl acetylene in an ambient atmosphere. We optimized the reaction under different conditions and the results are summarized in *Table 1*.

The reaction was performed using iodobenzene (1.0 mmol) and phenylacetylene (1.2 mmol) in the presence of 2.0 mmol of base and different loadings of catalyst at 90°C. Different solvents including DMF, water, THF and EtOH were tested. DMF was the optimum solvent with Et₃N and 20 mg composite (*Table 1*, entries 1–7). Other bases such as K_2CO_3 , NaOH or Cs_2CO_3 were also examined in DMF, but Et₃N turned out to be the best (*Table 1*, entries 8–10). When we changed the temperature of the reaction, the yield was decreased (*Table 1*, entries 11–13). So, the best results were achieved when the reaction was done in the presence of 0.02 g catalyst (0.18mol% Pd) at 80°C in DMF using Et₃N as base (*Table 1*, entry 1).

In order to assess the efficiency of the novel magnetic composite further, the substrate scope of the reactions for the Sonogashira coupling reaction was examined with a variety of arylhalides and different terminal alkynes as the substrates under the optimized

Entry	Amount of Catalyst (g)	Condition (solvent/ temperature °C)	Base	Time (h)	Yield ^b (%)
1	0.02	DMF/ 90	Et ₃ N	3	96
2	0.01	DMF/ 90	Et ₃ N	3	84
3	0.03	DMF/ 90	Et ₃ N	3	96
4	0.02	DMF/ 90	Et ₃ N	2	78
5	0.02	H ₂ O/ Reflux	Et ₃ N	4	93
6	0.02	THF/ Reflux	Et ₃ N	6	55
7	0.02	EtOH/ Reflux	Et ₃ N	6	89
8	0.02	DMF/ 90	K_2CO_3	3	86
9	0.02	DMF/ 90	NaOH	3	63
10	0.02	DMF/ 90	Cs_2CO_3	3	92
11	0.02	DMF/ 100	Et ₃ N	3	95
12	0.02	DMF/ 80	Et ₃ N	3	88
13	0.02	DMF/ r.t	Et ₃ N	3	Trace

 Table 1

 Optimization of Reaction Conditions in the Sonogashira Coupling Reaction of Iodobenzene with Phenylacetylene^a

^aReactions were run in 3 mL solvent with 1 mmol iodobenzene, 1.2 mmol phenylacetylene, and 2 mmol base. ^bIsolated yield.

reaction conditions, and the results are depicted in *Table 2*. As shown in *Table 2*, the h-Fe₃O₄@TiO₂-NH₂/Pd effectively catalyzed the coupling reactions of a variety of electron-neutral, electron-rich, electron-deficient and bulky aryliodides with phenylacetylene (*Table 2*, entries 1–6). Substituted phenylacetylenes and aliphatic alkynes were also good substrates and coupled with iodobenzene to give the corresponding products in good to excellent yields (*Table 2*, entries 7–12). Moreover, the arylbromide and arylchloride also worked well for this magnetic heterogeneous Sonogashira coupling reaction (*Table 2*, entries 13–17).

To define applicability of h-Fe₃O₄@TiO₂-NH₂/Pd, we have investigated its catalyst ability in the Heck cross-coupling reaction. The optimal conditions for the Heck reaction were also screened. As can be seen in *Table 3*, DMF and Et₃N were found to be suitable solvent and base for the model reaction of iodobenzene (1.0 mmol) and methyl acrylate (1.5 mmol) in the air. The optimal reaction temperature was 120° C.

Following obtaining the optimum reaction conditions, we explored the scope of our methodology using a variety of arylhalides with methyl and ethyl acrylates as olefins (*Table 4*). In all cases the desired (*E*)-products are obtained as confirmed from coupling values (*J*) in the NMR spectra.⁵² It was observed that a time of 2–4 h was required for complete reaction with good yield (86–95%). However a much longer reaction time (6 h) is required for the less reactive phenyl chloride with lower yield (62%) of the desired product.

