Ionic Liquid Immobilized Palladium Nanoparticle - Graphene Hybrid as Active Catalyst for Heck Reaction

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Abstract: We engineered, graphene based Pd -Nano composites (Pd/RGO) and tested them to catalyze the Heck reaction in [bmim] NTf₂ solvent system. High yield, easy product isolation, recycling of the catalytic system and ligand free approach are the main outcomes of this proposed protocol. The proposed protocol was further exploited for the successful synthesis of 3-styryl coumarins in good yield.

Keywords: Heck Reaction, Ionic liquid, Graphene, Palladium nano particle, Nano composites.

1. INTRODUCTION

Graphene is the two-dimensional sheet of sp² hybridized carbon allotrop, having extraordinary combination of thermoelectrical and mechanical properties [1-6]. The graphene (graphene oxide or reduced graphene oxide) has attracted a great interest of chemical researchers for the development of a new kind of composite materials, particularly as a host to carry metal nanoparticles such as palladium, gold, platinum, titanium, tin and zinc. [1,2,7,8]. These nanoparticals supported graphenes were further exploited as catalyst for different organic reactions like oxidation, reduction, dehydrogenation, hydration, condensation, esterification, hydrogenation and coupling reactions [1,7,9-15] in a facile, recyclable and eco-friendly manner [1,2,7]. It was found that immobilization as well as stabilization of metal nanoparticals on a carbon substance is favorable for improving their catalytic activity. The presence of functional groups and the highly specific surface area of chemically modified graphenes (CMGs) enhances their capability of loading metal nanoparticles (MNPs) with the aid of hydrophobic and electrostatic interactions. These graphene based MNPs serve excellent stability against air and moisture, hence they offer easy handling during the reaction.

In catalysis, palladium metal is considered as an important metal catalyst to catalyze various organic transformations [9-11], specially C-C bond forming coupling reactions. Palladium metal offers the most effective combinations of activity and selectivity throughout the reaction. Various approaches have been made to modify the palladium catalyzed coupling reactions like incorporation of different organic/inorganic bases, ligands, solvent systems, different organic-inorganic supports (polymers, ionic liquids, Mont-

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morillonite clay, silica, zeolite etc.) to anchor the palladium catalysts as well as substrates in order to improve the yield, selectivity along with the recycling of valuable palladium catalyst etc [10-13]. In recent reports, palladium nanoparticales immobilized reduced graphene oxide (Pd/rGO) was found nearer to other commercially available palladium catalysts (*e.g.* Pd on charcoal) in terms of yield and selectivity, but such Pd/rGO also undergoes with various shortcomings like high catalyst loading, catalyst leaching (*via* agglomeration of Pd metals into the clusters), limited substrate scope, requirement of polar solvents, etc.

A number of reports and reviews have been published on exploring the application of ionic liquids as a reaction medium for different organic transformations [16,17]. Recently graphene-supported Pt nanoparticles were immobilized into the [MTBD][bmsi] ionic liquid to catalyze electrocatalytic reaction with high catalytic activity [18]. Gao *et al.* also submitted report on the synthesis with complete characterization of Ag-Pd bimetallic nanoparticles on reduced graphene oxide (rGO), which were also used to catalyze Suzuki-Miyaura as well as Sonogashira carbon coupling reaction. This method offers simple reaction protocol along with the added advantages of catalyst recycling [19].

In the search of ligand free, recyclable, selective and stable catalytic system, we engineered the Pd/rGO composite and tested as a catalyst for the Heck reaction in $[bmim]NTf_2$ ionic liquid medium.

2. RESULTS AND DISCUSSION

Typically, Pd/rGO was prepared by reducing the mixture of graphene suspension (2.5mg/mL) and palladium acetate (10 mg) in water. Sodium dodecyl sulfate (SDS, 0.1 mol/L) was used as a surfactant as well as reducing agent [2] during the process. Size distribution of Pd nanoparticales further analyzed by transmission electron microscope (TEM) and the mean size of Pd nanoparticales dispersed on the graphene

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Scheme 1. Reaction optimization for Heck Reaction.

sheets were found about 5 nm (average size) (Supporting information Figure 1). The presence of a large number of Pd nanoparticals on graphene was also confirmed by energy-dispersive X-ray spectroscopy (EDX) (Supporting information Figure 2). The oxygen and sulfur signal appear due the presence of residual dodecanoate and sulfonate groups in EDX data. The significant copper peaks also appeared in the EDX data due to the presence of Copper grid.

