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Immobilized Palladium-pyridine Complex on γ-Fe_2O_3 Magnetic Nanoparticles as a New Magnetically Recyclable Heterogeneous Catalyst for Heck, Suzuki and Copper-free Sonogashira Reactions

S. Sobhani* and S. Esmaeilzadeh-Soleimani
Department of Chemistry, College of Sciences, University of Birjand, Birjand, Iran

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A new immobilized palladium-pyridine complex on γ-Fe_2O_3 magnetic nanoparticles was synthesized and characterized by SEM, TEM, TGA, ICP, XPS, XRD, FT-IR and CHN analyses. The catalytic activity of the synthesized catalyst has been investigated in Heck, Suzuki and Sonogashira coupling reactions using a series of aryl halides. The catalyst was easily isolated from the reaction mixture by an external magnetic field and reused several times with no significant loss of catalytic activity.

Keywords: Palladium, Iron oxide, Coupling reactions, Heterogeneous catalyst

INTRODUCTION

Palladium-catalysed cross-coupling reactions *via* Heck, Suzuki and Sonogashira have been emerged as the powerful method for the formation of carbon-carbon bonds in organic syntheses. These reactions generally proceed in the presence of a homogeneous palladium catalyst, which makes a tedious separation and recovery of the catalyst, and might result unacceptable palladium contamination of the products [1-7]. A way to overcome this difficulty would be the use of a heterogeneous Pd catalyst. Solid-phase organopalladium complexes, having high activity and selectivity, offer several practical advantages such as the ease of separation of the catalyst from the desired products and reducing the total cost of the process. Along this line, immobilization methods for depositing palladium onto heterogeneous solid beds have been studied extensively [8-10]. Among the solid supports, magnetic nanoparticles (MNPs) have been emerged as an attractive material for the immobilization of homogeneous catalysts. MNP-supported catalysts can be isolated efficiently from the reaction mixture through simple magnetic separation after the reaction completion. This kind of catalyst separation eliminates the need for the catalyst filtration and centrifugation [11-14]. In recent years, the use of nitrogen-based ligands in metal complexes has been received wide attention in organometallic chemistry [18-28]. Some of the beneficial features of these compounds making them attractive are their thermal stability, low price, high efficiency and simple preparation methods. To date, a large number of metal complexes containing *N*-ligand derivatives such as imidazole [15-17], Schiff bases [18-20], pyridine [21,22], NNN-pincer ligands [23-25], nitrogen-containing dendrimers [26,27] and DABCO [28] have been applied as catalysts in synthetic organic chemistry. Pyridine moieties are among the most important heterocyclic structural motifs that exist widely in a large number of ligands, natural products, pharmaceuticals and functional materials, and have been used as the active catalysts in organic syntheses [29-31]. In continues of our recent works on the development of new heterogeneous catalysts [24,28,32-39], herein, we have synthesized palladium-pyridine complex on γ-Fe_2O_3 magnetic nanoparticles (Pd-Py-γ-Fe_2O_3). After the characterization of this newly synthesized catalyst, we have used it as a heterogeneous catalyst for the C-C bond formation *via* Heck, Suzuki and Sonogashiro cross-coupling reactions.

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*Corresponding author. E-mail: ssobhani@birjand.ac.ir

EXPERIMENTAL

General Information

Chemicals were purchased from Merck Chemical Company. NMR spectra were recorded in ppm in $CDCl_3$ on a Bruker Advance DPX-400 and 250 instrument using TMS as internal standard. The purity of the products and the progress of the reactions were accomplished by TLC on silica-gel polygram SILG/UV254 plates. FT-IR spectra were recorded on a JASCO FT-IR 460 plus spectrophotometer. TEM analysis was performed using TEM microscope (Philips CM30). The morphology of the products was determined using Hitachi Japan, model s4160 scanning electron microscopy (SEM) at accelerating voltage of 15 KV. Thermo gravimetric analysis (TGA) was performed using a Shimadzu thermo gravimetric analyser (TG-50). Elemental analysis was carried out on a Costech 4010 CHN elemental analyser. Power X- ray diffraction (XRD) was performed on a X'Pert Pro MPD diffractometer with Cu K α ($\lambda = 0.154$ nm) radiation. Surface analysis spectroscopy of the catalyst was performed in an ESCA/AES system. This system was equipped with a concentric hemispherical (CHA) electron energy analyser (Specs model EA10 plus) suitable for X-ray photoelectron spectroscopy (XPS). The content of Pd in the catalyst was determined by OPTIMA 7300DV ICP analyser.

Synthesis of Pyridine Supported on Nano γ-Fe_2O_3

The γ-Fe_2O_3 nanoparticles were synthesized by a reported chemical co-precipitation technique of ferric and ferrous ions in alkali solution with minor modifications [28]. A mixture of γ-Fe_2O_3 (2 g) in toluene (40 ml) was sonicated for 30 min. 3-Mercaptopropyl trimethoxysilane (0.5 ml) was added to the dispersed γ-Fe_2O_3 in toluene and slowly heated to 105 °C and stirred at this temperature for 20 h. The resulting mercapto-functionalized γ-Fe_2O_3 was separated by an external magnet and washed 3 times with MeOH, EtOH and CH_2Cl_2 and dried under vacuum. 3-(Chloromethyl) pyridine hydrochloride (0.15 g) and triethylamine (0.13 ml) were added to mercapto-functionalized γ-Fe_2O_3 (1.7 g) in dry toluene (15 ml), and the mixture was refluxed for 18 h. The solid material was then filtered, washed with H_2O, MeOH, CH_2Cl_2 and dried at room temperature in vacuum to afford nano γ-Fe_2O_3-pyridine based catalyst.

Synthesis of Palladium-pyridine Complex Supported on γ-Fe_2O_3 (Pd-Py-γ-Fe_2O_3)

Pd-Py-γ-Fe_2O_3 (1.7 g) was added to a solution of $Pd(OAc)_2$ (0.008 g) in dry acetone (40 ml). The reaction mixture was stirred at room temperature for 24 h. After stirring, the solid was separated by an external magnet, and washed with acetone. It was then dried in an oven at 90 °C overnight to furnish Pd-Py-γ-Fe_2O_3.

