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Immobilized Pd(0) nanoparticles on phosphine-functionalized graphene as highly active catalyst for Heck, Suzuki and *N*-arylation reactions

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In this study, a phosphine group was chemically grafted to the surface of graphene in order to prepare a reusable ligand with high surface area incorporating a phosphine moiety. The treatment of graphene oxide (GO) with hydroxide followed by an aqueous work-up yields a OH-functionalized graphene material (GOH) via the ring-opening of the epoxide groups. Reaction of GOH with chlorodiphenylphosphine (CIPPh₂) gives a new material, GOPPh₂ (PFG), which can be used for stabilization of metal nanoparticles or complexation of transition metals in order to prepare a reusable metal catalyst. Stabilization of palladium nanoparticles on the surface of GOPPh₂ resulted in the production of an efficient heterogeneous Pd catalyst (PFG-Pd) for application in C-C and C-N bond formation reactions. The PFG-Pd catalyst was characterized using some different microscopic and spectroscopic techniques such as FT-IR, XRD, TEM, SEM, EDX, and ICP analysis. The applicability of PFG-Pd catalyst was evaluated in a Heck, Suzuki and *N*-arylation reactions. The catalyst system showed high catalyst activity in these process and target products were obtained in high isolated yields. The PFG-Pd catalyst was reusable in these reactions at least for 5 times with no significance decreasing in its catalytic activities.

Introduction

Transition metal catalysis is a powerful methodology in organic synthesis and for this reason there is particular attention on the introduction of new catalyst systems and their applicability in organic transformations.¹Palladium is a valuable transition-metal which act as catalyst in many organic transformations especially C-C and C-heteroatom bond formation reactions.²The Pd-catalyzed Suzuki³ and Heck⁴ reactions are among valuable strategies in organic synthesis due to their applicability in the synthesis of a wide range of materials with physical, chemical and biological activities. Also, *N*-arylation which has been known as Buchwald-Hartwig reaction is a key transformation especially in medicinal chemistry.⁵ Overall, these Pd-catalyzed reactions are strategic in organic chemistry having important application in synthesis of useful materials and for this reason there are many research in this field,

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especially on the recovery and reusability of used Pd catalysts.⁶The simple recovery and reuse of Pd catalyst systems is highly desirable from both economic and environmental points of view.⁷In addition to reusability, the reactivity is important factor in the design of a high performance Pd catalyst system.⁸ In view point of reactivity Pd complexes involving phosphorus ligands are one of the reactive classes of Pdcatalysts.⁹Accordingly, there is widespread interest in the recent years in design of heterogeneous Pd catalyst systems incorporating phosphine ligands.¹⁰

On the other hand, graphene derivatives are one of the applicable and interesting support materials for synthesis of heterogeneous catalysts.¹¹ Among graphene derivatives Graphene oxide (GO) is very interesting because it is possible to modified it with other functionalities. Thus, the development of chemically modified graphenes through GO is a topic of great interest to many researchers as this will allow the properties of graphene to be modified for specific applications. Graphene oxide (GO) is a graphene derivative with rich oxygen-containing functional groups (such as hydroxyl, epoxy, carbonyl and carboxyl groups) and is readily available and inexpensive.¹² This material has been widely used as a starting material to prepare graphene-based nanomaterials, which have displayed unique performances due to their remarkable electronic, mechanical and chemical properties.¹³ Especially, GO provides extraordinary potential in designing novel catalytic systems with enhanced performances. Due to the dimensional nature of this substrate and its high surface area, it is

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possible to immobilize metal nanoparticles on the surface for application as catalyst in organic transformations. For example, Pd/GO displayed a high activity in Suzuki-Miyaura, Heck and Sonogashira coupling reactions.¹⁴Also, Pt/RGO hybrid exhibited good catalytic activity for methanol oxidation and hydrogen conversion reactions.¹⁵ In other reports the surface of graphene was modified with organic or inorganic materials in order to improve the catalytic applicability of these class of nanocatalysts in organic transformations.¹⁶

In continuation of our program on the synthesis of heterogeneous catalysts,¹⁷ we would like to introduce a new strategy for the synthesis of a phosphine functionalized graphene (PFG) material as a reusable phosphorus ligand via grafting PPh2moieties on the surface of graphene plates. In this study, Pd nanoparticles were immobilized on PFG(PFG-Pd) toward synthesis of a reusable Pd catalyst for application in C-C and C-N bond formation reactions. Thus, we check the catalytic activity PFG-Pd in Heck, Suzuki and N-arylation reactions. To the best of our knowledge, there is no report in the literature on the synthesis of phosphine-functionalized graphene and immobilization of palladium nanoparticles on it for catalytic application purpose. Although, the synthesized phosphine modified graphene can be used in other applications but in this study we introduced it as a recyclable phosphine ligand for application in Pd-catalyzed coupling reactions.

