Received: 26 November 2015

Revised: 5 January 2016

(wileyonlinelibrary.com) DOI 10.1002/aoc.3449

Palladium–S-propyl-2-aminobenzothioate immobilized on Fe₃O₄ magnetic nanoparticles as catalyst for Suzuki and Heck reactions in water or poly(ethylene glycol)

Accepted: 10 January 2016

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A moisture- and air-stable heterogenized palladium catalyst was synthesized by coordination of palladium with *S*-propyl-2aminothiobenzamide supported on Fe_3O_4 magnetic nanoparticles. The prepared nanocatalyst was characterized using Fourier transform infrared, energy-dispersive X-ray and inductively coupled plasma atomic emission spectroscopies, X-ray diffraction, vibrating sample magnetometry, transmission and scanning electron microscopies, dynamic laser scattering and thermogravimetric analysis. This catalyst could be dispersed homogeneously in water or poly(ethylene glycol) and further applied as an excellent nano-organometal catalyst for Suzuki and Heck reactions. The catalyst was easily separated with the assistance of an external magnet from the reaction mixture and reused for several consecutive runs without significant loss of its catalytic efficiency or palladium leaching. The leaching of catalyst was examined using hot filtration and inductively coupled plasma atomic emission spectroscopy. Also, the effects of various reaction parameters on the Suzuki and Heck reactions are discussed. Copyright © 2016 John Wiley & Sons, Ltd.

Keywords: magnetic nanoparticle; palladium; C-C coupling; Heck reaction; Suzuki reaction

Introduction

Palladium is one of the most crucial metals in catalysis and it has been commonly applied as one of the most powerful tools for the formation of the carbon-carbon bond in organic synthesis.^[1,2] In particular, palladium-catalysed cross-coupling reactions of aryl halides such as Suzuki and Heck coupling reactions have become powerful methods in modern synthetic organic chemistry for the preparation of natural products, agrochemicals, pharmaceuticals, biologically active compounds, herbicides, UV screens, hydrocarbons, polymers, liquid crystal materials and advanced materials.^[3-6] Homogeneous palladium catalysts have been extensively studied in synthetic organic chemistry because of their high catalytic activity and selectivity.^[7] However, there are several drawbacks of homogeneous catalysts, such as the purification of the final products, recycling of the catalyst and deactivation of the catalyst.^[8,9] Additionally, removal of palladium from organic products at the end of a reaction is highly desirable because of its high cost and toxicity.^[10] Hence, the heterogenization of homogeneous catalysts can help in their use for practical processes to overcome the problems mentioned above.^[11] Therefore, to combine the advantages of both heterogeneous and homogeneous catalysts, immobilization of homogeneous catalysts on nanoparticles is the best choice, which efficiently bridges the gap between heterogeneous and homogeneous catalysts.^[12–14] However, the supporting nanocatalysts such as MCM-41,^[15,16] SBA- $15^{[17]}_{17}$ TiO₂ nanoparticles,^[18] heteropolyacids,^[19] ionic liquids,^[2] carbon nanotubes^[20] or some polymers^[21] have various disadvantages such as difficult or time-consuming and expensive separation of fine particles from a reaction mixture. Also some of them require high temperature for calcination or a lot of time and tedious conditions for their preparation. The separation drawback can be overcome by the use of magnetic nanoparticles (MNPs), which can be rapidly and easily isolated from a reaction mixture using an external magnet.^[22] More importantly, magnetic separation is more effective and easier than filtration or centrifugation, is simple, economical and clean separation, promising for industrial applications.^[23] One of the most promising MNP supports is superparamagnetic iron oxide with high surface area that can be prepared in water using commercially available materials such as FeCl₃·.4H₂O and FeCl₂·4H₂O.^[24]

We report here the synthesis and characterization of a palladium complex immobilized on Fe_3O_4 MNPs. This reusable catalyst was applied for the Suzuki and Heck reactions with a minimal leaching of palladium species.

