Journal of Molecular Catalysis A: Chemical 385 (2014) 61–67

Contents lists available at ScienceDirect

Journal of Molecular Catalysis A: Chemical

journal homepage: www.elsevier.com/locate/molcata

Functionalization of fullerene (C_{60}) with metformine to immobilized palladium as a novel heterogeneous and reusable nanocatalyst in the Suzuki–Miyaura coupling reaction at room temperature

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ARTICLE INFO

Article history:
Received 19 November 2013
Received in revised form 8 January 2014
Accepted 10 January 2014
Available online 22 January 2014

Keywords:
Biguanide-functionalized C_{60}
Metformine
Pd catalyst
Suzuki–Miyaura coupling

ABSTRACT

Pd supported on biguanide(metformine)-functionalized fullerene (C_{60}-Met/Pd^{2+}) hybrid materials was fabricated for the first time. The catalyst prepared was characterized by X-ray diffraction spectroscopy (XRD), Fourier transform infrared (FT-IR), thermogravimetric analysis (TGA), and transmission electron microscopy (TEM). The catalyst showed excellent activity Suzuki–Miyaura coupling reaction of different aryl iodides and bromides with phenylboronic acid at room temperature in the EtOH:H_2O (1:1) mixture as solvent. The yields of the products were in the range from 85% to 98%. The catalyst can be readily recovered and reused at least 6 consecutive cycles without significant loss in its catalytic activity. This is the new example for the development of fullerene (C_{60}-Met-Pd) complexes which can be used as efficient recyclable catalysts without palladium leaching.

1. Introduction

Fullerenes, the new molecular allotrope of carbon, were discovered in 1985 by H. W. Kroto, R. F. Curl and R. E. Smalley [1], who were awarded the Nobel Prize in Chemistry in 1996 due to this seminal scientific finding. The novel and promising fullerene (C_{60})-based carbon nanomaterial has attracted tremendous attentions over the recent years due to its exceptional properties, such as excellent mechanical, thermal, optical, high specific surface area, electronic, structural properties and also their promising preliminary biological activities, such as DNA photocleavage, HIV-protease (HIV-P) inhibition, neuroprotection and apoptosis [2–5]. The chemical versatility and tunability combined with solution processability make fullerene-based materials attractive for a wide range of applications in many field including catalysis, drug delivery, bioimaging, adsorption, electronic and photonic devices [6–10]. Since its large specific surface area and the large delocalized π-electron system of fullerene-related material can form strong hydrophobic and π-stacking interactions with organic molecules, it might be a promising candidate for a catalyst or a catalyst support. However, the development of covalent chemistry of C_{60} has opened the possibility to attach this spherical structure with several groups, which allows increment in the material science.

Recently, immobilization of Pd nanoparticles on solid supports have received considerable attention as a new generation of heterogeneous catalysts in various scientific fields because of their superior catalytic performance, good stability, ease of separation and satisfactory reusability in comparison to the traditional homogeneous $Pd(OAc)_2$, $PdCl_2$ catalysts [11–17]. However, the catalytic activity of Pd^{2+}-supported decrease gradually when the catalyst was used repeatedly. This could be ascribed to the weak interaction between palladium and the support material, as well as the agglomeration and accumulation of Pd nanoparticles on the surface of the material [18,19]. Therefore, it is desirable to improve the stability, recyclability, and catalytic activity of heterogeneous Pd nanocatalysts. Owing to these interests and also as a part of our ongoing research program on the application of catalysts for the development of useful new synthetic methodologies [20], herein, we report the synthesis of a heterogeneous palladium nanocatalyst supported on metformine-grafted-fullerene (C_{60}-Met/Pd(II)) and its catalytic activity of the catalyst prepared was investigated by employing Suzuki–Miyaura coupling reaction as a model reaction. The result showed that the new catalyst retains the reactivity characteristic of a homogeneous

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http://dx.doi.org/10.1016/j.molcata.2014.01.007

