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FACILE SYNTHESIS OF REDUCED GRAPHENE OXIDE-SUPPORTED Pd/CuO NANOPARTICLES AS AN EFFICIENT CATALYST FOR CROSS-COUPLING REACTIONS

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ABSTRACT

The present communication reports a scientific investigation of a simple and versatile synthetic route for the synthesis of palladium nanoparticles decorated with copper oxide and supported on reduced graphene oxide (rGO). They are used as a highly active catalyst of Suzuki, Heck, and Sonogashira cross coupling reactions with a remarkable turnover number of 7000 and a turnover frequency of 85000 h^{-1}. The Pd-CuO nanoparticles supported on reduced graphene oxide nanosheets (Pd-CuO/rGO) exhibit an outstanding performance through a high catalytic activity towards cross coupling reactions. A simple, reproducible, and reliable method is used to prepare this efficient catalyst using microwave irradiation synthetic conditions. The synthesis approach requires a simultaneous reduction of palladium and copper nitrates in presence of graphene oxide (GO) nanosheets using hydrazine hydrate as a strong reducing agent. The highly active and recyclable catalyst has many advantages including mild reaction conditions and short reaction durations in an environmentally benign solvent system. Moreover, the catalyst prepared can be recycled for up to five times with nearly identical high catalytic activity. Furthermore, the high catalytic activity and the recyclability of the catalyst prepared are due to the strong catalyst-support interaction. The defect sites of the reduced graphene oxide (rGO) act as nucleation centers that enable anchoring of both Pd and CuO nanoparticles and hence, minimize the possibility of agglomeration which leads to a severe decrease of the catalytic activity.

Keywords: graphene, cross-coupling, copper oxide, microwave-assisted synthesis, heterogeneous catalysis, catalyst recycling.

INTRODUCTION

Over the past few years, palladium, as a transition metal, has attracted researchers' interests especially when the palladium particles are in a nano scale. Palladium based catalysts have been widely investigated as potentially advanced catalysts in homogeneous and heterogeneous processes due to their unique properties that range between those of single metal atoms and a bulk metal. The accurate control of the particle size and the overall particle size distribution is one of the most important challenges to provide new compounds of unique chemical and physical properties [1 - 4]. Recently, the researchers have adopted new routes including the usage of nanostructured materials as heterogeneous catalysts comparing their performance with that of the traditional powder catalysts. This scientific investigation has led to the fact that the use of nanostructured materials exhibits extraordinary properties of the nanoparticles accompanied by new effects caused by the nanostructured materials referring to a remarkable enhancement including but not limited to the size, the shape, the reaction active sites, the catalytic selectivity, and the surface structure [5 - 7].

The nanoporous structure is considered a decisive factor that makes the copper oxide nano particles an ideal candidate for extremely wide applications in environmental, biological, biomedical, chemical, physical and other engineering fields [8 - 29]. Carbon supported catalysts based on a single thick layer of carbon atoms in two dimensional (2D) honeycomb lattice named Graphene have recently gained much significant research attention due to their thermal and mechanical properties, their electronic structure, as well as their unique and huge surface area [20, 21, 30 - 33]. Those distinctive characteristics make graphene one of the most promising and ideal supports of different metallic and bimetallic nanoparticle catalysts which can be used in a variety of chemical transformations. Besides, its large surface area, the high chemical, thermal, and mechanical stability determine graphene selection as the most favorable among other potential supports [19, 23, 25]. Moreover, the defects of graphene lattice structure show excellent behavior in anchoring the metals at a nanoscale and hence leading to a tunable metal-support interaction through surface functionalities. The high catalytic activity of metallic and bimetallic nanoparticles supported on graphene nanosheets and its defect sites is recently reported by many researchers in the catalysis research field [34 - 47]. It is well recognized that C-C coupling is one of the most important processes in the field of organic synthesis. Those types of reactions are widely used in many areas like agriculture, medicine, and pharmaceutical industry. The new synthetic trends referring to microwave assisted synthesis [48 - 54] are mainly focused on using catalysis at a nanoscale in response to green chemistry requirements.

There are several synthetic routes used to prepare graphene based Pd-copper oxide catalysts [55 - 58].

The method advanced in this investigation uses a microwave assisted synthesis to gain some favorable advantages including not only mild reaction conditions, a short reaction duration, but also a ligand free environmentally benign solvent system that provides high economic viability [19, 20, 23].

EXPERIMENTAL

All chemicals were purchased and used as received without further purifications. High-purity graphite powder was purchased from Alfa Aesar. Palladium nitrate, hydrazine hydrate, aryl bromide, bromobenzene, and potassium carbonate were obtained from Sigma Aldrich.