Experimental

+B: Preparation of Palladium–S-propyl-2-aminobenzothioate Immobilized on ${\rm Fe_3O_4}$ MNPs

Free Fe₃O₄ MNPs were synthesized according to our recently reported procedure via a chemical co-precipitation technique using $FeCI_3 \cdot 6H_2O$ and $FeCI_2 \cdot 6H_2O$ in basic solution at $80^{\circ}C$.^[23] The

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obtained $\ensuremath{\mathsf{Fe}_3\mathsf{O}_4}$ nanoparticles (1.5 g) were dispersed in 50 ml of ethanol–water (1:1 v/v) solution by sonication for 30 min, and then 2.5 ml of (3-mercaptopropyl)trimethoxysilane (MPTMS) was added to this mixture. The reaction mixture was stirred under nitrogen atmosphere at 40°C for 8 h. Then, the nanoparticles were washed with ethanol five times and separated through magnetic decantation. The prepared nanoparticles (SH-MNPs) were dried at room temperature. The obtained SH-MNPs (1 g) were dispersed in 50 ml of ethanol by sonication for 20 min, and then isatoic anhydride (2.5 mmol) was added to the reaction mixture. The reaction mixture was stirred under nitrogen atmosphere at 80°C for 8 h. Then, the resulting nanoparticles (ATBA-MNPs) were washed with ethanol several times and separated using magnetic decantation and dried at room temperature. The obtained ATBA-MNPs (0.5 g) were dispersed in 25 ml of ethanol by sonication for 20 min, and then palladium acetate (0.25 mmol) was added to the reaction mixture. The reaction mixture was stirred under nitrogen atmosphere at 80°C for 20 h. Then, NaBH₄ (0.3 mmol) was added to the reaction mixture and reaction was continued for 2 h. The final product was separated using magnetic decantation and washed with ethanol to remove the unattached substrates. The nanoparticle product (Pd-ATBA-MNPs) was dried at room temperature.

General Procedure for C–C Coupling Reaction using Sodium Tetraphenylborate (Suzuki Reaction)

A mixture of aryl halide (1 mmol), sodium tetraphenylborate (0.5 mmol), Na_2CO_3 (3 mmol) and Pd-ATBA-MNPs (0.004 g, 0.66 mol%) was stirred in water at 80°C. The progress of the reaction was monitored using TLC. After completion of the reaction, the mixture was cooled to room temperature and the catalyst was separated using an external magnet and washed with diethyl ether. The reaction mixture was extracted with water and diethyl ether. The organic layer was dried over Na_2SO_4 (1.5 g). Then the solvent was evaporated and pure biphenyl derivatives were obtained in good to excellent yields.

General Procedure for Coupling of Aryl Halides with Phenylboronic Acid (Suzuki Reaction)

A mixture of aryl halide (1 mmol), phenylboronic acid (1 mmol), Na_2CO_3 (3 mmol) and Pd-ATBA-MNPs (0.005 g, 0.82 mol%) was added to a reaction vessel. The mixture was stirred in water at 80°C and the progress of the reaction was monitored using TLC. After completion of the reaction, the catalyst was separated using an external magnet and washed with ethyl acetate. The reaction mixture was extracted with water and ethyl acetate and the organic layer dried over anhydrous Na_2SO_4 (1.5 g). Then the solvent was evaporated and pure biphenyl derivatives were obtained in good to excellent yields.

General Procedure for Coupling of Aryl Halides with Butyl Acrylate or Acrylonitrile (Heck Reaction)

A mixture of aryl halide (1 mmol), alkene (1.2 mmol), Na_2CO_3 (3 mmol) and Pd-ATBA-MNPs (0.010 g, 1.64 mol%) was stirred in poly(ethylene glycol) (PEG) at 100–120°C and the progress of the reaction was monitored using TLC. After completion of the reaction, the mixture was cooled to room temperature and the catalyst was separated using an external magnet and washed with diethyl ether. The reaction mixture was dried over Na_2SO_4

(1.5 g). Then the solvent was evaporated and pure products were obtained in yields of 81–98%.

Results and Discussion

Catalyst Preparation

The catalyst was prepared using a concise route, which is outlined in Scheme 1. Initially, SH-MNPs were prepared according to new reported procedure.^[23] Subsequently, ATBA-MNPs were synthesized by reaction of SH-MNPs with isatoic anhydride. Ultimately, Pd-ATBA-MNPs were obtained via coordination of palladium with 2aminothiobenzamide immobilized on Fe₃O₄ (Scheme 1). This catalyst was characterized using X-ray diffraction (XRD), transmission electron microscopy (TEM), scanning electron microscopy (SEM), energy-dispersive X-ray spectroscopy (EDS), dynamic laser scattering (DLS), Fourier transform infrared (FT-IR) spectroscopy, vibrating sample magnetometry (VSM), thermogravimetric analysis (TGA) and inductively coupled plasma atomic emission spectroscopy (ICP-OES).