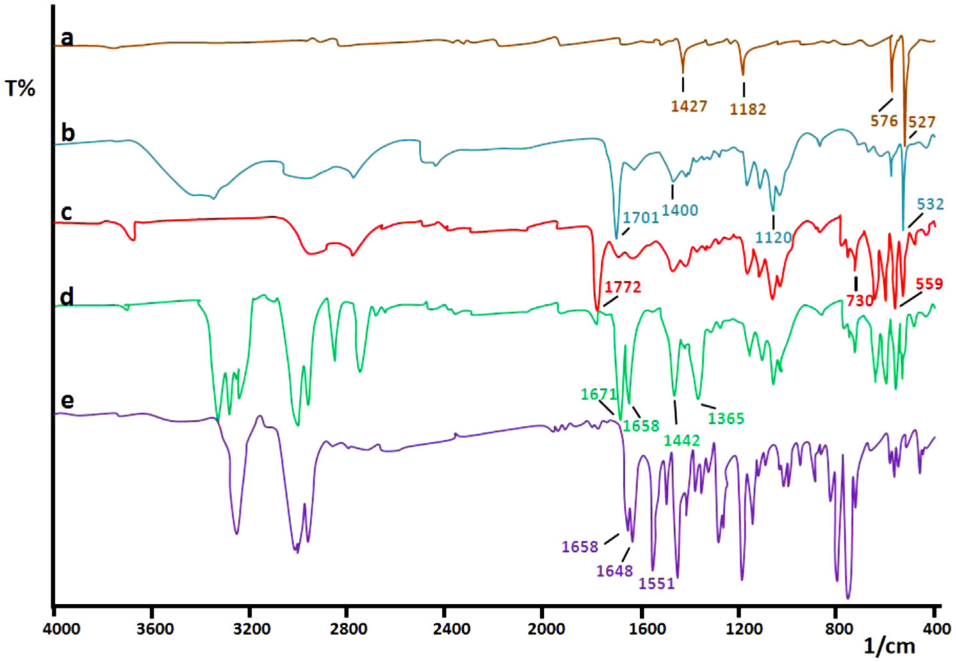


Fig. 1. FTIR spectra of (a) C_{60}, (b) C_{60}-COOH, (c) C_{60}-COCl, (d) C_{60}-CO-Met, and (e) C_{60}-CO-Met/Pd(II).

catalyst but at the same time it was easy to separate off and reuse.

2. Experimental

2.1. Materials

All the reagents were purchased from Aldrich and Merck used without any purification. The pure fullerene without functional groups was purchased from Petrol Co. (Tehran, Iran) (Fig. 1). $SOCl_2$, HCl, H_2SO_4, HNO_3, deionized water, anhydrous dimethyl formamide (DMF), CaH_2, and metformin hydrochloride were obtained from Sigma–Aldrich and Merck.

2.2. Preparation of free metformin

1.65 g of metformin hydrochloride (10 mmol) and 0.40 g of NaOH (10 mmol) were added to 100 ml of ethanol and the resulting suspension was stirred for 5 h. Then, the suspension was filtered and ethanol was removed with rotary evaporation leading to free metformine in 99% yield. The obtained free metformin was freshly used in the next experiments.

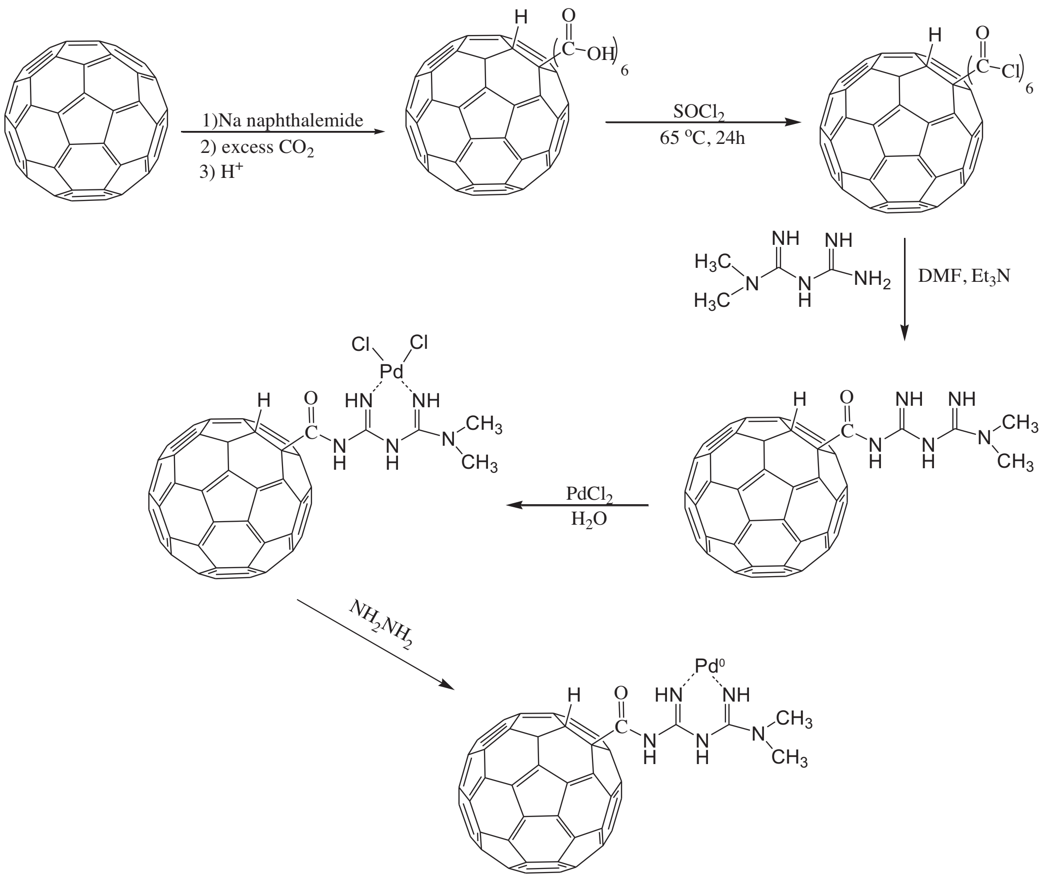
2.3. Covalent grafting of metformine to C_{60}

