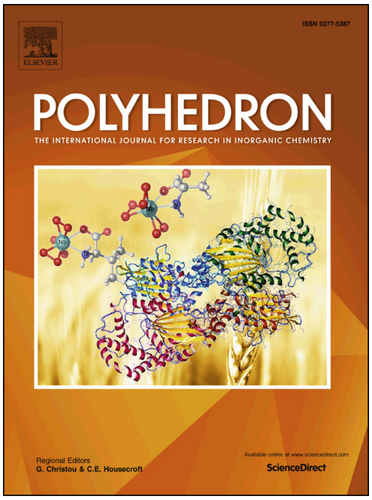

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Immobilization of palladium nanoparticles on Metformin-functionalized graphene oxide as a heterogeneous and recyclable nanocatalyst for Suzuki coupling reactions and reduction of 4-nitrophenol

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Abstract. In this study, Pd nanoparticles supported on Metformin modified graphene oxide (GO-Met-Pd) is proposed as a green heterogeneous catalyst. The structural properties of the as-synthesized nanocatalyst were determined by X-ray diffraction (XRD), Fourier transformed infrared (FT-IR) spectroscopy, transmission electron microscopy (TEM), field emission scanning electron microscopy (FESEM), energy dispersive X-ray spectroscopy (EDS), wavelength-dispersive X-ray spectroscopy (WDX) and inductively coupled plasma (ICP). Activity of the catalyst was investigated by focusing on the Suzuki-Miyaura coupling reaction and room-temperature reduction of 4-nitrophenol (4-NP), as model reactions. The catalyzed reactions provided high yields of biphenyl compounds through the Suzuki-Miyaura reaction and outlined highly efficient conversion of 4-NP to its reduced form. Moreover, no significant Pd leaching was detected in the reaction solutions and the catalyst could be recovered, at least, 6 times without any considerable loss of its catalytic activity.

Keywords. Graphene oxide, Metformin, Palladium, Nanocatalyst, Suzuki, 4-Nitrophenol

1. Introduction

Graphene is a one atom-thick material that is composed of a closely packed honeycomb two-dimensional lattice. This material exhibits high thermal stability, excellent electronic conductivity and good mechanical strength. Furthermore, it possesses a considerable adsorption capacity due to its high specific surface area (2630 m^2 g^{-1}). All these features represent graphene as an interesting option for supporting catalytic nanoparticles (NPs) [1-5]. Another advantageous characteristic of graphene sheets is that they can be decorated with various functional groups or combined with different nanomaterials to give graphene composites. Graphene composites provide exceptional properties that are beneficial for the development of a new generation of catalysts [6]. In other words, the noticeable characteristics of graphene can be combined with the properties of the NPs decorated on graphene's surface to promote performance of the designed catalyst. So that, supporting metal NPs on graphene advances synergistic interactions between the metal and graphene and, therefore, presents a detectable improvement in the electronic properties of the catalyst.

One of the metals that can be combined with graphene sheets is Palladium (Pd). Since the discovery of Pd-catalyzed cross-coupling reactions in 1970s, they have been of strategic importance in organic synthesis [7-11]. For example, they have been accepted as a general catalyst for preparation of bioactive functionalized biphenyls, which are essential compounds in pharmaceuticals and agricultural industries [7-11]. Due to the wide application of Pd-based catalysts for formation of C–C bonds, they have continuously gained interest. However, the focus of researchers has shifted towards developing highly efficient and recyclable catalysts that can be used for ecofriendly industrial purposes.

An important issue about Pd-based catalysts refers to the fact that cross-coupling reactions are usually performed under homogeneous conditions by adopting a ligand that can improve the activity and selectivity of the catalyst for specific reactions [7-11]. As it is well-known, homogeneous catalysis is challenging for pharmaceutical applications since homogenous catalysts cannot be recycled and residual metals might contaminate the reaction products [12, 13]. This problem can be overcome by developing heterogeneous catalysts. That is why many researchers have attempted to perform cross-coupling reactions using palladium particles fixed on different solid supports including activated carbon [14,15], zeolites [16,17], polymers [18,19] and NPs [20-24]. Though heterogeneous catalysts can be recycled efficiently, reduced activity of immobilized catalysts is observed frequently [25, 26]. Consequently, it is necessary to develop heterogeneous Pd nanocatalysts that can provide high activity, catalytic stability and recyclability, simultaneously. Otherwise, the catalyst would not be appropriate for potential applications in the chemical and pharmaceutical industries. To fabricate such ideal catalyst, the research activities of our research group have been devoted to immobilization of palladium NPs on Metformin-modified materials. Our proposed catalysts have been employed for efficient catalysis of C-C coupling reactions [27-30]. In continuation of our work, herein, we fabricate a new Pd catalyst supported on Metformin-modified graphene oxide sheets, for the first time, and investigate its performance in catalysis of the Suzuki-Miyaura coupling reaction, as a model reaction. According to the evaluations, this catalyst can demonstrate the high reactivity of homogeneous catalysts, in addition to possessing the recyclability characteristic of heterogenous catalysts.

2. Experimental

2.1. Materials

The required chemicals were purchased from the Merck and Aldrich companies. Since the materials were highly pure, they were used without any further purification. Reaction completion was assessed by performing TLC analysis on silica gel plates. For this purpose, the solvent of n-hexane-EtOAc (4:1) was used. A Bruker Tensor 27 spectrometer (Bruker, Karlsrohe, Germany) was employed to record the FT-IR spectra of the pressed KBr discs. Also, X-ray diffraction (XRD) spectroscopy was carried out by a Philips powder diffractometer (PW 1373 model; Cu Ka = 1.5406 Å). The XRD patterns were recorded over the 2θ range of 10 to 80º at a ... scanning rate. Moreover, field emission scanning electron microscopy (FE-SEM) (Cam scan MV2300) was utilized to determine the morphology and particle dispersion of the samples while an energy dispersive X-ray (EDS) detector was coupled to the SEM system to investigate the chemical composition of the nanostructures. Finally, TEM images of the samples were taken by a Philips-EM-2085 transmission electron microscope using 100.0 kV accelerating voltage.

2.2. General procedure for preparation of graphene oxide (GO)

Natural graphite powder was used to prepare the nanosheets of graphene oxide (GO) via the modified method of Hummer [16]. According to this method, 3 g graphite powder and 1 g sodium nitrate ($NaNO_3$) were gently mixed with a solution of 98% H_2SO_4 (46 mL). Meanwhile, the solution was stirred for 15 min in an ice bath at 0 to 5 ºC. Then, 6 g potassium permanganate ($KMnO_4$) was slowly mixed with the suspension, under vigorous stirring at 10 to 15 ºC. Stirring of the suspension continued for 2 h. The obtained reaction mixture was continuously stirred at 35 ºC for another 30 min. After that, 138 mL distilled water was gently added to the reaction suspension under vigorous stirring. Addition of water and maintenance of the solution at 95 to 98 ºC for 1 h resulted in a color change and provided a yellowish solution. The resultant solution was further diluted with 200 mL warm distilled water (40 ºC) and treated with 18 mL hydrogen peroxide (H_2O_2, 30%). Again, the solution color changed and converted to brown. The brown precipitate was centrifuged and washed by a solution of hydrochloric acid (HCl, 10%) several times. Finally, the brown GO particles were filtered and dried for 24 h under vacuum at 60 ºC.