General Procedure for Heck Cross-coupling Reaction

A mixture of aryl halide (1 mmol), olefin (1.1 mmol), Et_3N (2 mmol) and catalyst (0.015 g, 1 mol%) was stirred at 100 °C for an appropriate time (Table 2). EtOAc was added to the reaction mixture. The catalyst was separated by an external magnet, washed with EtOAc, dried and re-used for a consecutive run under the same reaction conditions.

General Procedure for Suzuki Cross-coupling Reaction

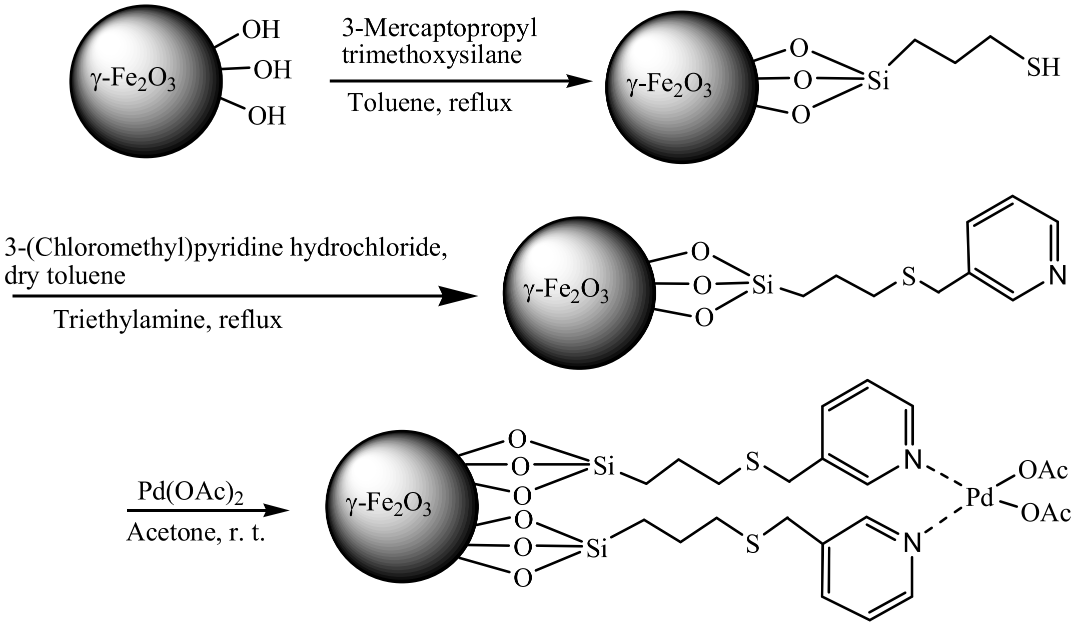
A mixture of aryl halide (1 mmol), phenylboronic acid (1.1 mmol), Et_3N (2 mmol) and catalyst (0.03 g, 2 mol%) was stirred at 100 °C for an appropriate time (Table 3). EtOAc was added to the reaction mixture. The catalyst was separated by an external magnet, washed with EtOAc, dried and re-used for a consecutive run under the same reaction conditions.

General Procedure for Sonogashira Cross-coupling Reaction

A mixture of aryl halide (1 mmol), phenylacetylene (1.1 mmol), Et_3N (2 mmol) and catalyst (0.03 g, 2 mol%) was stirred at 100 °C for an appropriate time (Table 4). The reaction mixture was diluted with EtOAc. The catalyst was separated by an external magnet, washed with EtOAc, dried and re-used for a consecutive run under the same reaction conditions.

RESULTS AND DISCUSSION

Immobilized palladium-pyridine complex on γ-Fe_2O_3 magnetic nanoparticles (Pd-Py-γ-Fe_2O_3) was synthesized following the steps in Scheme 1. At first, mercapto-functionalized γ-Fe_2O_3 was synthesized by the



Scheme 1. Synthesis of Pd-Py-γ-Fe_2O_3

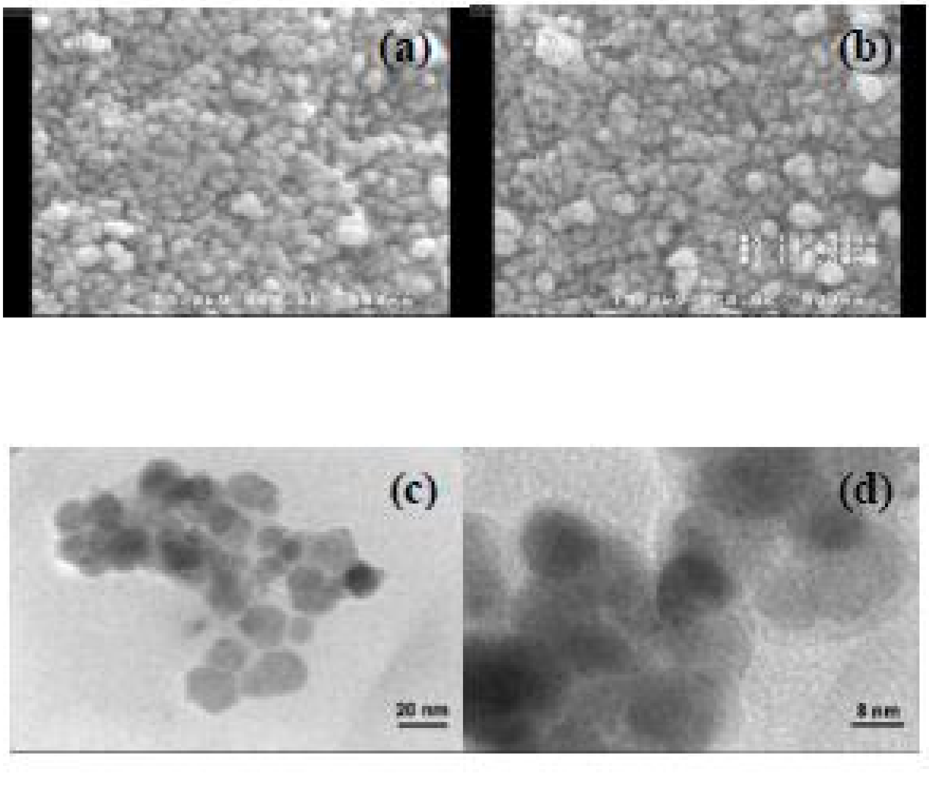


Fig. 1. SEM images (a and b) and TEM images (c and d) of Pd-Py-γ-Fe_2O_3.