Hexa(carboxyl)fullerene was synthesized following a well-known procedure [22–24]. C_{60} (400 mg, 0.556 mmol) was added to dry degassed 1,2-dimethoxyethane (DME) (250 mL). After stirring for 6 h, sodium naphthalenide (11.5 mmol) in DME (50 mL) was added and stirred until the color of this mixture was changed from dark green to dark brown. Purified carbon dioxide gas was then introduced into the reaction container continuously, accompanied by vigorous stirring for 3 days, to afford a brown suspension. The precipitates were separated from solution by the centrifugation. They were then dissolved in DMF, and the insoluble side products and unreacted C_{60} were separated from the DMF solution by centrifugation. The dark brown sodium salt solution was added dropwise to 4 M HCl with vigorous stirring to induce the precipitation of a chestnut brown product. The precipitates were then separated from solution by centrifugation. The solid products were then washed with a limited amount of deionized water and centrifuged several times to remove residual HCl until this product started to dissolve. The yield of chestnut brown solid of C_{60}-$(COOH)_6$ was 56%. It is soluble in water and other polar organic solvents, such as DMF, DMSO, THF. The carboxylated C_{60} (C_{60}-$(COOH)_6$) thus obtained were dried at 60 °C for 1 day under reduced pressure and reacted with excess of $SOCl_2$ at room temperature for 24 h. The product (fullerene having carbonyl chloride, (C_{60}-$COCl)_6$) was purified by centrifugation and subsequently washed with THF, which was then dried at 50 °C for 12 h. The final product was then subjected to functionalization with metformine. Free metformine (metformine-to-fullerene weight ratio was 10:1) were mixed with 1 mL solution of DMF and Et_3N (1 mL) and then stirred for 1 h. The obtained acyl chloride fullerene in 20 mL DMF was then added to the suspension. The reaction mixture was kept at 120 °C for 3 days. The solid was then separated by filtration and washed with CH_2Cl_2 and deionized water for several times and dried in vacuum.

2.4. Preparation of C_{60}-Met/Pd^{2+} and C_{60}-Met/Pd^0 nanocatalysts

The C_{60}-Met (1 g) was dispersed in 30 mL deionized water by sonication for 10 min and a aqueous solution of $PdCl_2$ (10 mL, 0.7 mmol) was added to dispersion of C_{60}-Met. The mixture was stirred for 24 h in room temperature to complete attainment of coordination. Thus yielded C_{60}-Met/Pd^{2+} nanocatalyst was subjected to centrifugation, washed with deionized water and dried in vacuum at 40 °C for 12 h. The overall synthesis of C_{60}-Met/Pd^{2+} nanocatalyst is schematically demonstrated in Scheme 1.

The reduction of C_{60}-Met/Pd^{2+} by hydrazine hydrate was performed as follows: 30 mg of C_{60}-Met/Pd^{2+} was dispersed in 60 mL of water, and then 100 μL of hydrazine hydrate (80%) was added. The pH of the mixture was adjusted to 10 with 25% ammonium hydroxide and the reaction was carried out at 95 °C for 2 h. The final product C_{60}-Met/Pd^0 was washed with water and dried in vacuum at 50 °C. Scheme 1 depicted the synthetic procedure of C_{60}-Met/Pd^{2+} and C_{60}-Met/Pd^0. The concentration of palladium in



Scheme 1. Schematic diagram of C_{60}-Met/Pd(II) and C_{60}-Met/Pd(0) fabrication.