Catalyst Preparation

Synthesis of Graphene Oxide (GO)

Hummers and Offeman method was used to prepare graphene oxide (GO)[59]. In accordance with the adopted synthetic approach, the high-purity graphite powder was oxidized using $H_2SO_4/KMnO_4$ mixture. The graphite powder (4.5 g, 0.375 mol) and $NaNO_3$ (2.5 g, 0.0294 mol) were mixed together in a conical flask and then the mixture was kept in an ice bath under continuous stirring. Solutions of concentrated H_2SO_4 (115 ml, 2.157 mol) and $KMnO_4$ (15 g, 0.095 mol) were subsequently added over a period of 2.5 h. This step was followed by addition of deionized water (230 ml) while keeping the temperature of the mixture around 80^oC. Then, the mixture was stirred for nearly 20 min. Deionized water (700 mL) along with (10 %) H_2O_2 (20 mL, 0.667 mol) were added and the reaction mixture was stirred for another 5 min. The resulting yellow-brownish cake was washed several times with 1M HCl (20 mL) and then by deionized water (3 L). The resulting GO solid was dried at 60°C overnight [20, 23].

Synthesis of Pd supported on CuO nanoparticles (Pd/CuO)

In this experimental procedure, catalysts of different weight percentage (5 wt. %, 10 wt. %, 20 wt. %, 30 wt. %) of palladium loading on copper oxide were prepared. In a 250 ml beaker, a solution containing 20 mL deionized water and the relevant weight of copper (II) nitrate hemipentahydrate (347.72 mg, 329.42 mg, 292.82 mg, 256.22 mg, respectively) were sonicated at a room temperature for approximately 1.5 h. Then a volume (97 µl, 194 µl, 388 µl, 582 µl, respectively) of palladium nitrate solution corresponding to the previously mentioned loading percents was introduced to the sonicated solution, while the stirring was continued for another 1.5 h. Hydrazine hydrate (1200 µl) was added at a room temperature and the solution was heated in a microwave for 30 s. Finally, the catalyst was dried in an oven till the catalyst reached a constant weight.

Synthesis of Pd Nanoparticles

Palladium nitrate (1940 µl) was added to 50 ml deionized water, and the solution was sonicated for 1 h. Then, the mixture was stirred for another hour. After that 1200 µl of hydrazine hydrate were added to the mixture. Then, it was heated using a microwave oven for 20 s, filtered, washed with deionized water and subsequently with ethanol. It was finally dried in an oven till the catalyst reached a constant weight.

Synthesis of Copper Oxide Nanoparticles

366 mg of copper (II) nitrate hemipentahydrate ($Cu(NO_3)_2.2.5H_2O$) were added to 50 mL of deionized water and sonicated for 1 h. The mixture was stirred for another hour. 1200 µl of hydrazine hydrate were added to the mixture following the step of stirring. Then, it was heated using a microwave oven for 20 s, filtered, washed with deionized water and subsequently with ethanol. It was finally dried in an oven till the catalyst reached a constant weight.

Synthesis of Pd-CuO nanoparticles (Pd/CuO) supported on Graphene

50 mg of GO were dispersed in 50 mL of water for 1 h in a sonication bath to produce an aqueous dispersion of graphene oxide. Then 50 mL of deionized water containing 194 µl of palladium nitrate ($Pd (NO_3)_2$) and 366 mg of copper (II) nitrate hemipentahydrate ($Cu(NO_3)_2.2.5H_2O$) were added and sonicated for 1 h. This solution was added to the aqueous dispersion of graphene oxide and stirred for 1 h. After that 1.2 ml hydrazine hydrate were added at a room temperature. The mixture turned reddish brown. The precursor suspension obtained was heated in a microwave within 60 s intervals. This resulted in a black product which was washed 2 - 3 times with hot deionized water, then 2 - 3 times with ethanol and finally dried in an oven at 80˚C.

Catalyst Characterization

TEM images were taken using JEOL JEM-1230 electron microscope. GC–MS analyses were used to monitor the product catalytic activity in respect to the reactions selected. Thermo Fisher Scientific ESCALAB was used to perform the X-ray photoelectron spectroscopy (XPS) analysis. X'Pert PRO PAN analytical X-ray diffraction unit was used to measure the X-ray diffraction patterns at a room temperature.

A general procedure of Suzuki and Heck Cross – Coupling reactions proceeding

In the typical procedure, aryl halide (0.32 mmol, 1 eq.) was dissolved in 4 mL of H_2O:EtOH (1:1) as a solvent system. Aryl boronic acid (0.382 mmol, 1.2 eq.) and potassium carbonate (0.96 mmol, 3 eq.) were added to this mixture. Then Pd/CuO (1 mol %) was added. This step was followed by heating under microwave irradiation at 80°C for 10 min. After the reaction was completed, the mixture was extracted and the solvent was removed from the filtrate. The solid product was further purified [20, 23].