Catalyst Characterization

The prepared catalyst was characterized using several techniques. In order to investigate the crystal phase of Pd-ATBA-MNPs, XRD analysis was performed and the pattern of this sample is shown in Fig. 1. As can be seen, the iron oxide phase is identified by the peak positions at 30.2° (2 2 0), 35.6° (3 1 1), 43.3° (4 0 0), 54.1° (4 2 2), 57.4° (5 1 1) and 63.1° (4 4 0), which is consistent with the standard Fe₃O₄ XRD spectrum.^[12] These results reveal that the surface modification of the Fe₃O₄ nanoparticles does not lead to their phase change. Also the XRD pattern of Pd-ATBA-MNPs contains a



Scheme 1. Synthesis of Pd-ATBA-MNPs.



Figure 1. XRD pattern of Pd-ATBA-MNPs.



Figure 2. (a, b) TEM and (c) SEM images of Pd-ATBA-MNPs. (d) EDS spectrum of Pd-ATBA-MNPs.

series of peaks (39.9°, 46.6° and 67.6°) which are indexed to Pd on the surface of Fe₃O₄.^[25] The average size of nanocatalyst particle diameter is calculated to be 12.14 nm from the XRD results using Scherrer's equation ($D = k\lambda/\beta \cos \theta$), which is confirmed from TEM (Figs 2(a) and (b)) and SEM (Fig. 2(c)) images. TEM and SEM images provide more accurate information as to the particle size and morphology of the catalyst particles. Figure 2 shows the SEM and TEM images of Pd-ATBA-MNPs. It can be seen that most of the particles are quasi-spherical with an average diameter of about 10–15 nm, which is in accord with the XRD results. Also, the size and morphology of Pd-ABA-MNPs are quite homogeneous.

To characterize the catalyst in terms of the supporting palladium metal on Fe₃O₄ surface, the metal content of Pd-ATBA-MNPs was investigated using EDS. As shown in Fig. 2(d), the EDS spectrum of Pd-ATBA-MNPs shows the presence of Fe, O, Si, C, S and N, as well as Pd species in the surface of the catalyst. In order to determine the exact amount of Pd in Pd-ATBA-MNPs, ICP-OES was used. From this analysis, the amount of Pd in the catalyst is found to be 1.64×10^{-3} mol g⁻¹.



Figure 3. DLS measurements of (A1, A2) $\rm Fe_3O_4$ nanoparticles and (B1, B2) Pd-ATBA-MNPs.

In order to extend the characterization of the catalyst, DLS analysis of Fe_3O_4 nanoparticles and Pd-ATBA-MNPs was performed. The DLS results for Fe_3O_4 nanoparticles and Pd-ATBA-MNPs are shown in Fig. 3. In this analysis we find that as-prepared Fe_3O_4 nanoparticles are 78.1 nm in diameter, while after immobilization of the palladium complex on Fe_3O_4 , the size is increased to 93.8 nm in diameter. This increase in particle diameter is due to the presence of organic layers and palladium complex on the surface of Fe_3O_4 nanoparticles. The observed particle size from DLS analysis is slightly larger than that found using TEM or XRD due to the effect of agglomeration of nanoparticles and solvation. On the basis of



Figure 4. Magnetization curves for (a) ${\rm Fe}_3{\rm O}_4$ and (b) Pd-ATBA-MNPs at room temperature.



Figure 5. FT-IR spectra of (a) Fe_3O_4 MNPs, (b) SH-MNPs, (c) ATBA-MNPs and (d) Pd-ATBA-MNPs.



Figure 6. TGA curves of Fe_3O_4 MNPs (black), SH-MNPs (blue), ATBA-MNPs (red) and Pd-ATBA-MNPs (green).



Scheme 2. Carbon–carbon coupling reaction using sodium tetraphenylborate in the presence of Pd-ATBA-MNPs.

this analysis, the successful immobilization of organic layers including palladium complex on the Fe₃O₄ surface is verified. The magnetic properties of Fe₃O₄ nanoparticles and Pd-ATBA-MNPs were measured using VSM at room temperature. The room temperature magnetization curves of Fe₃O₄ nanoparticles and Pd-ATBA-MNPs are shown in Fig. 4. VSM measurements for Fe₃O₄ nanoparticles show that the saturation magnetization (M_s) is 74.09 emu g⁻¹ (Fig. 4(a)), while M_s of Pd-ATBA-MNPs is decreased to 42.16 emu g⁻¹ (Fig. 4(b)).^[26] On the basis of these results, the successful grafting of organic layers including palladium complex on Fe₃O₄ is verified.

