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Pd–*S*-methylisothiourea supported on magnetic nanoparticles as an efficient and reusable nanocatalyst for Heck and Suzuki reactions

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ABSTRACT

Supported Pd–*S*-methylisothiourea on magnetic nanoparticles (Pd–SMU-MNPs) as an efficient and magnetically reusable nanocatalyst was prepared and applied for the Heck and Suzuki cross-coupling reactions. All coupling reactions proceeded in short reaction times with good to excellent yields. After completion of reactions, the catalyst was easily separated from the reaction mixture using an external magnetic field and reused for several consecutive runs without significant loss of its catalytic efficiency and activity. This nanomagnetic catalyst was characterized by FT-IR spectroscopy, XRD, VSM, ICP-OES, TEM and SEM techniques. The leaching of the catalyst has been examined by a hot filtration test and ICP-OES analysis.

1. Introduction

Palladium commonly has been applied as one of the powerful metals for C–C coupling reactions [1–3]. Cross-coupling reactions such as Heck and Suzuki reactions were used as significant procedures in modern synthetic organic chemistry for the preparation of natural products, pharmaceuticals, agrochemicals, herbicides, biologically active compounds, UV screens, polymers, hydrocarbons, liquid crystal materials and advanced materials [4–7]. Homogeneous Pd-catalysts have been widely reported in carbon–carbon coupling reactions because of their high catalytic activity [8], while, in the catalytic reactions, separation and reusability of the catalyst is an important factor because of stringent ecological and economical demands for sustainability [9–11]. Therefore, nanoparticles (NPs) have recently emerged as efficient alternatives for the immobilization of homogeneous catalysts [12,13]. Because, by decreasing the support size, the surface area is increased and consequently a semi-homogeneous media is obtained, which can be used as a bridge to improve the gap between homogeneous and heterogeneous catalysts [14]. However, in order to simplify catalyst recovery and reusability of the particles, magnetic nanoparticles (MNPs) have recently emerged in catalyst science, and they can be rapidly isolated from the reaction mixture using an external magnet [15]. More importantly, magnetic separation is more effective and easier than filtration or centrifugation [16]. Among the various magnetic nanoparticles, Fe_3O_4 MNPs have many advantages such as easy preparation, having a high surface-area, low toxicity, and easy availability [17,18]. Therefore, Fe_3O_4 MNPs are considered as ideal support for the heterogenization of homogeneous catalysts [10–13].

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2. Result and discussion

2.1. Catalyst preparation

In continuation of our studies about the application of new catalysts in organic functional group transformations [16,19], herein we report a simple and efficient method for the carbon–carbon cross-coupling reaction in the presence of catalytic amounts of Pd–SMU-MNPs. The Pd–SMU-MNPs were prepared by the concise route that has been outlined in Scheme 1. Initially, naked Fe_3O_4 MNPs were prepared by coprecipitation of iron(II) and iron(III) ions in basic solution at 80 °C [16], followed by modification using (3-chloropropyl)trimethoxysilane (CPTES). Subsequently, *S*-methylisothiourea immobilized on Fe_3O_4 magnetic nanoparticles (SMU-MNPs) via the reaction of Cl–Pr–⊖Si–Fe_3O_4 with a *S*-methylisothiourea hemisulfate salt. Finally, Pd–SMU-MNPs were prepared via coordination of palladium(II) with SMU-MNPs followed by reduction of Pd(II) to Pd(0) by $NaBH_4$. The catalyst has been characterized by scanning electron microscopy (SEM), transmission electron microscopy (TEM), vibrating sample magnetometry (VSM), inductively coupled plasma atomic emission spectroscopy (ICP-OES), X-ray diffraction (XRD) and Fourier transform infrared spectroscopy (FT-IR).

2.2. Catalyst characterization

The morphology and particle size of Pd–SMU-MNPs were evaluated by SEM and TEM analysis. The SEM image shows that these nanoparticles are spherical in shape with an average diameter of 24 ± 3 nm (Fig. 1). Also, TEM images reveal that the diameter of the Pd–SMU-MNPs is 15 ± 3 nm (Fig. 2).

In order to determine the exact amount of palladium in Pd–SMU-MNPs, the ICP-OES technique was performed. The amount of loaded palladium on the Pd–SMU-MNPs was found to be 1.54×10^{-3} mol g^{-1} based on inductively coupled plasma atomic emission spectroscopy (ICP-OES).