A general procedure of catalyst recycling

In this typical experimental procedure, aryl halide (0.32 mmol, 1 eq.) was dissolved in 6 mL of H_2O:EtOH (1:1). Aryl boronic acid (0.382 mmol, 1.2 eq.), potassium carbonate (0.96 mmol, 3 eq.) and palladium-copper oxide nanoparticles Pd/CuO (1 mol %) were subsequently added. Then, the mixture was heated at the assigned temperature and duration. Upon reaction completion, the catalyst was removed, purified and then transferred directly to another reaction tube[20, 23].

RESULTS AND DISCUSSION

The Suzuki cross-coupling reaction of bromobenzene and phenyl boronic acid in 50 vol. % of aqueous ethanol solution is investigated under various reaction conditions. A microwave reactor (Scheme 1) is used. In order to study the temperature effect on the catalytic activity, the cross-coupling reaction is carried out at a constant reaction time (10 min) and different temperature values (80^oC, 120^oC, 150^oC) using the synthesized Pd-CuO/rGO catalysts (1 mol %). A comparison is carried out in case of using Pd/CuO in absence of reduced graphene oxide. The results reveal that the temperature has a great effect on the reaction yield. The increase of the reaction mixture temperature favors the higher conversion to the product. The maximum conversion value is obtained at 150^oC. This behavior is identical for all

Table 1. Conversion percentages obtained in using different ratios of Pd/CuO and Pd-CuO/rGO.

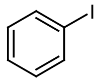
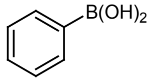
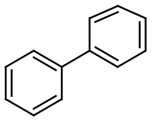
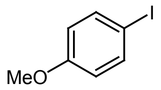
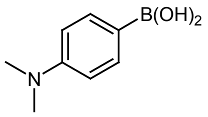
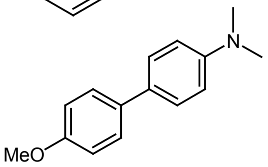
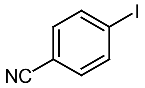
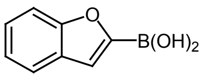
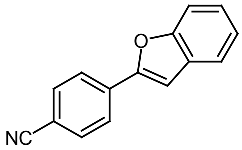
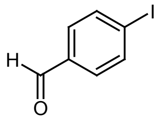
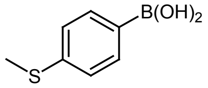
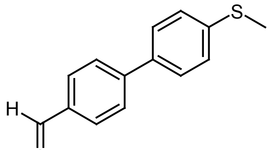
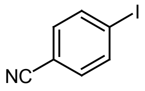
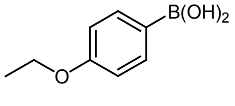
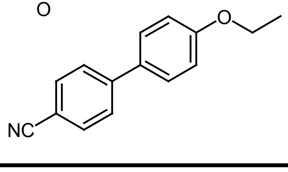
Catalysts	Temp (°C)	Time (min.)	Conversion %^{a*}	Conversion %^{b*}	Conversion %^{c*}	Conversion %^{d*}
5 wt % Pd-CuO	80°C	10	40	60	35	55
	120°C	10	72	78	64	75
	150°C	10	86	90	72	85
10 wt % Pd/CuO	80°C	10	57	65	47	60
	120°C	10	82	88	58	84
	150°C	10	94	98	84	88
20 wt % Pd/CuO	80°C	10	66	75	53	70
	120°C	10	93	96	66	85
	150°C	10	100	100	93	100
Pd nanoparticles	150°C	10	< 30	< 30	< 30	< 30
CuO nanoparticles	150°C	10	< 30	< 30	< 30	< 30

a,c The conversion was calculated for Suzuki and Heck cross coupling reactions using (1 mol%) Pd/CuO catalyst.

b,d The conversion was calculated for Suzuki and Heck cross coupling reactions using (1 mol%) Pd-CuO/rGO catalyst.

** The conversions were determined by GC–MS.*

Table 2. Suzuki cross coupling reactions proceeding with Pd/CuO and Pd-CuO/rGO catalyst on various substrates.

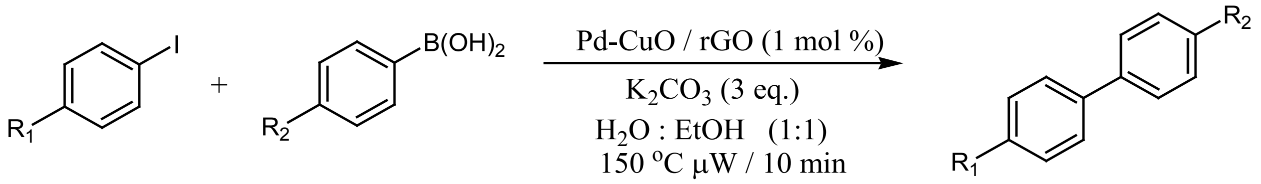
Entry	**Aryl halide**	**Boronic acid**	**Product**	**Conversion^a (%)**	**Conversion^b (%)**
1				**90 %**	**100 %**
2				**86 %**	**95 %**
3				**85 %**	**90 %**
4				**82 %**	**88 %**
5				**88 %**	**92 %**

