ORIENTAL JOURNAL OF CHEMISTRY
An International Open Free Access, Peer Reviewed Research Journal
www.orientjchem.org
Est. 1984
ISSN: 0970-020 X
CODEN: OJCHEG
2018, Vol. 34, No.(2):
Pg. 881-886

Carbon–Carbon Bond Formation Reaction with Pd/reduced Graphene Oxide Composite

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http://dx.doi.org/10.13005/ojc/340236

(Received: December 03, 2017; Accepted: February 01, 2018)

ABSTRACT

Palladium nanoparticles supported on reduced graphene oxide (Pd/rGO) catalyst was prepared by using alovera extract in sunlight. The catalyst (Pd/rGO) was employed for the Suzuki cross coupling reactions. The characterization of Pd/rGO was done by scanning electron microscopy (SEM), transmission electron microscopy (TEM) and X-ray diffraction analysis (XRD). The average particle size of Pd was found to be 7±2 nm. The compound showed excellent catalytic activity with good recyclability for C-C cross coupling reactions.

Keywords: Solar energy, Alo vera, Heterogeneous catalysis, Greener synthesis, Palladium nanoparticles, Reduced graphene oxide, Cross coupling reactions.

INTRODUCTION

In last decades Suzuki–Miyaura cross-coupling reaction has gained considerable attention because of its use in making active pharmaceutical ingredients, agrochemicals, polymers, bioinorganic materials and natural products on a laboratory as well as industrial scale[1]. In 1981 the first method was reported for the preparation of biaryls via C-C cross-coupling reaction[2]. In general, homogeneous palladium complexes are used as catalysts in the Suzuki reaction[3].

The reported homogeneous catalysts are found to have greater catalytic properties than heterogeneous catalysts in the formation of C-C coupling reactions[4-6]. The several researchers focused on the development of palladium complexes which efficiently catalyze the reaction[7].

The palladium complexes usually show greater catalytic activity. The main drawbacks of these catalysts are availability, stability, recovery, and high cost in addition to their sensitivity to air and moisture. So reactions catalyzed by

Pd-complxes are carried under nitrogen atmosphere.

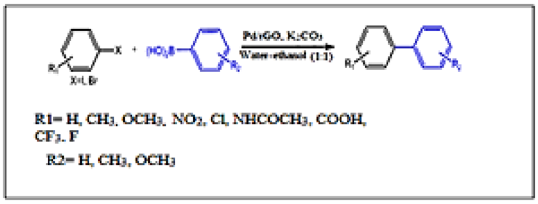
In order to overcome these challenges the efforts has been made to design heterogeneous Pd composites such as Pd supported on metal oxide, carbon, mesoporous zeolites and polymers, for use in Suzuki-Miyaura coupling reactions[8-10] Recently, the use of ligand-free heterogeneous palladium nanocomposites has drawn more attention of the researchers due to their simple handling, recovery, and recycling.

Further catalytic activity of Pd-based catalysts is increased by using different types of support materials[11-14]. The use of support facilitates stabilization and homogeneous dispersion of Pd supported catalyst[15].

We have previously reported the electrochemical preparation of Pd NPs supported on graphene and their applications in suzuki coupling reactions[11,13] These catalysts exhibited high efficiency and easy recycling. The major challenges in palladium nanoparticle synthesis are size control and agglomeration of Pd NPs[16,17].

The synthesis of Pd NPs nanoparticles by greener route is one of the most striking features of present research[18]. In recent past various biological methods of synthesis of metal nanoparticles have been employed[19-21]. In biological methods metal nanoparticles are reduced by using bacteria, fungus and plant extracts as a reducing agents. The biological methods are more ecofriendly, avoid use of toxic reducing agents, and cheap. In literature few reports are available on synthesis of metal nanoparticles using sunlight[22-27]. The main drawbacks these reported methods are high temperature operation, longer reaction time, toxic reducing agents and recovery of the catalyst. To overcome these drawbacks we herein, report synthesis of palladium nanoparicles supported on partially reduced graphene oxide (Pd/rGO) by using alovera extract and sunlight. In Aloe vera more than seventy five essential constituents such as enzymes, minerals, vitamins, sugars, lignin, saponins, amino acids and salicylic acids are present, which could facilitate the reduction of functional groups such as –COOH, -OH, epoxide, etc. in graphene oxide. The present protocol is novel, inexpensive and eco-friendly for the synthesis of Pd nanoparticles in which alovera acts as a mild reducing agent and sunlight as an energy source for the reduction. The catalytic application of prepared catalyst was examined in C-C Suzuki coupling reactions.