C_{60}-Met/Pd^{2+} and C_{60}-Met/Pd^{0} were 18 and 16 wt.%, respectively, which were determined by ICP-AES and TGA.

2.5. Catalytic activity

2.5.1. Suzuki–Miyaura coupling reaction

In a typical reaction, 10 mg of the catalyst (1 mol%) was placed in a 25 mL Schlenk tube, 1 mmol of the aryl halide in 5 mL of water/ethanol (1:1) was added 0.134 g (1.2 mmol) of phenyl boronic acid, 0.276 mg of K_2CO_3 (2 mmol). The mixture was then stirred for the desired time at room temperature. The reaction was monitored by thin layer chromatography (TLC). After completion of reaction, the catalyst was recovered by centrifuge and washed with ethyl acetate and ethanol. The combined organic layer was dried over anhydrous sodium sulfate and evaporated in a rotary evaporator under reduced pressure. The crude product was purified by column chromatography.

3. Results and discussion

3.1. Catalyst characterization

The synthesis of metformine-functionalized fullerene anchored palladium catalyst consists in: (i) surface modification of fullerene with nitric acid and sulfuric acid to introduce carboxyl group (ii) conversion of the surface carboxylic acid groups into acid chloride groups by reaction with thionyl chloride, (iii) attachment of metformine to the fullerene surface through reaction with the acid chloride groups and (iv) complexation of the metformine ligand to Pd by reaction with palladium chloride and then reduction with hydrazine hydrate and ammonium hydroxide (Scheme 1). The metformine-functionalized fullerene anchored palladium(II) complex (C_{60}-Met/Pd^{2+}) was conveniently synthesized from commercially available and cheap materials via immobilization on fullerene. The pathways of C_{60}-Met/Pd^{2+} fabrication are shown in Scheme 1.

The surface structure of the materials was confirmed using Fourier transform infrared (FTIR) spectroscopy. Fig. 1 shows the FT-IR spectra obtained for (a) C_{60}, (b) C_{60}-COOH, (c) C_{60}-COCl, (d) C_{60}-CO-Met, (e) C_{60}-CO-Met/Pd(II). Comparison of the FT-IR spectra of C_{60}-COOH (curve b) with C_{60} (curve a), a new band (1701 cm^{-1}) appeared in C_{60}-COOH due to C=O stretching vibration of the carboxylic acid group, which indicated the carboxylic derivative of C_{60} was prepared successfully. The converting of the carboxylic acid groups (C_{60}-COOH) into the acyl chloride intermediate (C_{60}-COCl) by treatment with thionyl chloride was confirmed by the appearance of peak near 1778 cm^{-1} stretching in curve c. Curve d shows the spectrum of C_{60}-Met and the absorption band at 1658 cm^{-1} was attributed to the carbonyl stretching of the amide groups (—CONH—). Also, the band in the spectral region of 1671 cm^{-1} can be assigned to the imine (C=NH) bond of the attached metformine. These results indicated that the metformine was bonded to the surface of fullerene through amidation reaction. The signals appeared at 1671 and 1658 cm^{-1} in curve **d** for the metal-ligand co-ordination [25,26] presumably leads to a shift of these two peaks to lower frequencies (1671–1658 cm^{-1}). This shift can be observed comparing curve **e**. These peaks at curves **d** and **e** displayed the successful attachment of metformine organic ligands and subsequent coordination of Pd^{2+} ions within the hybride material.

Transmission electron microscopy (TEM) investigations are carried out to observe the morphology and distribution of palladium

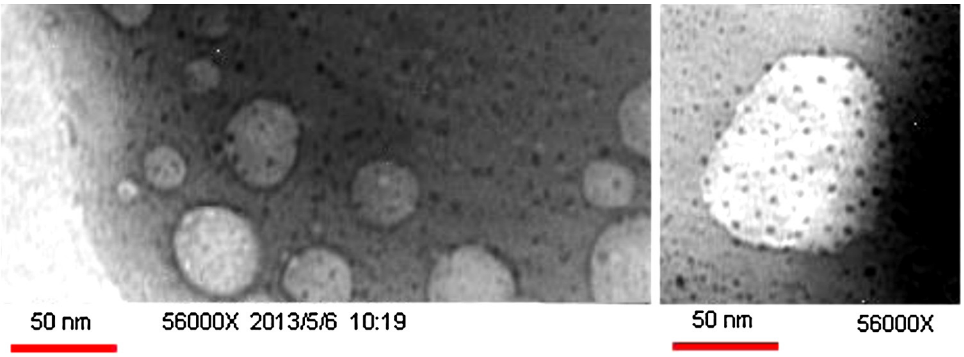


Fig. 2. TEM images of C_{60}-Met/Pd.

