An efficient and heterogeneous Pd-containing modified graphene oxide catalyst for preparation of biaryl compounds

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ABSTRACT

In this research, a novel palladium-containing modified-graphene oxide (GO-N$_2$S$_2$/Pd) catalyst is designed and synthesized for the Suzuki-Miyaura reaction. The prepared catalyst was characterized by different techniques, such as thermogravimetric analysis (TGA), transmission electron microscopy (TEM), scanning electron microscopy (SEM), Fourier transform infrared (FT-IR), energy-dispersive X-ray (EDX), Raman spectroscopy, X-ray diffraction (XRD), and inductively coupled plasma optical emission spectrometry (ICP-OES). The catalytic performance of the synthesized catalyst was evaluated in the Suzuki cross-coupling reaction of phenylboronic acid and aryl halides with K$_2$CO$_3$ as a base. Good recoverability and reusability of this heterogeneous catalyst at the end of the reaction were observed.

1. Introduction

The palladium-catalyzed cross-coupling reaction with halo benzenes and phenylboronic acid is commonly used in the synthesis of several crucial chemical complexes [1, 2, 3, 4, 5]. In this regard, for decades, significant efforts have been made to attach palladium complex on inorganic, different severable hybrid or organic supports [6, 7]. So attention is now focused on the preparation of heterogeneous catalysts based on this transition metal. This is owing to the easy recoverability and reusability of heterogeneous catalysts in the reactions [8, 9, 10, 11, 12, 13, 14, 15]. In heterogeneous catalysts, support plays important role in conversion as well as in the mechanical and thermal stability of the catalyst [16]. Graphene oxide (GO) has received considerable research interest as a novel support for homogeneous catalysts owing to its significant physical and chemical properties, including high stability, two-dimensional sheet-like structure, sizeable open surface area, high mechanical strength and substantial green environmental impact [16, 17, 18, 19, 20, 21]. Compared to non-covalent functionalization, the covalent functionalization of GO is particularly attractive due to the easy recovery of the reactive sites. The physical and chemical properties of graphene oxide can be tuned by oxidation of its surface to different functional groups such as epoxy, carbonyl (C=O), hydroxyl (C–OH), and carboxylic acid (COOH) [22, 23, 24, 25, 26]. The easy availability of these groups is important for their potential application as support [27, 28, 29, 30, 31, 32, 33, 34, 35, 36]. Recently, several Pd catalysts have been immobilized onto functionalized graphenes to prepare biaryls. An example, Qinrui et al. reported boron nitride nanosheet-attached to Pd–Fe core-shell (NPs), a catalyst for cross-coupling reaction [37]. Phuong et al. reported that Pd-complex grafted onto graphene oxide exhibits excellent catalytic performance in the C–C bond forming reactions [38]. Saptal et al. also reported that palladium nanoparticles decorated on the plane of modified graphene oxide (Pd@APGO) are suitable catalysts for the cross-coupling reactions [39]. In continuous of the aforementioned reports, herein, we describe successful immobilization of Pd complex on functionalized graphene oxide. The supported palladium catalyst was obtained using coordination between PdCl$_2$ and 1,2-bis(4-aminophenylthio) ethane ligand (N$_2$S$_2$) that was covalently grafted onto graphene oxide. This catalyst indicated high catalytic performance for Suzuki-Miyaura reaction between halobenzenes and phenylboronic acid (Scheme 1).

2. Experimental section

2.1. Materials

All chemicals, as well as all solvents, were purchased from Aldrich-Sigma company and were used without further purification.
2.2. Material characterization

Fourier-transform infrared spectrum was carried out in the region 400–4000 cm$^{-1}$ by a JASCO 6300D instrument. Thermogravimetric (TGA) analyses were regulated using a Perkin-Elmer -6000 instrument. The scanning electron microscope (SEM) images were taken using a Hitachi S-4800 fields. The transmission electron microscopy (TEM) images were recorded with a Philips CM10 microscope. The XRD measurement patterns were collected a Bruker D8-advance X-ray diffract meter. Raman spectroscopy was determined on a Renishaw Raman system model 1000 spectrometer with an excitation wavelength of 514 nm. The yields were estimated by gas chromatography tests that were by a Shimadzu (GC-16A) equipped with an FID detector. The metal content of the catalysts was recorded by utilizing inductively coupled plasma optical emission spectroscopy (ICP-OES) analysis conducted on a PerkinElmer emission spectrometer.