We report here the greener synthesis of Pd/rGO composite using alovera extract in sunlight and its applications in Suzuki coupling reactions. This environmentally benign catalyst is highly efficient, recyclable, stable for Suzuki coupling reactions.



Scheme 1. Suzuki reaction catalyzed by Pd/rGO

EXPERIMENITAL

Material and Methods

All the reagents used were procured from Sigma-Aldrich of AR grade and used without any purification.

Synthesis of graphene oxide

The synthesis of Graphene oxide was carried out by reported modified methods in the literature[28]. In typical procedure, 1 g of graphene and 1 g $NaNO_3$ was added to a round bottom flask containing 45 mL of concentrated H_2SO_4. The reaction mixture was maintained at 0-5 ^{0}C for 2 h and then charged 6 g of $KMnO_4$. The reaction mixture was diluted with water followed by heating at 98 ^{0}C for 15 minutes. A brown color solution was obtained after cooling reaction mixture to 30 ^{0}C. The reaction mixture was then treated with 20 mL hydrogen peroxide till color change from brown to yellow. The reaction mass was quenched in 100 mL distilled water and stirred for 1h at 30 ^{0}C. The solid obtained was centrifuged, washed with 10% HCl and finally with distilled water till neutral pH, and dried at 60 ^{0}C.

Preparation of Aloe vera Extract

100 g of fresh leaves of Aloe vera were chopped and mixed with 500 mL of distilled water.

Then mixture was boiled and concentrated to 100 mL. This reaction mass was cooled and filtered to obtain Aloe vera extract. The prepared extract was stored in a refrigerator at 4 °C.

Synthesis of Pd/rGO nanocomposite

A graphene oxide (800 mg) was charged to 500 mL beaker containing 200 mL distilled water. A $PdCl_2$ solution (0.8 g) and 100 mL Aloe vera extract was added to the reaction mixture and sonicated for 20 min. at 28-30 °C. The resulting mass was stirred under sunlight till the color changes from brown to black. The catalyst was filtered through whatman filter paper, washed with water, ethanol (50 mL), and dried at 110 °C to obtain a desired catalyst.

Characterization of Pd/rGO nano composite

The morphological study of Pd/rGO was done by different analytical techniques such as scanning electron microscopy (SEM) and transmission electron microscopy (TEM) and composition by X-ray Diffraction (XRD, Rigaku Miniflex model by using CuKα = 1.54 Å with scanning range 10–80°). Palladium content in the composite was determined by inductively coupled plasma-atomic emission spectroscopy (ICP-AES).

General procedure for Suzuki coupling reactions

A mixture of aryl halide (1 mmol), phenyl boronic acid (1.2 mmol), 3 mmol potassium carbonate and 3 mg of Pd/rGO catalyst was charged in 5 mL ethanol-water (1:1) and refluxed for 6 hours. The reaction was monitored by Gas Chromatography. After the completion, reaction mass was cooled the catalyst recovered by centrifugation. The recovered catalyst was washed with absolute alcohol, dried and used for next run. The pure products were obtained by column chromatography. The conversion of reactant was determined by Gas chromatography (GC). The final products of coupling reactions are characterized by ^{1}HNMR and Mass spectroscopy.

RESULTS AND DISCUSSION

(Pd/rGO) composite prepared by novel greener approach using alovera extract in presence of sunlight was characterized by ICP-AES, SEM, TEM and XRD.

The analysis of SEM image (Fig. 1) clearly shows the formation of PdNPs on reduced graphene oxide with mono and uniform dispersion of PdNPs.