Successful functionalization of the MNPs can be deduced from FT-IR spectra. The FT-IR spectra for bare Fe₃O₄ nanoparticles, SH-MNPs, ATBA-MNPs and Pd-ATBA-MNPs are shown in Fig. 5. The strong band at 580 cm^{-1} comes from the vibrations of Fe O bonds of Fe₃O₄.^[23] The spectrum of Fe₃O₄ shows a stretching vibration at 3440 cm⁻¹ which incorporates the contributions from both symmetric and asymmetric modes of O H bonds which are attached to the surface of Fe₃O₄ nanoparticles. Also, a peak appears at 1631 cm⁻¹ corresponding to the stretching vibrational mode of an adsorbed water layer.^[12,23] Immobilization of MPTMS on the surface of MNPs was indicated by the appearance of two peaks at 2922 and 2852 cm^{-1} , assigned to the CH stretching vibrations, and also S H stretching vibration modes as a weak band that appears near 2450 cm^{-1} (Fig. 5(b)) which is absent in the spectrum of ATBA-MNPs (Fig. 5(c)). Reaction of isatoic anhydride with MPTMS produces ATBA-MNPs for which the presence of carbonyl group is indicated by the band at 1630–1640 cm^{-1} (Fig. 5(c)). In addition, in the spectrum of Pd-ATBA-MNPs (Fig. 5(d)) the broad band in the range 1400-1650 cm⁻¹ is attributed to the formation of palladium complex. All of these bands reveal that the surface of Fe₃O₄ nanoparticles is successfully modified with organic layers.

Bond formation between the nanoparticles and the complex can be inferred from TGA. The TGA curve of the Pd-ATBA-MNPs shows

+ NaBPh ₄ Catalyst, Base						
Entry	Catalyst (mg)	Solvent	Base	Temperature (°C)	Time (min)	Yield (%)
1	_	PEG	Na ₂ CO ₃	80	300	b
2	10	PEG	Na ₂ CO ₃	80	10	98
3	8	PEG	Na ₂ CO ₃	80	20	96
4	6	PEG	Na ₂ CO ₃	80	25	96
5	4	PEG	Na ₂ CO ₃	80	30	97
6	2	PEG	Na ₂ CO ₃	80	60	74
7	4	EtOH	Na ₂ CO ₃	80	30	93
8	4	CH₃COOEt	Na ₂ CO ₃	80	70	45
9	4	H ₂ O	Na ₂ CO ₃	80	25	98
10	4	H₂O	NaHCO ₃	80	30	88
11	4	H₂O	Et₃N	80	30	61
12	4	H ₂ O	NaOH	80	30	60
13	4	H ₂ O	Na ₂ CO ₃	60	30	62
14	4	H ₂ O	Na ₂ CO ₃	40	30	47
15	4	H ₂ O	Na ₂ CO ₃	r.t.	30	21
16	4	H ₂ O	Na ₂ CO ₃	60	420	88
17	4	H ₂ O	Na ₂ CO ₃	r.t.	420	55

Table 1. Optimization of reaction conditions for C-C coupling reaction of iodobenzene with sodium tetraphenylborate in the presence of Pd-ATBA-

^b No reaction.

Table 2. Catalytic C–C coupling reaction of aryl halides using NaBPh ₄ in the presence of catalytic amount of Pd-ATBA-MNPs (4 mg, 0.66 mol%) in H ₂ O at 80°C						
Entry	Aryl halide	Time (min)	Yield (%) ^a	TOF (h^{-1})	Melting point (°C)	
1	lodobenzene	25	98	356.36	67–69 ^[16]	
2	4-lodotoluene	55	97	160.33	42-43 ^[27]	
3	2-lodotoluene	220	79	32.64	Oil ^[28]	
4	4-Bromotoluene	25	96	349.09	41–43 ^[27]	
5	4-Bromophenol	15	95	575.75	159–161 ^[29]	
6	Bromobenzene	30	95	287.87	68–69 ^[16]	
7	4-Bromochlorobenzene	10	94	854.54	70–72 ^[27]	
8	4-Bromobenzonitrile	10	96	872.72	80-83 ^[29]	
9	Chlorobenzene	350	81 ^b	8.41	64–66 ^[27]	

^a Isolated yield.