Results and discussion

Synthesis of PFG-Pd catalyst

Our strategy for the synthesis of immobilized Pd nanoparticles on phosphine-functionalized graphene(PFG-Pd) is shown in Scheme 1.



As shown in Scheme 1, PFG-Pd was synthesized in a three steps process. The GO substrate was treated with hydroxide anion, resulting in the opening of epoxied rings and generation of free hydroxyl group on the surface of graphene sheets.^{12b} The synthesized hydroxy functionalized graphene substrate (GOH), were reacted with chlorodiphenylphosphine (CIPPh₂)for the synthesis of phosphine-functionalized graphene (PFG).^{10c} Then, Pd(OAc)₂ in the presence of EtOH was reduced to Pd(0) nanoparticles to generate a

heterogeneous Pd catalyst system based on graphene.^{7a}Thus,PFG is a useful material for stabilization or complexation of transition metals such as Pd, Ru, Pt, ... on graphene for application in transition metal catalyzed reactions.

In this study, PFG was applied in order to immobilize Pd nanoparticles on surface of graphene for utilization in Heck, Suzuki and N-arylation reactions. The phosphine group on the surface of graphene can coordinate with Pd species, resulting in the efficient stabilization of them on graphene surface.

Characterization of PFG-Pd catalyst

The PFG-Pd catalyst was characterized using some different microscopic and spectroscopic techniques including FT-IR, TEM, SEM, DLS, XRD, EDX, TGA and ICP analysis. A comparison between the FT-IR spectra of GO, and PFG is shown in Figure 1.





The FT-IR of GO shows two bands at around 1735 and 1620 cm⁻¹, which are presumably due to stretching of C=O bond and C=C, respectively. The mentioned peaked appeared in PFG material at 1720 and 1574 cm⁻¹, respectively.¹⁸ The peak at 1427cm⁻¹ is related to C-O bond of carboxyl group. Also, the peak positioned at 1381cm⁻¹ related to the C-O bond of epoxide groups.¹⁹ Disappearance of this peak in PFG confirms the ring opening of this group during preparation process. Also, the peak positioned at 956cm⁻¹ related to the formation of P-O bond structure of PFG ligand. The absorptions of C–H out-of-plane deformation of the mono-substituted benzene ring and vibrations of P-C bond were observed at 694 and 1435 cm⁻¹, which confirm the presence of PPh₂ moiety on the surface of graphene sheets.²⁰

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Then, the PFG-Pd catalyst was investigated by TEM in order to represent the morphology and size of immobilized Pd nanoparticles on the surface of PFG. The TEM images of the PFG-Pd catalyst are shown in Figure 2.



Figure 2 The TEM images of PFG-Pd in different positions

As shown in Fig. 2, the nanoparticles were produced in near to spherical shape with good monodispersity (Fig. 2a & 2b). Also, some of the particles formed in hexagonal shape (Fig. 2c). The DLS analysis of PFG-Pd catalyst show that Pd nanoparticles have average size of 25 nm which is in good agreement with the data obtained from the TEM image (Fig. 2d). These results show that our methodology is efficient for the synthesis of Pd nanoparticles in small size on the surface of graphene sheets which are suitable for catalytic application.

The surface morphology of PFG-Pd material was also investigated by scanning electron microscopy (SEM). As shown in Fig. 3, Pd nanoparticles with spherical morphology are exist on the surface of graphene nano sheets. In these images both graphene sheets (as plates) and Pd nanoparticles (as sphere cores) are observable.



Figure 3 The SEM images of PFG-Pd catalyst

The EDX analysis of PFG-Pd catalyst system is shown in Figure 4.



Figure 4 EDX analysis of PFG-Pd catalyst

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Results of this analysis show the presence of elements of C, O, P and Pd in the structure of catalyst. Amount of P was 5.6 Wt%, which using a calculation it is possible to obtain amount of grafted PPh₂ group to the surface of graphene. The amount of PPh₂ group was estimated to be 1.8 mmol/g of substrate. Also the Wt% of Pd was 26.3, as a result 2.48 mmol/g of Pd is present in the structure of this catalyst system.

The thermogravimetric analysis (TGA) was used to investigate the thermal behavior of GO, PFG and PFG-Pd materials (Figure 5). The TGA of GO shows three main weight loses. The first one occurred at temperatures of 100-110 °C with attributed to the absorbed water. The second one which appeared at temperatures of 190-220 °C which can be related to the dehydration process of oxygen atoms in GO. The final weight loses related to the decomposition of graphene structure. In the TGA diagram of PFG a weight loss with a mild slope is observable which is different from the TGA diagram of GO. Also, the TGA of PFG-Pd show a weight loss with a little gradient in the temperature range of 100-450. This diagram show another weight loss in the temperature range of 500-700, which can be attributed to the decomposition of the graphene structure. As shown in TGA of PFG-Pd the remaining non-decomposable is about 27% which show the amount of loaded Pd in the structure of catalyst.