** Aryl halide (0.32 mmol, 1 eq.), aryl boronic acid (0.382 mmol, 1.2 eq.), potassium carbonate (0.96 mmol, 3 eq.), and Pd/CuO (1 mol %) in 4 mL (H2O:EtOH) (1:1) were heated at 150 ˚C (MWI) for 10 min.*

*** The conversions were determined by GC-MS.*

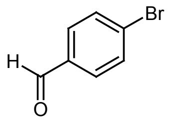
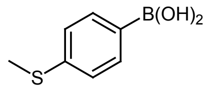
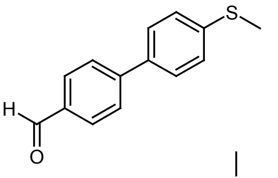
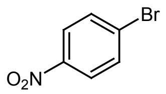
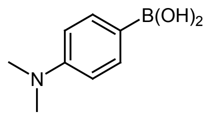
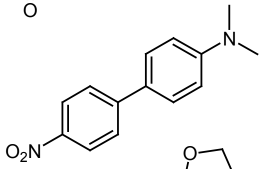
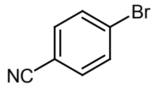
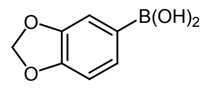
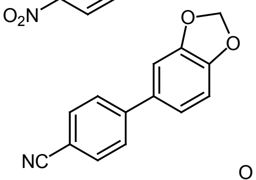
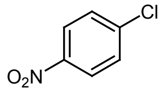
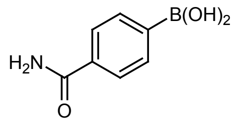
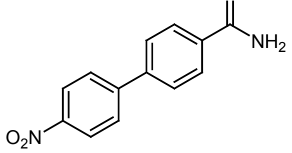
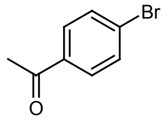
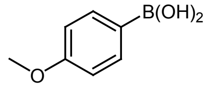
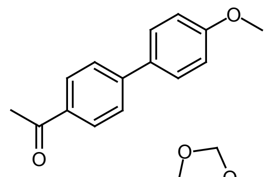
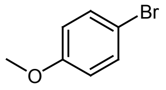
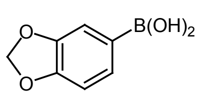
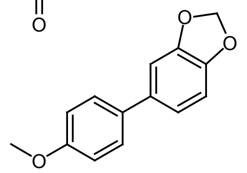
a The conversion was calculated for Suzuki cross coupling reactions using (1 mol %) Pd/CuO catalyst.

b The conversion was calculated for Suzuki cross coupling reactions using (1 mol %) Pd-CuO/rGO catalyst.



Scheme 1. Suzuki cross coupling reactions using Pd-CuO/rGO catalyst.

Table 3. Diversity of Suzuki cross coupling reactions using Pd/CuO and Pd-CuO/G catalyst.

Entry	Aryl halide	Boronic acid	Product	Conversion[a] (%)	Conversion[b] (%)
1				**90 %**	**96 %**
2				**87 %**	**95 %**
3				**91 %**	**98 %**
4				**60 %**	**78 %**
5				**88 %**	**92 %**
6				**82 %**	**87 %**

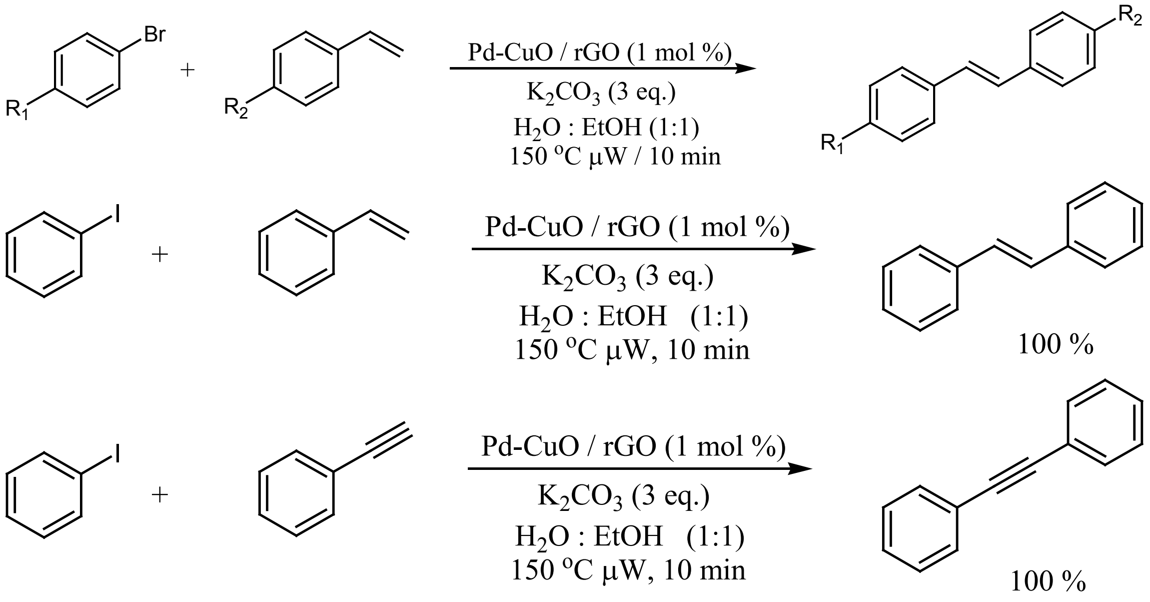
** Aryl halide (0.32 mmol), aryl boronic acid (0.382 mmol, 1.2 eq.), potassium carbonate (0.96 mmol, 3 eq.), and Pd/CuO (1 mol %) in 4 mL (H_2O:EtOH) (1:1) were heated at 150 ˚C (MWI) for 10 min.*