To obtain GO nanosheets, 100 mg GO was dispersed in 100 mL distilled water and sonicated to exfoliate the GO particles. Sonication was conducted in an ultrasonic bath with 100 W power. The sonication process was stopped when the solution became transparent. Then, the transparent solution was centrifuged for 10 min to separate any unexfoliated GO particle. At the end, the solution was dried for 24 h in a vacuum oven at 80 ºC to acquire the GO nanosheets. Therefore, in summary, aqueous GO nanosheets were produced through oxidization and, subsequently, exfoliation of graphite powder.

2.3. Synthesis of GO-Met-Pd(II) and GO-Met-Pd(0)

Metformin modified GO sheets (GO-Met) were prepared via condensation of Metformin and GO nanosheets. In this way, 50 mg GO nanosheets was added to a DMF solution (50 mL) and ultrasonicated for 1 h. Then, the sonicated solution was cooled down to 0 °C and 6 mmol NHS and 6 mmol EDC were added. The reaction mixture was stirred for 2 h at 0 °C. After that, 10 mmol Metformin was added, the temperature was raised to 100 ºC and the solution was stirred at that temperature for 24 h. This process gave GO-Met. The GO-Met sheets were filtered, washed with acetone and water, respectively, and dried in vacuum at 40 °C. In the next step, 50 mg GO-Met was dispersed in 100 mL water to synthesize GO-Met-Pd(II) and GO-Met-Pd(0). After sonicating the suspension for 15 min, 5 mg $PdCl_2$ was poured in the solution and the suspension was again sonicated for 10 min. The sonicated solution was kept on a working magnetic stirrer overnight. Then, the resultant GO-Met-Pd(II) particles were filtered, washed subsequently with water and acetone and dried at 40 °C. To obtain GO-Met-Pd(0) from GO-Met-Pd(II), 30 mg GO-Met-Pd(II) was dispersed in 50 mL water. After that, 90 μL hydrazine hydrate (80%) was mixed with the suspension and 25% ammonium hydroxide was added to adjust pH of the solution on 10. The Pd(II) reduction reaction was performed at 95 °C for 2 h to obtain the final product of GO-Met-Pd(0). Then, the reduced particles were washed using water and dried at 50 °C. Scheme 1 illustrates the synthetic procedure conducted for preparation of GO-Met-Pd(II) and GO-Met-Pd(0). Based on the ICP-AES measurements, the concentration of palladium in GO-Met-Pd(II) and GO-Met-Pd(0) was 4.3 and 4.2 wt%, respectively.

2.4. General procedure for Suzuki-Miyaura reactions

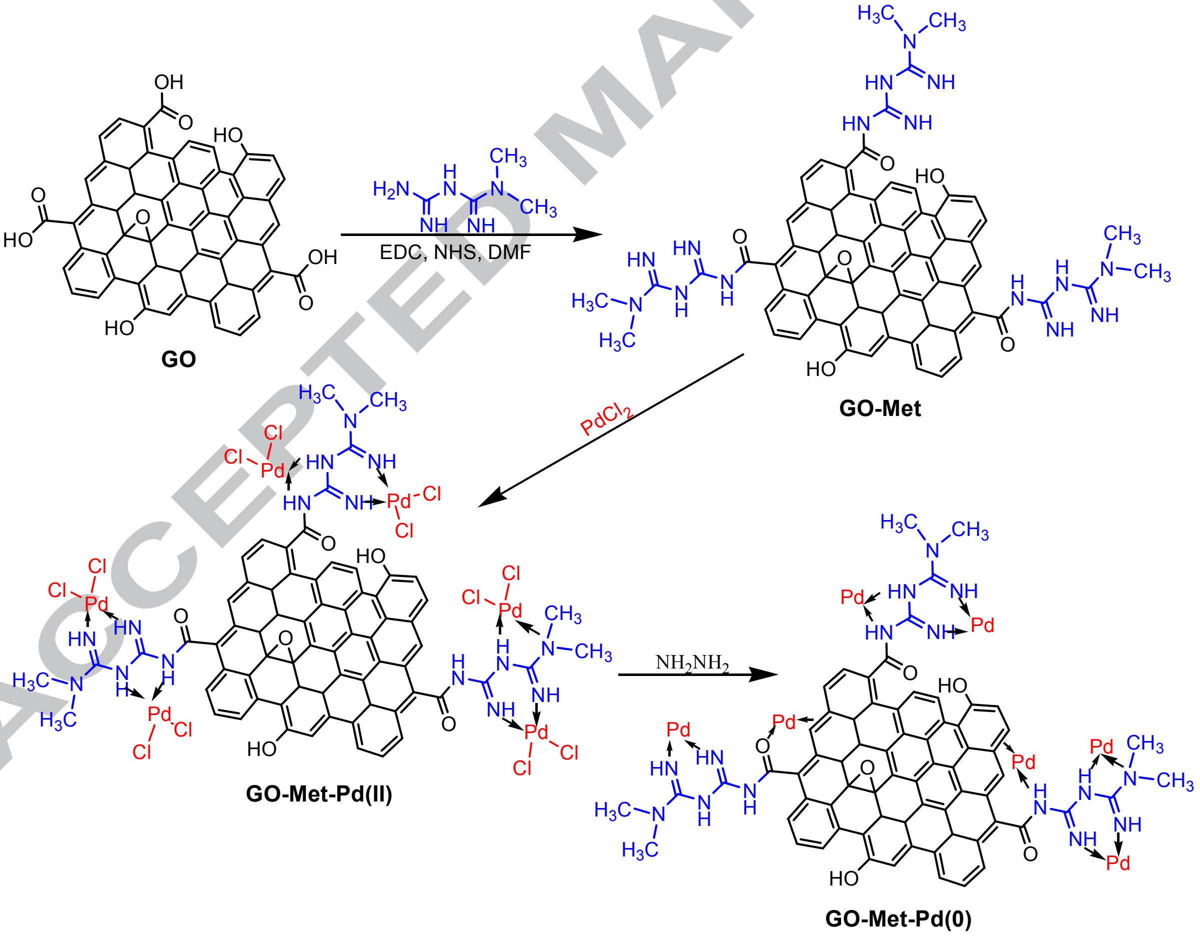
1.0 mmol aryl halide was dissolved in a 3-mL mixture of H_2O-EtOH (1:1, v/v), in a 25-mL round bottom flask. After that, 1.0 mmol aryl boronic acid, 2 mmol K_2CO_3 and 10 mg nanocatalyst (0.1 mol %) were added to the flask. The reaction mixture was stirred for the desired time at 60 °C. The reaction times are reported in Table 2. After confirming completion of the reaction by TLC, the reaction solution was diluted with 10 mL distilled water and the products were extracted using ethyl acetate (3 × 10 mL). The solvent was evaporated under vacuum and the mixture of the organic compounds was dried over anhydrous Na_2SO_4. The products were purified by flash chromatography using hexane:ethylacetate (4:1) as mobile phase.

2.5. General procedure for reduction of 4-NP

To investigate the catalytic performance of the GO-Met-Pd nanocomposite, the reactant solutions of 4-NP (3 mM) and $NaBH_4$ (0.3 M) were prepared, freshly. Then, the reactants (1 mL each) were mixed by magnetic stirring and transferred to a quartz cuvette. 2 mg of the catalyst was added to the cuvette to initiate the reaction. To monitor reduction of 4-NP to 4-AP, absorption intensity of 4-NP was recorded at 400 nm excitation wavelength by an ultraviolet-visible (UV-vis) spectrophotometer.