^b Reaction conditions: aryl halide (1 mmol), Pd-ATBA-MNPs (10 mg, 1.65 mol%), sodium tetraphenylborate (0.5 mmol) and Na₂CO₃ (3 mmol) in PEG at 100°C.





the mass loss of the organic functional groups as the catalyst decomposes upon heating. Figure 6 shows the TGA curves for bare Fe₃O₄ nanoparticles, SH-MNPs, ATBA-MNPs and Pd-ATBA-MNPs. The TGA curves of all samples show a small amount of weight loss below 200°C, attributed to desorption of physically adsorbed solvents and surface hydroxyl groups.^[12] In the TGA curve of the catalyst, a weight loss of about of 22% from 200 to 600°C results from the decomposition of immobilized organic moieties on the Fe₃O₄ surface. Meanwhile, weight losses of about 2, 5 and 9% from 200 to 600°C occur for Fe₃O₄ MNPs, SH-MNPs and ATBA-MNPs, respectively. These results indicate that the palladium complex has been supported on the surface of Fe₃O₄ nanoparticles.

Catalytic Study

After characterization of the catalyst structure, its catalytic activity was studied in C–C coupling reactions, namely Suzuki and Heck reactions. Initially, we were interested in finding a simple and efficient method for carbon–carbon coupling bond formation in the presence of Pd-ATBA-MNPs as an efficient nanocatalyst (Scheme 2).

In order to optimize reaction conditions, initially we examined the reaction of iodobenzene (1 mmol) with sodium tetraphenylborate (0.5 mmol) as a model reaction and the effects of various parameters such as solvent, temperature, base and amount of catalyst were studied for this model reaction (Table 1). At first, we find that the reaction does not proceed in the absence of Pd-ATBA-MNPs (Table 1, entry1). Then, we examined the effect of various solvents, PEG, EtOH, CH₃COOEt and water, at 80°C (Table 1, entries 6–9). The best results are obtained for water. Also, the effect of temperature was studied (Table 1, entries 9, 13–17) and excellent yield of the product is obtained at 80°C (Table 1, entry 9). Also, the coupling of iodobenzene and sodium tetraphenylborate was performed in the presence of Pd-ATBA-MNPs in water at 80°C using 3 equiv. of

Table 3. Optimization of Suzuki reaction conditions for coupling of 4-nitrobromobenzene (1 mmol) with PhB(OH)₂ (1 mmol) in the presence of Pd-ATBA-MNPs

+ Catalyst, Base Solvent, Temperature									
Entry	Catalyst (mg)	Solvent	Base	Amounts of base (mmol)	Temperature (°C)	Time (min)	Yield (%) ^a		
1		H₂O	Na ₂ CO ₃	3	80	120	b		
2	3	H ₂ O	Na ₂ CO ₃	3	80	120	98		
3	5	H ₂ O	Na ₂ CO ₃	3	80	30	98		
4	10	H ₂ O	Na ₂ CO ₃	3	80	20	99		
5	5	EtOH	Na ₂ CO ₃	3	80	30	52		
6	5	CH ₃ COOEt	Na ₂ CO ₃	3	80	30	75		
7	5	PEG	Na ₂ CO ₃	3	80	30	20		
8	5	H ₂ O	NaHCO ₃	3	80	30	91		
9	5	H ₂ O	Et₃N	3	80	30	38		
10	5	H ₂ O	Na ₂ CO ₃	3	60	30	51		
11	5	H ₂ O	Na ₂ CO ₃	3	r.t.	30	Trace		
12	5	H ₂ O	Na ₂ CO ₃	1.5	80	30	42		
^a Isolated	^a Isolated yield.								

Table 4.	Coupling of aryl halides with $PhB(OH)_2$ ir	n the presence of catalytic	amount of Pd-ATBA-MN	IPs (5 mg, 0.82 mol%) in	water at 80°C
Entry	Aryl halide	Time (min)	Yield (%) ^a	TOF (h^{-1})	Melting point (°C)
1	lodobenzene	40	97	177.44	68 ^[16]
2	4-lodotoluene	50	92	134.63	44–45 ^[27]
3	4-Bromophenol	15	99	482.93	157–160 ^[29]
4	4-Bromotoluene	60	85	103.66	45 ^[27]
5	4-Bromoaniline	310	93	21.95	53-54 ^[30]
6	Bromobenzene	70	90	94.08	68 ^[16]
7	4-Bromonitrobenzene	30	98	239.02	111–113 ^[27]
8	4-Bromobenzonitrile	25	93	272.19	83 ^[29]
9	4-Bromochlorobenzene	35	75	156.79	68-70 ^[27]
10	4-Chlorobenzonitrile	135	68 ^b	36.86	83 ^[29]

^a Isolated yield.