The well characterized Pd/rGO was further tested for the Heck reaction in [bmim]NTf₂ ionic liquid medium. Here it was expected that ionic liquids not only work as good solvents for the Heck reaction (due to their physiochemical properties), but their exceptional ionic environs may change the progress of the reaction, activating and/or stabilizing intermediates or transition states in the Heck reaction mechanisms. As a result, while running the Heck reaction in ionic liquids increases the reaction kinetics with respect to conventional solvent systems. It is well documented that onic liquids offer physiochemical stabilization of the metal nanoparticales and also influences the regio- and stereoselectivity of the Heck reaction products [20,21]. The Pd nanoparticles before and after the coupling reaction were also studied by TEM (Supporting information Figure 1). The presence of Pd metal leaching in the reaction phase was confirmd with the help of atomic absorption spectroscopy (AAS). The results derived from above mentioned analytical studies, indicate the proper dispersion of Pd/rGO species into the 1-butyl-3-methylimidazolium bis(trifluoromethylsulfonyl) imide([bmim]NTf₂) ionic liquid. Here, [bmim]NTf₂ ionic liquid works as a reservoir of catalytically active Pd/rGO species. It was expected that Heck reaction probably proceeds via the oxidative addition of aryl halides on the surface of Pd nanoparticles. After the reaction, the product was easily recovered by simple extraction with diethyl ether followed by decantation of the upper organic layer. No aqueous work-up and additives were required during the reaction.

2.2. Application of Pd/rGO Catalysts for Heck Reaction

Model test reaction was carried out with iodobenzene, ethyl acrylate and potassium carbonate in different solvents using Pd/rGO as catalyst (Scheme 1, Table 1, Entry 1-25). The highest yield was obtained with Pd/rGO in [bmim]NTf₂ solvent system and because of that [bmim]NTf₂ was used as a reaction solvent to optimize rest of the reaction parameters like time, temperature, catalyst loading, screening of bases and ligands etc (Table 1, Entry 1-25). Pd/rGO/ [bmim]NTf₂ system gave the best result in terms of yield, reaction time, temperature and catalyst loading (Table 1, Entry 5). After completion the reaction, the corresponding reaction product was isolated by simple diethyl ether extraction method in case of ionic liquid while in case of organic solvents, aqueous work-up was required to isolate the reaction product from reaction mass along with the heavy loss of catalyst as well as the reaction product.

Under conventional reaction conditions, homogeneous Pd catalyst gets deteriorated and offers the deposition of Pd black after the reaction. Recovery of the Pd catalyst is usually unrealistic, thus eliminating the possibility of recycling the Pd catalyst. On the other hand, ionic liquid containing Pd/rGO can be recycled as a catalyst itself, as shown in Figure 1. No significant loss in yield was found during catalyst recycling experiments up to 10 runs but after extending the recycling experiments up to 13th cycle, 5-7% drop in yield was observed (Scheme 2). The drop in catalytic activity during recycling experiments was mainly observed because of agglomeration of rGO immobilized Pd nanoparticles, as the particale size of Pd nanoparticales increased from 5 nm to 20 nm while performing the TEM analysis of Pd/rGO (13th run) (Supporting information Figure 1b).

The optimized reaction conditions were further tested for various combinations of aryl halides with different olifines (Table 2, Entry 1-15) [22]. The C-X bond strength affects the activity towards the Heck reaction as the general cross coupling reaction follows the C-I>C-Br reactivity order. The yield of coupling reactions with different alkyl acrylates was found to be more comparable to styrene. Boromobenzene with electron withdrawing groups offered almost similar activity with respect to iodobenzene towards Heck reaction (Table 2, Entry 5-12) while substituted bormobenzenes with an electron donating groups gave the coupling product in lower yield.