3. Results and Discussion

Scheme 1 depicts the synthesis steps that were carried out to prepare the catalyst. In the first step, the Hummer's method helped to oxidize graphite powder to GO and provide hydrophilic oxygen containing functional groups, e.g. epoxy, carboxyl and hydroxyl, on the surfaces of the GO nanosheets. These hydrophilic groups stabilized dispersion of GO nanosheets in aqueous solutions [31]. In the next step, GO was treated with Metformin to functionalize the GO and obtain Metformin modified GO sheets. In the last step, Pd NPs were immobilized on the Metformin functionalized GO sheets. With respect to ICP analysis, 0.39 mmol Pd/g of the catalyst was loaded on the GO-Met nanosheets.



Scheme 1. Schematic diagram of GO-Met-Pd fabrications.

Fig. 1a shows the XRD patterns of the samples. The XRD pattern of GO-Met-Pd (Fig. 1a) contains the well-defined peaks of 39.8°, 46.3°, 67.2° and 80.7°, which correspond to the distinctive crystalline planes of (111), (200), (220), and (311), respectively. These crystal planes represent the face centered cubic lattice of Pd(0) [32]. In addition, there is a peak at 10°, in Fig. 1a. This peak refers to the (002) plane of GO nanosheets and indicates restoration of the well-ordered lamellar structure of GO nanosheets in GO-Met-Pd.

The FT-IR spectra of GO, GO-Met and GO-Met-Pd(II) are presented in Fig. 1b. In the FT-IR spectrum of GO-Met, the band located around 2950 cm^{-1} is related to C-H stretching while the bands observed at 3350 and 1580 cm^{-1} correspond to N-H stretching. Also, the peak positioned at 1658 cm^{-1} can be ascribed to the stretching mode of C=NH in the metformin functional groups. Therefore, these vibrational bands verify that Metformin is successfully bound to the surface of the GO sheets through the amidation reaction. Curve **b** of Fig. 1b displays the FT-IR spectra of GO-Met-Pd(II). In this spectrum, the characteristic peak of C=NH stretching is shifted from 1658 to 1652 cm^{-1} due to the coordination of Pd to the Metformin groups. This shift is evident from comparison of the spectra and confirms coordination of Pd^{2+} ions to the Metformin ligands.

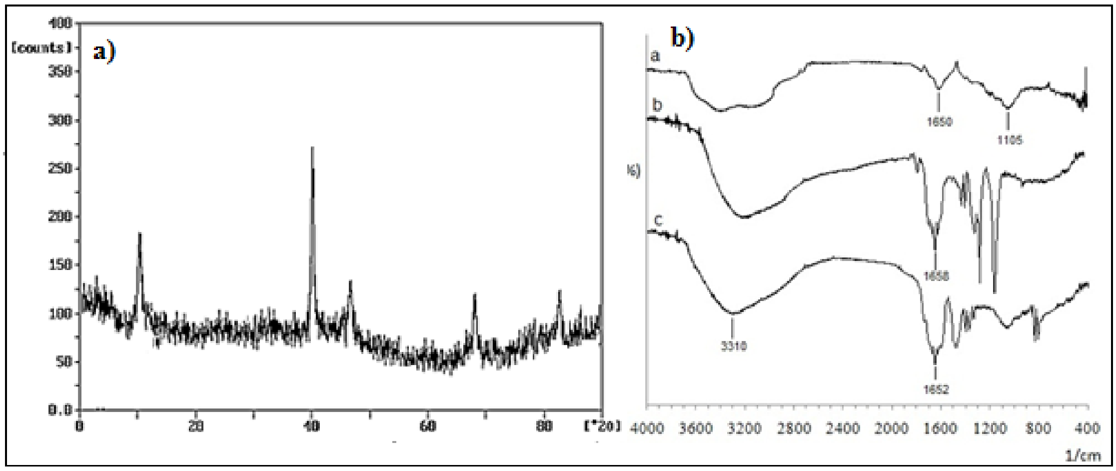


Fig. 1. a) XRD pattern of GO-Met-Pd; b) FT-IR spectra for (a) GO, (b) GO-Met, and (c) GO-Met-Pd(II).

Figs. 2a and 2b illustrate morphology of the GO-Met sheets and the GO-Met-Pd particles, respectively. According to the FE-SEM images of Fig. 2, a noticeable quantity of Pd NPs has dispersed on the surface of the GO-Met sheets. Furthermore, observation of a strong EDX peak at 3 keV (Fig. 2c) approves the presence of elemental Pd NPs. Also, the EDX analysis unravels the existence of carbon, oxygen and nitrogen, as well as Au, in the GO-Met-Pd particles. This elemental composition indicates that the presence of Metformin is responsible for capping and stabilization of Pd NPs on the surface of the GO sheets. In consistent with the SEM results, the TEM images (Fig. 2d) exhibit a homogenous distribution of Pd NPs on the surface of the Metformin modified GO sheets. In general, the characterization results demonstrate the important role of Metformin in enhancing dispersibility of Pd. Furthermore, the histogram clearly defined the average hydrodynamic size of Pd NPs to be in the around of 5.24 nm (Fig. 3).