Reusability is an important issue for catalytic reactions to make the method cheap, industrially profitable and environmentally sustainable. So the reaction between aryliodide (1 mmol) and phenylacetylene (1.2 mmol) under optimal conditions was selected to investigate the constancy of the catalyst activity. After completion of the reaction, the catalyst was easily separated using an external magnet. The h-Fe₃O₄@TiO₂-NH₂/Pd could be employed five times in the Sonogashira coupling reaction with no significant decrease in catalytic activity. The product percent yields for the five runs were found to be 96, 96,

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Table 2

 $107 - 109(108 - 110)^{48}$ 57-59 (57.8-61.1)⁴⁷ 59-60(58.2-59.6)⁴⁷ 68-69(69.4-70.5)⁴⁷ $Mp^{\circ}C$ (Lit. mp)^{Ref} h-Fe₃O₄@TiO₂-NH₂-Pd Catalyzed Sonogashira Reaction of Aryl Iodides and Bromides with Terminal Alkynes^a Yield^b (%) 96 95 92 $-R_1$ 91 Time (h) 2.5 ŝ \mathfrak{c} \mathfrak{c} ъ reaction condition Product $-R_1$ Me0- O_2N- + Ř × Terminal alkyne ó Aryl halide ,v 0,v ž Entry 2 \mathfrak{c} 4

MeO

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10 9 8 7 6 5

yellow oil⁴⁷

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(Continued on next page)

'ontinued)	$Mp^{\circ}C$ (Lit. mp) ^{Ref}	96-97(95-97) [58]	77–79(77–79) ⁵¹	57–59(57.8–61.1) ⁴⁷	107–109(108–110) ⁴⁸	68–69(69.4–70.5) ⁴⁷
	Yield ^b (%)	95	06	70	89	80
	Time (h)	3.5	4	9	9	6
	Product	HO	MeO		O ₂ N	Me
	Terminal alkyne	HO	HO			
	Aryl halide		Meo	Br	Br	Mc
	Entry	11	12	13	14	15

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^aReaction conditions: aryl halide(1.0 mmol), terminal alkyne (1.2 mmol), h-Fe₃O₄@TiO₂-NH₂/Pd catalyst (20 mg), Et₃N (2.0 mmol) in DMF (3.0 mL) at 90°C. ^bIsolated yield.

Entry	Amount of Catalyst (g)	Condition (solvent/ temperature °C)	Base	Time (h)	Yield ^b (%)
1	0.02	DMF/ 120	Et ₃ N	2	95
2	0.01	DMF/ 120	Et ₃ N	2	74
3	0.03	DMF/ 120	Et ₃ N	2	94
4	0.02	DMF/ 120	Et ₃ N	1.5	80
5	0.02	H ₂ O/ Reflux	Et ₃ N	3	45
6	0.02	DMSO/ 120	Et ₃ N	2	85
7	0.02	EtOH/ Reflux	Et ₃ N	3	60
8	0.02	DMF/ 120	K_2CO_3	2	82
9	0.02	DMF/ 120	NaOH	2	67
10	0.02	DMF/ 120	Cs_2CO_3	2	73
11	0.02	DMF/ 130	Et ₃ N	2	93
12	0.02	DMF/ 110	Et ₃ N	2	83
13	0.02	DMF/ r.t	Et ₃ N	10	Trace

 Table 3

 Optimization of Reaction Conditions for Heck Cross Coupling Reactions of Iodobenzene and Methylacrylate^a

^aReactions were run in 3 mL solvent with 1 mmol iodobenzene, 1.5 mmol methyl acrylate, and 2 mmol base. ^bIsolated yield.

94, 94 and 92, respectively. It is worth mentioning that the XRD of the catalyst was not changed after five cycles.

To verify whether the observed catalysis activity was due to the heterogeneous catalyst $h-Fe_3O_4@TiO_2-NH_2/Pd$ or to a leached Pd species in solution, we performed a hot filtration test.⁵⁶ Before the completion of the model reaction, we excluded the catalyst using an external magnet and allowed the reaction to occur. No increase in the yield was observed by GC analysis, showing a negligible amount of leached Pd species from the catalyst. It was confirmed by ICP analysis that no Pd could be detected in the hot filtered solution. The palladium is heterogeneous and remains on the support during the reaction.

Conclusion

A novel and low-density $h-Fe_3O_4$ @TiO₂-NH₂/Pd was effectively prepared in a four step procedure using simple starting materials. It exhibited high catalytic efficiency in the ligand-free Heck and copper-free Sonogashira cross-coupling reactions. The magnetic composite could be facilely recovered using an external magnet. This methodology had the advantages of high yield and elimination of ligand or copper for cross-coupling reactions. In addition the catalyst is moisture-stable, which was much superior to commercial Pd catalysts. In this catalytic process an inert atmosphere is not necessary, thus overcoming the high operating costs of the traditional method.

Experimental Section

All chemicals, including $FeCl_3 \cdot 6H_2O$, NH_4Ac , ethylene glycol, ethanol, acetonitrile, $NH_3 \cdot H_2O$, tetrabutyl orthotitanate (TBOT) and polyvinylpyrrolidone (PVP) were analytical grade reagents, purchased from Sigma-Aldrich, and used without further purification.