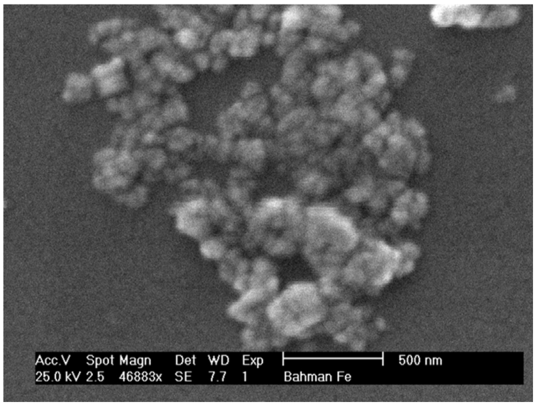
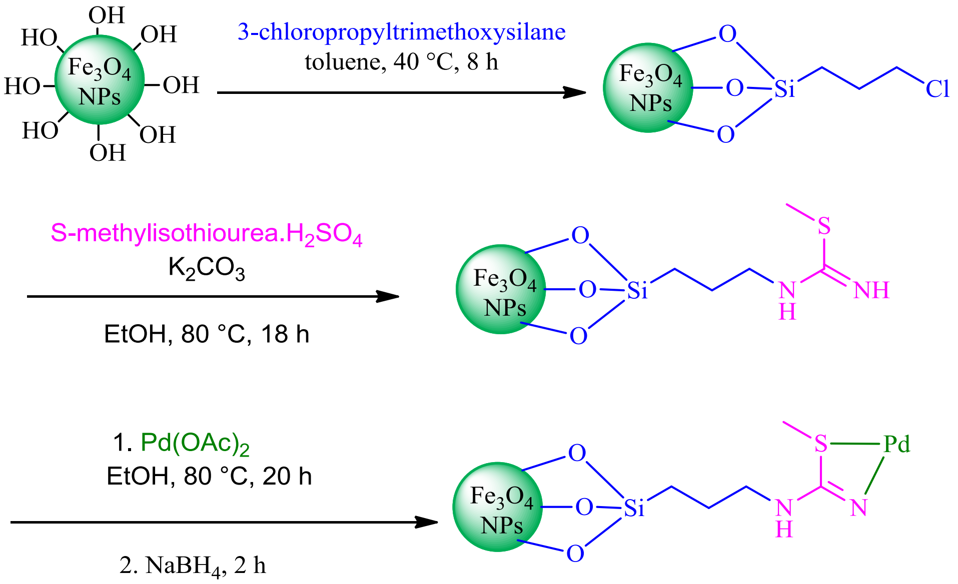


Fig. 1. SEM image of Pd–SMU-MNPs.

The XRD patterns of the Fe_3O_4 nanoparticles and catalyst showed several peaks at 2θ values of 30.5°, 35.8°, 43.6°, 54.3°, 57.5° and 63.2° related to crystal planes in the Fe_3O_4 cubic lattice (Fig. 3). Also the XRD pattern of Pd–SMU-MNPs shows a series of peaks (40.0°, 46.4° and 67.4°), and these results revealed that the surface modification of the Fe_3O_4 nanoparticles didn't destroy their cubic lattice structures [20].

Successful functionalization of the Fe_3O_4 NPs can be inferred from the FT-IR technique. Fig. 4 shows FT-IR spectra of Fe_3O_4, Cl-MNPs, SMU-MNPs and Pd–SMU-MNPs. The FT-IR spectrum for bare Fe_3O_4 shows a stretching vibration at 3390–3440 cm^{-1} from both symmetrical and asymmetrical modes of O–H bonds, which are attached to the surface of MNPs. The presence of Fe_3O_4 was shown in FT-IR by two strong absorption bands around 582



Scheme 1. Preparation process of Pd–SMU-MNPs.

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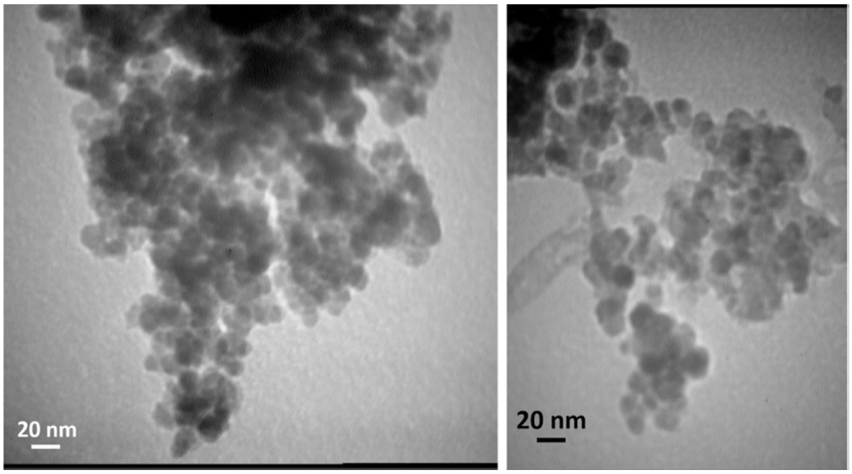

Fig. 2. TEM images of Pd–SMU-MNPs.

