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ORIGINAL PAPER

Immobilization of a palladium(II) bis(imidazolium) complex onto graphene oxide by noncovalent interactions: an efficient and recyclable catalyst for Suzuki–Miyaura reaction

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Abstract

In this research, the Suzuki–Miyaura coupling reaction catalyzed by a palladium(II) complex containing bis(imidazolium) ligand, Pd^{II}(BIM), immobilized on graphene oxide (GO) as heterogeneous, recyclable and active catalyst is reported. The catalyst, Pd^{II}(BIM)@GO, was characterized by FT-IR, diffuse reflectance UV–Vis spectroscopy, ICP, field emission scanning electron microscopy, energy-dispersive X-ray analysis, and elemental analysis. It was demonstrated that the GO-supported palladium(II) complex can act as an efficient catalyst and is reusable several times without a significant loss of their catalytic activity.

Keywords Heterogeneous catalyst · Graphene oxide · Palladium(II) complex · Suzuki coupling reaction · Aryl halides

Introduction

Graphene's unique hexagonal atomic carbon-layered nanostructure has attracted an increasing research attention since its discovery in 2004 [1]. The unusual properties of these exfoliated graphene sheets, including fast charge mobility at room temperature, have motivated the generating novel hybrid materials for nanoelectronics, photovoltaics, batteries, supercapacitors, and related devices [2–6].

However, other properties of graphene such as their large specific surface area, unique chemical and thermal stability, high mechanical strength, chemical versatility and tunability, and low manufacturing cost represent graphene-based materials as potential applications in fuel cells, chemical sensors, hydrogen storage, and heterogeneous catalysis [7–9]. Chemically derived graphenes such as graphene oxide (GO) and reduced graphene oxide (rGO) are suitable candidates for the immobilization of catalytically active species for heterogeneous catalysis due to their inertness, large surface area, stability, and availability [10, 11].

Palladium (Pd)-catalyzed C–C cross-coupling reactions play a key role in modern organic synthesis [12]. Among these reactions, Suzuki coupling is the most powerful method for the synthesis of biaryl units which are important molecular components in pharmaceuticals, herbicides, and natural products, as well as in engineering materials such as conducting polymers, molecular wires, and liquid crystals [13–17]. In these cross-coupling reactions, two molecules are assembled on the metal via the formation of metal–carbon bond. The catalytic steps contain oxidative addition, transmetalation, and reductive elimination [18]. In this way, the carbon atoms bound to palladium are brought very close to one another. In the next step, they couple to one another and this leads to the formation of a new carbon–carbon single bond.

Applications of homogenous palladium catalysts in Suzuki reaction are limited on an industrial scale because of high cost of the catalysts and their low efficiency in separation and recovery from reaction media. Therefore, considerable efforts have been used to immobilize Pd compounds on various separable supports such as activated carbon, silica gel, polymers, metal oxides, porous aluminosilicates, clays, and other organic, inorganic, or hybrid materials for decades [19–21].

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Graphene oxide, which is obtained by the oxidation of graphite, has several oxygen-containing functional groups such as hydroxyl and epoxy groups on the basal planes, and carbonyl and carboxyl groups at the edges that give rise to its unique physical and chemical properties. Due to these polar functional groups in GO, the sorption and intercalation of ions and molecules are possible [22–28]. During these years, graphene (G) and graphene oxide (GO) have been considered as a potential support for palladium-catalyzed C–C coupling reactions [29–36].

In continuation of our interest in the application of palladium-based catalysts for organic transformations [37–43], here we report the preparation and characterization of a palladium(II) complex of a functionalized bis(imidazolium) ligand, Pd^{II}(BIM), immobilized on graphene oxide via non-covalent method. The catalytic activity of the heterogeneous and recyclable Pd^{II}(BIM)@GO catalyst was investigated in Suzuki C–C coupling reactions.