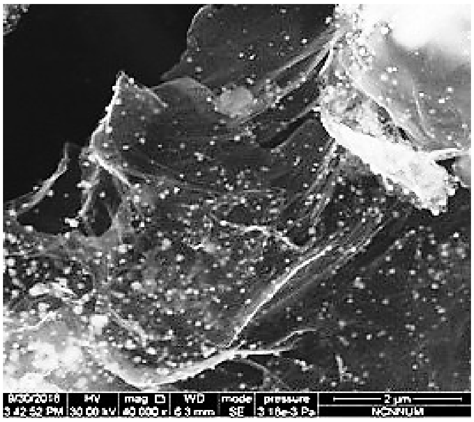


Fig. 1. SEM of Pd/rGO

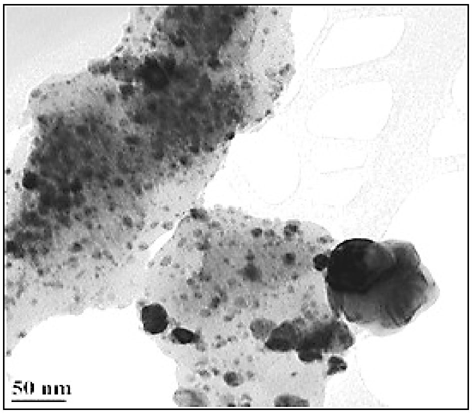


Fig. 2. TEM of Pd/rGO

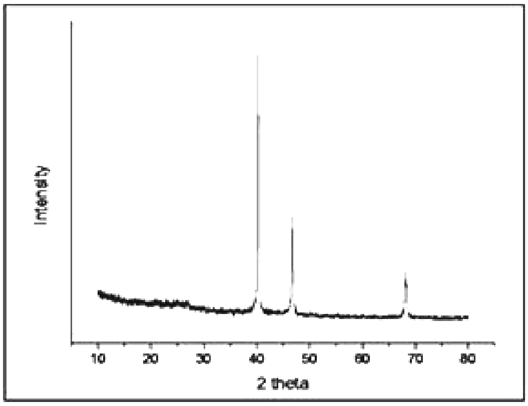


Fig. 3. XRD spectra of Pd/rGO

The TEM images (Fig. 2) show the presence of well dispersed Pd nanoparticles on rGO. The size of Pd NPs varies from 2-19 nm. Fig. 3 represents the XRD pattern of (Pd/rGO) composite. The broad weak diffraction peak appears at 24.61°, which indicates the reduction and exfoliation of GO into reduced graphene oxide. The peaks at around $2\theta = 40.1°$, 46.5°, 68.1°, for the Pd NPs on rGO are assigned to the (111), (200) and (220), crystalline planes of the face centered cubic structured palladium. It also confirms that the intensity of peak corresponds to $2\theta = 40.1°$ is more and this could be major crystal facet. The average crystalline size was obtained by using Scherrer's equation: $D=0.9\lambda/\beta\cos\theta$ (where D is the average crystalline size, λ is the wavelength of CuKα, β is the fullwidth at half maximum of the diffraction peaks, and θ is the Bragg's angle). The average crystalline size of PdNPs was found to be around 7±2 nm. The pd loading in Pd/rGO composite was found to be 7.2 wt.%.

In order to accomplish promising results, the effect of various solvents, bases, and catalyst amounts has been examined using iodobenzene and arylboronic acid as a representative reaction. Among the various solvents, ethanol-water mixture (1:1) was a better solvent (Table 1, entries 1-7). The reaction proceeded well in ethanol-H_2O mixture compared to that in pure H_2O or ethanol (Table 1, entries 8-9). Among the various bases K_2CO_3 (3 mol eq.) was identified as efficient base (Table 1, entries 1 and 10-13). The effect of catalyst loading was investigated. It is to be noted that the quantity of catalyst plays a significant role in the product yields. We assessed this reaction with various pd content from 0.1-0.3 mol%. The result demonstrates that 0.2 mol% palladium loading favours the reaction (Table 1, entries 14–17). The most favourable reaction conditions for the model reaction are Palladium: 0.2 mol%, Solvent: ethanol–water (50%, v/v), Base: K_2CO_3, and Temperature:t 80 °C.

Table 1: Optimization of reaction parameters for Suzuki reaction catalyzed by Pd/rGO[a]

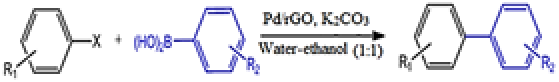
Entry	Solvent	Base	Pd loading(mol %)	Time (h)	Yield (%)[b]
1	Ethanol/H_2O	K_2CO_3	0.2	2	96
2	Methanol	K_2CO_3	0.2	2	81
3	Acetonitrile	K_2CO_3	0.2	2	53
4	DMF	K_2CO_3	0.2	2	33
5	Water/methanol	K_2CO_3	0.2	3	90
6	DMF	K_2CO_3	0.2	4	22
7	Water/toluene /1,2dioxane	K_2CO_3	0.2	6	22
8	Water	K_2CO_3	0.2	12	20
9	Ethanol	K_2CO_3	0.2	14	16
10	Ethanol/H_2O	Na_2CO_3	0.2	2	60
11	Ethanol/H_2O	TEA	0.2	2	28
12	Ethanol/H_2O	N-methyl morpholine	0.2	3	60
13	Ethanol/H_2O	NaOH)	0.2	2	46
14	Ethanol/H_2O	K_2CO_3	0.3	2	96
15	Ethanol/H_2O	K_2CO_3	0.2	2	96
16	Ethanol/H_2O	K_2CO_3	0.15	6	61
17	Ethanol/H_2O	K_2CO_3	0.1	12	52