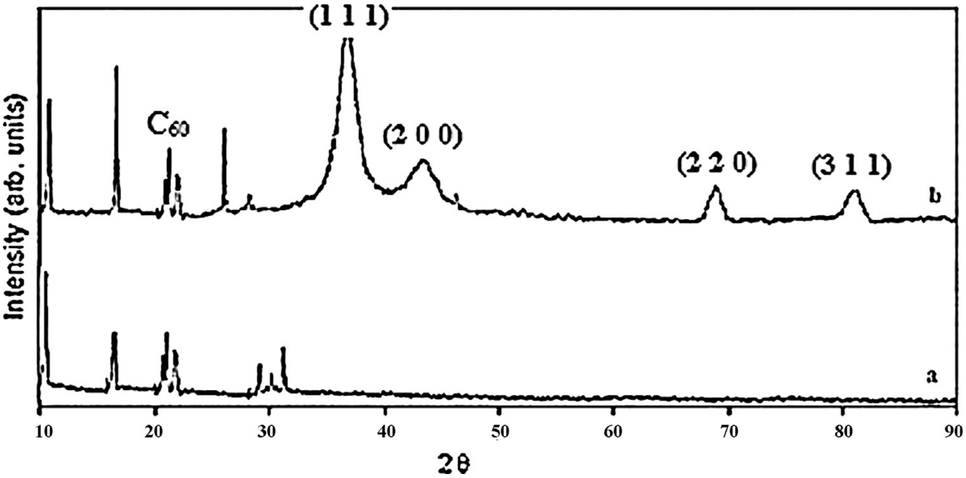


Fig. 3. XRD spectra of (a) C_{60} and (b) C_{60}-Met-Pd.

particles supported on C_{60}-Met/Pd. The existence of Pd nanoparticles, deposited on modified-fullerene was clearly distinguishable as dark spots in Fig. 2. The TEM images of C_{60}-Met/Pd (Fig. 2) show a uniform diameter distribution of palladium particles with near spherical morphology supported on C_{60}-Met. The diameters of palladium particles range from 3 to 5 nm and there is no large agglomerate of the palladium particles. The results indicated that metformine play an important role to improve the dispersibility of Pd. The different size aggregation of functionalized fullerenes is observable from the TEM that shown the self-assembly behavior of substituted water-soluble C_{60}-containing metformines ligand [21].

The metal loading was determined using ICP-AES, and the results showed Pd loading of 1 mmol g^{-1} (18%). Thus for the supported Pd catalyst approximately 20% of the ligand are occupied by metal.

The X-ray diffraction spectroscopy (XRD) pattern of pure fullerene C_{60} (curve "a" in Fig. 3) is clear and appears at $2\theta = 10.8$, 17.6, and 20.7. Solid C_{60} forms a face-centered-cubic structure at room temperature [27,28]. The XRD pattern of C_{60}-Met/Pd complex (curve "b" in Fig. 3) confirmed the presence of C_{60} in catalysts. This means that the crystallinity and morphology of C_{60} were preserved during the functionalized method. XRD pattern of Pd(0) complex as shown four major peaks at a $2\theta^\circ$ of 39.9, 47.4, 68.7 and 82.0 can be assigned to the diffraction from the four reflection indexes of (1 0 0), (2 0 0), (2 2 0) and (3 1 1), respectively (card 05-0681 in the JCPDS file).

The thermogravimetric analysis (TGA) in inert atmosphere (N_2) is shown in Fig. 4. These curves are related to C_{60} (curve "a" in Fig. 4), C_{60}-Met-Pd(II) (curve b) and C_{60}-Met-Pd(II) (curve c). Two main mass loss regions are observed for C_{60}. The first weight loss occurred at a temperature range of 100–650 °C and was moderate. Another weight loss was observed the temperature range of 660–780 °C. The results shown that solvent loss such as water start at 100 °C and carbon cage and amorphous carbon decompose start at 650 °C. [20] Curve "b" showsthat several weight losses were observed for C_{60}-Pd(II) complex. The first mass loss occurs at temperature range of 100–310 °C that is related to the loss of solvent trap in complex. The second mass loss occurs at temperature range of 310–450 °C that is related to the loss of ligand in complex and third mass losses occur at 600–800 °C and that related