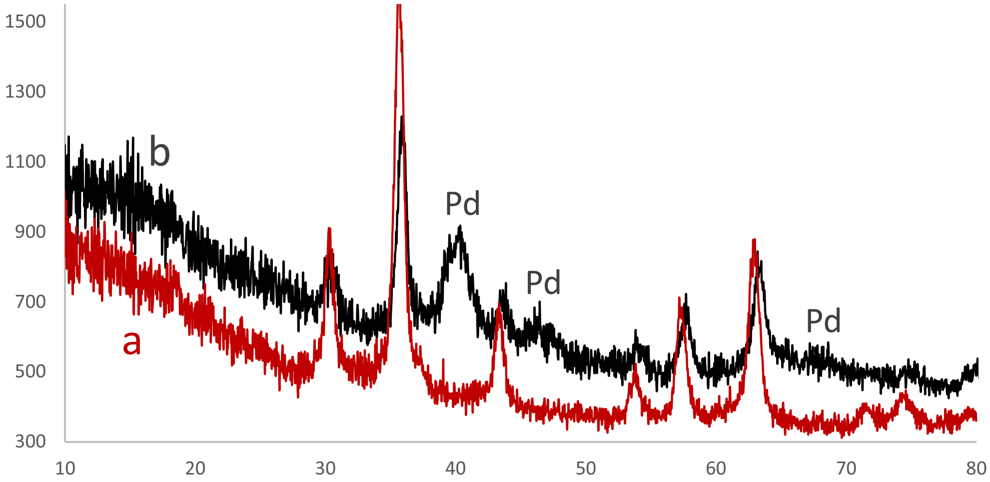

Fig. 3. XRD patterns of Fe_3O_4 nanoparticles (a) and Pd–SMU-MNPs (b).

and 443 cm^{-1}, which corresponds to the Fe–O bond of Fe_3O_4 [13]. The stretching vibrations at 990 cm^{-1} (corresponding to Fe–O–Si bonds) and 1057 and 780 cm^{-1} (related to O–Si bonds) indicate that the silica organic group was successfully coated on the surface of Fe_3O_4 nanocrystals [16,21]. Furthermore, the presence of the anchored organic groups including propyl silane is confirmed by C–H stretching vibrations that appear at 2885 and 2973. Also, in the FT-IR spectrum of SMU-MNPs, the located bands around 1629 cm^{-1} correspond to the C═N stretching vibrations, indicating that Cl of Cl-MNPs has been successfully replaced by *S*-methylisothiourea.

The superparamagnetic properties of particles were measured using the VSM technique. The magnetization curves of Fe_3O_4 MNPs and Pd–SMU-MNPs are shown in Fig. 5. The magnetic measurements show that Pd–SMU-MNPs have a saturated magnetization value of 42 emu g^{-1} and Fe_3O_4 MNPs have a saturated magnetization value of 74 emu g^{-1}. Decreasing the magnetic properties of the Pd–SMU-MNPs (74 → 42 emu g^{-1}), compared with the Fe_3O_4 MNPs is due to the coating of the Fe_3O_4 MNPs by organic layers and a palladium complex.

2.3. *Catalytic study*

In order to study the catalytic activity of Pd–SMU-MNPs, Suzuki reaction has been performed using sodium tetraphenyl borate ($NaBPh_4$) and phenylboronic acid ($PhB(OH)_2$) in the presence of this nanostructural compound (Scheme 2).

In order to optimize the reaction conditions, the effect of various parameters such as temperature, solvent (DMF, DMSO, toluene, water or PEG), bases (Et_3N, KOH, NaOEt or K_2CO_3) and amount of catalyst were examined for the cross-coupling of iodobenzene with $PhB(OH)_2$ (Table 1). We found that the reaction did not proceed in the absence of Pd–SMU-MNPs (Table 1, entry 9). As shown in Table 1, the best results were observed in the presence of 0.006 gr, 0.92 mol % of Pd–SMU-MNPs (Table 1, entry 4). Also, different bases and various solvents have been examined

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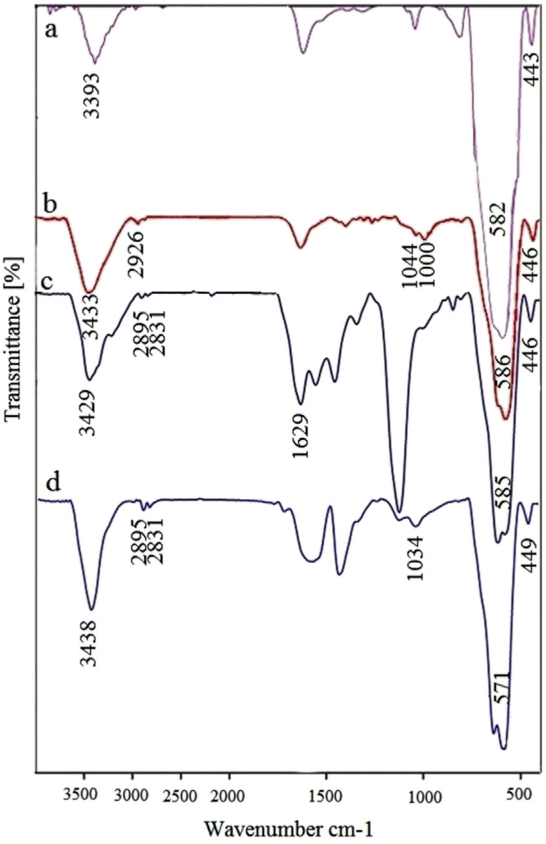
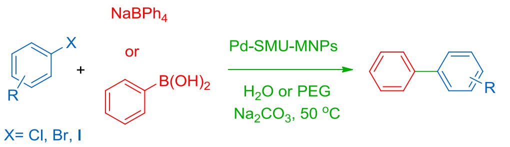