^b Reaction conditions: aryl halide (1 mmol), Pd-ATBA-MNPs (5 mg, 0.82 mol%), PhB(OH)₂ (1 mmol) and Na₂CO₃ (3 mmol) in PEG at 100°C.



Scheme 4. Pd-ATBA-MNP-catalysed Heck reaction.

various bases (Table 1, entries 10–12). The most effective base is Na_2CO_3 . Therefore, the best result is obtained by carrying out the reaction with Pd-ATBA-MNPs (0.004 g, 0.66 mol%), iodobenzene (1 mmol), sodium tetraphenylborate (0.5 mmol) and Na_2CO_3 (3 mmol) in water at 80°C (Table 1, entry 9).

In order to show the efficiency of this catalytic system, a variety of aryl iodides, chlorides and bromides were coupled with sodium tetraphenylborate in the presence of Pd-ATBA-MNPs (4 mg, 0.66 mol%) to produce corresponding biphenyls (Table 2). The reactions of the various aryl halide derivatives, including those with electron-

donating (Table 2, entries 2–5) and electron-withdrawing (Table 2, entries 7 and 8) groups on the aromatic ring, with sodium tetraphenylborate were then investigated to confirm the generality of the present method. However, the reaction with aryl chloride shows less reactivity towards coupling and requires much more Pd-ATBA-MNPs (10 mg, 1.65 mol%) than that for aryl iodides and bromides (Table 2, entry 9). It is worth mentioning that all products are obtained in good to excellent yields. Therefore, the results reveal that this methodology is effective for a wide range of aryl halides including chlorides, bromides and iodides.

In order to extend the general application of Pd-ATBA-MNPs as a catalyst, reactions of various aryl halides with phenylboronic acid were studied (Scheme 3). In order to optimize the reaction conditions and obtain the best catalytic system, the reaction of 4-nitrobromobenzene (1 mmol) with phenylboronic acid (1 mmol) was used as a model reaction, and was examined under various reaction parameters such as base, solvent, temperature and amount

Table 5. Optimization of reaction conditions for C–C coupling reaction of iodobenzene with butyl acrylate								
COOBu + COOBu Solvent, Temperature								
Entry	Catalyst (mg)	Solvent	Base	Amounts of base (mmol)	Temperature (°C)	Time (min)	Yield (%) ^a	
1	3	PEG	Na ₂ CO ₃	3	100	90	42	
2	5	PEG	Na ₂ CO ₃	3	100	90	51	
3	7	PEG	Na ₂ CO ₃	3	100	50	60	
4	10	PEG	Na ₂ CO ₃	3	100	40	90	
5	15	PEG	Na ₂ CO ₃	3	100	30	90	
6	10	DMSO	Na ₂ CO ₃	3	100	70	40	
7	10	PEG	Na ₂ CO ₃	3	100	70	55	
8	10	H ₂ O	Na ₂ CO ₃	3	100	70	Trace	
9	10	PEG	Na ₂ CO ₃	3	80	180	63	
10	10	PEG	Et₃N	3	100	70	51	
11	10	PEG	NaOEt	3	100	70	10	
12	10	PEG	NaHSO ₄	3	100	70	20	
13	10	PEG	NaHCO ₃	3	100	70	40	
14	10	PEG	NaOH	3	100	70	15	
15	10	PEG	Na_2CO_3	1.5	100	85	51	
^a Isolated	vield.							

Table 6. Coupling of aryl halides with butyl acrylate or acrylonitrile (Heck reaction) in the presence of catalytic amount of Pd-ATBA-MNPs (10 mg, 1.64 mol%)								
Entry	Aryl halide	Alkene	Time (min)	Yield (%) ^a	TOF (h^{-1})	Melting point (°C)		
1	lodobenzene	Butyl acrylate	40	90	82.32	Oil ^[31]		
2	4-lodotoluene	Butyl acrylate	80	94	42.99	Oil ^[32]		
3	4-lodoanisole	Butyl acrylate	125	98 ^b	28.68	Oil ^[31]		
4	2-lodotoluene	Butyl acrylate	200	82 ^b	15	Oil ^[32]		
5	4-Bromotoluene	Butyl acrylate	1560	81 ^b	1.90	Oil ^[32]		
6	4-Bromoanisole	Butyl acrylate	215	94 ^b	15.99	Oil ^[31]		
7	Bromobenzene	Butyl acrylate	500	86	6.29	Oil ^[31]		
8	3-Bromopyridine	Butyl acrylate	60	82	50	Oil ^[32]		
9	4-Bromonitrobenzene	Butyl acrylate	105	91	31.71	59–60 ^[32]		
10	4-Chloronitrobenzene	Butyl acrylate	2880	87 ^b	1.1	60 ^[32]		
11	lodobenzene	Acrylonitrile	240	97 ^b	14.79	Oil ^[33]		
12	Bromobenzene	Acrylonitrile	1080	93 ^b	3.15	Oil ^[33]		
13	4-lodotoluene	Acrylonitrile	295	96 ^b	11.90	Oil ^[34]		
14	4-Bromotoluene	Acrylonitrile	480	95 ^b	7.24	Oil ^[34]		
^a Isolated ^b Reactio	° Isolated yield. [™] Reaction temperature: 120°C.							