Coumarins or benzopyranones, have attracted a great interest of researchers due to their unique pharmacological activities towards cancer, bacteria, etc [23-25]. We exploited our proposed protocol for the synthesis of 3-styryl coumarins using 3-bromo-6,7-dimethoxycoumarin with three different derivatives of vinyl benzene (Table 2, Entry 13-15). The overall yield for 3-styryl coumarin derivatives was isolated in quantitative yield.

3. EXPERIMENTAL

All the chemicals were purchased from Sigma Aldrich, Acros or Fluka. Nuclear Magnetic Resonance (NMR) spectra were recorded on standard Bruker 300WB spectrometer with an Avance console at 400 and 100 MHz for ¹H and ¹³C NMR respectively. The residue was purified by flash chromatography (FC) with hexane/ethyl acetate. The detailed ¹H NMR and ¹³C NMR of each eck reaction products were found similar to the reported analytical data [25-27]. The purity of reaction products (Table **2**, Entry 1-15) was checked by gas chromatographic analysis (Shimadzu GC-17A gas chromatograph with either a DB-Wax or a RTX-5 column). 1-butyl-3-methylimidazolium *bis* (trifluoromethylsulfonyl)

Table 1. Catalyst optimization fo	r Heck reaction.
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Entry ^a	Catalyst (0.25 mol%)	Solvent ^b (2mL)	Base/Ligands	Temperature (°C)	Reaction Time (Minutes)	Yield ^c (%)
1.	Pd/rGO	DMSO	K ₂ CO ₃	100	60	57
2.	Pd/rGO	DMF	K ₂ CO ₃	100	60	53
3.	Pd/rGO	THF	K ₂ CO ₃	100	60	53
4.	Pd/rGO	NMP	K ₂ CO ₃	100	60	57
5.	Pd/rGO	[bmim]NTf ₂	K ₂ CO ₃	100	60	98
6.	Pd/rGO	Water: ⁱ prOH	K ₂ CO ₃	100	60	65
7.	Pd/rGO	Water:EtOH	K ₂ CO ₃	100	60	61
8.	Pd/rGO	Water:MeOH	K ₂ CO ₃	100	60	63
9.	Pd/rGO	[bmim]NTf ₂ (3mL)	K ₂ CO ₃	100	60	97
10.	Pd/rGO	[bmim]NTf ₂ (1mL)	K ₂ CO ₃	100	60	90
11.	Pd/rGO	[bmim]NTf ₂	K ₂ CO ₃	50	60	73
12.	Pd/rGO	[bmim]NTf ₂	K ₂ CO ₃	150	60	97
13.	Pd/rGO	[bmim]NTf ₂	K ₂ CO ₃	120	60	98
14.	Pd/rGO	[bmim]NTf ₂ + DMSO	K ₂ CO ₃	100	60	97
15.	Pd/rGO	[bmim]NTf ₂	K ₂ CO ₃	100	30	47
16.	Pd/rGO	[bmim]NTf ₂	K ₂ CO ₃	100	90	98
17.	Pd/rGO	[bmim]NTf ₂	K ₂ CO ₃	100	120	97
18.	Pd/rGO	[bmim]NTf ₂	Pyridine	100	60	77
19.	Pd/rGO	[bmim]NTf ₂	ET ₃ N	100	60	72
20.	Pd/rGO	[bmim]NTf ₂	Na ₂ CO ₃	100	60	80
21.	Pd/rGO	[bmim]NTf ₂	K ₂ CO ₃ :PPh ₃	100	60	89
22.	PdCl ₂	[bmim]NTf ₂	K ₂ CO ₃	100	60	95
23.	Pd (OAc) ₂	[bmim]NTf ₂	K ₂ CO ₃	100	60	96
24.	Pd/rGO (4 mol%)	[bmim]NTf ₂	K ₂ CO ₃	100	60	98
25.	Pd/rGO (1 mol%)	[bmim]NTf ₂	K ₂ CO ₃	100	60	71

(a.) The reaction was carried out with iodobenzene (0.50 mmol), ethyl acrylate (1 mmol), base (1.5 mmol), PPh₃ as ligand (0.05 mmol) solvent (2 mL). (b.) The water : organic solvent ration 1:1.(c.) Isolated yields after column chromatography.