*** The conversions were determined by GC-MS*

a The conversion was calculated for Suzuki cross coupling reactions using (1 mol%) Pd/CuO catalyst.

b The conversion was calculated for Suzuki cross coupling reactions using (1 mol%) Pd-CuO/rGO catalyst.

prepared Pd/CuO and Pd-CuO/ rGO catalysts containing different Pd loadings (5 wt. %, 10 wt. %, and 20 wt. %) as seen in Table 1. It is also found that the increase of the catalyst weight percentage on the solid support from 5 wt. % to 10 wt. and finally to 20 wt. % enhances the product conversion (at all temperature values studied). The maximum product conversion reaches 100 % in case of 20 wt. % load of Pd catalyst at 150°C. Surprisingly, the



Scheme 2. Reactivity of Pd-CuO/rGO catalyst towards Heck and Sonogashira coupling reactions.

further Pd content increase (30 wt. %) leads to a sharp drop of the catalytic performance and a lower conversion (about 60 %) in respect to the desired product which may be due to the harmful effect of the agglomeration that accompanies the palladium loading increase.

It is also worth noting that the cross-coupling reaction taking place under the optimized conditions (10 min and 150°C) in presence of 1 mol % CuO nanoparticles or 1 mol % Pd nanoparticles instead of 1 mol % Pd-CuO/rGO catalyst results in a very low conversion to the cross-coupling product desired (less than 30 %).

Those findings reflect on one hand the superiority of Pd metal over copper in respect to these reactions catalysis. On the other hand, it shows the crucial role played by the copper oxide solid support (found in Pd/CuO catalyst and not in Pd nanoparticles catalyst) in minimizing the agglomeration effect of the Pd nanoparticles responsible for the catalyst activity reduction.

The versatility of the substrates that can be used in Suzuki cross-coupling reaction in presence of the synthesized catalyst is illustrated in Tables 2 and 3.

The versatility of the substrates that can be used in Heck cross-coupling reaction in presence of the synthesized catalyst is presented in Table 4. It is obvious from the data obtained that the use of reduced graphene oxide (rGO) as a support has a great effect on the catalytic activity

The study of the TEM images shows the well dispersed palladium nanoparticles of a size of 25 ± 2 nm in Fig. 1a. The use of graphene provides obtaining well dispersed and smaller nanoparticles of a size of 8 ± 2 nm as shown in Fig. 1c. The TEM images presented here illustrate the higher catalytic activity obtained in case of Pd/CuO and Pd-CuO/G when compared to that registered in presence of the same catalysts but after the fifth run. The difference considered is due to the particles agglomeration that probably takes place in the course of the reaction. This is shown in Figs. 1b and 1d.

Fig. 2 displays the XRD pattern of palladium-copper oxide supported on reduced graphene oxide (rGO) prepared by the microwave method. There is an additional peak at 26.1 (002) ascribed to reduced graphene oxide (rGO). This is an indication of the reduction of grapheme oxide (GO) into reduced graphene oxide (rGO). The exact palladium content of Pd-CuO/ rGO catalysts prepared by microwave synthesis is determined by inductively coupled plasma (ICP-OES). It is found equal to 3.5 wt. %, 6.5 wt. %, 10 wt. %, 18 wt. % of Pd, while