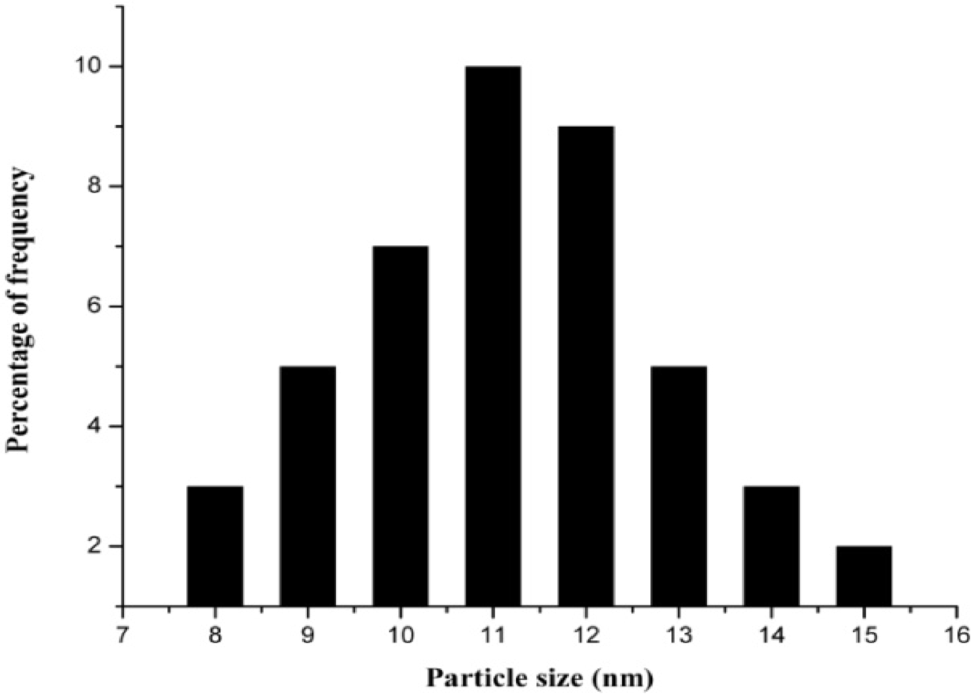


Fig. 2. Particle size distribution of Pd-Py-γ-Fe_2O_3.

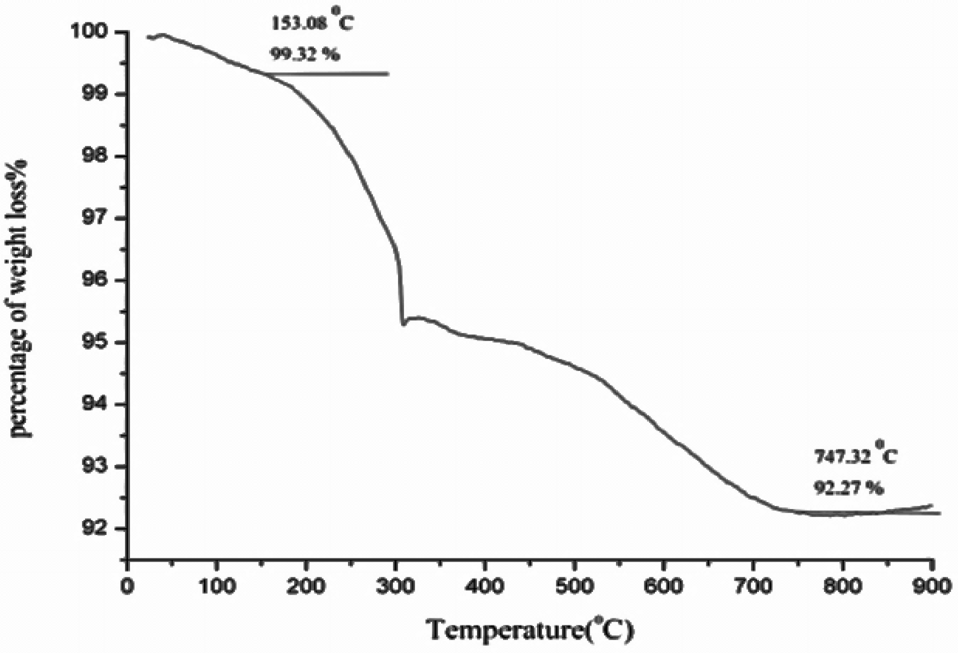


Fig. 3. TGA diagram of Pd-Py-γ-Fe_2O_3.