Experimental

Materials and methods

All the reagents were of analytical grade and used without further purification. The chemicals used in this work were purchased from Fluka, Merck, and Sigma-Aldrich chemical companies. The FT-IR and DR FT-IR spectra were recorded with potassium bromide pellets on a JASCO 6300 spectrophotometer in the range 400–4000 cm^{-1}. Diffuse reflectance UV–Vis spectra (DR UV–Vis) were recorded by a JASCO V-670 UV–Vis spectrophotometer. The scanning electron micrographs for morphological features of Pd^{II}(BIM)@GO were taken on a Philips XL20 field emission scanning electron microscope (FE-SEM), equipped with an energy-dispersive X-ray analysis (EDAX) detector. Elemental analysis was carried out on a LECO CHNS-932 analyzer. The ICP for Pd content analyses of the catalyst was determined by a PerkinElmer Optima 7300 DV spectrometer. The substances were identified and quantified by gas chromatography (GC) on an Agilent GC 6890 equipped with a 19096C006 80/100 WHP packed column and a flame ionization detector (FID) using *n*-decane as an internal standard.

Synthesis of palladium(II) bis(imidazolium) complex

The palladium(II) complex of a functionalized bis(imidazolium) ligand, Pd^{II}(BIM), was prepared according to the literature method [44]. First, 1,3-bis(1-methylimidazolium-3-yl) propan2-one diiodide **1** as a bisimidazolium ligand was prepared by the reaction of 1,3-dichloroacetone with 1-methylimidazole and NaI in acetone. The resulting brown precipitate was extracted with diethyl ether and ethanol (m.p. 223 °C). Elemental analysis calcd (%) for $C_{11}H_{16}I_2N_4O$: C, 27.87; H, 3.40; N, 11.82. Found: C, 27.58; H, 3.47; N, 11.51.

Then, the Pd^{II}(BIM) complex was obtained by adding $Pd(OAc)_2$ to a solution of compound **1** in DMSO. The palladium(II) bis(imidazolium) complex as a yellow powder was obtained from recrystallization from DMSO and acetonitrile. Elemental analysis calcd (%) for $C_{11}H_{14}I_2N_4OPd$: C, 23.78; H, 3.07; N, 8.53. Found: C, 23.52; H, 3.07; N, 8.53.

Preparation of graphene oxide-supported palladium(II) bis(imidazolium) complex, Pd^{II}(BIM)@GO

The GO was prepared by the oxidation of graphite powder with H_2SO_4 and $KMnO_4$, according to the method described by Hummers and Offemann [45, 46]. The GO (200 mg) was added to a solution of Pd^{II}(BIM) (10 mg) in H_2O/DMSO (100 ml, 100:1), and the brown suspension was sonicated for 15 min. The mixture was vigorously stirred at room temperature for 24 h. At the end of the reaction, the resulting suspension was filtered and thoroughly washed with water several times. Finally, the Pd^{II}(BIM)@GO catalyst was obtained after a freeze-drying procedure (Yield: 89%).

General procedure for Suzuki–Miyaura cross-coupling reaction of aryl halides with phenylboronic acid catalyzed by Pd^{II}(BIM)@GO

A mixture of aryl halide (1 mmol), phenylboronic acid (1.3 mmol), K_2CO_3 (2 mmol), and catalyst (0.35 mol% for Pd^{II}(BIM)@GO) in DMF/H_2O (5 ml, 2:1) was stirred at 60 °C under air atmosphere. The progress of the reaction was monitored by GC. After the completion of the reaction, the catalyst was separated by centrifugation and the products were extracted with ethyl acetate. The organic phase was separated and dried over $MgSO_4$ and evaporated under reduced pressure.

Catalysts recovery

Due to the importance of recovery and reuse of heterogeneous catalysts from green chemistry aspects, the reusability of the Pd^{II}(BIM)@GO catalyst was investigated in the Suzuki–Miyaura reaction of 4-iodoanisole with phenylboronic acid under the optimized reaction conditions. At the end of each reaction, the reaction mixture was worked up as described above and the filtered catalyst was successively reused in the same reaction and the filtrate was used for the determination of amount of Pd leached using ICP analysis.