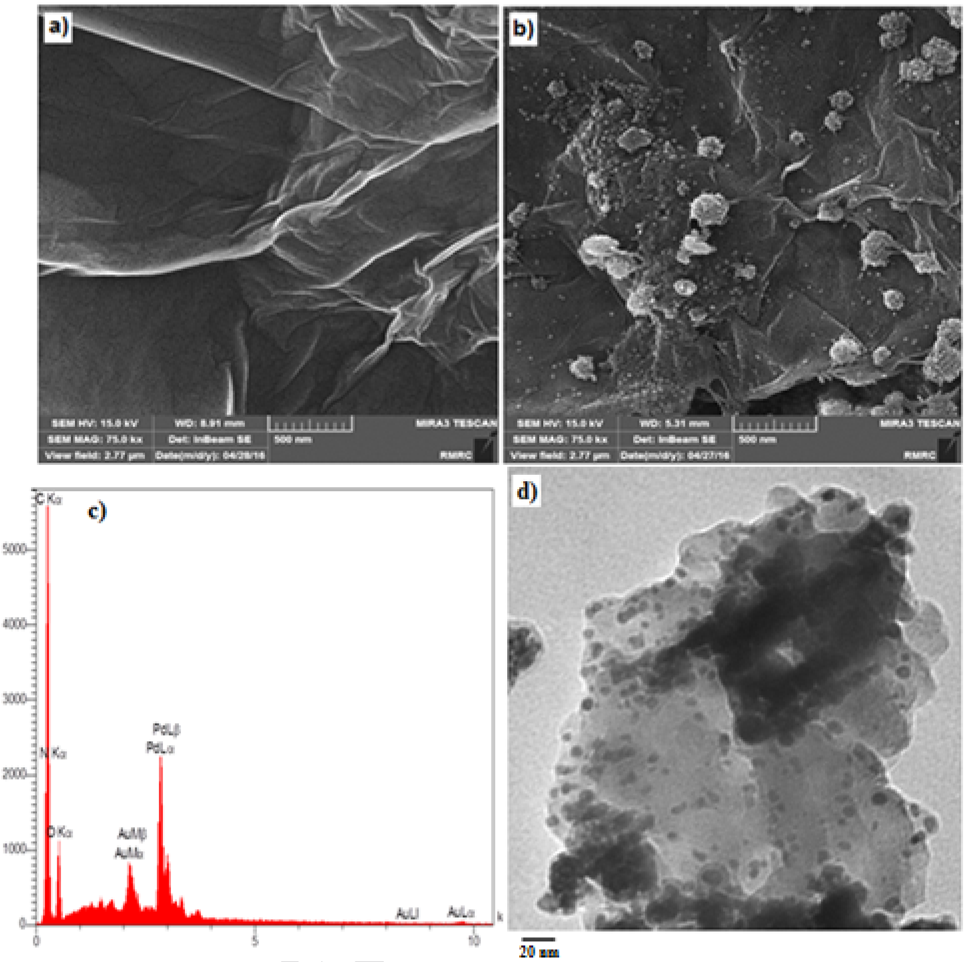


Fig. 2. (a) FESEM image of GO, (b) FESEM image of GO-Met-Pd, (c) EDX of GO-Met-Pd and (d) TEM image of GO-Met-Pd.

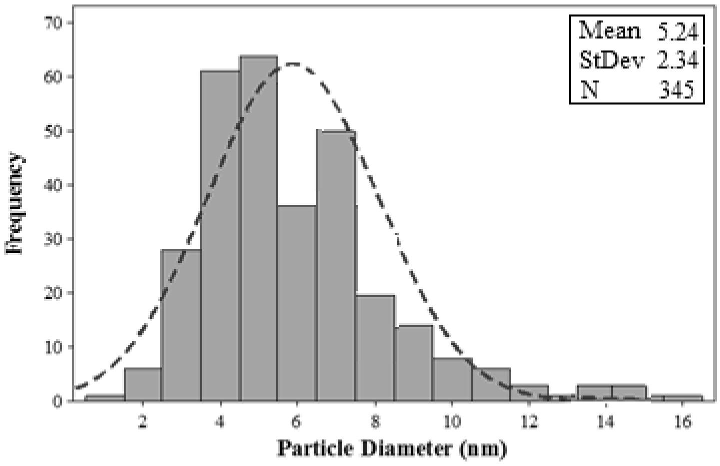


Fig. 3. The particle size distribution of Pd NPs.

In addition to XRD, FT-IR, SEM and TEM analysis, the samples were studied by wavelength-dispersive X-ray spectroscopy (WDX) coupled with quantified FESEM mapping (Fig. 4). This research tool can present qualitative information about distribution of various chemical elements in the context of different catalysts. As the compositional maps of C, N and Pd show, the Pd NPs have well dispersed throughout the GO-Met-Pd composite.

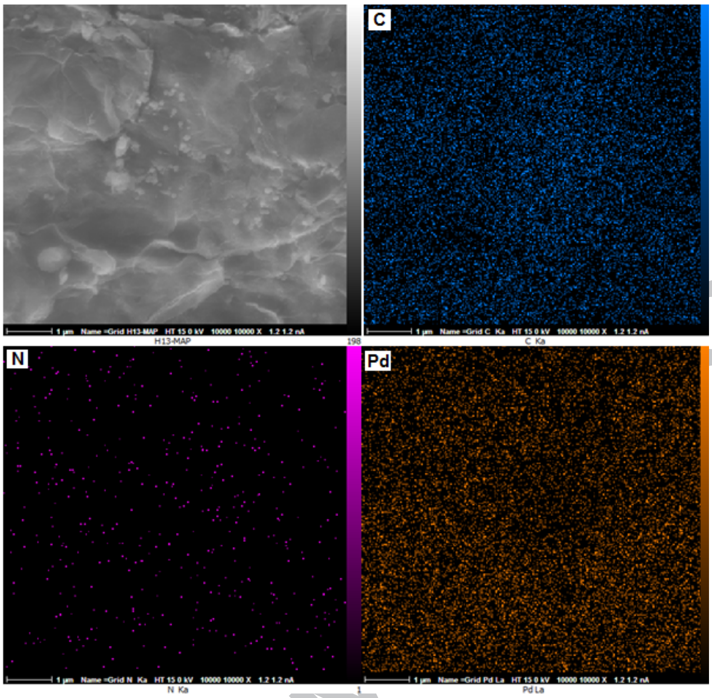


Fig. 4. FESEM image of GO-Met-Pd and elemental maps of C, N and Pd atoms.

X-ray photoelectron spectroscopy (XPS) analysis of GO-Met and GO-Met-Pd in the N1s region as evidence of coordination has also been investigated (Figure 5). To investigate the sitting position of the Pd NPs in GO-Met-Pd, curve fittings of N1s region in the XPS spectra of GO-Met and GO-Met-Pd are produced. tree binding energies of N1s at approximately 400 eV are observed in both cases of GO-Met and GO-Met-Pd (Figure 5 a,b). The comparison shows that there is small shift of binding energy of N1s (400.02 eV to 401.05 eV) with or without Pd NPs, and the proportion of binding energy at 401 eV increases from 35% to 65% after the deposition of Pd NPs. This change in N1s spectra confirm the interaction or proximity between the Pd atoms and the N atoms.

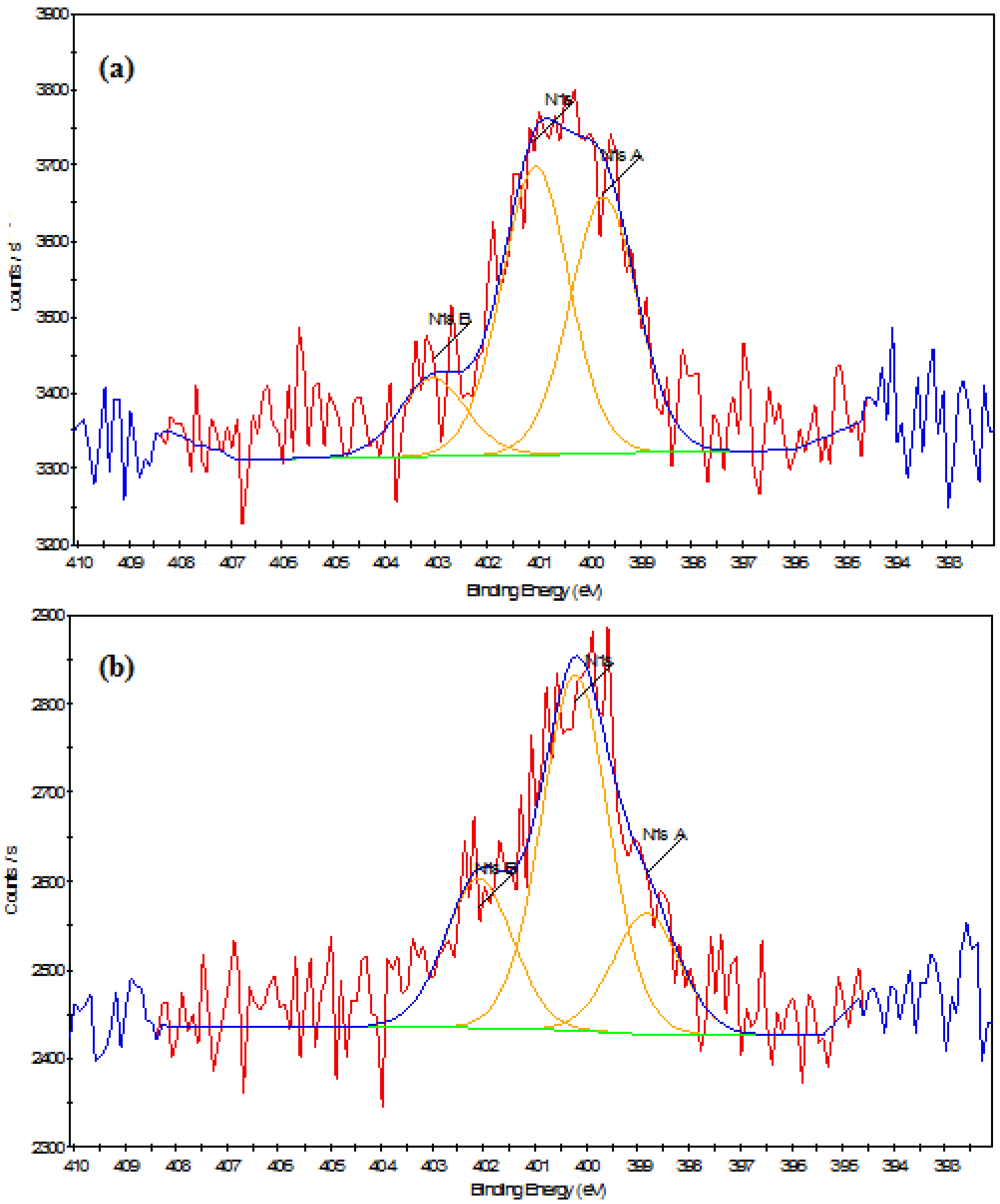
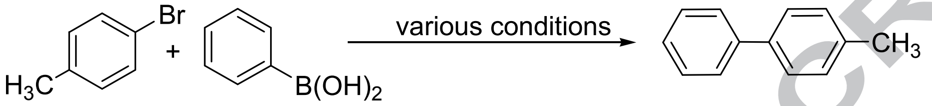