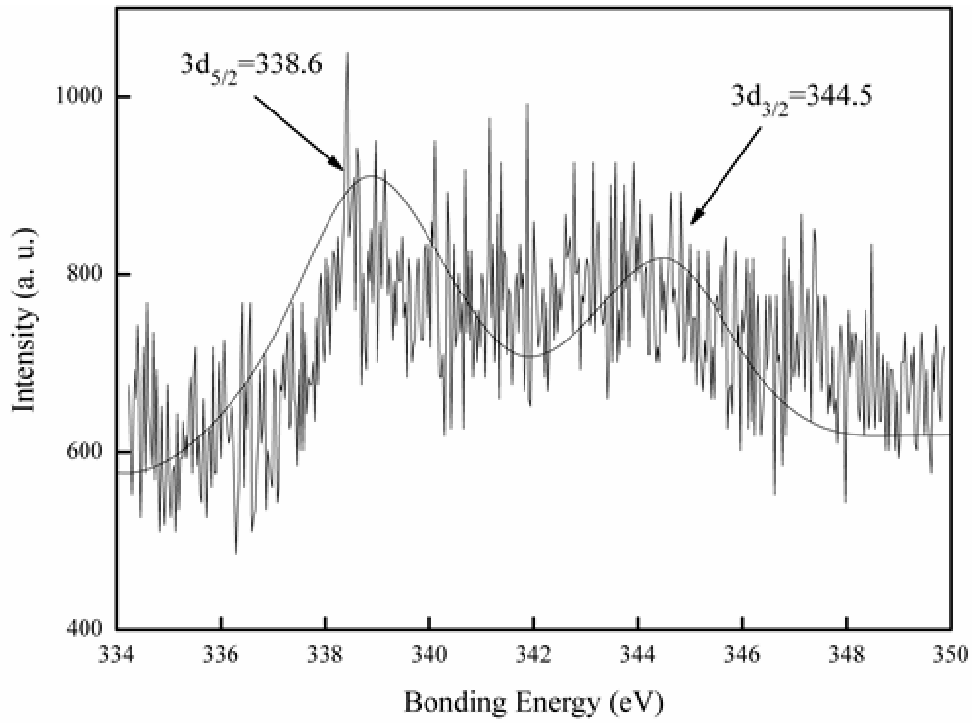


Fig. 4. X-ray photoelectron spectroscopy (XPS) of Pd-Py-γ-Fe_2O_3.

reaction of γ-Fe_2O_3 with 3-mercaptopropyl trimethoxysilane. It was then subjected to react with 3-chloromethylpyridine hydrochloride to give the supported pyridine on γ-Fe_2O_3. Pd-Py-γ-Fe_2O_3 was obtained from the reaction of supported pyridine on γ-Fe_2O_3 with $Pd(OAc)_2$ in acetone at room temperature. The synthesized Pd-Py-γ-Fe_2O_3 was fully characterized by SEM, TEM, TGA, ICP, XRD, XPS, FT-IR and CHN analyses.

According to the SEM (Figs. 1a and b), the synthesized Pd-Py-γ-Fe_2O_3 has uniformity spherical morphology. Nanoparticles are spherical in shape and relatively monodispersed in TEM images (Figs. 1c and d). The particle size distribution of Pd-Py-γ-Fe_2O_3 was also evaluated using TEM and showed that the average diameter of the particles was 11 nm (Fig. 2). The SEM images show particles with an average diameter of 50-60 nm.

The TGA diagram of the catalyst is shown in Fig. 3. A significant decrease in the weight percentage of the catalyst at about 150 °C is related to the desorption of water molecules from the catalyst surface. Another decreasing peak started at 380 °C was related to the decomposition of functionalized groups on the catalyst surface.

The amount of immobilized pyridine ligands on γ-Fe_2O_3 was calculated to be 0.43 mmol g^{-1} according to the elemental analysis (N = 0.61%). The Pd content of Pd-Py-γ-Fe_2O_3 was quantified by ICP. The ICP analysis showed that 0.16 mmol of Pd was anchored on 1 g of Pd-Py-γ-Fe_2O_3.

The X-ray photoelectron spectroscopy (XPS) diagram pertaining to Pd-Py-γ-Fe_2O_3 is shown in Fig. 4. This spectrum indicates peaks at 338.6 and 344.5 eV corresponding to the electron levels of $3d_{5/2}$ and $3d_{3/2}$, respectively. These peaks imply the presence of Pd(II) in Pd-Py-γ-Fe_2O_3.

The XRD pattern of Pd-Py-γ-Fe_2O_3 is shown in Fig. 5. In this figure, the diffraction peaks of γ-Fe_2O_3 at around 2θ = 30.4°, 35.8°, 43.6°, 53.7°, 57.6°, 63.2° corresponding to (2 2 0), (3 1 1), (4 0 0), (4 2 2), (5 1 1) and (4 4 0) are easily recognizable. This indicated that the γ-Fe_2O NPs are mostly existed in the face centred cubic structure. The XRD pattern of Pd-Py-γ-Fe_2O_3 showed a weak peak at 2θ = 39.4° that corresponds to the 1 1 1 reflection of supported Pd.