Fig. 4. FT-IR spectra of Fe_3O_4 (a), Cl-MNPs (b), SMU-MNPs (c) and Pd–SMU-MNPs (d).



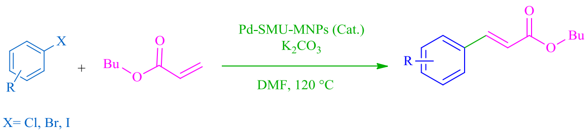
Scheme 2. Pd–SMU-MNPs catalyzed the Suzuki reaction.

and the best results were obtained in H_2O as solvent using 3 mmol of K_2CO_3 at 50 °C.

After optimization conditions, we examined the catalytic activity of Pd–SMU-MNPs for various aryl halides and the results are summarized in Table 2. In this study, various aryl iodides (Table 2, entries 1–3), bromides (Table 2, entries 4–10) and chlorides (Table 2, entries 11–13) were reacted with phenylboronic acid efficiently. All products were obtained in good yields. Therefore, this methodology is an efficient protocol for the cross-coupling a wide range of aryl halide including Cl, Br and I.

Also, the same reaction conditions have been applied for the cross-coupling of aryl halides with $NaBPh_4$ in the presence of Pd–SMU-MNPs (Table 2, entries 14–24). Aryl halides including electron-neutral, electron-rich and electron-poor substituents reacted with $NaBPh_4$ to produce the corresponding biphenyl in good to excellent yields (88–99% yield of products).

Also, we examined the catalytic activity of Pd–SMU-MNPs in the Heck reaction (Scheme 3). In order to find out the best reaction conditions, the coupling reaction of iodobenzene with butyl acrylate was selected as the model reaction (Table 3). The reaction conditions, such as the solvent (Table 3, entries 1–5), base (Table 3, entries 6–9), and amount of catalyst (Table 3, entries 9–13), were optimized in this model reaction (Table 3). Also, the effect of



Scheme 3. Pd–SMU-MNPs catalyzed the Heck reaction.

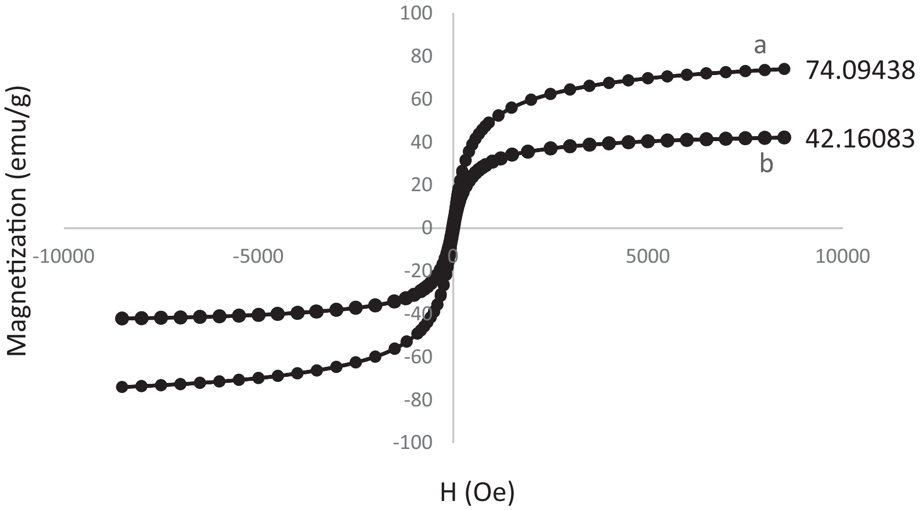


Fig. 5. Magnetization curves of Fe_3O_4 (a) and Pd–SMU-MNPs (b) at room temperature.

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Table 1
Optimization of reaction conditions for the C–C coupling reaction of iodobenzene (1 mmol) with phenylboronic acid (1 mmol) in the presence of Pd–SMU-MNPs.