Results and discussion

Characterization of graphene oxide-supported palladium(II) bis(imidazolium) complex, Pd^{II}(BIM)@GO

The preparation pathway for Pd^{II}(BIM)@GO catalyst is shown in Scheme 1. As can be seen, the palladium(II) complex of a functionalized bis(imidazolium) ligand as a zwitterionic complex, with the negatively charged ligands at the Pd(II) center balanced by the positive charges on the pendant imidazolium groups [47], can be immobilized onto GO nanosheets giving the Pd^{II}(BIM)@GO as heterogeneous catalyst. The prepared catalyst was characterized by FT-IR and DR UV–Vis, FE-SEM, EDX, ICP, and elemental analysis.

The FT-IR spectra of GO, Pd^{II}(BIM) complex, and Pd^{II}(BIM)@GO catalyst are shown in Fig. 1. In the FT-IR

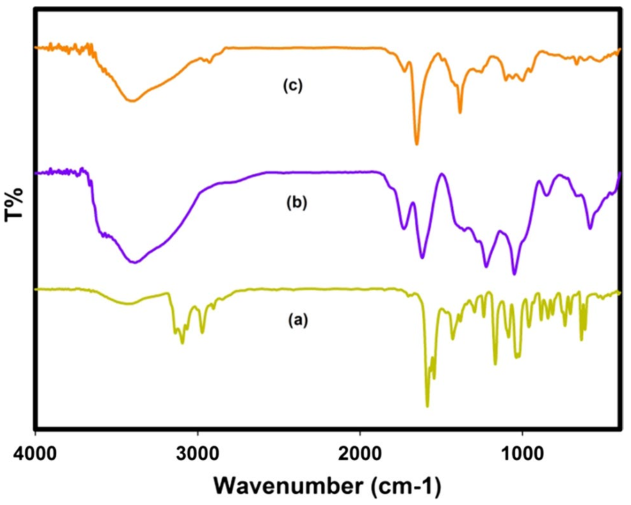
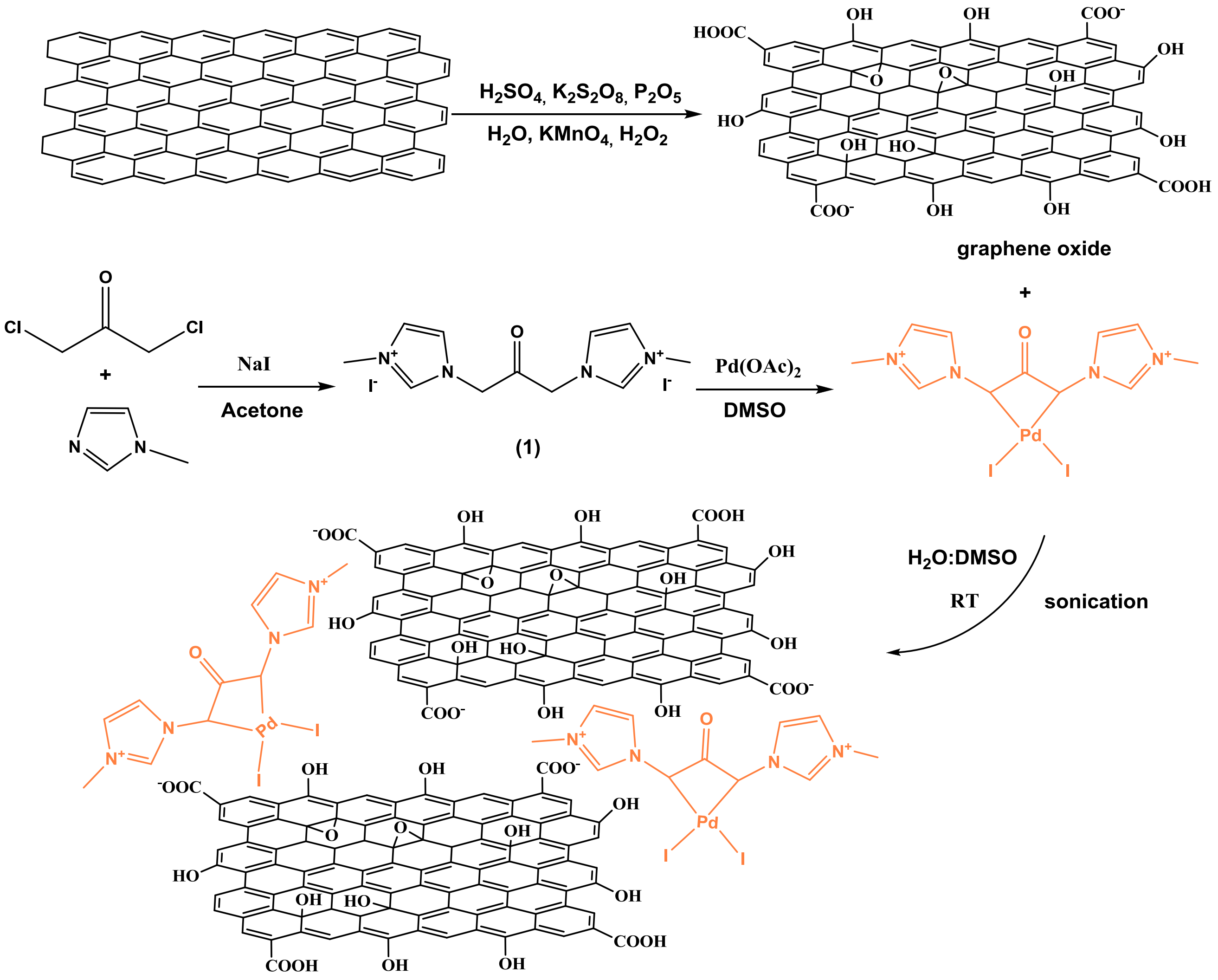