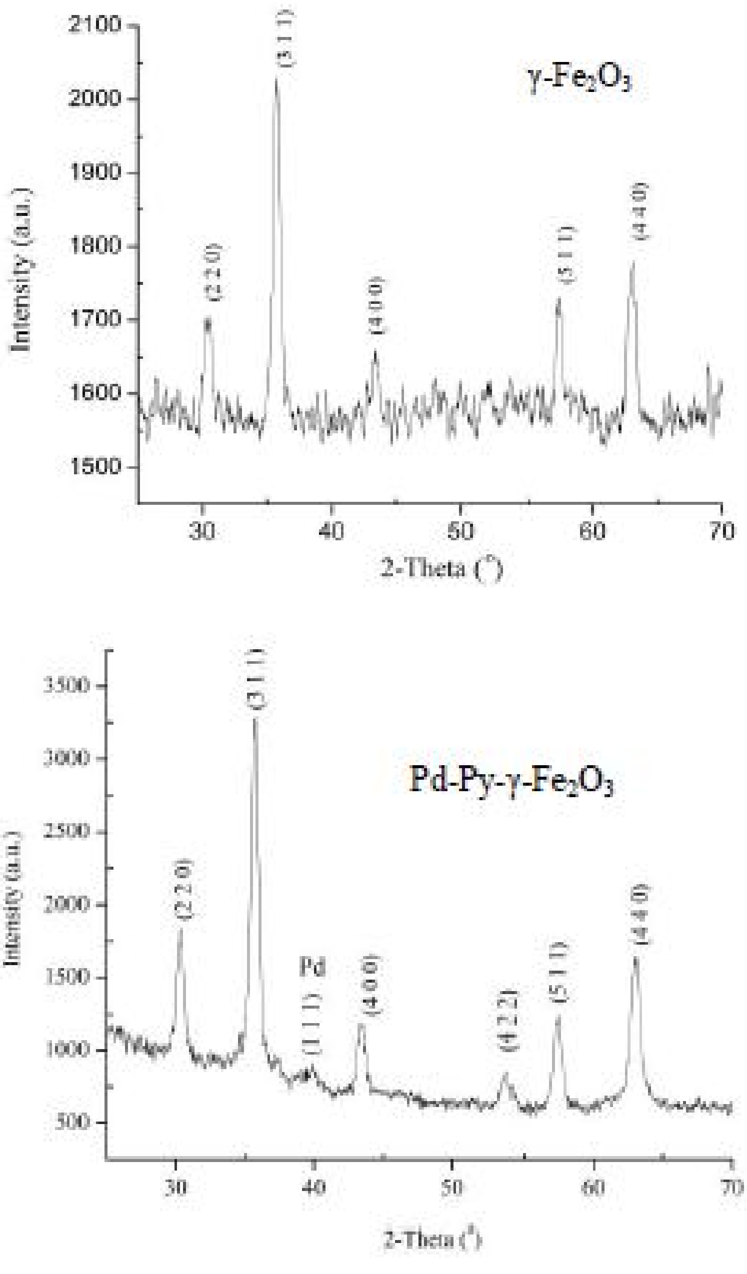
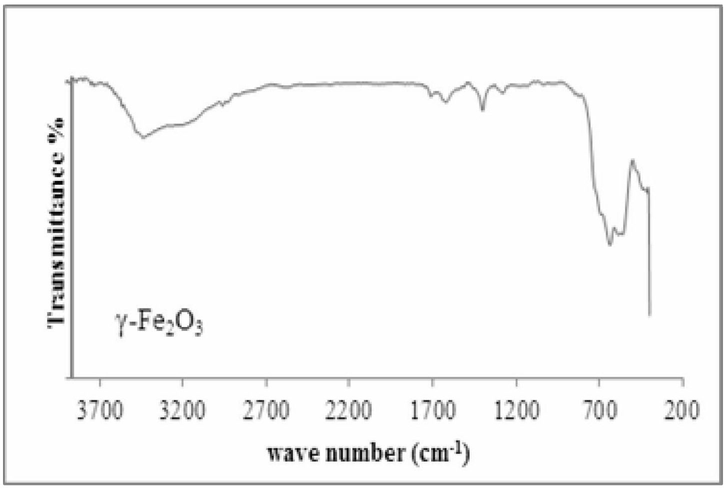


Fig. 5. XRD pattern of γ-Fe_2O_3 and Pd-Py-γ-Fe_2O_3.

The FT-IR spectra of γ-Fe_2O_3 and Pd-Py-γ-Fe_2O_3 are compared in Fig. 6. The peak placed at 650 cm^{-1} is related to the stretching vibrations of the Fe-O bonds in these compounds. Characteristic peaks at 1104, 1448 and 1474 cm^{-1} observed in the spectrum of Pd-Py-γ-Fe_2O_3, are related to the stretching vibrations of Si-O, C=C and C=N bonds in this compound.

Heck, Suzuki and Sonogashira Reactions in the Presence of Pd-Py-γ-Fe_2O_3

The efficiency of metal-catalysed cross-coupling reactions is mainly affected by the amount of the catalyst,



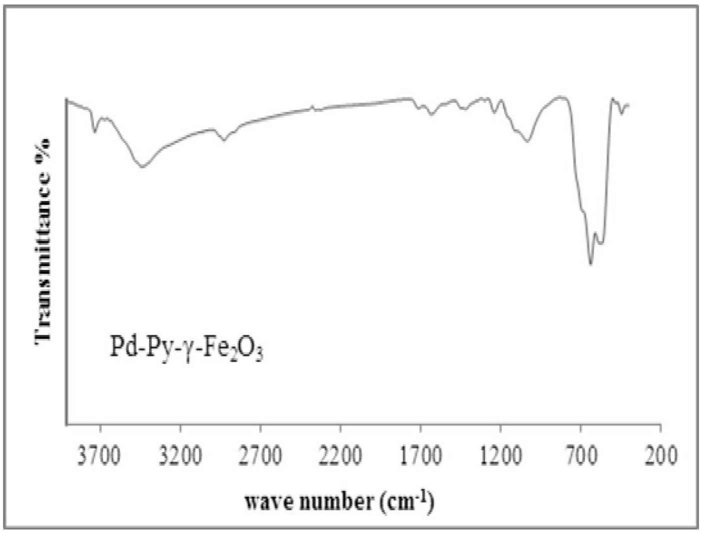


Fig. 6. FT-IR spectra of γ-Fe_2O_3 and Pd-Py-γ-Fe_2O_3.

type of the solvent, base, and reaction temperature. In order to optimize the reaction conditions for using Pd-Py-γ-Fe_2O_3 as a heterogeneous catalyst in the Heck reaction, the reaction of iodobenzene and *n*-butyl acrylate in the presence of 1 mol% of the catalyst and Et_3N at 100 °C was chosen as a model reaction. The solvent effect was first examined for the model reaction using different solvents, and also under solvent-free conditions (Table 1, entries 1-7). The best result was obtained in the absence of any solvent (Entry 7). The model reaction was carried out with different bases and also without a base (Table 1, Entries 8-11). The best yield of the product was obtained when the reaction was accomplished in the presence of Et_3N as the base. The amount of the catalyst was another estimated factor (Table 1, Entries 12-14). A further increasing of catalyst loading does not have any effect on the yield of the product (Table 1, Entry 14). The product was produced in 70% and trace amount in the presence of 0.5 and 0 mol% of the catalyst, respectively (Table 1, Entries 13 and 12). The temperature effect was also investigated. The reaction was carried out at some other temperatures (Table 1, Entries 15-17). The results showed that 100 °C was the best temperature for this reaction.