Entry	Solvent (2 mL)	Base (3 mmol)	Catalyst (g)	Temperature (°C)	Time (min)	Yield %[a]
1	DMSO	K_2CO_3	0.006 (0.92 mol %)	50	25	91
2	DMF	K_2CO_3	0.006 (0.92 mol %)	50	25	95
3	Toluene	K_2CO_3	0.006 (0.92 mol %)	50	30	43
4	H_2O	K_2CO_3	0.006 (0.92 mol %)	50	30	96
5	PEG	K_2CO_3	0.006 (0.92 mol %)	50	30	97
6	H_2O	$(Et)_3N$	0.006 (0.92 mol %)	50	30	56
7	H_2O	KOH	0.006 (0.92 mol %)	50	30	61
8	H_2O	NaOEt	0.006 (0.92 mol %)	50	30	18
9	H_2O	K_2CO_3	–	50	600	–[b]
10	H_2O	K_2CO_3	0.002 (0.31 mol %)	50	30	37
11	H_2O	K_2CO_3	0.003 (0.46 mol %)	50	30	49
12	H_2O	K_2CO_3	0.005 (0.75 mol %)	50	30	68
13	H_2O	K_2CO_3	0.006 (0.92 mol %)	40	30	55
14	H_2O	K_2CO_3	0.006 (0.92 mol %)	r.t.	100	34

[a] Isolated yields.
[b] No reaction.

Table 2
C–C Coupling reaction of aryl halides (1 mmol) using $PhB(OH)_2$ (1 mmol) or $NaBPh_4$ (0.5 mmol) in the presence of Pd–SMU-MNPs (0.006 g, 0.92 mol %).

Entry	Aryl halide	Phenylating reagent	Time (min)	Yield (%)[a]	Melting point (°C) [Ref.]
1	Iodobenzene	Phenylboronic acid	30	96	62–65 [22]
2	4-Iodotoluene	Phenylboronic acid	60	94	42–44 [22]
3	2-Iodotoluene	Phenylboronic acid	300	90	Oil [23]
4	4-Bromonitrobenzene	Phenylboronic acid	20	99	115–117 [24]
5	4-Bromochlorobenzene	Phenylboronic acid	90	95	70–72 [23]
6	4-Bromobenzonitrile	Phenylboronic acid	60	96	82–84 [23]
7	Bromobenzene	Phenylboronic acid	40	91[b]	64–66 [22]
8	4-Bromotoluene	Phenylboronic acid	40	92[b]	42–44 [22]
9	4-Bromophenol	Phenylboronic acid	40	92[b]	161–163 [23]
10	4-Bromobenzaldehyde	Phenylboronic acid	70	88	55–57 [25]
11	4-Chloronitrobenzene	Phenylboronic acid	100	90[b,c]	115–116 [24]
12	Chlorobenzene	Phenylboronic acid	125	89[b,c]	63–66 [22]
13	4-Chlorobenzonitrile	Phenylboronic acid	140	92[b,c]	82–84 [23]
14	Iodobenzene	Sodium tetraphenyl borate	30	97	64–66 [22]
15	4-Iodotoluene	Sodium tetraphenyl borate	45	94	43–44 [22]
16	2-Iodotoluene	Sodium tetraphenyl borate	280	91	Oil [23]
17	4-Bromonitrobenzene	Sodium tetraphenyl borate	40	98	116–117 [24]
18	4-Bromochlorobenzene	Sodium tetraphenyl borate	20	99	70–72 [23]
19	4-Bromobenzonitrile	Sodium tetraphenyl borate	60	90	82–85 [23]
20	4-Bromophenol	Sodium tetraphenyl borate	60	90	161–163 [23]
21	4-Bromobenzaldehyde	Sodium tetraphenyl borate	100	89	56–58 [25]
22	4-Chloronitrobenzene	Sodium tetraphenyl borate	90	93[b,c]	115–117 [24]
23	Chlorobenzene	Sodium tetraphenyl borate	140	90[b,c]	62–65 [22]
24	4-Chlorobenzonitrile	Sodium tetraphenyl borate	170	93[b,c]	82–85 [23]

[a] Isolated yield.
[b] PEG used as the solvent.
[c] Pd–SMU-MNPs was 8 mg, 1.2 mol %.

temperature (Table 3, entries 12–15) was examined. As shown in Table 3, the best conditions were obtained in the presence of Pd–SMU-MNPs (8 mg, 1.2 mol %) in DMF using K_2CO_3 at 120 °C (Table 3, entry 2).

This optimized reaction conditions was then applied for the cross-coupling of different aryl halides including iodides (Table 4, entries 1–5), bromides (Table 4, entries 6–9) and chlorides (Table 4, entries 10–12) in the presence of Pd–SMU-MNPs and all products were obtained in good yield (91–97%). The reaction of various aryl halides (including electron-donating and electron-withdrawing groups) with butyl acrylate was investigated to confirm the generality of the present methodology.