Fig. 1 FT-IR spectrum of *a* Pd^{II}(BIM) complex, *b* GO, and *c* Pd^{II}(BIM)@GO catalyst



Scheme 1 Preparation route for the Pd^{II}(BIM)@GO catalysts

spectrum of GO (Fig. 1a), the strong band at 1729 cm^{-1} (C=O) represents carboxylic acid, and the bands at 1052, 1618, and 1226 cm^{-1} are attributed to the C–O (epoxy), C=C, and C–OH groups in graphene oxide, respectively. In addition, a broad band at 3428 cm^{-1} is attributed to the stretching mode of O–H bonds, due to the presence of many hydroxyl groups.

The spectrum of catalyst (Fig. 1c) shows the parent characteristic bands of GO and more new bands at 2927 and 1384 cm^{-1} related to the stretching vibration of CH_3(N) and C=N in the imidazolium ring, respectively, that proved the immobilization of palladium(II) bis(imidazolium) complex on GO nanosheets. On the other hand, the presence of nitrogen in the elemental analysis of the catalyst related to imidazolium groups confirms the immobilization of Pd^{II}(BIM) complex onto GO nanosheets.

The DR UV–Vis spectra of GO, Pd^{II}(BIM) complex, and Pd^{II}(BIM)@GO catalyst are shown in Fig. 2. The UV–Vis spectrum of GO shows a strong absorption peak at 214 nm related to discrete units of *sp*^{2}-bonded carbons and a peak around 300 nm, which is attributed to $n - \pi^*$ transition of C=O bonds (Fig. 2a). In the DR UV–Vis spectrum of the Pd^{II}(BIM)@GO, the absorption peaks were appeared at 323, 214, 309, 341, and 389 nm (Fig. 2c) which showed the characteristic peaks of the palladium(II) complex and also the GO support.

The field emission scanning electron microscopy (FE-SEM) micrograph of the Pd^{II}(BIM)@GO catalyst shows the morphology of the surface GO used in this study. As can be seen, there are large flakes of GO with macroscopic wrinkled layered structure and smooth surface. Also, the spectrum of energy-dispersive X-ray (EDX) coupled to the SEM confirmed the presence of Pd in the catalyst texture and showed that the major elements are carbon and oxygen (Fig. 3).