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Scheme 2. Optimized reaction condition for Heck reaction.



Fig. (1). Recycling Results of $Pd/rGO/[bmim]NTf_2$ for Heck reaction.

Table 2. Application of Pd/rGO catalysts for Heck reaction.

Entry ^a	Aryl Halide	Olefin	Reaction Product	Yield ^b (%)
1				98
2				92
3				73
4				90
5	Br			95
6	0 Br			92
7	HO		HO	65

Entry ^a	Aryl Halide	Olefin	Reaction Product	Yield ^b (%)
8	Br			58
9	H ₂ N Br		H ₂ N O O	65
10	Br			93
11	N Br		O N Br	78
12	Br		s o o	71
13	O O O O O O O			63
14	Br 0 0 0 0 0	NO ₂		67
15	o o l			45

(a.) The reaction was carried out with Pd/rGO (0.25mol%), haloaryl (0.50 mmol), olifin (1 mmol), K₂CO₃ (1.5 mmol), [bmim] [NTf₂] (2 mL) at 100°C for 60 minutes.
 (b.) Isolated yields after column chromatography.

imide ([bmim]NTf₂) was synthesized as per reported procedure [28]. The Pd/rGO material was characterized by trans-

mission electron microscope (TEM) (Philips CM200) and energy-dispersive X-ray spectroscopy (EDX) (PerkinElmer, PHI 1600 spectrometer). The palladium contents of the samples were determined quantitatively by atomic absorption spectroscopy (AAS) on a HITACHI Z-2300 instrument.

3.1. General Procedure for Heck Reaction

Add 50 mL round bottom flask with aryl halide (0.5 mmol), vinyl compound (1.5 mmol), catalyst in a solvent system as per reported quantity in Table 1, Entry 1-25. Base (1.5 mmol) and phosphine ligand (0.05 mmol) were added as per requirement (Table 1, Entry 1-25). The resulting reaction mass was allowed to heat at the 100°C for 1 hour. After cooling the reaction mass the volatile materials were under reduced pressure at 40°C for 20 minutes. Then the reaction product was isolated with diethyl ether (5x2mL) washing. Then the purification of reaction product was carried out with flash chromatography (eluent: AcOEt: *n*-hexane=1: 3) to achieve the pure Heck reaction product.

3.2. Catalyst Recycling Experiment

Add 50 mL round bottom flask with with aryl halide (0.5 mmol), vinyl compound (1.5 mmol), Pd/rGO (0.25 mole %) in [bmim]NTf₂ (2 mL) with K_2CO_3 (1.5 mol). The resulting reaction mass was allowed to heat at 100 °C for 1 hour. The reaction mass was allowed to cool at room temperature (20-25°C). Then the volatile materials were evaporated from the reaction mass under reduced pressure at 40°C for 20 minutes. The reaction product was isolated after washing with diethyl ether (5x2mL) and the catalytic system was dried under reduced pressure at 50°C for 30 minutes. Then the next slot of reactants was added for the next recycling run.

CONCLUSION

We have successfully developed a highly efficient ligand free method for Heck reaction. Ionic liquid mediated Pd/rGO catalyst in an ionic liquid medium which afforded the coupling products with excellent yield. One of the major advantages of the proposed protocol is that the catalyst system can be easily re-used without loss of catalytic activity, thereby multiplying catalyst turnover. Another advantage is that the reaction proceeds without phosphine ligands, which are expensive, toxic and contaminants of product. The Green nature of ionic liquid and its operational simplicity makes the present Heck reactions more attractive.

CONFLICT OF INTEREST

The authors confirm that this article content has no conflict of interest.

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Declared none.

SUPPLEMENTARY MATERIAL

Supplementary material is available on the publishers Web site along with the published article.

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