Fig. 5. XPS spectra of a) curve fitting of N1s region in the XPS spectrum of GO-Met; b) curve fitting of N1s region in the XPS spectrum of GO-Met-Pd.

3.1. Catalytic activity of GO-Met-Pd in the Suzuki-Miyaura reaction

The composite catalyst, i.e. GO-Met-Pd, was applied to C-C bond formation between aryl halides and phenyl boronic acid to evaluate its catalytic performance. Such reaction is usually known as the Suzuki-Miyaura cross coupling reaction. At first, the catalytic conditions were optimized by focusing on the Suzuki coupling reaction of 4-methylbromobenzene with phenyl boronic acid, as a model reaction. The optimized parameters included reaction solvent, temperature, base, and catalyst dosage. The optimization results are summarized in Table 1. As expected, no target product was produced in the absence of the catalyst (Table 1, Entry 11) whereas addition of the GO-Met-Pd particles to the reaction mixture prompted high-yield synthesis of the desired product. Based on the optimization trials, H_2O/EtOH (1:1) was selected as the best solvent. Also, among the examined bases, K_2CO_3 was identified as the most effective base. The effect of catalyst dosage was evaluated by adopting several catalyst quantities ranging from 0.050 mol% to 0.200 mol% (Table 1, Entries 7 to 9). The best product yield was achieved using 0.010 g (0.1 mol%) catalyst (Table 1, entry 8). Also, the optimal reaction temperature was found to be 60 °C (Table 1, Entry 8 vs. Entries 12 to 14). So that, at 50 °C, the product yield was lower than the yield obtained at 60 °C and increasing the reaction temperature to 100 °C did not result in any significant improvement in the yield of the desired product.

Table 1. The optimization of reaction parameters for the Suzuki reaction of 4-methylbromobenzene with phenyl boronic acid.[a]



Entry	Pd (mol%)	Solvent	Base	T (°C)	Time (h)	Yield (%)[b]
1	0.1	DMF	K_2CO_3	80	2	80
2	0.1	Toluene	K_2CO_3	80	2	78
3	0.1	EtOH	K_2CO_3	60	2	77
4	0.1	H_2O	K_2CO_3	90	5	55
5	0.1	EtOH/H_2O[c]	NaOAc	60	2	65
6	0.1	EtOH/H_2O[c]	Et_3N	90	4	80
7	0.05	EtOH/H_2O[c]	K_2CO_3	60	2	75
8	0.1	EtOH/H_2O[c]	K_2CO_3	60	1	98
9	0.2	EtOH/H_2O[c]	K_2CO_3	60	1	96
10	0.1	EtOH/H_2O[c]	No base	60	12	Trace
11	0.0	EtOH/H_2O[c]	K_2CO_3	60	12	0.0
12	0.1	EtOH/H_2O[c]	K_2CO_3	25	6	65
13	0.1	EtOH/H_2O[c]	K_2CO_3	50	2	80
14	0.1	EtOH/H_2O[c]	K_2CO_3	100	1	98

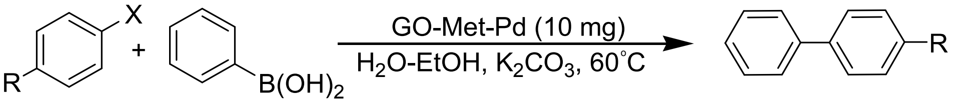
[a] Reaction conditions: 4-methylbromobenzene (1.0 mmol), phenylboronic acid (1.0 mmol), catalyst, base (2 mmol) and solvent (3 mL).

[b] Isolated yield.

[c] 3 mL (1:1)

After determination of the optimal conditions, several coupling reactions between different aryl halides (I, Br and Cl) and phenyl boronic acid were performed under the optimal conditions. The results are reported in Table 2. Based on Table 2, 0.1 mol GO-Met-Pd can efficiently catalyze the reaction of phenyl iodides, bromides and chlorides with phenylboronic acid (Entries 1 to 17). So that, aryl halides with electron-donating or withdrawing groups were observed to react with phenylboronic acid to provide high yields of the associated products. Notably, the reaction of the 2-bromothiophene and 2-iodothiophene heteroaryl halides with phenylboronic acid gave the related coupled products in 96% and 90% yields, respectively (Table 2, Entries 16 and 17). It was noticed that the coupling reaction of aryl chlorides with phenylboronic acid requires a longer reaction time and leads to a moderate reaction yield, with respect to aryl iodides and bromides (Table 2, Entries 3, 6 and 9).