Figure 5 The TGA curves of GO, PFG and PFG-Pd.

The XRD pattern of the PFG-Pd catalyst is shown in Figure 6. The peaks are indexed as the (111), (200), and (220) planes of the Pd nanoparticles.^{7a} The strongest peaks of the XRD pattern correspond to graphene (002),²⁰ demonstrating the existence of Pd nanoparticles on the surface of PFG substrate. The XRD pattern of recovered catalyst is same to the fresh catalyst and the peaks of both Pd nanoparticles and graphene are observable, representing that the PFG-Pd act as a heterogeneous catalyst in practice.



Figure 6 The X-ray diffraction (XRD) pattern of the PFG-Pd catalyst before recovery (up) and after recovery (down)

PFG-Pd-catalyzed Heck reaction

The PFG-Pd catalyst was used as a reusable Pd catalyst in the Heck reaction. The reaction between 1-bromo-4-methylbenzene (1a) and styrene (2a) was selected as model reaction in order to find optimum condition. The results of optimization study are shown in Table 1.

 Table 1 Optimization of Heck reaction in the presence of PFG-Pd catalyst



Entry	Base	Solvent	T (°C)	Time (h)	Yield (%) ^b
1	K ₂ CO ₃	DMF	120	6	88
2	K ₂ CO ₃	DMAc	120	6	76
3	K ₂ CO ₃	Toluene	110	12	55
4	K ₂ CO ₃	EtOH	80	12	32
5	K ₂ CO ₃	H ₂ O	reflux	12	20
6	Na ₂ CO ₃	DMF	120	6	85
7	K ₃ PO ₄	DMF	120	12	73
8	NaOH	DMF	120	12	70
9	Cs ₂ CO ₃	DMF	120	6	89
10	K ₂ CO ₃	DMF	100	12	70
11	K ₂ CO ₃	DMF	130	6	90
12	K ₂ CO ₃	DMF	rt	48	0
13	K ₂ CO ₃	DMF	120	6	92 [°]
14	K ₂ CO ₃	DMF	120	6	92 ^d
15	K ₂ CO ₃	DMF	120	6	78 ^e
16	K ₂ CO ₃	DMF	120	24	75 ^f
17	K ₂ CO ₃	DMF	120	6	89 ^g

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18	K ₂ CO ₃	DMF	120	6	88 ^h		
^a Reaction conditions: 1a (1 mmol), 2a (1.2 mmol) base (2 mmol),							
solvent (3 mL). ^b Isolated yield. ^c 7 mg of catalyst was used. ^d 10mg							
of catalyst was used. ^e 3 mg of PFG-Pd was used. ^f 1mg of PFG-Pd							
was used. ^g 1.5 mmol styrene was used. ^h 1.0 mmol styrene was							
used.							

As shown in Table 1, different parameters such as base, solvent, temperature, reaction time were investigated in order to obtain optimum condition for this process. Among solvents tested DMF was recognized as the best solvent (Table 1, entries 1-5). Also, K_2CO_3 was selected as base for the Heck reaction in the presence of PFG-Pd catalyst (Table 1, entries 6-9).Different temperatures checked and it was observed that temperature of 120 °C is suitable for this reaction (Table 1, entries 10-12). Also amount of catalyst loading was optimized and in the presence of 7mg (1.7 mol%) of PFG-Pd catalyst, maximum yield of product was produced (Table 1, entries 13-16).By use of 1.5 and 1.0 equivalent of styrene the yield was decreased, so 1.2 eq of styrene was optimal. As a result the entry 13 of Table 1 was selected as optimized conditions for Heck reaction using PFG-Pd as catalyst.

In order to show the generality of PFG-Pd catalyst in the Heck reaction, different substrates of aryl halides and alkenes were checked and results are shown in Scheme 2.



Scheme 2 Products of Heck reaction using PFG-Pd catalyst. All yields are isolated. Reaction conditions: aryl halide (1 mmol), alkene (1.2 mmol) base (2 mmol), solvent (3 mL).

The results in Scheme 2 show that by use of PFG-Pd catalyst it is possible to synthesize divers alkene derivatives using appreciate

alkene and aryl halides. Aryl iodides reacted efficiently in high yield and low reaction time. A good yield of products was observed for aryl bromide substrates. However moderate yields for aryl chloride substrates were detected. Overall, both electron donating and withdrawing groups of aryl rings have not significance effect on reaction time and isolated yields; however, the reaction yield for electron-poor rings was better. Two classes of alkenes including styrene and acrylate were used and it was observed that the reaction yields for styrene is higher than acrylate and PFG-Pd catalyst system is efficient for both alkene substrates used.

Then, in order to show the heterogeneous capability of PFG-Pd catalyst in Heck reaction, the level of reusability was checked in model reaction and it was observed that this catalyst system is reusable at least for 5 times without any significant decreasing in its catalytic activities. The reusability of PFG-Pd catalyst system is shown in Figure 7.