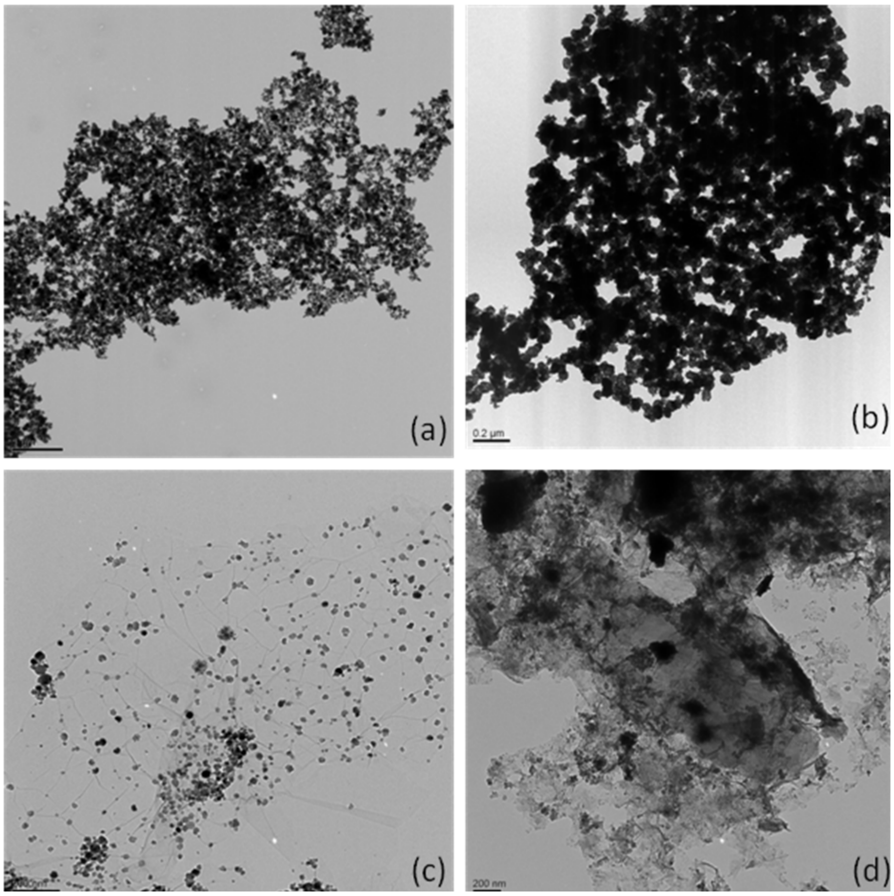


Fig. 1. TEM - images of Pd/CuO prior to the reaction and after the 5 th run of the reaction (a.b) and of Pd-CuO/rGO prior to the reaction and after the 5 th run of the reaction (c,d).

the initial palladium amount of Pd/CuO catalysts refers to 5 wt %, 10 wt %, 20 wt %, 30 wt %, respectively. The further characterization of the microwave synthesized palladium-copper oxide supported on reduced graphene oxide catalyst (Pd-CuO/ rGO) is achieved on the ground of the XRD pattern of the catalyst sample as seen in Fig. 2. The sharp diffraction peak at 2θ = 40^0 characteristic of palladium is readily noticed. The XRD reflections of CuO match that of JCPDS no. 48-1548 corresponding to a monoclinic structure [60, 61]. The diffraction peaks are ascribed to (110), (111), (112), (020), (202), (112), (311), and (113) planed of copper oxide NPs as shown in Fig. 2 [19, 20, 23].

The XPS technique is widely used as it is more sensitive in analyzing the surface oxides than XRD. The surface composition of the catalysts prepared is characterized by XPS measurements. Fig. 3 shows the results referring to 20 wt % Pd/CuO catalyst. All samples have C1s binding energy around 284.5 eV due to carbon contamination. The existence of copper oxide in

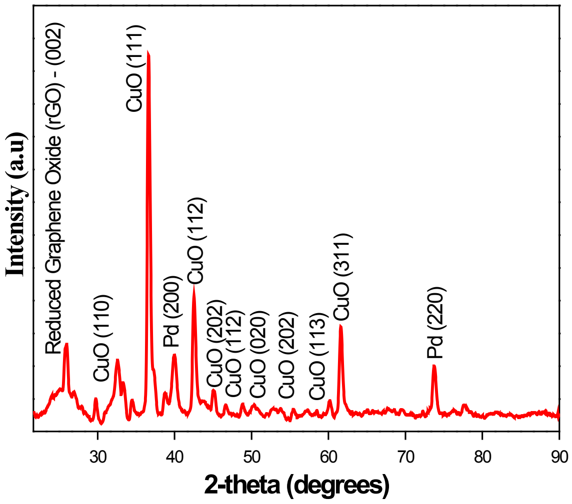


Fig. 2. An XRD pattern of Pd-CuO/rGO nanoparticles.