	$Mp^{\circ}C^{Ref}$	91–91.5 ⁵⁴	71-73 ⁵³	colorless oil ⁵³	yellow oil ⁵³
Table 4 h-Fe ₃ O ₄ @TiO ₂ -NH ₂ -Pd Catalyzed Heck Reaction of Aryl Halides with Alkenes (Continued)	Yield ^b (%)	90	89	92	06
	Time (h)	3.5	0	2.5	ω
	Product	Meo	CI	OE	OEt
	Alkene	OMe	OMe	OEt	OEt
	Aryl halide	Meo			Me
	Entry	4	Ś	Q	7

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The progress of the reaction was monitored by TLC on commercial aluminum-backed plates of silica gel 60 F254, visualized using ultraviolet light. Melting points were determined in open capillaries using an Electro thermal 9100 without further correction. ¹H NMR and ¹³C NMR spectra were recorded using a Bruker DRX-400 spectrometer. Magnetic h-Fe₃ O_4 @m-Ti O_2 /Ag hollow spheres were characterized by the following methods: FT-IR spectra were obtained with potassium bromide pellets in the range of 400-4000 cm⁻¹ using a Shimadzu 8400 s spectrometer; X-ray diffraction (XRD) was detected by a Philips instrument using Cu-Ka radiation of wavelength 1.54 Å; scanning electron microscopy, FE-SEM-EDX, analysis was performed using a Tescanvega II XMU Digital Scanning Microscope. Samples were coated with gold at 10mA for 2min prior to analysis; transmission electron microscope (TEM) images were taken with a CM30300Kv field emission transmission electron microscope; the magnetic properties were characterized using a vibrating sample magnetometer (VSM, Lakeshore 7407) at room temperature. Thermo-gravimetric analyses (TGA) were conducted with a LINSEIS modele STS PT 16000 thermal analyzer in air at a heating rate of 5°C min⁻¹. For oils, the ¹H and ¹³C NMR spectra matched those reported in the literature references indicated in Tables 2 and 4 and were submitted for review.

Synthesis of magnetic Fe_3O_4 hollow spheres

Hollow magnetic particles were synthesized through a solvothermal reaction.⁴⁴ Briefly, PVP (1.0 g) was dissolved in 40 mL of ethylene glycol (EG) and then 5 mmol of ferric chloride hexahydrate (FeCl₃·6H₂O) and 30 mmol of sodium acetate (NaAc) were added. The resulting mixture was stirred vigorously for 15min, and was transferred to a Teflon-lined stainless-steel autoclave (100 mL capacity). Then, the autoclave was heated to 200° C for 10 h, and the autoclave was subsequently cooled to room temperature. The resulting black solid was washed several times with ethanol and deionized water and dried at 80° C in a vacuum oven overnight.

Synthesis of hollow- Fe_3O_4 @Ti O_2 core shell

The Fe₃O₄@TiO₂ hollow spheres were synthesized by directly coating a layer of TiO₂ on the Fe₃O₄ by hydrolyzing tetrabutyl orthotitanate (TBOT) in ethanol and acetonitrile solution.³⁸ Hence, 50 mg of the hollow Fe₃O₄ was dispersed in a mixed solvent containing 90 ml of ethanol and 30 ml of acetonitrile with the aid of ultrasound. Then, 0.5 ml of NH₃/H₂O was added to the mixture. After that, 1 ml of TBOT was added to the above suspension with stirring for 1.5 h. The products were collected by magnetic separation and washed three times with ethanol.

Synthesis of Aminopropyl-modified hollow Fe₃O₄@TiO₂ core shell (h-Fe₃O₄@TiO₂-NH₂)

Hollow-Fe₃O₄@TiO₂-NH₂ was synthesized by a procedure explained previously.⁴⁶ Hence, 500 mg of h-Fe₃O₄@TiO₂ was dispersed in 20 mL dry toluene for 30 min using ultrasound assistance. To the resulting solution, 2 mmol of 3-aminopropyltriethoxysilane was added and the mixture was refluxed for 24 h under a nitrogen atmosphere. The (3aminopropyl)triethoxysilane functionalized hollow Fe₃O₄@TiO₂ was subjected to magnetic separation and was washed sequentially with ethanol (3 × 20 mL) and dried under vacuum for 24 h.