The ICP analysis of the catalyst after 5 times of reusability show that a low amount of Pd content (1.7 %) lost. These results show that PFG-Pd catalyst is heterogeneous for Heck reaction in practice.

To confirm this point that the activity resulted from the supported palladium nanoparticles on the PFG and not from leached Pd, we did the hot filtration test.²³ When the reaction between bromobenzene and styrene was complete, hot filtration had been done and the obtained filtrate solution from the filtration was applied for the next run. After purification processes, the products from the Heck reaction were obtained in less than 3% isolated yield. The ICP analysis of the hot filtrate aqueous solution is in good agreement with these results, because only 0.9 ppm of Pd being observed in this solution.



Figure 7 Reusable capability of PFG-Pd in Heck reaction. Model reaction and optimized conditions was used to check the reusability. Reaction time is 12h.

In order to show that the morphology and structure of the reused PFG-Pd catalyst system does not change significantly, it was analyzed with XRD and SEM. The comparison between the XRD patterns of the fresh and reused PFG-Pd catalyst (Figure 5) demonstrates negligible change in its structure. Also, XRD peaks of reused catalyst show that Pd nanoparticles do not removed from the PFG surface during the reaction progress. The SEM images (see supporting information) of reused catalyst are not considerably

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different from the fresh catalyst, representing that the morphology of catalyst remained unchanged after running the reaction.

To compare the efficiency of our catalyst with the reported heterogeneous Pd-catalysts in the Heck reaction, we have tabulated the results of these catalysts for the synthesis of compounds **3a**, in Table 2. As shown in Table 2, our catalyst is superior to some of the previously reported catalysts in terms of reaction condition, reaction time, and yield. Also similar tables were made for Suzuki and N-arylation reaction results (Table 4, 6).

Table 2 Results Comparison of compound **3a** synthesis, using PFG-Pd catalyst with those obtained by the reported catalysts

Entry	Catalyst and reaction conditions	х	Yield(%) ^a
This work	PFG-Pd(0) (1.7 mol% Pd), K ₂ CO ₃ , DMF, 6h, 120 °C	Br	88
2 ^{24a}	Pd(dba) ₂ -CNT (0.2 mol% Pd), K ₃ PO ₄ , DMF, 12h, 140 °C	Br	75
3 ^{24b}	PCA-GNS-Pd (0.2 mol% Pd), Na ₂ CO ₃ , H ₂ O, TBAB, 15h, 90 °C.	Br	71
4 ^{24c}	Pd@CD-GNS (0.05 mol% Pd), Na2CO3, H2O, TBAB, 24h, 90 °C.	Br	75
5 ^{7a}	SSS-PNP (1.2 mol% Pd), K ₂ CO ₃ , H ₂ O, 5h, reflux.	Br	92
6 ^{24d}	Cell–OPPh₂-Pd(0) (0.1 mol% Pd), Bu₃N, DMF, 7h, 110.	Br	81
7 ^{24e}	PdNPore (0.01 mmol), NaOAc (1.5 mmol), DMAc, 140 °C, 48h	Br	92
8 ^{24f}	MPCS-TI/Pd (0.1 mol%), DMF/H ₂ O,Et ₃ N, 110 °C,TBAB, 4h.	Br	93
9 ^{24g}	MCM(Pd)-41 (0.005 g), n-Pr3N, solvent free, 130 °C, 0.5h.	Br	92

^a Isolated yield.

PFG-Pd-catalyzed Suzuki reaction

In this part of study the Suzuki reaction was checked as another important Pd-catalyzed C-C coupling reaction. The reaction between arylboronic acid and aryl halides in the presence of Pd catalyst resulted in the generation of a biaryl moiety which is an important structural moiety in many organic compounds. In order to find suitable conditions for the Suzuki reaction using PFG-Pd catalyst, the reaction between 1-bromo-4-methylbenzene (**1a**) and phenylboronic acid (**4a**) was used as a model and different conditions were investigated.

Table 3 Optimization study for Suzuki reaction using PFG-Pd catalyst^a



Entry	Base	Solvent	T(°C)	Time (h)	Yield (%) ^b
1	K ₂ CO ₃	H ₂ O	80	12	55
2	K ₂ CO ₃	DMF	100	12	78
3	K ₂ CO ₃	DMF:H ₂ O (1:1)	100	12	80
4	K ₂ CO ₃	DMF:H ₂ O (5:1)	100	12	88
5	K_2CO_3	EtOH	80	12	75
6	K ₂ CO ₃	EtOH:H ₂ O (1:1)	80	12	93
7	Na₂CO ₃	EtOH:H ₂ O (1:1)	80	12	88
8	NaOH	EtOH:H ₂ O (1:1)	80	15	85
9	K_3PO_4	EtOH:H₂O (1:1)	80	15	80
10	K_2CO_3	EtOH:H₂O (1:1)	90	12	92
11	K_2CO_3	EtOH:H ₂ O (1:1)	50	12	72
12	K ₂ CO ₃	EtOH:H ₂ O (1:1)	rt	24	35
13	K ₂ CO ₃	EtOH:H ₂ O (1:1)	80	12	92 [°]
14	K ₂ CO ₃	EtOH:H ₂ O (1:1)	80	12	93 ^d
15	K ₂ CO ₃	EtOH:H ₂ O (1:1)	80	24	78 ^e
16	K ₂ CO ₃	EtOH:H ₂ O (1:1)	80	12	91 ^f
17	K ₂ CO ₃	EtOH:H ₂ O (1:1)	90	24	93 ^g