2.4. *Recyclability of the catalyst*

The reusability of catalysts is an important advantage from an industrial point of view. Therefore, the recovery and recyclability of Pd–SMU-MNPs were examined in the coupling reaction of iodobenzene with phenylboronic acid. After completion of the reaction, the catalyst was rapidly isolated from the reaction mixture by magnetic decantation and washed with diethyl ether to remove residual organic materials. Then, the reaction vessel was charged with fresh substrates and subjected to the next run. As shown in Fig. 6, the catalyst can be reused over eight times without any significant loss of its catalytic activity or

Table 3
Optimization of reaction conditions for the C–C coupling reaction of iodobenzene (1 mmol) with butyl acrylate (1.2 mmol) in the presence of Pd–SMU-MNPs.

Entry	Solvent (2 mL)	Base (3 mmol)	Catalyst (g)	Temperature (°C)	Time (min)	Yield %[a]
1	DMSO	K_2CO_3	0.008 (1.2 mol %)	120	90	30
2	DMF	K_2CO_3	0.008 (1.2 mol %)	120	90	95
3	Toluene	K_2CO_3	0.008 (1.2 mol %)	120	90	15
4	DMSO:H_2O	K_2CO_3	0.008 (1.2 mol %)	120	90	45
5	PEG	K_2CO_3	0.008 (1.2 mol %)	120	90	60
6	DMF	$(Et)_3N$	0.008 (1.2 mol %)	120	90	65
7	DMF	KOH	0.008 (1.2 mol %)	120	90	30
8	DMF	NaOEt	0.008 (1.2 mol %)	120	90	Trace
9	DMF	K_2CO_3	–	120	1200	–[b]
10	DMF	K_2CO_3	0.004 (0.6 mol %)	120	90	35
11	DMF	K_2CO_3	0.005 (0.75 mol %)	120	90	60
12	DMF	K_2CO_3	0.007 (1.05 mol %)	120	90	70
13	DMF	K_2CO_3	0.008 (1.2 mol %)	60	90	25
14	DMF	K_2CO_3	0.008 (1.2 mol %)	80	90	55
15	DMF	K_2CO_3	0.008 (1.2 mol %)	100	90	70

[a] Isolated yield.
[b] No reaction.

Table 4
Cross-coupling of aryl halides (1 mmol) with butyl acrylate (1.2 mmol) (Heck reaction) in the presence of catalytic amounts of Pd–SMU-MNPs (8 mg, 1.2 mol %).

Entry	Aryl halide	Time (min)	Yield (%)[a]	Melting point (°C) [Ref.]
1	Iodobenzene	90	96	Oil [23]
2	4-Iodotoluene	120	95	Oil [23]
3	2-Iodotoluene	350	91	Oil [23]
4	4-Iodoanisole	90	93	Oil [23]
5	2-Iodoanisole	450	92	Oil [26]
6	4-Bromonitrobenzene	90	97	60–62 [23]
7	4-Bromochlorobenzene	720	91	Oil [27]
8	4-Bromobenzonitrile	75	95	40–42 [27]
9	Bromobenzene	80	95	Oil [23]
10	Chlorobenzene	300	93	Oil [23]
11	4-Chlorobenzonitrile	420	90	39–42 [27]
12	4-Chloronitrobenzene	330	91	60–63 [23]

[a] Isolated yields.

palladium leaching. The average isolated yield for eight runs was 94.5%, which clearly proved the practical recyclability of this catalyst.

In order to show that Pd–SMU-MNPs act heterogeneously in the reaction media, a hot filtration test was performed in the coupling reaction of iodobenzene with butyl acrylate. In this study, we obtained the yield of product in the half time of the reaction that was 63%. Then the reaction was repeated and in half time of the reaction, the catalyst separated and allowed the filtrate to react further. The yield of reaction in this stage was 64% confirming that the Pd–SMU-MNPs act heterogeneously in the reaction media.

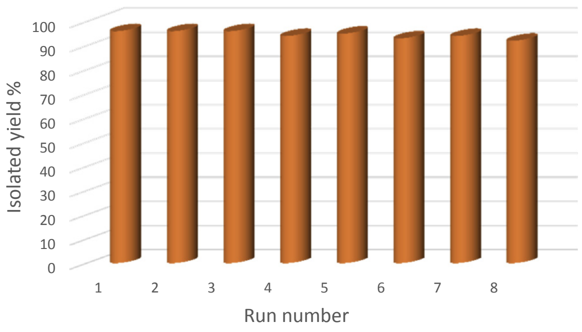

Fig. 6. Recyclability of Pd–SMU-MNPs in the coupling of iodobenzene with phenylboronic acid.

Also, to determine the exact leaching of palladium in the catalyst, the amount of Pd in Pd–SMU-MNPs was determined by ICP-OES after six times recycling. The amount of Pd in the recovered catalyst was found to be 1.49×10^{-3} mol g^{-1} based on ICP-OES. Therefore the amount of Pd in the catalyst after six times recovery is comparable with the fresh catalyst (1.54×10^{-3} mol g^{-1} for fresh Pd–SMU-MNPs). Therefore, only 3% leaching of palladium from the catalyst was observed after six runs. The results from the hot filtration test and ICP-OES technique showed that leaching of palladium during the reaction is negligible.