Figure 7. Recyclability of Pd-ATBA-MNPs in the coupling of iodobenzene (1 mmol) with (a) NaBPh₄ (0.5 mmol) and (b) PhB(OH)₂ (1 mmol) under reaction conditions.

of Pd-ATBA-MNPs (Table 3). As expected, no product is observed in the absence of the catalyst (Table 3, entry 1). Initially, the model reaction was carried out in several solvents, EtOH, water, CH₃COOEt and PEG, and it is found that water gives the best yield; in other solvents lower yields are observed (Table 3, entries 4–7). The reaction is significantly affected by the nature of base and the additive used. Therefore, a variety of bases were tested (Table 3, entries 7–9). The best result is observed using 3 mmol of Na₂CO₃. Therefore, the best results are obtained in water at 80°C in the presence of 5 mg (0.82 mol%) of Pd-ATBA-MNPs using 3 mmol of Na₂CO₃ (Table 3, entry 3).

After the optimization of the reaction conditions, various aryl halides including several functional groups were reacted under optimum conditions and the corresponding biphenyl are obtained in short reaction times with good to excellent yields (Table 4). The experimental procedure is very simple and also a wide range of aryl halides (chloride, bromide and iodide) possessing electron-donor and electron-withdrawing substituents can be successfully employed to prepare the corresponding biphenyls in excellent yields at room temperature. Aryl bromides and aryl iodides react in shorter times compared to aryl chlorides (Table 4, entry 10). Our prepared catalyst not only shows high efficiency in the Suzuki reaction, but also exhibits good performance in the Heck reaction. Therefore, we investigated the Heck reaction in the presence of Pd-ATBA-MNPs via coupling of various aryl halides with butyl acrylate or acrylonitrile (Scheme 4).

In order to establish the optimum conditions, a model reaction using iodobenzene and butyl acrylate was selected to optimize the reaction under various conditions. The activity of the catalyst in various amounts was studied, and comparable yields are obtained (Table 5). The best result is observed with 10 mg (1.64 mol%) of Pd-ATBA-MNPs (Table 5, entry 4). Several solvents were also tested; among them PEG gives the best result. Next we examined the effect of the base on the outcome of the coupling reaction (Table 5, entries 9–15). It is found that Na₂CO₃ gives a better result than Et₃N, NaOEt, NaHSO₄, NaHCO₃ and NaOH.

The scope of this methodology was evaluated in the Heck reaction for other substrates and the results are summarized in Table 6. This methodology is applicable for a wide range of aryl halides with both electron-donating groups (Table 6, entries 2–6, 13, 14) and electron-withdrawing groups (Table 6, entries 9 and 10) in the reaction with butyl acrylate. In this study, acryloni-trile was applied as another alkene (Table 6, entries 11–14) under the optimized conditions with various aryl halides (bromides and iodides) and all products are obtained in good to excellent yields. This procedure is very simple and has the ability to tolerate a variety of aryl halides.

Reusability of Catalyst

The reusability of catalysts is an important advantage for commercial applications. Therefore, the recovery and recyclability of Pd-ATBA-MNPs were studied in the coupling reaction of iodobenzene with phenylboronic acid and sodium tetraphenylborate. After completion of the reaction, the catalyst was easily and rapidly recovered from the reaction mixture using an external magnet. The remaining magnetic nanocatalyst was further washed with diethyl ether to remove residual product and decantation of the reaction mixture. Then, the reaction vessel was charged with fresh substrate and subjected to the next run. As shown in Fig. 7, the catalyst can be recycled over nine