^a Reaction conditions: 1a (1 mmol), 4a (1.2 mmol) base (2 mmol), solvent (3 mL). ^b Isolated yield. ^c 5 mg of PFG-Pd catalyst was used. ^d 8 mg of PFG-Pd catalyst was used. ^e 3 mg of PFG-Pd catalyst was used. ^f 2.5 mmol base was used. ^g 1.5 mmol phenyl boronic acid was used.

Different conditions were checked in order to obtain appreciate conditions for efficient synthesis of biaryls using Suzuki reaction in the presence of PFG-Pd catalyst. As demonstrated in Table 2, among tested solvents, a mixture of EtOH:H₂O (1:1) was selected as the best media for the reaction (Table 2, entries 1-6). Some bases were also evaluated and K₂CO₃ was chosen as the superior base for this reaction (Table 2, entries 7-9).By change of temperature the reaction yield was changed and temperature of 80 °C was selected as the best condition for Suzuki reaction using PFG-Pd catalyst (Table 2, entries 10-12). The optimum amount of catalyst loading was selected 5mg which is equal to 1.2 mol% of Pd (Table 2, entries 13-15).As a result of this optimization study the best condition for Suzuki reaction using PFG-Pd catalyst was entry 6 of Table 2. The GC analysis of the reaction show that the amount of homocoupling byproduct (biphenyl) is about 2%, demonstrating that this catalyst system is highly efficient for Suzuki reaction under heterogeneous conditions.

After optimization study of Suzuki reaction in the presence of PFG-Pd catalyst, several biaryl compounds using aryl halides and arylboronic acids were synthesized (Scheme 3).

The represented products in Scheme 3 demonstrate that different aryl halides and arylboronic acids can be applied to synthesis desired biaryl compounds using PFG-Pd catalyst under optimized conditions. Aryl halides with both electron donating and electron withdrawing groups were resulted to products in good to excellent yields. Heterocyclic substrates were also used and products were obtained in good yields but with more reaction time.

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Biphenyl and naphthalene substrates produced coupling products under same conditions.



Scheme 3 Products of Suzuki coupling in the presence of PFG-Pd catalyst. All yields are isolated. Reaction conditions: aryl halide (1 mmol), aryl boronic acid (1.2 mmol), base (2 mmol), and solvent (3 mL).

The level of reusability of PFG-Pd catalyst was also investigated in the Suzuki reaction. For this purpose the model reaction and optimized conditions were applied and it was observed that the PFG-Pd catalyst is reusable at least for 5 times in this process without any treatments in its catalytic activities (Figure 8).



Figure 8 Reusable capability of PFG-Pd in Suzuki reaction. Reaction time is 12h.

The hot filtration test was accomplished for Suzuki reaction as same as Heck reaction between 4-bromotoluene and phenylboronic acid. After careful purification processes, about 5% of the coupling product was isolated from the reaction mixture, demonstrating that the PFG-Pd catalyst act heterogeneous in practice. As well, the obtained ICP data from the reused catalyst show that only a low amount of Pd (1.6 %) is lost from the substrate. Consequently, these results confirmed that PFG-Pd catalyst provides good catalytic activity without significant leaching of palladium.

 Table 4 Comparison of the results of the synthesis of compound 5a, using PFG-Pd catalyst with those obtained by the reported catalysts

Entry	Catalyst and conditions	х	Yield(%) ^a
This work	PFG-Pd(0) (1.2 mol% Pd), K₂CO₃, H₂O:EtOH, 12h, 80 °C	Br	93
2 ^{25a}	GO-2N-Pd(II) (0.5 mol% Pd), K ₂ CO ₃ , EtOH, 4h, 80 °C	Br	77
3 ^{25b}	GO-NH2-Pd(II) (1 mol% Pd), K_2CO_3 , EtOH:H ₂ O, 4h, 80 °C	Br	71
4 ^{25c}	Pd-Schiff base@MWCNTs (0.1 mol% Pd), K2CO3, DMF:H2O, 2h, 60 °C	Br	98
5 ^{25d}	GO-NHC-Pd(II) (0.1 mol% Pd), K ₂ CO ₃ , EtOH:H ₂ O, 20h, 60 °C	Br	94
6 ^{25e}	NHC-Pd/GO-IL (0.1 mol% Pd), K ₂ CO ₃ , EtOH:H ₂ O, 2.5h, 60 °C	Br	85
7 ^{25f}	GO-NHC-Pd (1 mol% Pd), Cs ₂ CO ₃ , DMF:H ₂ O, 1h, 50 °C	Br	89
¹ Isolate	ed vield.		