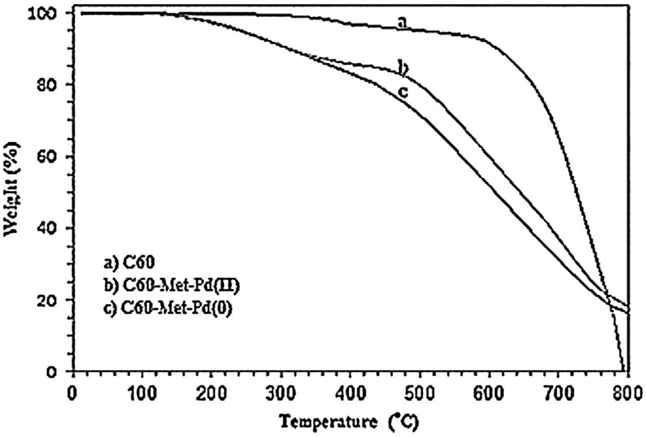
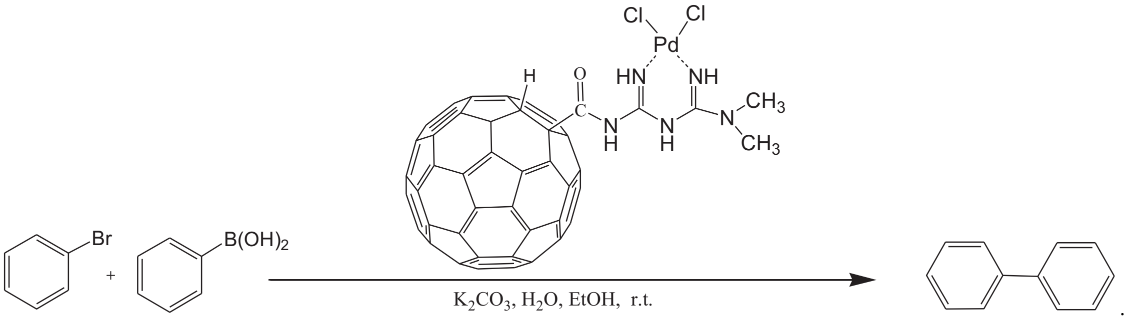


Fig. 4. TGA spectra of (a) C_{60}, (b) C_{60}-Met-Pd(II), and (c) C_{60}-Met-Pd(0).

Table 1
Optimization of the conditions for the Suzuki–Miyaura reaction of bromobenzene with phenylboronic acid.



Entry	Solvent	Pd catalyst (mg)	Base	Time (min)	Yield (%)[a]
1	DMF	10	K_2CO_3	60	88
2	Toluene	10	K_2CO_3	60	70
3	EtOH	10	K_2CO_3	80	75
4	H_2O	10	K_2CO_3	120	55
5	EtOH/H_2O[b]	10	K_2CO_3	45	98
6	EtOH/H_2O[b]	10	NaOAc	60	70
7	EtOH/H_2O[b]	10	Et_3N	60	85
8	EtOH/H_2O[b]	5	K_2CO_3	60	85
9	EtOH/H_2O[b]	15	K_2CO_3	60	98
10	EtOH/H_2O[c]	10	K_2CO_3	60	75
11	EtOH/H_2O[d]	10	K_2CO_3	120	85

Reaction conditions: bromobenzene (1 mmol), PhB(OH)$_2$ (1.2 mmol), C_{60}-Met/Pd(II) (10 mg, 1 mol%), solvent (4 ml).

[a] Isolated yield.

[b] EtOH/H_2O = 1:1.

[c] EtOH/H_2O = 2:1.

[d] EtOH/H_2O = 1:2.

to the decomposition of C_{60}. This part of the thermogram reveals the amounts of supported ligand on fullerene which is estimated to be ~20% (w/w). Curve "c" that related to C_{60}-Pd(0) complex, is similar to curve "b". The remaining weight percent up to the temperature of 800 °C is equal to 0, 18 and 19 are related to curves "a", "b" and "c", respectively. The remaining weight of C_{60} is zero because all fullerene carbons, at a temperature of 800 °C, burned and converted to carbon dioxide. The remaining weights percent of complexes (18 and 19) show the presence of metal palladium installed on the fullerene. These results confirm that our applied strategy can be considered as a good and practical method for the modification of the C_{60} substrate by various functional groups such as amines.