The loading of the palladium(II) complex on GO, determined by measuring the pd content by ICP, was obtained about 0.077 mol per gram of the catalyst.

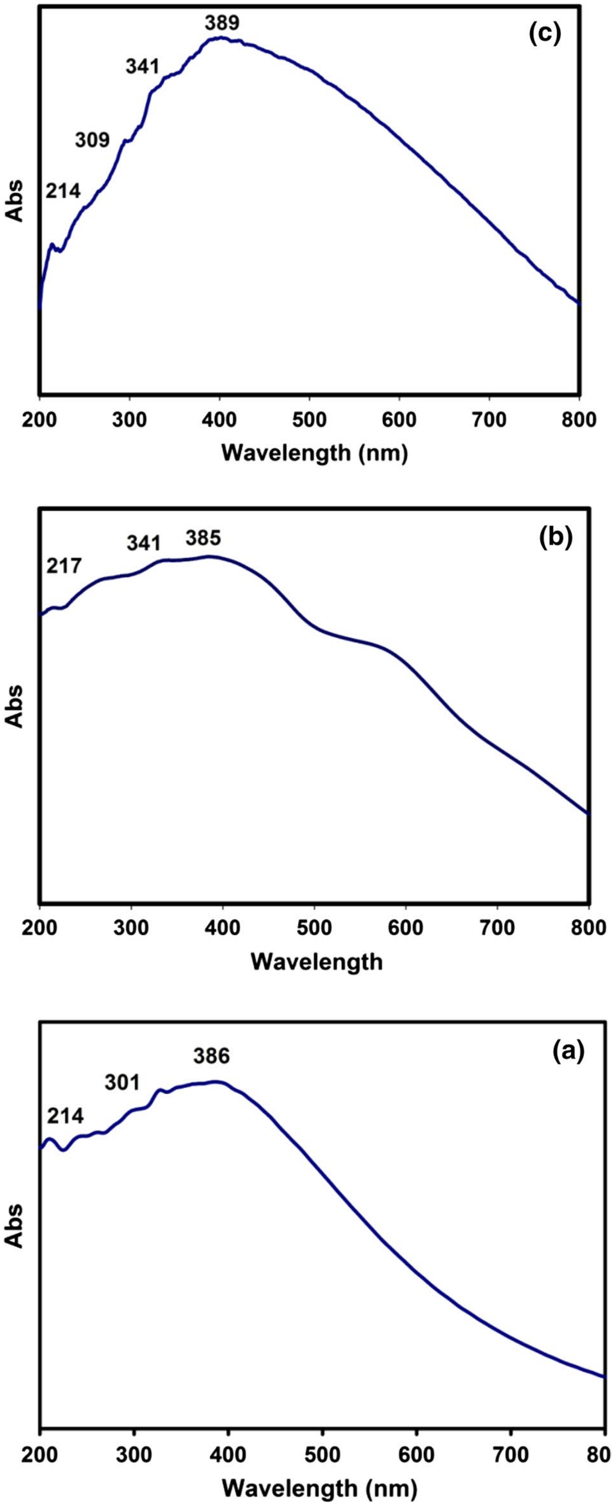


Fig. 2 The DR UV–Vis spectrum of **a** GO, **b** Pd^{II}(BIM) complex, and **c** Pd^{II}(BIM)@GO catalyst

Investigation of catalytic activity of Pd^{II}(BIM)@GO catalyst in the Suzuki–Miyaura cross-coupling of aryl halides with phenylboronic acid reaction

The catalytic activity of Pd^{II}(BIM)@GO heterogeneous catalyst was investigated in the Suzuki–Miyaura reaction of aryl halides with phenylboronic acid. In this manner, as shown in Table 1, the reaction parameters such as kind of solvent and base, temperature, and catalyst amount were optimized in the