To explore the scope of this reaction, we investigated the coupling reaction of various aryl halides carrying either

Table 1. Heck Cross-coupling Reaction of Iodobenzene with *n*-Butyl Acrylate under Different Conditions

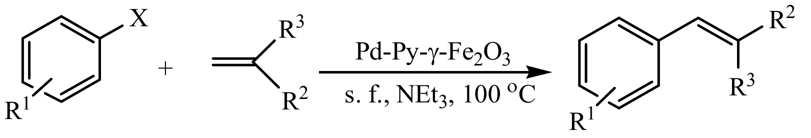
Entry	Base	T (°C)	Catalyst (%)	Solvent	Time (h)	Yield (%)[a]
1	NEt_3	100	1	H_2O	2	46
2	NEt_3	Reflux	1	DMF	2	82
3	NEt_3	Reflux	1	EtOH	2	61
4	NEt_3	Reflux	1	CH_3CN	2	29
5	NEt_3	Reflux	1	EtOAc	2	59
6	NEt_3	Reflux	1	Toluene	2	73
7	NEt_3	100	1	-	1	92
8	K_2CO_3	100	1	-	2	86
9	KOH	100	1	-	24	12
10	KOAC	100	1	-	2	15
11	-	100	1	-	24	26
12	NEt_3	100	-	-	1	Trace
13	NEt_3	100	0.5	-	1	71
14	NEt_3	100	1.5	-	2	92
15	NEt_3	r.t.	1	-	1	11
16	NEt_3	80	1	-	1	81
17	NEt_3	130	1	-	1	92

[a]Isolated yield. Reaction conditions: iodobenzene (1 mmol), *n*-butyl acrylate (1.1 mmol), Et_3N (2 mmol.), Pd-Py-γ-Fe_2O_3 (1 mol%, except for Entries 12-14), temperature = 100 °C.

electron-withdrawing or electron-releasing constituents in aromatic rings with different alkenes under optimized reaction conditions (Scheme 2, Table 2).

As seen in Table 2, the reaction of different iodobenzene and bromobenzene with olefins including methyl/ethyl/*n*-butyl acrylate and styrene proceeded well and produced the desired products in good to high yields. The Heck coupling reaction of chlorobenzene with *n*-butyl acrylate was also studied. The product was obtained in 20% yield after 24 h catalyzed by Pd-Py-γ-Fe_2O_3.

Encouraged by the above results of Heck reactions, the catalytic activity of Pd-Py-γ-Fe_2O_3 was then evaluated for Suzuki coupling reactions (Scheme 3, Table 3). Aryl halides (iodides, bromides and chlorides) containing electron-withdrawing or electron-realizing groups underwent the Suzuki coupling reaction with phenylboronic acid and gave the corresponding coupling products in good to high yields.



R^1 = H, OMe, Me, Cl, CN, NO_2
X = I, Br

R^2 = Ph, CO_2R^4
(R^4 = Me, Et, *n*-Bu)
R^3 = H, Me

Scheme 2. Heck cross-coupling reaction of aryl halides with olefins catalyzed by Pd-Py-γ-Fe_2O_3.

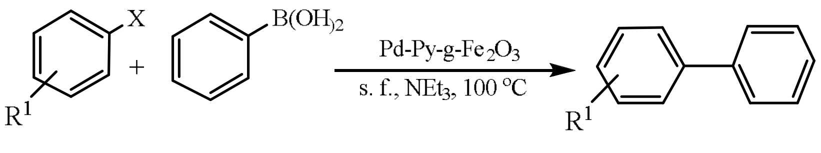
Table 2. Heck Cross-coupling Reaction of Aryl Halides with Olefins Catalyzed by Pd-Py-γ-Fe_2O_3

Entry	Aryl halide	Olefin	Time (h)	Yield (%)[a]	Obtained M.P. (°C)	Reported M.P. (°C) [Ref.]
1	PhI	CH_2=CH-CO_2Bu^n	1	92	141-143	140-142 [40]
2	PhI	CH_2=CH_2-CO_2Me	3	91	34-36	35-37 [40]
3	PhI	CH_2=C(Me)-CO_2Me	3	90	-	-
4	PhI	CH_2=CH-CO_2Et	2	86	-	-
5	4-$MeOC_6H_4I$	CH_2=CH-CO_2Bu^n	7	82	91-93	90-92 [40]
6	4-ClC_6H_4I	CH_2=CH-CO_2Bu^n	4	84	37-39	37-39 [40]
7	PhBr	CH_2=CH-CO_2Bu^n	10	71[b]	141-143	140-142 [40]
8	4-$O_2NC_6H_4Br$	CH_2=CH-CO_2Bu^n	13	82	68-70	67-69 [40]
9	4-NCC_6H_4Br	CH_2=CH-CO_2Bu^n	4	63	42-44	43-46 [41]
10	PhI	PhCH=CH_2	3	81	122-124	122-124 [42]
11	4-$MeOC_6H_4I$	PhCH=CH_2	2	73	131-133	132-134 [42]
12	4-ClC_6H_4I	PhCH=CH_2	4	75	37-39	37-39 [43]
13	4-$O_2NC_6H_4Br$	PhCH=CH_2	7	71[b]	156-157	156-157 [44]

[a] Isolated yield. Reaction conditions: aryl halide (1 mmol), olefin (1.1 mmol), Et_3N (2 mmol), catalyst (1 mol%, except for Entries 7 and 13), 100 °C. [b] Catalyst = 3 mol%.

We have also evaluated the catalytic activity of this catalytic system in the copper-free Sonogashira reaction (Scheme 4). The coupling reaction successfully occurred between different aryl iodides, bromides and cholorides and phenylacetylene, and the corresponding products were obtained in good to high yields (Table 4).