2.3. Synthesis of 3-chloropropyl functionalized GO (GO-CP)

Graphene oxide was oxidized from graphite using the Hummer method [40]. In a round-bottom flask, graphene oxide (1 g) was dissolved in 50 mL of dry toluene for 30 min, followed by dropwise addition of 2 mL of 3-chloropropyltrimethoxysilane. The resulting mixture was heated to reflux with continuous stirring for 12 h under nitrogen protection. After cooling to ambient condition, the obtained mixture was filtered and washed with EtOH five times. The product was dried at a temperature 70 °C and denoted as GO-CP.

2.4. Synthesis of N$_2$S$_2$ ligand

To do this, 4-amino thiophenol (1.25 g, 10 mmol) was dissolved in dry ethanol (10 mL) containing sodium (0.23 g, 10 mmol). Then, ethylene dibromide (0.43 mL, 5 mmol) in ethanol (5 mL) was added and this mixture was refluxed for 12 h. This was cooled to ambient temperature. The resulted ligand was washed with water and dried at ambient temperature. This sample was recrystallized in ethanol and a yellowish product was obtained.

2.5. Immobilization of palladium on GO-N$_2$S$_2$ (GO-N$_2$S$_2$/Pd)

To do this, 1 g of GO-CP was added in dry toluene (60 mL) and then, 100 mg of N$_2$S$_2$ ligand and trimethylamine (3 mL) were added in the reaction vessel. The obtained mixture was refluxed for 30 h under N$_2$ protection. Then, the sample was filtered, washed with dry EtOH and denoted as GO-N$_2$S$_2$. Finally, 200 mg of as-obtained GO-N$_2$S$_2$ was added to a CH$_3$OH solution of PdCl$_2$ (1 mmol), and this was stirred at 25 °C for
24 h. Finally, the resulting sample was filtered, washed thoroughly with ethanol, dried at 70 °C for 8 h. The successful immobilization of the palladium on GO-N2S2 support was confirmed by ICP-OES, which showed 0.19 mmol Pd g⁻¹.

2.6. Catalytic activity

A mixture of phenylboronic acid (1.3 mmol), aryl halide (1 mmol), GO-N2S2/Pd catalyst (0.5 mol% Pd), and K₂CO₃ (1.2 mmol) in 5 mL C₂H₅OH was stirred at temperature 75 °C under ambient condition. The catalyst was easily separated from the mixture by simple centrifugation, evaluated by TLC. Also, pure products were prepared after recrystallization in ethanol or using column chromatography on silica.

3. Results and discussion

Using the modified Hummer method, the graphene oxide is usually obtained by harsh oxidation of graphite powder with H₂SO₄ and KMnO₄. The GO-CP was synthesized by functionalization of graphene oxide with Cl(CH₂)₃Si(OCH₃)₃ (CPTMS), as formerly reported [41]. Afterward, GO-CP was reacted with N₂S₂ ligand to give GO-N₂S₂. The final GO-N₂S₂/Pd catalyst was synthesized using the reaction of GO-N₂S₂ with Pd (II) chloride (Scheme 1).

3.1. Characterization of the catalyst

The graphene oxide and GO-N₂S₂/Pd catalyst were characterized by FT-IR analysis (Figure 1) Comparison study the spectra of graphene oxide and heterogeneous catalyst identified the incorporation of Pd (II) complex onto the graphene oxide surface. The FT-IR spectroscopy of the GO (Figure 1a) revealed the appearance of different functional groups, including C–O (1056 cm⁻¹), C–OH (1223 cm⁻¹), C–C (1621 cm⁻¹), carboxylic acid (1731 cm⁻¹), and stretching band of O–H (3421 cm⁻¹) on the GO [42]. Furthermore, for the designed catalyst (Figure 1b), the stretching vibrations at 1571 cm⁻¹, 3100–3450 cm⁻¹, and a new band at 1713 cm⁻¹ can be corresponding to the C–N linker, N–H/O–H bonds, and amide (-NH-C-) group, respectively [43]. The new peak at 1486 cm⁻¹ is related to the skeletal vibration of the benzene. The band at 1433 cm⁻¹ and also the low-intensity bands at around 1013-1138 cm⁻¹ are corresponded to the bending vibration of aromatic C–H. These results indicate the successful immobilization of the palladium complex onto the GO surface.