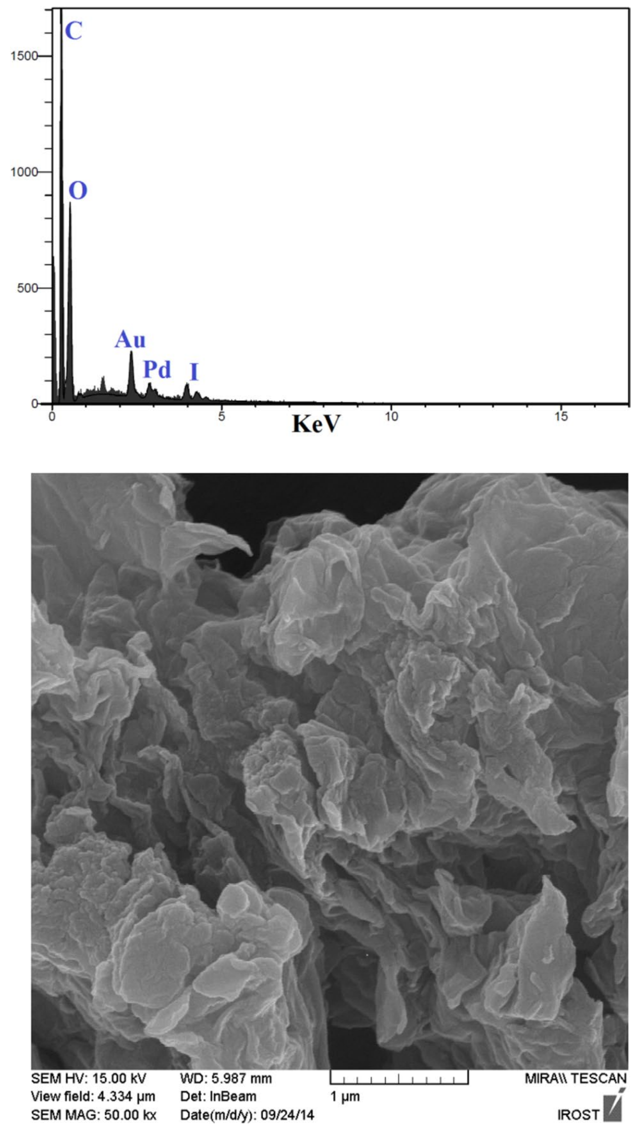


Fig. 3 The FE-SEM images and EDX spectrum of Pd^{II}(BIM)@GO catalyst

coupling of 4-iodoanisole (1 mmol) with phenylboronic acid (1.3 mmol) in the presence of Pd^{II}(BIM)@GO monitored by GC. In the optimization of the amount of catalysts, different amounts of catalyst were used and the best results were obtained using 0.0035 mol of Pd^{II}(BIM)@GO (Table 1, entries 1–4). No product was detected, in the absence of catalyst. This coupling reaction was found to be highly sensitive to the reaction temperature (Table 1, entries 5–7). A reaction temperature of 60 °C was found to be optimal. When the model reaction was carried out at room temperature, only 52% of corresponding product was observed (entry 6). Then, the model reaction was carried out in different organic/aqueous media (Table 1, entries 11–13). Different aqueous solvents such as DMF, EtOH, DMSO, and toluene were used as reaction media, and higher yields were produced. When DMF/H_2O (2:1) was used as solvent, higher yields of the desired cross-coupling product were obtained, while in a nonpolar solvent such as toluene the product yield was very low. This can be attributed to the better solubility of reactants in this solvent. Different organic and inorganic bases such as NEt_3, Na_3PO_4, and K_2CO_3 were used in the model reaction (Table 1, entries 8–10). Among them, K_2CO_3 was found to be the most efficient base. Comparison of inorganic bases utilized showed that carbonate base was more stable than the other one and an organic base like NEt_3 was not as efficient as K_2CO_3. Therefore, it was concluded that 4-iodoanisole (1 mmol), phenylboronic acid (1.3 mmol), K_2CO_3 (2 mmol), and Pd^{II}(BIM)@GO (0.35 mol% Pd) in DMF/H_2O (5 ml, 2:1) at 60 °C were selected as optimized conditions (Table 1, entries 3). Also, as can be seen from Table 1, longer time of reaction has no effect on reaction yield in comparison with optimized conditions (Table 1, entry 14).