PFG-Pd-catalyzed N-arylation reaction

Carbon-heteroatom bond formation reaction is one of the most important strategies in organic synthesis due to the emergency of the introduction of heteroatoms on the structure of many useful compounds.²¹Along this line, C-N bond formation using Pd catalyst has been considered as a very powerful strategy in the synthesis of aryl amines and there are many research groups that work on this field. In this part of study we decided to use PFG-Pd catalyst in the *N*-arylation reaction in order to increase the applicability of our designed catalyst in more Pd-catalyzed reactions.

The reaction between 1-bromo-4-methylbenzeneand indole was selected as model reaction. The result of optimization study is shown in Table 3.

In our initial selection for the optimization of reaction conditions, toluene was used as solvent and 70% of product after 12h at 100 °C was obtained (Table 3, entry 1). Then the type of base was changed and NaOtBu was selected as the best tested base (Table 3, entries 2-6). Then, some solvents were tested to obtain suitable reaction medium for the *N*-arylation reaction catalyzed by PFG-Pd and it was observed that the maximum yield was produced in toluene solvent (Table 3, entries 7-10). At 110 °C the reaction yield was 93%, thus this temperature was selected as optimum (Table 3, entries 11-13). Then catalyst loading was investigated and 7 mg of catalyst was optimal which is equal to 1.7 mol% of Pd. Under solvent-free conditions 55% of product was observed. Also increasing the amount of indole has no effect on the reaction yield. Thus, entry 11 of Table 3 was selected as optimized conditions for *N*-arylation reaction using PFG-Pd catalyst.

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H ₃ C	1a	~~ (6a	conditions	9	7a	
Entry	Base	solvent	T (°C)	Time(h)	Yield (%) ^b	
1	K ₂ CO ₃	toluene	100	12	70	
2	Na₂CO ₃	toluene	100	12	50	
3	Cs ₂ CO ₃	toluene	100	12	86	
4	NaO <i>t</i> Bu	toluene	100	12	90	
5	K₃PO₄	toluene	100	12	55	
6	NaOH	toluene	100	12	30	
7	NaO <i>t</i> Bu	THF	80	24	70	
8	NaO <i>t</i> Bu	dioxane	100	24	84	
9	NaO <i>t</i> Bu	DMF	100	24	66	
10	NaO <i>t</i> Bu	EtOH	reflux	24	0	
11	NaOtBu	toluene	110	12	93	
12	NaOtBu	toluene	80	24	81	
13	NaO <i>t</i> Bu	toluene	rt	24	0	
14	NaO <i>t</i> Bu	toluene	110	12	94 ^c	
15	NaOtBu	toluene	110	24	80 ^d	
16	NaOtBu	toluene	110	24	65 ^e	
17	NaOtBu	-	110	24	55	
18	NaOtBu	toluene	100	12	93 ^f	
19	NaO <i>t</i> Bu	toluene	100	12	91 ^g	

 Table 5
 Optimization
 study
 of
 PFG-Pd-catalyzed
 N-arylation

 reaction^a

^a Reaction conditions: 1a (1 mmol), 4a (1.2 mmol) base (2 mmol), solvent (3 mL).^b Isolated yield.^c10 mg of PFG-Pd catalyst was used. ^d5 mg of PFG-Pd catalyst was used. ^e3 mg of PFG-Pd catalyst was used. ^f2 mmol base was used.^g 1.5 mmol indole was used.

To determine the scope of the this reaction for preparation of aryl amine derivatives, a number of commercially available amines have coupled with some aryl halides under optimized reaction conditions, and the results are depicted in Scheme 4.



Scheme 4 Products of N-arylation coupling in the presence of PFG-Pd catalyst. All yields are isolated. Reaction conditions: aryl halide (1 mmol), amine (1.2 mmol), base (2 mmol), and solvent (3 mL).

As shown in Scheme 4, *N*-arylation reaction can be accomplished efficiently in the presence of PFG-Pd catalyst system. The *N*arylation reactions of both aromatic and aliphatic amines were investigated and the optimized conditions were suitable for all substrates. Aryls halides of iodide, bromide and chloride were applicable in our methodology. Indole was effectively coupled with aryl amines in the presence of PFG-Pd catalyst system and *N*arylated products were produced in good to excellent yields. Some of products were synthesized using carbazole, imidazole and benzimidazole as valuable heterocyclic amine coupling partners. Morpholine and pyrrolidine was used as aliphatic amines in order to show the applicability of PFG-Pd catalyst in *N*-arylation of arylhalides with these classes of amines. Overall, our methodology is efficient for N-arylation under mild conditions.