Figure 2 shows the SEM image, EDS and EDS mapping of catalyst. According to SEM, there are large flakes of graphene oxide with a smooth plane and a macroscopic wrinkled sheeted structure. Also, the element distribution analysis demonstrated that the elements N, S, and Pd (Figure 2a) are homogeneously distributed on the modified GO.

The EDS spectrum also showed the signals of expected elements S, N, C, Pd, and O (Figure 2b). These results confirm the successful immobilization of the N₂S₂/Pd complex onto the GO plane. Moreover, TEM analysis was used for the characterization of the GO-N₂S₂/Pd catalyst. The TEM image of the catalyst (Figure 3) revealed some agglomeration and crumpling of the nanosheets owing to the modification of the plane of graphene oxide support [44,45]. Also, according to the TEM image, palladium nanoparticles were appeared similar to dark spots on the GO surface.
The TG curves of the samples were also performed to evaluate the thermal stability of graphene oxide and heterogeneous catalyst (Figure 4). For both samples, the first weight decrease up to 150 °C is owing to the evaporation of adsorbed H2O. The second weight decrease, at temperature of 150–260 °C, is related to the decomposition of oxygen-carrying functionalities groups and removal of more stable oxygen functionalities decomposing at higher temperatures (such as quinone, carbonyl, and phenol) [46,47]. The TGA of GO-N2S2/Pd (Figure 4b) catalyst illustrated the main weight decrease, at about 220 °C corresponding to the removal of oxygen functionalities and also the decomposition of the N2S2/Pd moieties suggesting that the catalyst is desired thermally stable. These results also confirm well immobilization of N2S2/Pd complex onto the GO surface.

The structural and chemical changes of GO and GO-N2S2/Pd catalyst reflected in the Raman spectrum (Figure 5). Graphene oxide (Figure 5a) exhibited two diffraction peaks at approximately 1350 and 1585 cm\(^{-1}\) due to the D-band and G-band, respectively [48]. Compared to GO, in GO-N2S2/Pd catalyst (Figure 5b), a minimal shift of D- and G-band toward a lower wavenumber has appeared. This event is high likely owing to anchored of compounds to several small graphitic aromatic domains that emerged on the plane of GO. The shifting of the G band of the GO-N2S2/Pd catalyst from 1585 cm\(^{-1}\) to 1591 cm\(^{-1}\) is the same as the G band of pure graphite. The peak shift can be related to the gradual change of local stress caused by using chemical rectification [49]. This shift also shows an impact charge transfer between the GO layers and the chemical rectification [50]. Also, the amount of dropped intensity ratio reflects the number of C sp\(^2\) atoms increasing during the synthesis processes of the GO-N2S2/Pd catalyst. So the change of the number of C sp\(^2\) atoms is not due to a reduction of graphene oxide but is due to the attachment of the palladium complexes onto the GO plane.

The XRD patterns of graphene oxide and GO-N2S2/Pd catalyst are displayed in Figure 6. The characteristic diffraction peaks of GO (Figure 6a) were seen at approximately 20 of 10.84 and 42.46°, which are related the (d002) surface of GO and to the (100) surface of the hexagonal structure of carbon [51]. Compared with graphene oxide, the XRD pattern of the GO-N2S2/Pd catalyst (Figure 6b) showed a new peak at 20 = 28.4°, corresponding to the graphite (d002) surfaces, suggesting that the immobilization of Pd complex is taken place on the graphene oxide support [52,53].

### 3.2. Catalytic activity and reaction conditions

GO-N2S2/Pd catalyst was systematically examined in the Suzuki coupling reaction (Figure 7). Here, the activity of the catalyst in the C–C coupling reaction was studied following some of the appropriate variations in the catalyst amount, base and solvents. The initial tests for the cross-coupling reaction of aryl halides start with the reaction between 4-iodoanisole (1.0 mmol), phenylboronic acid (1.2 mmol) in the attendance of Cs2CO3 (1.0 mmol) and GO-N2S2/Pd (0.5 mol%) in EtOH at 65 °C delivering the biphenyl in 36% yield (Table 1, entry 1). Afterward, the temperature was elevated to 75 °C, together with the increase in the value of the base to improve the yield to 68% (Table 1, entries 2, 3). Then, different bases were examined in EtOH at 75 °C. The study showed in the presence of potassium carbonate, the best result is achieved (Table 1, entries 4–6).