3.2. *Catalytic testing*

3.2.1. *Suzuki–Miyaura coupling reaction*

In order to evaluate the catalytic performance of C_{60}-Met/Pd(II), the Suzuki–Miyaura reactions of aryl halides and phenylboronic acid were studied. Initially, we explored the catalyst ability for the reaction mentioned and the conditions optimized of coupling reaction between bromobenzene and phenylboronic acid as a model reaction with different amounts of the catalyst, solvents and bases (Table 1).

The influences of various reaction parameters such as base (Et_3N, AcONa and K_2CO_3), solvent (nonpolar, protic and aprotic), and catalyst amount on the reaction were tested (Table 1). Among the bases evaluated, K_2CO_3 was found to be the most effective and other bases were substantially less effective. We also investigated the effect of solvents on the Suzuki–Miyaura cross-coupling reaction and found that H_2O/EtOH (1:1) was the best media. It was found that C_{60}-Met/Pd(II) (10 mg, 1 mol% Pd) gave the optimum results using H_2O/EtOH (1:1) as solvent at room temperature. Thus, the optimum conditions selected are: bromobenzene (1 mmol), phenylboronic acid (1.2 mmol), C_{60}-Met/Pd(II) (10 mg, 1 mol% Pd), H_2O/EtOH (4 mL, 1:1), K_2CO_3 (2 mmol) and 25 °C as the reaction temperature.

To generalize the application of the C_{60}-Met/Pd^{+2}catalyst, the coupling reactions of various substituted aryl halides and phenylboronic acids were carried out using 1 mol% C_{60}-Met/Pd^{+2} as catalyst at room temperature (Table 2). The reactions proceeded well with a wide range of aryl iodides and bromides. For most of the substrates, the reaction could be completed in 0.75–4 h with moderate or excellent yields, with the substrates having either electron-donating groups or electron-withdrawing groups.

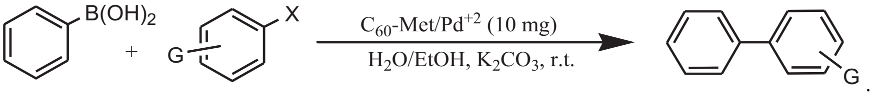
As it is seen, under optimized conditions, phenyl iodide and bromide was reacted efficiently with phenylboronic acid (Table 2, entries 1, 2). Both electron-withdrawing and releasing groups with phenylboronic acid afforded the corresponding products in high yields (Table 2, entries 3–14). It was found that the yield of reaction *ortho*-position aryl bromide is lower (Table 2, entry 13) than those of *para*- or *meta*-substituted aryl bromides (Table 2, entries 3–12). Notably, when 2-iodothiophene was used as coupling partner, the desired product was obtained and no poisoning of palladium catalyst occurred (Table 2, entry 14).

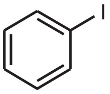
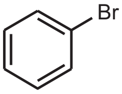
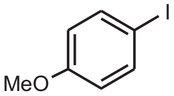
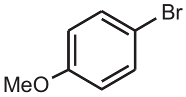
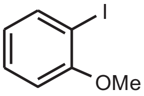
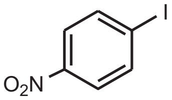
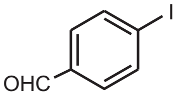
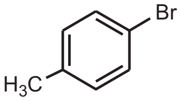
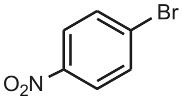
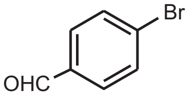
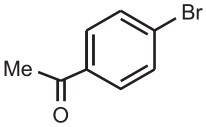
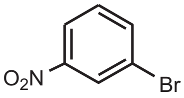
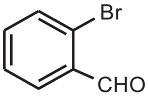
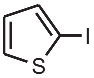
Finally, to assess the present protocol with respect to other reported methods for the preparation of biaryls, the catalytic performance of the C_{60}-Met/Pd^{+2} was compared with some of the reported catalysts. From Table 3, it can be seen that present catalyst exhibited higher conversions and yields compared to the other reported system [17,29–32].

3.3. *Recycling of the catalyst*

In order to investigate the recycling of the catalyst, the Suzuki–Miyaura cross-coupling reaction between iodobenzene and phenylboronic acid catalyzed by 1–mol% of C_{60}-Met/Pd^{+2} was chosen as a model reaction. The results indicated that C_{60}-Met/Pd^{+2} can be reused 6 times without significant loss of catalytic activity (Fig. 5). The result indicated that the palladium leaching of the

Table 2
Suzuki cross-coupling reaction of aryl halides with phenylboronic acid.