Table 2. Suzuki-Miyaura coupling reaction of different aryl halides with phenylboronic acid.[a]

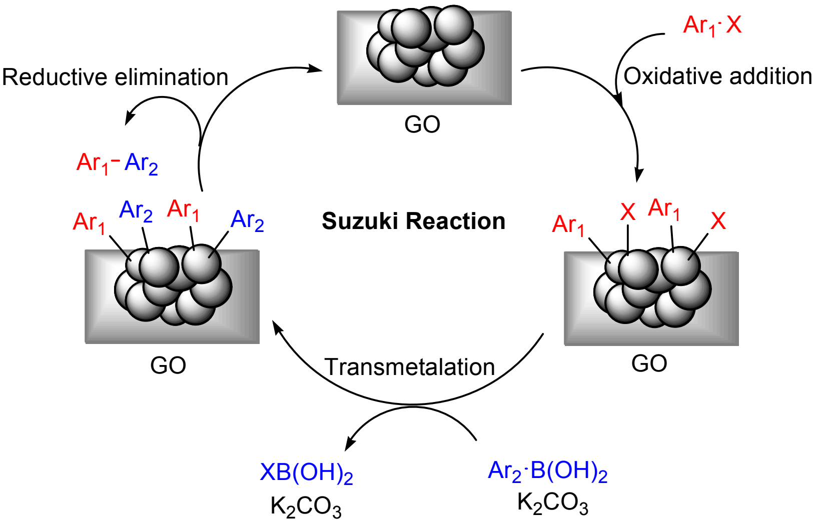


Entry	RC_6H_4X	R	X	Time (h)	Yield (%)[b]
1	H	H	I	0.25	98

2	H	H	Br	1.0	98
3	H	H	Cl	12	70
4	4-CH_3	H	I	0.25	98
5	4-CH_3	H	Br	1.5	98
6	4-CH_3	H	Cl	12	75
7	4-$COCH_3$	H	I	0.5	98
8	4-$COCH_3$	H	Br	2	96
9	4-$COCH_3$	H	Cl	12	65
10	4-CH_3O	H	I	0.5	98
11	4-CH_3O	H	Br	1.5	96
12	4-NH_2	H	I	1.0	96
13	4-NH_2	H	Br	2.0	88
14	4-OH	H	I	3.0	92
15	4-OH	H	Br	5.0	85
16	2-Thienyl	H	I	1.5	96
17	2-Thienyl	H	Br	5.0	90

[a] Reactions were carried out under aerobic conditions in 3 mL of H_2O/EtOH (1:1), 1.0 mmol arylhalide,1.0 mmol phenylboronic acid and 2 mmol K_2CO_3 in the presence of catalyst (0.010 g, 0.1 mol% Pd) at 60 ºC.
[b] The yield is detected by ^1H NMR.

To investigate reusability of the catalyst, the GO-Met-Pd particles were recovered conveniently through centrifugation and reused for five more catalytic cycles. It was observed that application of the catalyst to the Suzuki coupling of phenylboronic acid with 4-methylbromobenzene for 6 consecutive catalytic runs can give 98%, 98%, 96%, 95%, 90% and 83% yield, respectively. Moreover, the reaction mixture was centrifuged after completion of the reaction to separate the catalyst. The separated particles were washed with deionized water and ethanol several times and, then, dried in an oven at 50 °C. The recovered catalyst was saved for the next reaction cycle. To indicate any Pd leaching from the nanocomposite catalyst during the reactions, several samples of the filtrates, in addition to the washings obtained from the conducted standard reactions, were analyzed by ICP. The concentration of Pd detected in each sample was below 3.0 ppm. Furthermore, the model reaction was re-performed using the recovered filtrate. However, no reaction product could be isolated. In this way, the results declared that the GO-Met-Pd nanocomposite, rather than the leached Pd particles, are responsible for catalysis of the reaction and provision of high catalytic activity. According to these observations, a plausible reaction mechanism was proposed for catalysis of the Suzuki coupling reaction by the synthesized particles (Scheme 2).



Scheme 2. Possible mechanism of Suzuki coupling reaction catalyzed by GO-Met-Pd.

3.2. Catalytic activity of GO-Met-Pd for reduction of 4-NP

Catalysis of the reduction of 4-NP to 4-AP by the prepared GO-Met-Pd particles was carried out at room temperature, in the presence of $NaBH_4$ as a hydrogen donor. As the reaction progressed, the yellow color of the reaction solution turned into colorless. Therefore, the reaction progress was monitored by recording the UV-Vis spectra of the solution at short intervals. During the reaction, the characteristic peak of 4-NP attenuated at 400 nm and the indicative absorption peak of 4-AP appeared and intensified at 304 nm (Fig. 6a). The rate of the reduction reaction was assumed to be independent of $NaBH_4$ concentration since an excess amount of this reagent was used. With respect to this assumption, the catalyzed reduction of 4-NP was considered as a pseudo-first-order reaction and the absorption data were fitted into the first-order rate law. As Fig. 6b illustrates, a linear relationship was obtained between $\ln(A/A_0)$ and reaction time. According to the plotted relationship, the rate constant of the reaction, k, was calculated as 0.069 s^{-1}. Also, the parameter of catalyst activity ($Ka= k/m$) was calculated as 69 $s^{-1}g^{-1}$ for the GO-Met-Pd nanocomposite by dividing the determined rate constant by the amount of catalyst utilized for the reaction. This parameter was estimated to compare the catalytic activity of GO-Met-Pd with the performance of the other catalysts that have been used for catalysis of 4-NP reduction (see Table 3). As Table 3 demonstrates, the catalytic activity of GO-Met-Pd is considerably higher than activities of the outlined nanocatalysts. Therefore, it can be stated that GO-Met-Pd can present superior catalytic activity for reduction reactions.

Table 3. The comparison of catalytic activities for the reduction of 4-NP with catalysts reported in literatures.

Catalyst	K (s^{-1})	Ka ($s^{-1}g^{-1}$)	Ref
TAC-Ag-10	5.19 10^{-3}	1.03	[33]
P(AMPS)-Ni	9.38 10-4	0.019	[34]
P(AMPS)-Co	2 10^{-3}	0.04	[35]
P(AMPS)-Cu	1.72 10^{-3}	0.172	[36]
GO-Met-Pd	69 10^{-3}	69	This work

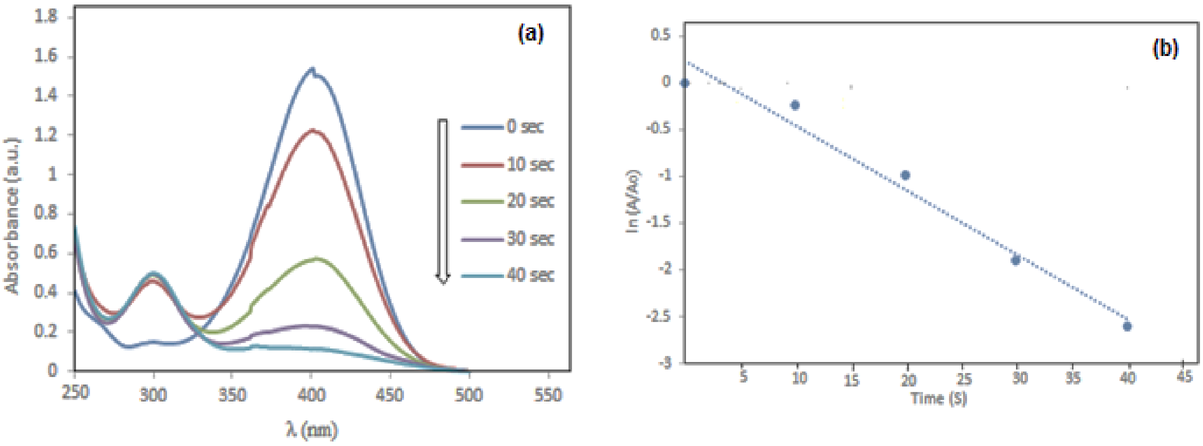


Fig. 6. (a) UV-visible spectra for catalytic reduction of 4-NP to 4-AP, (b) Plot of the $Ln(At/A_0)$ against the reaction different times.