We used ethanol as a solvent due to it is safe as well as cost-effective and efficiently promoted the Suzuki reaction. The effect of different solvents, such as DMF, EtOH, CH2Cl2 and acetonitrile was also checked. Among these, ethanol was recognized to be the best one (Table 1, entries 7–10). It was also found that the Pd catalyst is necessary for the Suzuki-Miyaura coupling transformation owing to no product appeared, in the absence of the GO-N2S2/Pd catalyst (entry 11).

The decrease in the temperature to 55 °C slightly decreased the yield (entry 12). The examination of the catalyst showed that the use of 0.5 mol% of supported palladium led to higher yield at shorter reaction times (Table 1, entries 13, 14).

To discover the applicability and limitation of the current method, reactions of aryl bromides, substituted/unsubstituted aryl chlorides, and aryl iodides with arylboronic acids were studied under optimized conditions (Figure 8). It was found that the rate of the Suzuki reaction is depended on the nature of substituents of aryls. Aryl halides bearing both electron-donating and electron-withdrawing groups were efficiently reacted with phenylboronic acid and the desired C–C coupling reaction...
Figure 7. Optimized experiment for Suzuki coupling reaction.

Table 1. Optimization experiments for the GO-N₂S₂/Pd catalyzed Suzuki coupling reaction.

| Entry | Solvent | Base           | Pd (mol %) | Time (h) | Yield (%) |
|-------|---------|----------------|------------|----------|-----------|
| 1     | EtOH    | Cs₂CO₃ (1.0)   | 0.5        | 10       | 36        |
| 2     | EtOH    | Cs₂CO₃ (1.0)   | 0.5        | 8        | 49        |
| 3     | EtOH    | Cs₂CO₃ (1.3)   | 0.5        | 10       | 68        |
| 4     | EtOH    | KOH (1.3)      | 0.5        | 10       | 57        |
| 5     | EtOH    | K₂CO₃ (1.3)    | 0.5        | 3        | 79        |
| 6     | EtOH    | Et₃N (1.3)     | 0.5        | 10       | 51        |
| 7     | CH₂Cl₂  | K₂CO₃ (1.3)    | 0.5        | 10       | 45        |
| 8     | CH₃CN   | K₂CO₃ (1.3)    | 0.5        | 10       | 39        |
| 9     | DMF     | K₂CO₃ (1.3)    | 0.5        | 10       | 26        |
| 10    | EtOH    | K₂CO₃ (1.3)    | 0.5        | 3        | 98        |
| 11    | EtOH    | K₂CO₃ (1.3)    | -          | 19       | 0         |
| 12    | EtOH    | K₂CO₃ (1.3)    | 0.5        | 3        | 83        |
| 13    | EtOH    | K₂CO₃ (1.3)    | 0.25       | 12       | 65        |
| 14    | EtOH    | K₂CO₃ (1.3)    | 0.1        | 12       | 51        |

Figure 8. Synthesis of biaryl compounds.

Table 2. Results of Suzuki reactions using GO-N₂S₂/Pd catalyst.

| Entry | X      | R      | GC Yield (%) |
|-------|--------|--------|--------------|
| 1     | I      | H      | 94           |
| 2     | I      | Me     | 91           |
| 3     | I      | OMe    | 93           |
| 4     | I      | NO₂    | 99           |
| 5     | Br     | H      | 82           |
| 6     | Br     | Me     | 80           |
| 7     | Br     | OMe    | 78           |
| 8     | Br     | NO₂    | 84           |
| 9     | Cl     | H      | 43           |
| 10    | Cl     | Me     | 48           |
| 11    | Cl     | NO₂    | 58           |
| 12    | Cl     | OMe    | 51           |

*a The reactions were run with phenylboronic acid (1.2 mmol), base (1.3 mmol), aryl halide (1 mmol), catalyst (0.5 mol% Pd), EtOH (5 mL). Temperature 75 °C for 3 h.