The reusability of the catalyst is a very important theme, especially for commercial applications. Therefore, the recovery and reusability of the catalyst were investigated using the reaction of iodobenzene with *n*-butyl



R^1 = H, OMe, Cl, CN, NO_2
X = I, Br, Cl

Scheme 3. Suzuki cross-coupling reaction of aryl halide with phenylboronic acid catalyzed by Pd-Py-γ-Fe_2O_3

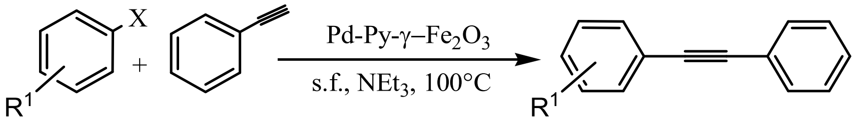
Table 3. Suzuki Cross-coupling Reaction of Aryl halides with Phenylbornic Acid Catalyzed by Pd-Py-γ-Fe_2O_3

Entry	Aryl halide	Time (h)	Yield (%)	Obtained M.P. (°C)	Reported M.P. (°C) [Ref.]
1	PhI	1	97	68-70	68-69 [45]
2	4-$MeOC_6H_4I$	3	63	80-82	81-83.5 [46]
3	4-ClC_6H_4I	3	91	75-77	76-77 [45]
4	PhBr	1	96	68-70	68 -69 [45]
5	4-$MeOC_6H_4Br$	7	72	80-82	81-83.5 [46]
6	4-$O_2NC_6H_4Br$	4	99	107-109	109-111 [46]
7	4-NCC_6H_4Br	4	98	87-89	89-92 [46]
8	PhCl	4	95	68-70	68-69 [45]
9	4-$O_2NC_6H_4Cl$	1	96	107-109	109-111 [46]
10	4-CNC_6H_4Cl	3	92	87-89	89-92 [46]

[a]Isolated yield. Reaction conditions: aryl halide (1 mmol), phenylboronic acid (1.1 mmol), Et_3N (2 mmol), catalyst (2 mol%), 100 °C.

acrylate, phenylboronic acid and phenylacetylene under the present reaction conditions. After the reaction was completed, EtOAc was added and the catalyst was separated by an external magnetic field (Fig. 7), washed with EtOAc, dried and recycled for another run. The average isolated yield of the products for five consecutive runs in Heck, Suzuki and Sonogashira reactions were 86.0, 91.2 and 92.2%, respectively (Fig. 8). ICP analysis of Pd-Py-γ-Fe_2O_3 after five times reuse indicates a very small amount of Pd leaching (less than 1%). A slight agglomeration is observed in the TEM image of the catalyst after five times reuse (Fig. 9). These results clearly demonstrate the practical reusability of this catalyst.

Comparison of the activity of various Pd catalysts with Pd-Py-γ-Fe_2O_3 in the Heck, Suzuki and Sonogashira reactions published in the literature are listed in Table 5.



R^1 = H, OMe, Me, Cl, CN, NO_2
X = I, Br,Cl

Scheme 4. Sonogashira cross-coupling reaction of aryl halides with phenylacetylene catalyzed by Pd-Py-γ-Fe_2O_3

Table 4. Sonogashira Cross-coupling Reaction of Aryl halides with Phenylacetylene Catalyzed by Pd-Py-γ-Fe_2O_3

Entry	Aryl halide	Time (h)	Yield (%)	Obtained M.P. (°C)	Reported M.P. (°C) [Ref.]
1	PhI	1	97	58-60	59-60 [47]
2	4-$MeOC_6H_4I$	3	61	58-60	58-59 [47]
3	4-ClC_6H_4I	3	92	82-84	84 [48]
4	PhBr	1	96	58-60	59-60 [47]
5	4-$MeOC_6H_4Br$	7	73	58-60	58-59 [47]
6	4-MeC_6H_4Br	4	92	70-72	72-73 [49]
7	4-$O_2NC_6H_4Br$	4	98	118-120	119-121 [47]
8	4-NCC_6H_4Br	4	99	105-107	107-109 [50]
9	PhCl	4	96	58-60	59-60 [47]
10	4-$O_2NC_6H_4Cl$	1	94	118-120	119-121 [47]
11	4-CNC_6H_4Cl	3	92	105-107	107-109 [50]
12	4-MeC_6H_4Cl	3	90	70-72	72-73 [49]

[a]Isolated yield. Reaction conditions: aryl halide (1 mmol), phenylacetylene (1.1 mmol), Et_3N (2 mmol), catalyst (2 mol%), 100 °C.

From Table 5, it is appeared that Pd-Py-γ-Fe_2O_3 showed good catalytic activity for the Heck, Suzuki and Sonogashira reactions. More importantly, among supported Pd catalysts, our catalyst like those which are supported on the magnetic nanoparticles could be easily separated from the reaction mixture by using an external magnet.

CONCLUSIONS

In summary, we have synthesized immobilized

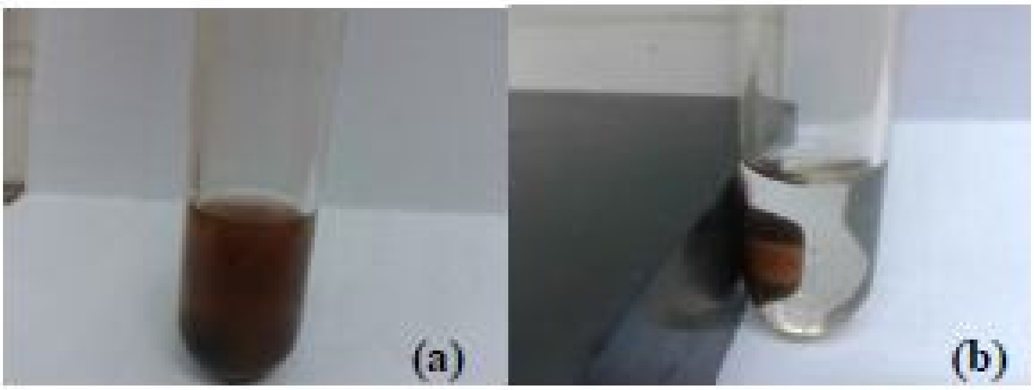


Fig. 7. a) Reaction mixture, b) Separation of Pd-Py-γ-Fe_2O_3 by an external magnetic field.