Also, in order to determine leaching of palladium in the reaction mixture, the Suzuki reaction through the coupling of iodobenzene with phenylboronic acid was performed and the obtained biphenyl has been characterized by ICP-OES to detect amounts of palladium in products. Interestingly, in this analysis even trace amounts of palladium weren't observed in the biphenyl product.

2.5. *Comparison of the catalyst with previously reported ones*

In order to examine the efficiency of the described procedure, we compared the results of the coupling of iodobenzene with phenylboronic acid with those of the previously reported procedures in the literature (Table 5). This catalyst showed a shorter reaction time and higher reaction yield than the other catalysts. Also Pd–SMU-MNPs are superior in terms of price, bio-compatibility, stability and easy separation than the previously reported works. In addition, the recoverability and recyclability of Pd–SMU-MNPs is more rapid and easier than the other catalysts. As is evident Pd–SMU-MNPs (in this work) have many

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Table 5
Comparison results of Pd–SMU-MNPs with other catalysts for the coupling of iodobenzene with phenylboronic acid.

Entry	Catalyst (mol % of Pd)	Size of catalyst (nm)	Condition	Temperature (°C)	Time (min)	Yield (%)[a]	TON	TOF (h^{-1})	Ref.
1	NHC–Pd(II) complex (1.0 mol %)	–	THF, Cs_2CO_3	80 °C	12 h	88	88	7.33	[28]
2	Pd NP (1.0 mol %)	2.5–14	H_2O, KOH	100 °C	12 h	95	95	7.92	[29]
3	CA/Pd(0) (0.5–2.0 mol %)	3.2 ± 0.4	H_2O, K_2CO_3	100 °C	120	94	188	47	[30]
4	Pd/Au NPs (4.0 mol %)	80	EtOH/H_2O, K_2CO_3	80 °C	24 h	88	22	0.92	[31]
5	Pd(II)–NHC complex (1 mol %)	–	DMF, Cs_2CO_3	100 °C	24 h	99	99	4.12	[32]
6	*N*,*N′*-Bis(2-pyridinecarboxamide)-1,2-benzene palladium complex (1 mol %)	10–20	H_2O, K_2CO_3	100 °C	180	97	97	32.33	[33]
7	Pd-MPTAT-1 (0.02 g)	50	NaOH, DMF: H_2O (1:5)	85 °C	8 h	95	–	–	[34]
8	LDH-Pd(0) (0.3 g)	6–10	K_2CO_3, 1,4-dioxane: H_2O (5:1)	80 °C	10 h	96	–	–	[35]
9	PANI-Pd (2.2 mol %)	150–300	K_2CO_3, 1,4-dioxane: H_2O (1:1)	95 °C	240	91	41.36	10.34	[36]
10	Pd–SMU-MNPs (0.006 mg, 0.92 mol %)	15 ± 3	H_2O, K_2CO_3	50 °C	30	96	104	208	This work

[a] Isolated yield.

advantages such as a low reaction time, high number of TNO and TOF, high yield of products, reacting at low temperature and use of water as the solvent.

3. Experimental

3.1. Preparation of the catalyst

The Fe_3O_4 MNPs were synthesized according to our recently reported procedure via a chemical coprecipitation technique using $FeCl_3 \cdot 6H_2O$ and $FeCl_2 \cdot 6H_2O$ in basic solution at 80 °C [23]. The obtained Fe_3O_4 nanoparticles (1.5 g) was dispersed in 50 mL toluene by sonication for 30 min, then 2.5 mL of (3-choloropropyl)triethoxysilane (CPTES) was added to the mixture. The reaction mixture was stirred under a N_2 atmosphere at 40 °C for 8 h. Then, the prepared nanoparticles (Cl–MNPs) were washed with ethanol, separated by magnetic decantation and dried at room temperature. In the next step, the obtained Cl-MNPs (1 g) were dispersed in 50 mL ethanol for 20 min, then *S*-methylisothiourea hemisulfate salt (2.5 mmol) and potassium carbonate (2.5 mmol) were added to the reaction mixture and stirred for 24 h at 80 °C under a N_2 atmosphere. Then, the resulting nanoparticles (SMU-MNPs) were washed with ethanol and separated using magnetic decantation and dried at room temperature. The obtained SMU-MNPs (1 g) were dispersed in 25 mL ethanol by sonication for 20 min; subsequently, palladium acetate (0.5 g, 1.95×10^{-3} mol) was added to the reaction mixture. The reaction mixture was stirred at 80 °C for 20 h. Then, $NaBH_4$ (0.5 mmol) was added to the reaction mixture and it was continued for two more hours. The final product (Pd–SMU-MNPs) was separated by magnetic decantation, washed with ethanol and dried at room temperature.