[a]Reaction condition: Iodobenzene (1 mmol), phenyl boronic acid (1.2 mmol), base (3 mmol), solvent (5 mL), Catalyst Pd/rGO . Temp. 80 °C [b]Isolated yield

The catalytic applicability of Pd/rGO was assessed for different substituents of aryl iodides and bromides (Table 2).

The aryl iodides with both electron donating and withdrawing substituents are found to be more reactive and gave exceptional yields within 2 h (Table 2, entries 2–10). The aryl bromides were less reactive in presence of the prepared catalyst. (Table 2, entries 12–15). The aryl iodide with bulky substituents also demonstrated good catalytic activity with moderate yields with a longer reaction time (Table 2, entry 11). The yields of reactions of 4-bromochlorobenzene, 4-iodoflurorobenzene, and 4-iodochlorobenzene with arylboronic acids were 94%, 89 %, 87% and 93% respectively (Table 2, entries 5, 12, 16 and17). The unsubstituted aryl iodide and bromide reacted efficiently with phenylboronic acid to give excellent yields (Table 2, entries 1, 6 and11) and less reactive cholorobenzene proceeded with longer reaction time.

Table 2: Substrate study by Pd/rGO[a]



Entry	R_1	X	R_2	Time (h)	Yield[b] (%)
1	H	I	H	2	96
2	p-Me	I	H	3	92
3	p-OMe	I	H	3	87
4	p-NO_2	I	H	2	93
5	p-Cl	I	H	2	94
6	H	I	p-Me	2	92
7	p-$NHCOCH_3$	I	H	2.5	96
8	p-OMe	I	p-Me	3	92
9	p-COOH	I	H	2	91
10	p-Cl	I	p-Me	2	95
11	p-CF_3	I	H	8	64
12	p-F	I	p-OMe	2	89
13	H	Br	H	6	91
14	p-Me	Br	H	7	89
15	p-Me	Br	p-Me	4	90
16	p-Cl	Br	H	4	87
17	p-Cl	Br	p-Me	5	93
18	H	Cl	H	22	40

[a]Reaction condition: Ar-X (1 mmol), Ar-$B(OH)_2$ (1.2 mmol), base (3.0 mmol), solvent (5 .0 mL), catalyst Pd/rGO (3.0 mg).Temp. 80 °C [b]Isolated yield

Table 3: Recyclability study[a]

Run	Ist	IInd	IIIrd	IVth	Vth	VIth	VIIth	VIIIth
Conversion	100	100	99	98	96	95	93	89

[a]Reaction condition: Iodobenzene (1 mmol), phenyl boronic (1.2mmol), base (3 mmol), solvent (5 mL), catalyst Pd/rGO (3mg). Temp. 80 °C

We have also investigated the recyclability of Pd/rGO catalyst for the aryl iodide with phenylboronic acid. The Pd/rGO catalyst was simply separated from the reaction mixture through centrifugation. Then it was washed with water and finally ethanol to remove the traces of products. It was then dried in air and used for the next runs. As seen from Table 3 prepared catalyst could be successfully reused seven times without much loss in yield of the product. The loss in activity after 7th cycle could be due to agglomeration and increase in particle size of palladium nanoparticles on reduced graphene oxide.

CONCLUSION

We have developed a novel 'greener' method for the preparation of Pd/rGO catalyst using aloe vera extract in sunlight. The various substituted aryl halides and substituted phenyl boronic acids were successfully coupled in the presence of prepared catalyst. This catalyst (Pd/rGO) showed high efficiency, stability and recyclability up to 7th cycles for the Suzuki–Miyaura C-C coupling reactions.

ACKNOWLEDGEMENT

The authors are thankful to the KET'S V. G. Vaze College Mulund (E) Mumbai (INDIA) for funding.

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