Table 3. Comparison of the catalytic activity of GO-N₂S₂/Pd catalyst with other Pd catalysts.

| Entry | Catalyst                  | Reaction condition | Recyclability | Time (h) | Yield (%) |
|-------|---------------------------|--------------------|---------------|----------|-----------|
| 1     | GO-N₂S₂/Pd                | 75 °C, EtOH        | 5             | 3        | 99 [This work] |
| 2     | PFG-Pd                    | 80 °C, H₂O, EtOH   | 5             | 10       | 95 [56]   |
| 3     | GO-2N-Pd(III)             | 80 °C, EtOH        | 6             | 4        | 77 [57]   |
| 4     | GO-PdNPS                  | 100 °C, dioxane    | 5             | 24       | 99 [58]   |
| 5     | NHC-Pd/GO-IL              | 60 °C, EtOH, H₂O   | 5             | 2.5      | 85 [59]   |
| 6     | Pd(II)-N-heterocyclic carbone | 110 °C, toluene    | -             | 20       | 80 [60]   |
| 7     | PdNPs-TDTAT               | 80 °C, H₂O         | 5             | 12       | 90 [61]   |
| 8     | Pd(II)-N(HCO₂)₄@nSiO₂     | 60 °C, H₂O         | 5             | 6        | 97 [62]   |
products were produced in excellent yields. Table 2 summarizes the outcomes.

As anticipated, iodobenzenes and bromobenzenes gave maximum yields of corresponding biphenyl products [54,55]. Evaluation, the advantage of the present study, the ability, and efficiency of GO-N2S2/Pd catalyst for the preparation of biaryl compound, were compared with those previously reported catalysts (Table 3). The results suggest that the present catalytic system is better than most of the former systems in terms of reaction times and yield. This confirms the high efficiency of obtained catalyst for the synthesis of a set of different biaryls.

A mechanism for the Suzuki reaction is proposed in Scheme 2. The support, substrates and solvent in the Pd-catalyzed reaction can act as reducing factors. In this current work, EtOH and the GO-support act as a reducing factors for Pd [63]. The efficient catalytic species are palladium (0) that are formed during the reaction process. In the initial part of the oxidative addition reaction, palladium nanoparticles are oxidized to palladium (II) to produce an aryl-palladium compound A. In the attendance of aryl boronic acid, the intermediate B is formed. The second part includes the reductive elimination reaction that biaryl product is generated and palladium nanoparticles are regenerated to complete the cycle [64,a,b,65]. The kinetics of the cross-coupling reaction in the attendance of the GO-N2S2/Pd catalyst was studied using the reactions between phenylboronic acid with 4-halo (Cl, I and Br) nitrobenzene. For all of the reactions it was observed that with increasing the reaction time, no further improvement of the yield is attained. Also, concentration of the GO-N2S2/Pd catalyst affects on the reaction yields and has a positive effect on the time of the reaction.

3.3. Catalyst stability and recyclability

Recovery and recyclability are among the quintessential advantages of heterogeneous catalysts. The reusability of the GO-N2S2/Pd catalyst was performed for the C-C coupling reaction between phenylboronic acid and 4-iodobenzene. The heterogeneous catalyst was recovered from the reaction sample using filtration and reused in consecutive cycles. As seen in Figure 9, the catalytic efficiency approximately did not lessen after being reused four times. After five runs, the palladium content of the recovered product was monitored using the ICP technique, and the result revealed only minimum leaching of the Pd (less than 1.3 %). The high resistance and recoverability of the catalyst can be attributed to the high efficiency of 4-aminophenylthio ethane ligand in the immobilization of Pd species.

4. Conclusion

In summary, a new GO supported palladium catalyst was obtained using covalent attachment of the Pd/N2S2 complex on graphene oxide. This catalyst was characterized by utilizing different techniques such as XRD, FT-IR, TEM, Raman, SEM, and TGA. These analyses showed strong attachment and desired stability of the Pd/ligand complex onto GO. The catalyst showed desired efficiency and selectivity in the Suzuki reaction.

Declarations

Author contribution statement

Ali Zarnegaryan: Conceived and designed the experiments; Contributed reagents, materials, analysis tools, or data; Wrote the paper.

Dawood Elhamifar: Performed the experiments; Analyzed and interpreted the data; Contributed reagents, materials, analysis tools, or data; Wrote the paper.

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Competing interest statement

The authors declare no conflict of interest.

Additional information

No additional information is available for this paper.

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