After monitoring the reaction of 4-NP reduction, the catalyst was removed by centrifugation, washed with water and ethanol several times and reused to evaluate reusability of the catalyst for practical applications. It was observed that the performance of the catalyst declines negligibly even after 8 catalytic cycles (Fig. 7). No significant Pd leaching was detected in any of the evaluated reactions, which demonstrates one of the advantageous features of this catalyst.

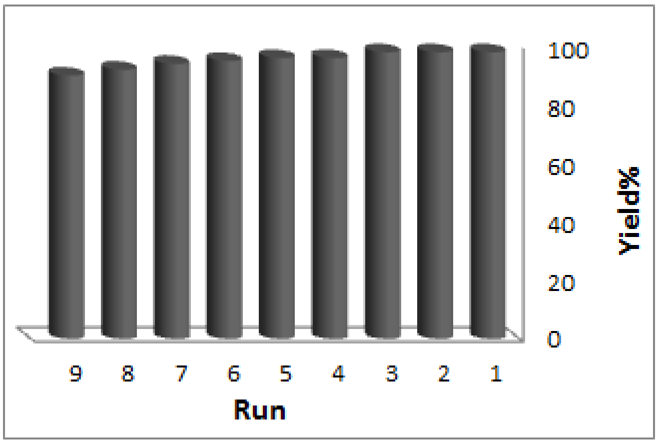


Fig. 7. Recyclability of GO-Met-Pd.

After the 5th catalytic run, ICP analysis was conducted to determine Pd leaching into the reaction solution. 1.65% Pd was detected, which signifies stability of GO-Met-Pb under the reaction conditions. Moreover, the TEM and SEM images of the catalyst after the 5th catalytic cycle (Fig. 8) depicted conservation of the catalyst’s nanostructure. Also, the TEM image of the recovered catalyst showed that the Pd NPs remain well dispersed without aggregation over the GO nano-sheets even after 5 catalytic runs. Also, the histogram clearly defined that the average size of Pd NPs did not significant change (Fig. 9).

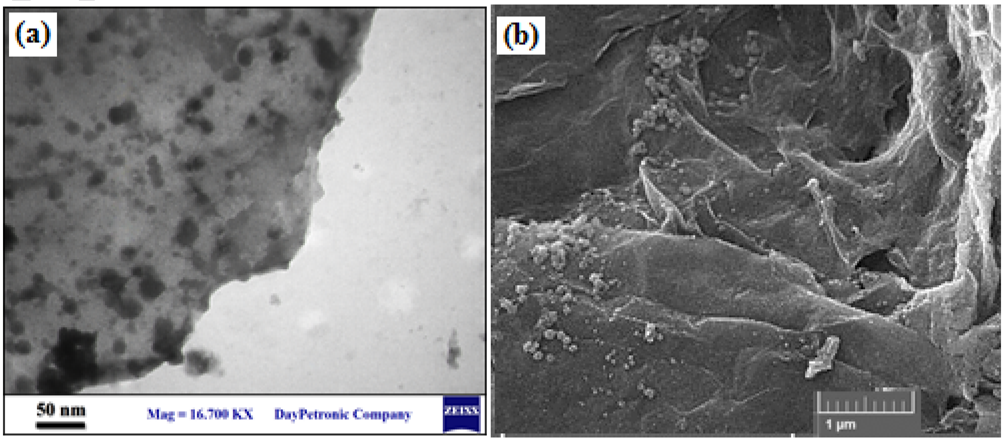


Fig. 8. a) TEM and b) SEM images of reused catalyst after the 5 runs.

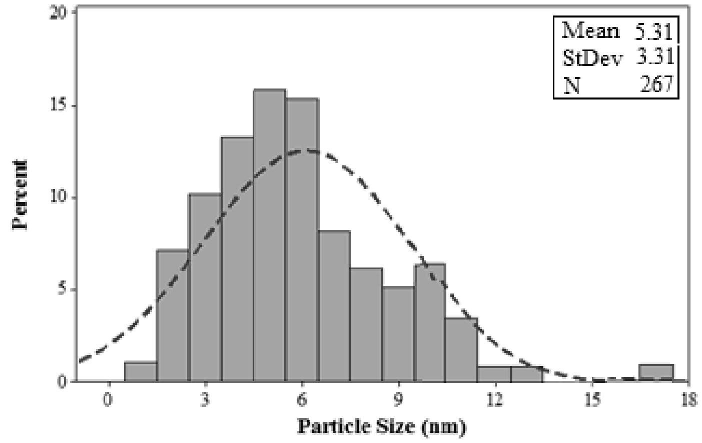


Fig. 9. The particle size distribution of Pd NPs in the reused catalyst after the 5 runs.

To investigate heterogeneity of the catalyst, a hot filtration test was performed on the GO-Met-Pd-catalyzed Suzuki reaction of 4-bromotoluene with phenylboronic, under the optimal conditions. In this test, after 30 min reaction time, 60% yield was obtained. Then, the catalyst was removed and the reaction was sustained for another 30 min, in the absence of the catalyst. No increase in the yield of the desired product was observed, which confirms heterogeneity of the GO-Met-Pd catalyst.

4. Conclusions

This study introduced a recyclable palladium catalyst supported on Metformin modified graphene oxide (GO) nanosheets. Characterization of the synthesized catalyst by the techniques of XRD, FT-IR, FESEM, TEM, ICP, WDX and EDX verified successful functionalization of the GO sheets and homogeneous dispersion of Pd nanoparticles on the modified sheets. Findings of this research unraveled that immobolization of Pd particles on the Metformin functionalized sheets can enhance stability of the active Pd species and provide an efficient and reusable catalyst for Suzuki-Miyaura cross-coupling reactions. The proposed catalyst was found to be a promising tool for preparation of biphenyl compounds. Furthermore, it could be conveniently recycled and reused without any noticeable loss of its catalytic activity. In addition to cross-coupling reactions, the catalyst was applied to reduction of 4-NP to 4-AP in water, at room temperature, and the catalyst was recycled by an external magnet and reused several times without any significant activity loss. No significant Pd leaching was detected in any of the evaluated reactions, which demonstrates one of the advantageous features of this catalyst. In general, the devised catalyst was declared as a green approach towards Pd-based catalysis and elimination of toxic contaminants, e.g. nitro-aromatics, from the environment.

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References

[1] M.D. Stoller, S. Park, Y. Zhu, J. An, R.S. Ruoff, Nano Lett. 8 (2008) 3498-3502.

[2] A.R. Siamaki, A.S. Khder, V. Abdelsayed, M.S. El-Shall, B.F. Gupton, J. Catal. 279 (2011) 1-11.

[3] J. Liu, S. Fu, B. Yuan, Y. Li, Z. Deng, J. Am. Chem. Soc. 132 (2010) 7279-7281.

[4] G.M. Scheuermann, L. Rumi, P. Steurer, W. Bannwarth, R. Mulhaupt, J. Am. Chem. Soc. 131 (2009) 8262-8270.

[5] A. Mastalir, Z. Kiraly, A. Patzko, I. Dekany, P. L'Argentiere, Carbon 46 (2008)1631-1637.

[6] B.F. Machado, P. Serp, Catal. Sci. Technol. 2 (2012) 54-75.

[7] D. Vanderbilt, Phys. Rev. B 41 (1990) 7892-7895.

[8] J. P. Perdew, K. Burke, M. Ernzerhof, Phys. Rev. Lett. 77 (1996) 3865-3868.