The reusability of PFG-Pd catalyst was also evaluated in the *N*-arylation reaction and results are shown in Figure 7. The model reaction and optimized conditions was selected for reusability study.

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Figure 9 Reusable capability of PFG-Pd in N-arylation reaction. Reaction time is 12h.

As shown in Fig. 9, the PFG-Pd catalyst system is reusable in the Narylation reaction at least for 5 times. No significant decreasing in the catalytic activities of the catalyst was observed after 5 run of reusability. Also the ICP analysis data showed that a small amount of Pd (about 1.5%) was lost after 5 run of reusability in comparison with fresh catalyst. Thus, PFG-Pd catalyst is introduced as an efficient heterogeneous catalyst in the N-arylation reaction.

 Table 6 Comparison of the results of the synthesis of compound 7a,
 using PFG-Pd catalyst with those obtained by the reported Pd catalysts

Entry	Catalyst and conditions	х	Yield(%) ^a
This work	PFG-Pd(0) (1.7 mol% Pd), NaOtBu, toluene, 10h, 110 °C	I	95
This work	PFG-Pd(0) (1.7 mol% Pd), NaOtBu, toluene, 15h, 110 °C	Br	92
1 ^{26a}	SWCNT-Met/Pd (0.2 mol% Pd), Et ₃ N, DMF, 6h, 110 °C	I	98
2 ^{26a}	SWCNT-Met/Pd (0.2 mol% Pd), Et ₃ N, DMF, 6h, 110 °C	Br	0 ^b
3 ^{26b}	SBA-15/AO/Pd(0) (0.3 mol% Pd), Et₃N, DMF, 4h, 110 °C	I	98
4 ^{26c}	biaryl(dialkyl)phosphine/Pd₂(dba)₃(1 mol% Pd), NaOt-Bu, Toluene, 100 °C	I	90
5 ^{26c}	biaryl(dialkyl)phosphine/Pd2(dba)3 (1 mol% Pd), NaOt-Bu, Toluene, 100 °C	Br	88

^a Isolated yield.^b C3-arylation of indole was observed.

Conclusions

In conclusion, we have introduced an efficient and simple method for chemically modification of graphene with phosphine groups. This is a new example of the grafting of PPh₂ group on the surface of graphene sheets using our methodology. In this study, Pd nanoparticles were immobilized on the surface of PFG in order to synthesis an efficient heterogeneous Pd catalyst system for application in Pd-catalyzed C-C and C-heteroatom coupling reactions. The PFG-Pd was used as an efficient heterogeneous View Article Online DOI: 10.1039/C5NJ02227D **ARTICIF**

catalystin Heck, Suzuki and N-arylation reactions under mild, and heterogeneous conditions. This graphene based nano-palladium catalyst system was reusable for 5 times in the reactions without significant decreasing in its catalytic activity. We believed that our strategy will be open up a new direction for the development of new phosphine functionalized graphene-based materials. Also, the PFG-Pd catalyst can be used in other Pd-catalyzed organic transformations.

Experimental Section

General. Chemicals were purchased from Fluka and Aldrich chemical companies and used as received. GO nanosheets were synthesized using graphite powders by a modified Hummer's method.²²FT-IR spectroscopy (Shimadzu FT-IR 8300 spectrophotometer) was employed for characterization of the catalyst and synthesized compounds. The scanning electron micrograph (SEM) for the catalyst was obtained by SEM instrumentation (SEM, XL-30 FEG SEM, Philips, at 20 kV). Transmission electron microscopy (TEM) was obtained using a TEM apparatus (CM-10-Philips, 100 kV) for characterization of the PFG-Pd catalyst. The X-ray diffraction (XRD, D8, Advance, Bruker, axs) was employed for characterization of the PFG-Pd catalyst. EDX analysis was accomplished using a Fe-SEM instrument (Sigma, Zeiss). ICP analysis was determined, using an inductively coupled plasma (ICP) analyzer (Varian, Vista-Pro). For recorded ¹H and ¹³C NMR spectra, we used a Bruker (250 MHz) Advance DRX in pure deuterated CDCl₂ solvents with tetramethylsilane (TMS) as the internal standard. The reaction monitoring was accomplished by TLC on silica gel PolyGram SILG/UV254 plates. Column chromatography was carried out on columns of silica gel 60 (70-230

Catalyst preparation

Preparation of GO. Typically, 5.0 g of natural graphite powder and 2.5 g of sodium nitrate were mixed with 115 mL of sulfuric acid (98%) in a 1000 mL round-bottom flask equipped with a magnetic stirrer and condenser place in an ice bath. The obtained solution was stirred and slowly added 15.0 g of potassium permangenate, the stirring was continued for 2 h. The mixture solution was transferred to a 35 °C water bath and stirred for 30 min. After this step, 230 mL of deionized water was slowly added into the solution and the solution temperature monitored was about 98 °C and stirred for 15 min. Then, 700 mL of deionized water and 50 mL of H_2O_2 (30%) was sequentially added to the mixture solution to terminate the reaction. The resulting materials was filtered and washed with 5% HCl solution followed by distilled water for several times. The solution was filtered under reduced pressure by vacuum pump over sinter-glass (G4). The graphite oxide powder was obtained after drying in vacuum at 60 °C for 12 h. The graphite oxide was dispersed in distilled water to make concentration of 0.5 mg/mL, and exfoliated by ultrasonication (75 w) for 30 min to

mesh).