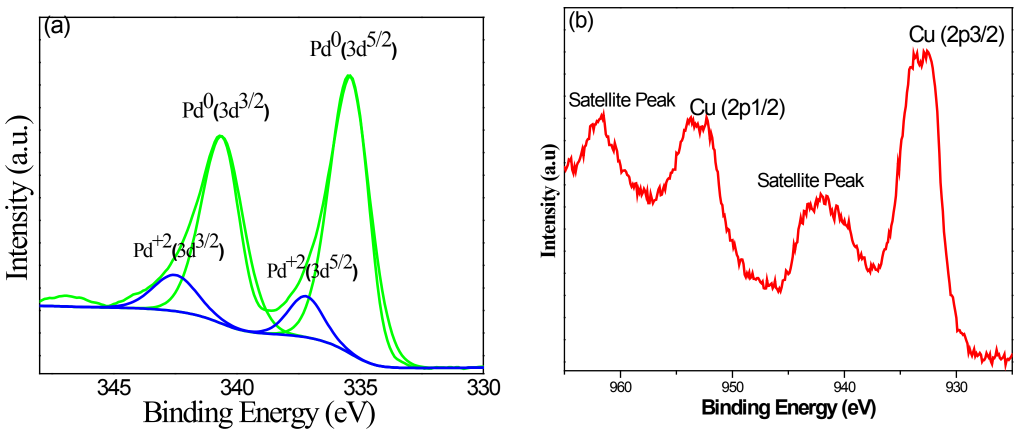
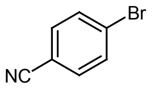
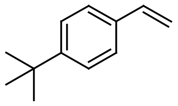
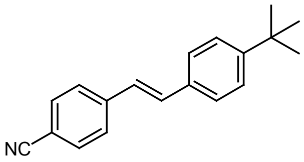
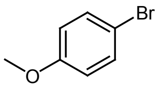
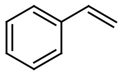
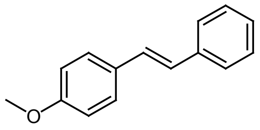
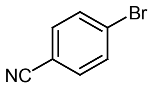
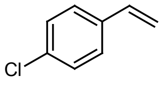
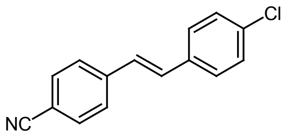
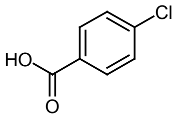
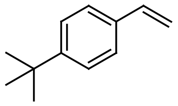
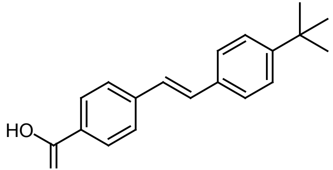
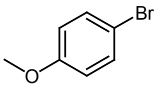
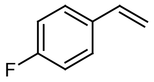
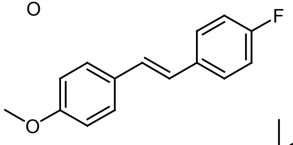
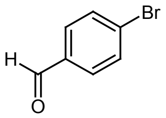
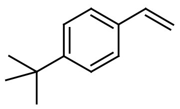
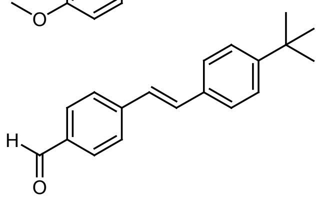


Fig. 3: (a) XPS (Pd3d) and (b) XPS (Cu2p) of Pd-CuO/rGO.

Table 4. Diversity of Heck coupling reactions using Pd/CuO and Pd-CuO/rGO catalyst.

Entry	**Aryl halide**	**Alkene**	**Product**	**Conversion[a] (%)**	**Conversion[b] (%)**
1				**87 %**	**90 %**
2				**90 %**	**95 %**
3				**93 %**	**100 %**
4				**88 %**	**90 %**
5				**75 %**	**85 %**
6				**82 %**	**88 %**

** Aryl bromide (0.32 mmol), alkene (0.64 mmol), potassium carbonate (0.96 mmol), and Pd/CuO (2 mol%) in 4 mL (H_2O:EtOH) (1:1) were heated at 150 °C (MWI) for 10 min.*

*** The conversions were determined by GC-MS.*

a The conversion was calculated for Heck cross coupling reactions using (1 mol%) Pd/CuO catalyst.

b The conversion was calculated for Heck cross coupling reactions using (1 mol%) Pd-CuO/rGO catalyst.

Table 5. Recycling experiments carried out with Pd-CuO/rGO catalyst of a concentration of 0.5 mol % and 1 mol %. %[a].

Run	Conversion (%)[b] (0.5 mol %)	Conversion (%)[b] (1 mol %)
1	100	100
2	97	100
3	95	98
4	93	96
5	90	94
6	80	85

a Bromobenzene (50 mg, 0.32 mmol), boronic acid (47 mg, 0.382 mmol, 1.2 eq.), potassium carbonate (133 mg, 0.96 mmol, 3 eq.), and Pd/CuO (0.5 mol%) or (1 mol %) in 4 mL (H_2O:EtOH) (1:1) were heated at 1500C (MWI) for 10 min.

b The conversions were determined by GC-MS.

the samples is confirmed as seen in Figs. 3(a) and 3(b). The XPS measurements show that there are shake-up satellite peaks located at 941.9 eV and 961.7 eV. The binding energy of Pd $3d^{5/2}$ is evaluated equal to 334.8 eV, while that of Pd $3d^{3/2}$ amounts to 340.1 eV. This indicates that Pd is ascribed to Pd^0. Similarly, the binding energy of Pd $3d^{3/2}$ is found equal to 341.38 eV, while that of Pd $3d^{5/2}$ is 336.23 eV. This indicates that Pd is present as PdO (Pd^{2+}). The binding energy of Cu $2P^{3/2}$ is located at 933.1 eV, while that of Cu $2P^{1/2}$ is located at 953.1 eV. This indicates that the copper present is ascribed to Cu^{2+}.