3.2. General procedure for the Suzuki reaction

A mixture of aryl halide (1 mmol), phenylboronic acid (1 mmol) or sodium tetraphenyl borate (0.5 mmol), K_2CO_3 (3 mmol), and Pd–SMU-MNPs (0.006 g, 0.92 mol %) was added to a reaction vessel. The resulting mixture was stirred in H_2O or PEG-400 at 50 °C and the progress of the reaction was monitored by TLC. After completion of the reaction, the catalyst was separated by an external magnet and washed with ethylacetate. The reaction mixture was extracted with H_2O and ethylacetate and the organic layer was 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.

3.3. General procedure for the Heck reaction

A mixture of aryl halide (1 mmol), *n*-butyl acrylate (1.2 mmol), K_2CO_3 (3 mmol), and Pd–SMU-MNPs (0.008 g, 1.2 mol %) was stirred in DMF at 120 °C (the progress of the reaction was monitored by TLC). After completion of the reaction, the mixture was cooled down to room temperature and the catalyst was separated by an external magnet, washed with diethyl ether and the reaction mixture was extracted with H_2O and diethyl ether. The organic layer was dried over Na_2SO_4 (1.5 g); the solvent evaporated and pure products were obtained in 81–98% yields.

3.4. Selected spectral data

3.4.1. 1,1′-Biphenyl

^{1}H NMR (400 MHz, $CDCl_3$): $\delta_H = 7.66–7.64$ (m, 4H), 7.52–7.41 (m, 4H), 7.42–7.38 (tt, $J = 7.6$, 1.2 Hz, 2H) ppm.

3.4.2. [1,1′-Biphenyl]-4-carbonitrile

^{1}H NMR (400 MHz, $CDCl_3$): $\delta_H = 7.79–7.76$ (m, 2H), 7.74–7.71 (m, 2H), 7.65–7.62 (m, 2H), 7.55–7.51 (m, 2H), 7.49–7.45 (m, 1H) ppm.

3.4.3. 4-Chloro-1,1′-biphenyl

^{1}H NMR (400 MHz, $CDCl_3$): $\delta_H = 7.61–7.59$ (m, 2H), 7.58–7.55 (m, 2H), 7.51–7.44 (m, 4H), 7.43–7.39 (tt, $J = 6$, 1.6 Hz, 1H) ppm.

3.4.4. Butyl cinnamate

^{1}H NMR (400 MHz, $CDCl_3$): $\delta_H = 7.75–7.71$ (d, $J = 16$ Hz, 1H), 7.58–7.56 (m, 2H), 7.44–7.41 (m, 3H), 6.55–6.47 (d,

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J = 16 Hz, 1H), 4.27–4.24 (t, J = 6.4 Hz, 2H), 1.77–1.71 (m, 2H), 1.51–1.46 (m, 2H), 1.03–0.99 (t, J = 7.6 Hz, 3H) ppm.

3.4.5. *Butyl 3-(p-tolyl)acrylate*

^{1}H NMR (400 MHz, $CDCl_3$): δ_H = 7.72–7.68 (d, J = 16 Hz, 1H), 7.48–7.46 (d, J = 8 Hz, 2H), 7.24–7.22 (d, J = 8 Hz, 2H), 6.46–6.42 (d, J = 16 Hz, 1H), 4.26–4.23 (t, J = 13.2 Hz, 2H), 2.42 (s, 3H), 1.77–1.70 (quint, J = 6.4 Hz, 2H), 1.51–1.45 (sixt, J = 7.6 Hz, 2H), 1.03–0.99 (t, J = 7.6 Hz, 3H) ppm.

3.4.6. *Butyl 3-(4-methoxyphenyl)acrylate*

^{1}H NMR (400 MHz, $CDCl_3$): δ_H = 7.69–7.65 (d, J = 15.6 Hz, 1H), 7.52–7.50 (d, J = 6.8 Hz, 2H), 6.94–6.93 (d, J = 7.2 Hz, 2H), 6.37–6.33 (d, J = 16 Hz, 1H), 4.25–4.22 (t, J = 6.4 Hz, 2H), 3.86 (s, 3H), 1.74–1.68 (quint, J = 6.8 Hz, 2H), 1.52–1.43 (sixt, J = 8 Hz, 2H), 1.02–0.98 (t, J = 7.6 Hz, 3H) ppm.

4. Conclusion

In conclusion, an efficient heterogeneous nanocatalyst (Pd–SMU-MNPs) was synthesized by immobilization of palladium on modified Fe_3O_4 nanoparticles. This catalyst was characterized by FT-IR, SEM, TEM, XRD, VSM and ICP-OES techniques. The Pd–SMU-MNPs exhibit an excellent catalytic activity, high reusability and air or moisture stability for the Suzuki and Heck reactions. This methodology is effective for a wide range of aryl halide including Cl, Br and I. Also, the catalyst can be recovered and recycled over eight times and used without any significant loss of its activity or palladium leaching.

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