[9] H. J. Monkhorst, J. D. Pack, Phys. Rev. B 13 (1976) 5188-5192.

[10] N. Marzari, D. Vanderbilt, A. DeVita, M. C. Payne, Phys. Rev. Lett. 82 (1999) 3296-3299.

[11] G. Zanti, D. Peeters, Eur. J. Inorg. Chem. (2009) 3904-3911.

[12] J.-A. Yan, M. Y. Chou, Phys. Rev. B 82 (2010) 125403.

[13] L.-L. Wang, D. D. Johnson, J. Am. Chem. Soc. 129 (2007) 3658-3664.

[14] U. Ravon, G. Chaplais, C. Chizallet, B. Seyyedi, F. Bonino, S. Bordiga, N. Bats, D. Farrusseng, ChemCatChem. 2 (2010) 1235-1238.

[15] C. J. Pickard, F. Mauri, Phys. Rev. B 63 (2001) 245101.

[16] W. S. Jr. Hummers, R. E. Offeman, J. Am. Chem. Soc. 80 (1958) 1339-1339.

[17] K.-H. Liao, A. Mittal, S. Bose, C. Leighton, K. A. Khoyan, C. W. Macosko, ACS Nano 5 (2011) 1253-1258.

[18] K. Niedermann, J. M. Welch, R. Koller, J. N. CvengrošSantschi, P. Battaglia, A. Togni, Tetrahedron 66 (2010) 5753-5761.

[19] S. Santra, K. Dhara, P. Ranjan, P. Bera, J. Dash, S. K. Mandal, Green Chem. 13 (2011) 3238-3247.

[20] S. Santra, P. Ranjan, P. Bera, P. Ghosh, S. K. Mandal, RSC Adv. 2 (2012) 7523-7533.

[21] M. Ganesan, R. G. Freemantle, S. O. Obare, Chem. Mater. 19 (2007) 3464-3471.

[22] T.-F. Yeh, J.-M. Syu, C. Cheng, T.-H. Chang, H. Teng, Adv. Funct. Mater. 20 (2010) 2255-2262.

[23] A. K. Diallo, C. Ornelas, L. Salmon, J. Ruiz Aranzaes, D. Astruc, Angew. Chem. Int. Ed. Engl. 46 (2007) 8644.

[24] J. Shen, Y. Hu, M. Shi, N. Li, H. Ma, M. Ye, J. Phys. Chem. C 114 (2010) 1498-1503.

[25] J. S. Carey, D. Laffan, C. Thomson, M. T. Williams, Org. Biomol. Chem. 4 (2006) 2337-2347.

[26] M. E. Matheron, M. Porchas, Plant Dis. 88 (2004) 665-668.

[27] (a) H. Veisi, A. Khazaei, M. Safaei, D. Kordestani, J. Mol. Catal. A: Chem. 382 (2014) 106; (b) H. Veisi, S. Taheri, S. Hemmati, Green Chem. 18 (2016) 6337; (b) F. Bonyasi, M. Hekmati, H. Veisi, J. Colloid. Interface Sci., 496 (2017 0 177; (c) M. Pirhayati, H. Veisi, A. Kakanejadifard, RSC Adv., 6 (2016) 27252; (d) B. Abbas Khakiani, K. Pourshamsian, H. Veisi, Appl. Organometal. Chem. 29 (2015) 259; (e) H. Veisi, A. Rashtiani and V. Barjasteh, Appl. Organometal. Chem., 30 (2016) 231 (f) H. Veisi, R. Ghorbani-Vaghei, S. Hemmati, M. Haji Aliani, T. Ozturk, Appl. Organometal Chem. 29 (2015) 26; (g) R. Ghorbani-Vaghei, M. Chegini, H. Veisi, M. Karimi-Tabar, Tetrahedron Lett., 50 (16), 1861; (h) H. Veisi, B. Maleki, M. hamelian, S. Sedigh Ashrafi, RSC Adv., 5 (2015) 6365; (i) B. Maleki, D. Azarifar, R. Ghorbani-Vaghei, H. Veisi, S. F. Hojati, M. Gholizadeh, H. salehabadi, M. Khodaverdian Moghadam, Monatsh Chem. 140 (2009) 1485.

[28] S. Lebaschi, M. Hekmati, H. Veisi, J. Colloid. Interface Sci., 485 (2017) 223.

[29] H. Veisi, R. Masti, D. Kordestani, M. Safaei, O. Sahin, J. Mol. Catal. A: Chem. 385 (2014) 61.

[30] H. Veisi, M. Ghadermazi and A. Naderi, Appl. Organometal. Chem., 30 (2016) 341.

[31] R. Bissessur, S. F. Scully, Solid State Ionics, 178 (2007) 877.

[32] N. Shang, C. Feng, H. Zhang, S. Gao, R. Tang, C. Wang, Z. Wang, Catal. Commun. 40 (2013) 111-115.

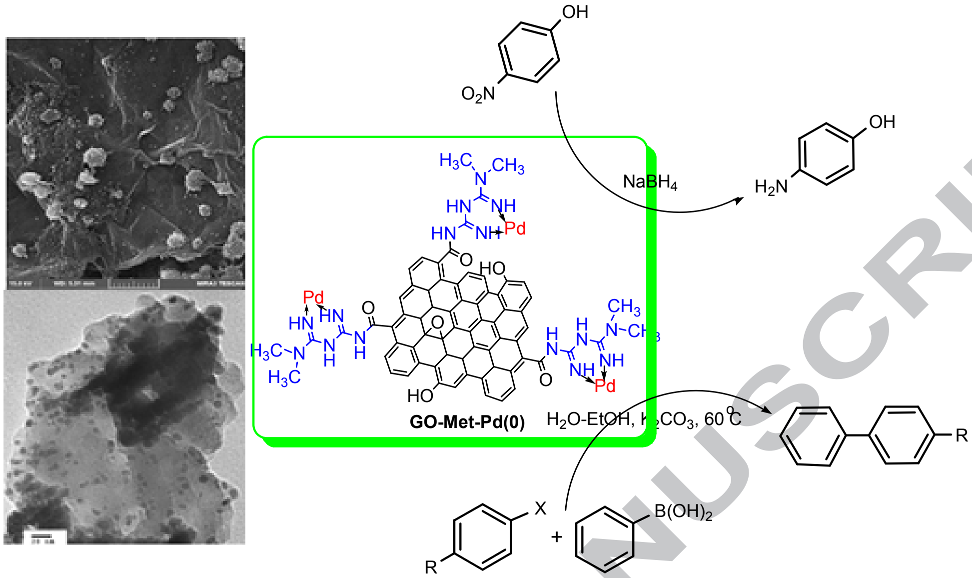
[33] M.H. Rashid, T.K. Mandal, J. Phys. Chem. C 111 (2007) 16750–16760.

[34] N. Sahiner, H. Ozay, O. Ozay, N. Aktas, Appl. Catal. A: Gen. 385 (2010) 201–207.

[35] N. Sahiner, H. Ozay, O. Ozay, N. Aktas, Appl. Catal. B: Environ. 101 (2010)137–143.

[36] N. Sahiner, O. Ozay, Curr. Nanosci. 8 (2012) 367–374.

Graphical Abstract



Pd nanoparticles supported on Metformin modified graphene oxide (GO-Met-Pd) is proposed as a green heterogeneous catalyst for Suzuki coupling reactions and reduction of 4-nitrophenol.