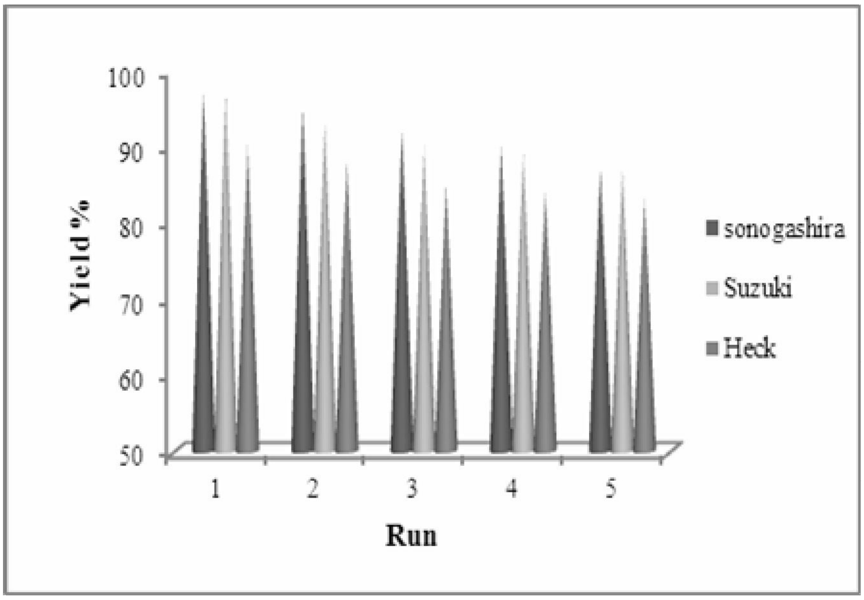


Fig. 8. Reusability of Pd-Py-γ-Fe_2O_3 as a magnetically recyclable catalyst.

Pd-pyridine on γ-Fe_2O_3 magnetic nanoparticles (Pd-Py-γ-Fe_2O_3). After its characterization by different methods, we have used this newly synthesized catalyst as a magnetically recyclable heterogeneous catalyst in Heck, Suzuki and Sonogashira cross-coupling reactions under solvent-free conditions. By this method, various aryl halides (iodides, bromides and chlorides) were coupled with olefins, phenylboronic acid and phenyl acetylene to generate the desired products in good to high yields. The catalyst was isolated with the aid of an external magnetic field and reused for five consecutive cycles without any drastic loss of its reactivity. Moreover, the Pd content and morphology of the catalyst remained intact after five times reuse.

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We are thankful to University of Birjand Research

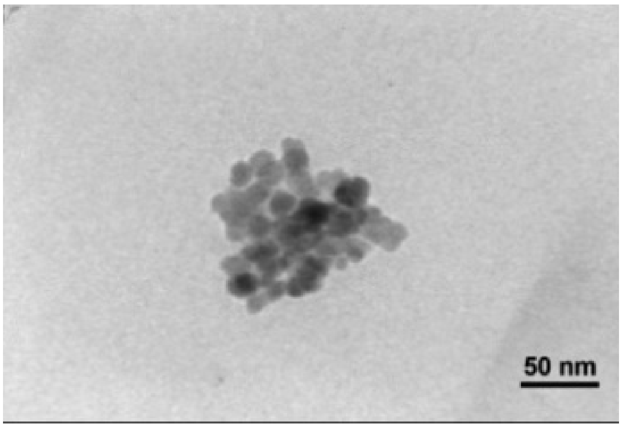

Fig. 9. TEM of Pd-Py-γ-Fe_2O_3 after five times reuse.

Table 5. Catalytic Activity of Pd-Py-γ-Fe_2O_3 in Comparison with other Pd Catalysts Used for Heck, Suzuki and Sonogashira Cross-coupling Reactions

Entry	Reaction	Catalyst (mol%)	Halide	Condition	Time (h)	Yield (%)	Ref.
1	Heck	Pd(0)-NH_2-Fe_3O_4 (5)	I	K_2CO_3, NMP, 130 °C	10	99	[51]
2	Heck	HMMS[a]-NH_2-Pd (4)	I	K_2CO_3, NMP, 130 °C	8	98	[52]
3	Heck	Pd(0)-$ZnFe_2O_4$ (4.62)	I	Et_3N, DMF, 120 °C	3	90	[53]
4	Heck	$PdCl_2$(2.3)/DPPPEG[b] 200(6.0)	I	Solvent-free, Pr_3N, 80 °C	0.08	95	[54]
5	Heck	Pd-Py-γ-Fe_2O_3 (1)	I	Solvent-free, Et_3N, 100 °C	1	92	This work
6	Suzuki	Bis(oxamato)palladate(II) complex[c] (5)	I, Br	Et_3N, *n*-Bu_4NBr, 120 °C	2	78, 65	[55]
7	Suzuki	Pd(0)-$ZnFe_2O_4$ (4.62)	I	K_2CO_3, EtOH, Reflux	4	92	[53]
8	Suzuki	Pd-Py-γ-Fe_2O_3 (2)	I	Solvent-free, Et_3N, 100 °C	1	97	This work
9	Sonogashira	Pd-NH-complexes (7.3)	I	Na_2CO_3, DMF, 50 °C	12	94	[56]
10	Sonogashira	[$PdCl_2(CH_3CN)_2$] (2.5)	Cl	Cs_2CO_3, H_2O/CH_3CN, 100 °C	12	88	[57]
11	Sonogashira	Pd-Py-γ-Fe_2O_3 (2)	I	Solvent-free, Et_3N, 100 °C	1	97	This work

[a]HMMS: hollow magnetic mesoporous sphere. [b]DPPPEG = bis-[diphenylphosphinite] PEG. [c]Bis[oxamato]palladate [II] complex: $[n\text{-}Bu_4N]_2[Pd(2\text{-}Mepma)_2].4H_2O$.

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