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generate GO nanosheets, followed by centrifugation at 3500 rpm for 30 min to remove unexfoliated graphite oxide.²²

Preparation of GOH. GO was converted to GOH via ring opening of epoxide in the presence of sodium hydroxide. In a canonical flask, 0.5 g of GO was dissolved in 20 mL of deionized water. Then, NaOH 0.5 g was added to the reaction mixture and permit it stir for 1h at room temperature. Subsequently, the temperature of mixture was enhanced to 90 °C and the solution was stirred for 24h. Afterward, the reaction mixture cold down to room temperature and neutralized with HCI (0.1 M) until pH = 7 reached. The GOH as a dark solid were isolated from the solution by simple filtration and washed with deionized water and dried in oven under vacuum.

Preparation of PFG. To a canonical flask containing 10 mL of dry dichloromethane, 0.3 g of GOH was added. Then 0.25 mL of Et_3N was added to the mixture and the solution was stirred for 10min at rt. After the specified time, 0.18 mL (0.22 g) of CIPPh₂ was added to the solution and it was stirred continuously for another 12 h under Ar gas. Subsequently, the reaction mixture cooled down to rt and precipitation was filtered and washed with dry dichloromethane (3 x 10) and deionized water (3 x 10). In order to obtain the PFG product it was dried under vacuum overnight.

Synthesis of PFG-Pd. In a three-necked flask (50 mL) containing 10 mL of EtOH and 0.3 g of PFG, 0.10 g of Pd(OAc)₂was added. When the addition was completed, the mixture was stirred for 24h at 35 °C. Then, the reaction mixture was filtered and the obtained solid was dried in vacuum to obtain PFG-Pd catalyst.

General procedure for the Heck reaction using PFG-Pd catalyst. To a mixture of arylhalide (1 mmol), styrene (1.2 mmol), and K_2CO_3 (2 mmol) in 3 mL DMF, PFG-Pd catalyst (7 mg g, 1.7 mol %) was added and heated in an oil bath at 120 °C for the time specified in Scheme 2. The reaction was followed by TLC. After completion of the reaction, the mixture was cooled to room temperature and filtered, and the remaining solid was washed with dichloromethane (3 × 5 mL) in order to separate the catalyst. After washing the dichloromethane with water (3 x 5 mL), the organic phase was extracted and dried over Na₂SO₄. The organic solvent was evaporated and to obtain crude product. For further purification it was purified by column chromatography (hexane/ethyl acetate).

General procedure for the Suzuki reaction using PFG-Pd catalyst. To a mixture of arylhalide (1 mmol), arylboronic acid (1.2 mmol), and K_2CO_3 (2 mmol) in 3 mL EtOH:H₂O (1:1), PFG-Pd catalyst (5 mg, 1.2 mol %) was added and heated in an oil bath at 80 °C for the time specified in Scheme 3. The reaction was followed by TLC. The separation of catalyst, work up process and purification is same to Heck reaction.

General procedure for the *N*-arylation reaction using PFG-Pd catalyst. To a mixture of arylhalide (1 mmol), amine (1.2 mmol), and K_2CO_3 (2 mmol) in 3 mL toluene, PFG-Pd catalyst (7 mg, 1.7 mol %) was added and heated in an oil bath at 110 °C for the time specified

in Scheme 4. The reaction was followed by TLC. The separation of catalyst, work up process and purification is same to Heck reaction.

Procedure for recovery of catalyst. After completion of the reaction, the mixture was cooled to room temperature and filtered, and the remaining solid was washed with dichloromethane $(3 \times 5 \text{ mL})$ in order to separate the catalyst. The reused catalyst was dried in oven (in order to washing with water be efficient), and then was washed with water $(3 \times 5 \text{ mL})$. The washed catalyst with water was dried in oven to ready for next run.

Procedure for hot filtration test. In this way that, after completion of the reaction, the mixture immediately was filtered and it was washed with hot DMF in order to separate the catalyst. Afterward, the filtrate solution was used for next run without adding catalyst.

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Immobilized Pd(0) nanoparticles on phosphine-functionalized graphene as highly active catalyst for Heck, Suzuki and *N*-arylation reactions

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Phosphine functionalized graphene was introduced for immobilization of Pd nanoparticles to be applied in C-C and C-N bond formation reactions.