Table 7.	Table 7. Comparison of results for Pd-ATBA-MNPs with those for other catalysts in the coupling of iodobenzene with phenylboronic acid							
Entry	Catalyst (mol% of Pd)	Conditions	Time (h)	Yield (%) ^a	Ref.			
1	Polymer-anchored Pd(II) Schiff base complex (0.5 mol%)	K ₂ CO ₃ , DMF–H ₂ O (1:1), 80°C	5	99	[3]			
2	NHC–Pd(II) complex (1.0 mol%)	THF, Cs ₂ CO ₃ , 80°C	12	88	[31]			
3	Fe ₃ O ₄ @SiO ₂ @mSiO ₂ -Pd(II) (0.5 mol%)	EtOH, K ₂ CO ₃ , 80°C	3	98	[35]			
4	PVP–Pd NPs (0.8 \times 10 ⁻³ mol%)	K ₂ PO ₄ , EtOH/H ₂ O, 90°C	2	94	[36]			
5	Pd NPs (1.0 mol%)	H ₂ O, KOH, 100°C	12	95	[37]			
6	CA/Pd(0) (0.5–2.0 mol%)	H ₂ O, K ₂ CO ₃ , 100°C	2	94	[38]			
7	PdCl ₂ (0.05 mol%)	DMF, Cs ₂ CO ₃ , 130°C	2	95	[39]			
8	Pd/Au NPs (4.0 mol%)	EtOH/H ₂ O, K ₂ CO ₃ , 80°C	24	88	[40]			
9	Pd(II)–NHC complex (0.01 mmol)	DMF, Cs ₂ CO ₃ , 100°C	24	99	[41]			
10	<i>N,N</i> '-bis(2-pyridinecarboxamide)-1,2-benzene palladium complex (1 mol%)	H ₂ O, K ₂ CO ₃ , 100°C	3	97	[42]			
11	Pd-MPTAT-1 (0.02 g)	NaOH, DMF–H ₂ O (1:5), 85°C	8	95	[43]			
12	LDH–Pd(0) (0.3 g)	K ₂ CO ₃ , 1,4-dioxane–H ₂ O (5:1), 80°C	10	96	[44]			
13	PANI–Pd (2.2 mol%)	K ₂ CO ₃ , 1,4-dioxane–H ₂ O (1:1), 95°C	4	91	[45]			
14	Pd-ATBA-MNPs (0.82 mol%)	H ₂ O, Na ₂ CO ₃ , 80°C	0.67	97	This work			
^a Isolated	* Isolated yield.							

runs without any significant loss of its catalytic activity. The average isolated yield for nine successive runs is 92.5 and 94.8%, which clearly demonstrates the practical recyclability of this catalyst.

In order to determine any leaching of palladium in the reaction mixture and to show that Pd-ATBA-MNPs are a heterogeneous catalyst, a hot filtration test was performed in the Suzuki reaction of iodobenzene with phenylboronic acid. In this study we find that the yield of product in half the reaction time is 52%. Then the reaction was repeated and in half of the reaction time the catalyst was separated and the filtrate allowed to react further. The yield of reaction in this stage is 54%, confirming that the leaching of palladium does not occur.

Also, to measure the exact leaching of palladium in the catalyst, the amount of palladium in Pd-ATBA-MNPs was determined using ICP-OES after five recycles. The amount of palladium in the catalyst is found to be 1.62×10^{-3} mol g⁻¹ based on ICP-OES for the catalyst after five re-use runs, meaning that the catalyst leaching is only 0.11%. The results from hot filtration test and ICP-OES technique show that leaching of palladium during the reaction is negligible.

Comparison of Catalyst

In order to examine the efficiency of the procedures presented, we compared the results of the coupling of iodobenzene with phenylboronic acid (Table 7) with previously reported results. This catalyst shows shorter reaction time and higher reaction yield than the other catalysts. Also this nanomagnetic catalyst is superior in terms of price, non-toxicity, stability and ease of separation than the previously reported ones. In addition, the recoverability and recyclability of this catalysts.

Conclusions

An efficient heterogeneous catalyst (Pd-ATBA-MNPs) was synthesized. This catalyst was characterized using several techniques, namely FT-IR spectroscopy, XRD, VSM, TEM, SEM, EDS and ICP- OES. The Pd-ATBA-MNPs exhibit excellent catalytic activity, high reusability and air and moisture stability for the Heck and Suzuki reactions. This methodology is effective for a wide range of aryl halides including chlorides, bromides and iodides. A high conversion of substrates was obtained in C–C coupling reactions using sodium tetraphenylborate, phenylboronic acid, acrylonitrile and butyl acrylate in the presence of this catalyst. Also, the catalyst can be reused up to nine times without any significant loss of its activity or palladium leaching.

Acknowledgments

This work was supported by the research facilities of Ilam University, Ilam, Iran.

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