A diversity of aryl halides was reacted with phenylboronic acid and 4-methoxyphenylboronic acid to produce the substituted biphenyls under optimized conditions. As can be seen from Table 2, different aryl iodides, bromides, and chlorides bearing electron-withdrawing and electron-donating groups reacted efficiently with phenylboronic acid and 4-methoxyphenylboronic acid to afford the desired cross-coupling products in high yields. As expected, aryl iodides were found to be more reactive than aryl bromides and chlorides.

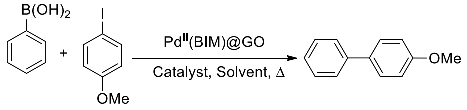
The complex is a Pd(II) complex, and many Pd(II) complexes have been reported to catalyze this reaction [37–42]. In the mechanism of Suzuki–Miyaura reaction catalyzed by Pd^{II}(BIM)@GO, the Pd(II) is responsible for Pd(0) species.

Table 3 compares the activity of the Pd^{II}(BIM)@GO catalyst (yield, time, reaction conditions) with various heterogeneous GO-based palladium catalysts in Suzuki reaction of aryl iodide and phenylboronic acid. It is clear from Table 3 that our catalyst is more efficient and less time-consuming for the Suzuki reaction.

Catalyst recovery and reuse

The recovery and reuse of a heterogeneous catalyst are of great importance from economical, industrial, and green chemistry points of view. The reusability of the Pd^{II}(BIM)@

Table 1 Optimization of conditions in the Suzuki reaction of 4-iodoanisole and phenylboronic acid catalyzed by Pd^{II}(BIM)@GO

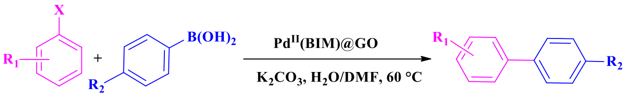


Entry	Solvent	Pd (mol%)	Base	T (°C)	Time (min)	Yield (%)[a]
1	DMF/H_2O (2:1)	0	K_2CO_3	60	–	0
2	DMF/H_2O (2:1)	0.1	K_2CO_3	60	35	64
3	DMF/H_2O (2:1)	0.35	K_2CO_3	60	10	100
4	DMF/H_2O (2:1)	1	K_2CO_3	60	4	99
5	DMF/H_2O (2:1)	0.35	K_2CO_3	80	6	98
6	DMF/H_2O (2:1)	0.35	K_2CO_3	r.t.	40	52
7	DMF/H_2O (2:1)	0.35	K_2CO_3	40	25	32
8	DMF/H_2O (2:1)	0.35	No Base	60	55	7
9	DMF/H_2O (2:1)	0.35	Na_3PO_4	60	15	74
10	DMF/H_2O (2:1)	0.35	NEt_3	60	20	56
11	DMSO/H_2O (2:1)	0.35	K_2CO_3	60	10	91
12	EtOH/H_2O (2:1)	0.35	K_2CO_3	60	10	76
13	Toluene/H_2O (2:1)	0.35	K_2CO_3	60	10	34
14	DMF/H_2O (2:1)	0.35	K_2CO_3	60	25	100

Reaction conditions: 4-iodoanisole (1 mmol), phenylboronic acid (1.3 mmol), base (2 mmol), solvent (5 ml) under air atmosphere