The results of the catalyst recycling are previously discussed. They are summarized in Table 5. Table 5 and Fig. 4 confirm that the catalyst has a high catalytic activity. For example, a catalyst containing 0.5 mol % can be recycled four times with almost 100 % conversion. On the other hand, the increase of the mole percentage to 1 mol % leads to five times-recycling with a conversion of nearly 100 %.

The TEM images of Pd/CuO confirm the deactivation of the catalyst after the 5th run, which happens due to the negative effect of the agglomeration process of

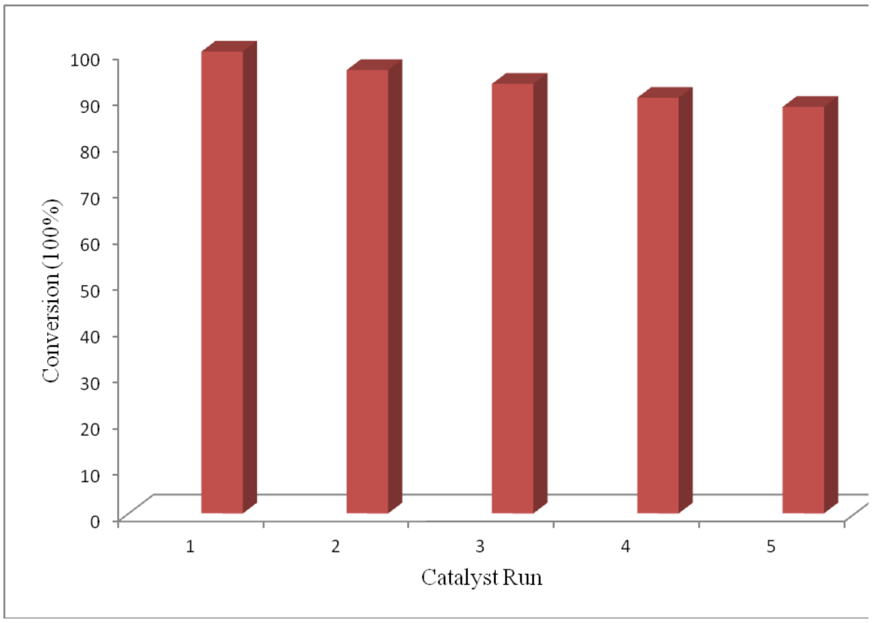


Fig. 4. Recycling experiments carried out with Pd-CuO/rGO catalyzing Suzuki cross coupling reaction.

both Pd and CuO nanoparticles on the surface as shown in Fig. 1b. The extent of Pd leaching from the catalyst prepared is investigated through performing the reaction within10 min at 150°C in presence of 0.5 mol % of a catalyst. The microwave assisted synthesis technique is used. The resulting mixture is filtered upon reaction completion. The filtrate content of Pd is measured. It is found to be 185 ppm based on the ICP-MS analysis.

CONCLUSIONS

In summary, the effect of using reduced graphene oxide as an ideal support is thoroughly investigated through determination of the catalytic activity of several types of catalysts in presence and absence of reduced graphene oxide as a support. A simple and reliable microwave irradiation method is used as a clean heating source to prepare Pd nanoparticles decorated with copper oxide and supported on reduced graphene oxide. The mixtures of palladium nitrate and copper (II) nitrate hemipentahydrate are reduced with hydrazine hydrate. The catalysts prepared are stable and have a high catalytic performance in respect to Suzuki, Heck, and Sonogashira cross–coupling reactions with nearly 100 % conversion for the first run of the catalyst, an excellent turnover number of 7000 and a turnover frequency of 85000 h^{-1}. Moreover, the catalysts are stable and can be reused up to five times with the same high catalytic performance for a wide range of substrates under batch reaction conditions.

In conclusion, a reliable method is developed to prepare highly active palladium-copper oxide based catalysts at a nano scale supported on reduced graphene oxide (rGO). Microwave irradiation is used to reduce chemically an aqueous mixture consisting of palladium nitrate, copper (II) nitrate hemipentahydrate and sheets of graphite oxide. The bimetallic material at the nano scale can be experimentally anchored directly to the reduced graphene oxide (rGO) which offers a unique combination of favorable advantages including not only mild reaction conditions, a high catalytic activity, a short reaction duration, and a ligand free environmentally benign solvent system, but also recyclability of the heterogeneous catalyst providing high economic viability.

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