Entry	Aryl halide	Time (min)	Yield (%)[a]
1		45	98
2		80	95
3		45	96
4		80	92
5		50	98
6		60	95
7		60	92
8		120	93
9		75	90
10		80	95
11		180	92
12		80	90
13		240	70
14		60	93

[a] Isolated yield.

Table 3
Comparison of the activity of different catalysts in the Suzuki cross-coupling reaction.

Reaction	Catalyst	Reaction conditions	Yield (%)	Refs.
Iodobenzene + phenylboronic acid	C_{60}-Met/Pd^{+2}	K_2CO_3, H_2O/EtOH (1:1), 25 °C, 45 min	98	This study
	Graphene oxide-NH_2-Pd^{2+}	K_2CO_3, H_2O/EtOH (1:1), 60 °C, 30 min	87	29
	Cell-$OPPh_2$-Pd^0	K_2CO_3, EtOH, 78 °C, 20 min	85	31
	Pd-$ZnFe_2O_4$	K_2CO_3, EtOH, 78 °C, 4 h	92	32
	Chitosan-Schiff base-Pd(II)	K_2CO_3, xylene, 130 °C, 6 h	34	17
p-Nitrobromobenzene + phenylboronic acid	C_{60}-Met/Pd^{+2}	K_2CO_3, H_2O/EtOH (1:1), 25 °C, 75 min	90	This study
	Graphene oxide-NH_2-Pd^{2+}	K_2CO_3, H_2O/EtOH (1:1), 60 °C, 4 h	80	29
	Polystyrene-supported palladium(II) dithizone complex	K_2CO_3, H_2O, 70 °C, 5 h	80	30
	Chitosan-Schiff base-Pd(II)	K_2CO_3, xylene, 130 °C, 6 h	76	31

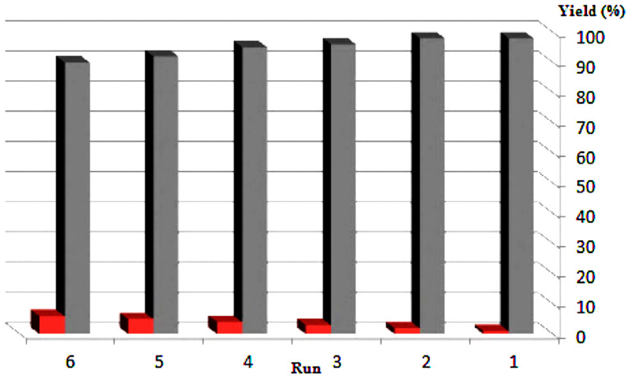


Fig. 5. The recycling of the C_{60}-Met/Pd^{+2} for the Suzuki coupling reaction.

catalyst was low. The results demonstrated that metformine play a key role to improve the stability of the C_{60}-Met/Pd^{+2} catalyst. Also, it is notably, after using C_{60}-Met/Pd^{+2}, no palladium ion could be detected in the liquid reaction mixtures by atomic absorption spectroscopy.

3.4. *Leaching test*

In order to investigate the leaching of Pd during the reaction in our catalytic system, we conducted a filtration test for the Suzuki reaction between iodobenzene and phenylboronic acid using C_{60}-Met/Pd^{+2} as catalyst. After 15 min (the reaction was completed in 45 min), the reaction was stopped and the reaction mixture was centrifuged at 10000 rpm for 10 min. Then the mixture without the solid catalyst was allowed to continue under the same conditions for another 30 min, and the conversation did not proceed significantly. This suggests that the leaching of Pd species from the solid support is low and the prepared catalyst is stable. On the other hand, atomic absorption spectroscopy of the filtrate also confirmed that the Pd content in the solution was below the detection limit (0.1 ppm).

4. Conclusion

In conclusion, a novel and recyclable palladium catalyst supported on metformine modified fullerene was fabricated for the first time. The results indicated that the stability of the catalyst was much improved and C_{60}-Met/Pd^{+2} were an efficient and recyclable catalyst for the Suzuki–Miyaura cross-coupling reaction. The catalyst can be readily recovered and reused without significant loss of its catalytic activity. The proposed method can be a promising alternative approach for the preparation of biphenyl compounds. This is the new example for the development of fullerene (C_{60}-Met-Pd) complexes which can be used as efficient recyclable catalysts without palladium leaching.

Acknowledgement

We are thankful to Payame Noor University (PNU), Iran and Istanbul Technical University, Turkey for partial support of this work.

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