[a] Yields were determined by GC

Table 2 Suzuki cross-coupling reaction catalyzed by Pd^{II}(BIM)@GO



Entry	R^1	R^2	X	Pd^{II}(BIM)@GO[a]	
				Time (min)	Yield (%)[b]
1	H	H	I	12	99
2	H	4-MeO	I	15	93
3	4-Me	H	I	8	97
4	4-Me	4-MeO	I	8	94
5	4-MeO	H	I	10	100
6	4-NO_2	H	I	15	87
7	4-NO_2	4-MeO	I	17	83
8	H	H	Br	35	93
9	4-MeO	H	Br	30	89
10	4-NO_2	H	Br	26	93
11	4-NO_2	4-MeO	Br	29	91
12	4-Ac	H	Br	32	95
13	H	H	Cl	75	67
14	H	4-MeO	Cl	80	66
15	4-Ac	H	Cl	45	98
16	4-MeO	H	Cl	75	34
17	4-NO_2	H	Cl	70	92

Reaction conditions: aryl halide (1 mmol), phenylboronic acid (1.3 mmol), K_2CO_3 (2 mmol), DMF/H_2O (2:1, 5 ml) under air

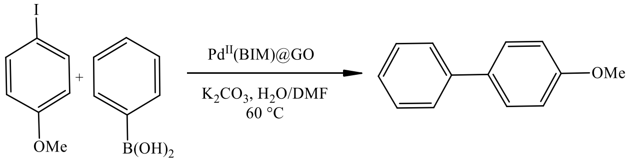
[a] 60 °C, catalyst (0.35 mol% Pd)

[b] Yields determined by GC

Table 3 Comparison of efficiency of various heterogeneous GO-based palladium catalysts in Suzuki reaction of aryl iodide and phenylboronic acid

Catalyst	Conditions	Yield (%)	Time	References
PdII(BIM)@GO (0.35 mol%)	K_2CO_3, DMF/H_2O (2:1), 60 °C	100	10 min	This work
GO–NHC–Pd (0.25 mol%)	K_2CO_3, EtOH/H_2O (1:1), 80 °C	96	1 h	[48]
NHC–Pd/GO–IL (0.1 mol%)	K_2CO_3, EtOH/H_2O (1:1), 60 °C	98	2.5 h	[49]
GO–Pd (0.5 mol%)	K_2CO_3, EtOH, 60 °C	93	30 min	[50]
GO–Pd (1.1 mol%)	K_3PO_4, H_2O, 100 °C	93	5 min	[33]

Table 4 Recycling and reuse of Pd^{II}(BIM)@GO in the Suzuki–Miyaura reaction



Entry	Pd^{II}(BIM)@GO	
	Yield (%)[a]	Pd leached (%)[b]
1	100	1
2	99	0.5
3	99	–
4	97	–
5	95	–

Reaction conditions: 4-iodoanisole (1 mmol), phenylboronic acid (1.3 mmol), K_2CO_3 (2 mmol), catalyst (0.35 mol% Pd), DMF/H_2O (2:1, 5 ml) under air at 60 °C after 10 min

[a] Yields determined by GC

[b] Determined by ICP analysis

GO catalyst was investigated in the reaction of 4-iodoanisole (1.0 mmol), phenylboronic acid (1.3 mmol), K_2CO_3 (2 mmol), and catalyst (0.35 mol%) at 60 °C. At the end of each reaction, the catalyst was filtered and washed thoroughly with diethyl ether, acetone, and water and reused with fresh 4-iodoanisole and phenylboronic acid. The results are summarized in Table 4. As can be seen, the catalyst was recovered and recycled five consecutive times without remarkable loss of its catalytic activity (95%). The amount of Pd leached was determined by ICP analysis. As can be seen, after second run, no catalyst was leached from catalyst.

Conclusion

In summary, we developed a new type of heterogeneous catalyst by the immobilization of palladium(II) complex of functionalized bis(imidazolium) ligand on graphene oxide (GO) as a stable support for the immobilization and stabilization of Pd nanoparticles. Simple preparation of catalyst, high catalytic activity, and good reusability with low leaching of Pd after the completion of the reaction, are noteworthy advantages of this catalytic system in the Suzuki–Miyaura coupling reaction. Further applications of this new catalytic system in other palladium-catalyzed reactions are under investigation in our laboratory.

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