Loading of nano-Pd on Aminopropyl-modified hollow-Fe₃O₄@TiO₂ (h-Fe₃O₄@TiO₂-NH₂-Pd)

Doping of Pd nanoparticles onto hollow-Fe₃O₄@TiO₂- NH₂ (h-Fe₃O₄@TiO₂-NH₂), was performed according to the previous literature report.⁴⁵ Therefore, 500 mg of h-Fe₃O₄@-TiO₂-NH₂ was dispersed in 20 mL ethanol solution under ultra-sonication for 0.5 h. Then, a solution of PdCl₂ (12.5 mg, 0.07 mmol) in 10 mL hot water was added. To the resulting mixture, a solution of 1 mmol NaBH₄ in 5 mL water was added and the mixture was stirred for 12 h at room temperature. The solid catalyst was separated by external magnet, washed sequentially with EtOH (3 × 20mL) and dried under vacuum for 24 h.

General procedure for the Heck coupling reaction

Aryl halide (1 mmol), alkene (1.5 mmol), triethylamine (2 mmol) and h-Fe₃O₄@mTiO₂-NH₂-Pd (20 mg) were added to 3 mL DMF and the reaction mixture was stirred at 120°C for the required time. After completion of the reaction, the reaction mixture was cooled to room temperature and diluted with hot ethanol (10 ml). Then, the catalyst was separated by an external magnet from the cooled mixture, washed with acetone, dried in an oven and re-used for a consecutive run under the same reaction conditions. The filtrate was concentrated and the resulting residue was purified by short column chromatography on silica gel to afford the desired product.

General procedure for the Sonogashira coupling reaction

Aryl halide (1 mmol), terminal alkyne (1.2 mmol), triethylamine (2 mmol) and h- $Fe_3O_4@mTiO_2-NH_2-Pd$ (20 mg) were added to 3 ml DMF and the reaction mixture was stirred at 90°C for the appropriate time. After completion of the reaction, the reaction mixture was cooled to room temperature and diluted with hot ethanol (10 ml). After that, the catalyst was separated by an external magnet from the cooled mixture, washed with acetone, dried in an oven and re-used for a consecutive run under the same reaction conditions. The filtrate was concentrated and the resulting residue was purified by short column chromatography on silica gel to afford the desired product.

Selected spectra data

1,2-Diphenylethyne (Table 2, entry 1)

¹H NMR (400MHz, CDCl₃) δ 7.52–7.36 (m, 4H), 7.29–7.11 (m, 6H); ¹³C NMR (100MHz, CDCl₃) δ 130.55, 128.12, 127.29, 122.22, 88.35.

1-Chloro-4-(phenylethynyl)benzene (Table 2, entry 6)

¹H NMR (400MHz, CDCl₃) δ 7.43 (dd, J = 6.6, 3.0Hz, 2H), 7.38–7.31 (m, 3H), 7.29–7.17 (m, 4H); ¹³C NMR (100MHz, CDCl₃) δ 133.20, 131.76, 130.55, 127.64, 127.43, 127.35, 121.88, 120.73, 89.29, 87.22.

Methyl (E)-3-(p-tolyl)acrylate (Table 4, entry 3)

¹H NMR (400MHz, CDCl₃) δ 2.40 (s, 3H), 3.82 (s, 3H), 6.42 (d, J = 16.0Hz, 1H), 7.21 (d, J = 8.0Hz, 2H), 7.44 (d, J = 8.0Hz, 2H), 7.70 (d, J = 16.0Hz, 1H); ¹³C NMR (100MHz, CDCl₃) δ 21.4, 51.6, 116.7 128.0, 129.6, 131.6, 140.7, 144.8, 167.6.

(E)-Ethyl 4-nitrocinnamate(Table 4, entry 8)

¹HNMR (400MHz, CDCl₃) δ (ppm): 1.38 (t, *J* = 6.8, 3H),4.35–4.29 (m, 2H), 6.58 (d, *J* = 16, 1H), 7.80–7.69 (m, 3H), 8.28 (d, *J* = 8.4, 2H); ¹³C NMR (100MHz, CDCl₃) δ (ppm):166.06, 148.47, 141.63, 140.60, 128.64, 124.19, 122.60, 61.04, 14.28.

Calculation of h-Fe₃O₄ density

It is important to determine the physical properties of the shell in hollow-sphere particles, because it directly affects the functionality of the final catalyst. So, in this study the shell density was determined using specific surface area and shell thickness as reported earlier in the literature.⁵⁷

The ρ_{shell} was calculated with shell thickness of "t" (nm) (obtained from XRD), inner radius of "r" (nm) [obtained from BET (Brunauer-Emmett-Teller)] and specific surface area SA (m². g⁻¹) [obtained from BJH (Barrett-Joyner-Halenda)].⁵⁸ Therefore, the ρ_{shell} value was calculated as follows: 4.73 g.cm⁻³. The magnetite's density is established at 5.18g.cm⁻³,⁵⁹ so the as-synthesized hollow spheres have a lower density than solid sphere-like Fe₃O₄.

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