Palladium nanoparticles supported on copper oxide as an efficient and recyclable catalyst for carbon(sp^2)–carbon(sp^2) cross-coupling reaction

Mahmoud Nasrollahzadeh [a,*], S. Mohammad Sajadi [b], Akbar Rostami-Vartooni [a], Abbas Azarian [c]

[a] Department of Chemistry, Faculty of Science, University of Qom, Qom 37185-359, Iran
[b] Department of Petroleum Geoscience, Faculty of Science, Soran University, P.O. Box 624, Soran, Kurdistan Regional Government, Iraq
[c] Department of Physics, University of Qom, Qom, Iran

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ABSTRACT

A convenient, mild and cost-effective synthesis of Pd/CuO nanoparticles by arc discharge of Cu in deionized (DI) water and electroless deposition of palladium was reported. The obtained nanoparticles were thoroughly characterized by using techniques like TEM, XRD, FE-SEM and EDS. The synthesized nanoparticles demonstrated excellent catalytic activity in Heck coupling reaction under aerobic conditions. The effects of catalyst composition, solvent and bases, aryl halides or olefins species on corresponding products were systematically investigated. High product yields, elimination of ligand and homogeneous catalysts, broad substrate scope and easy work up are important features of this method. In addition, the catalyst could be reused for five more consecutive recycles.

1. Introduction

Palladium catalyzed carbon–carbon coupling reactions are extensively used in the synthesis of a variety of compounds. Among the Pd-catalyzed cross-coupling reactions, Heck cross-coupling reactions have shown to be powerful tools for the synthesis of new molecules, and there are a considerable number of examples in which this reaction has reached industrial application [1–3].

The Heck cross-coupling reaction has been widely used in the synthesis of pharmaceuticals, natural products, and advanced materials [1–3]. Till date several methods were reported for the Heck-coupling reactions using palladium complexes and toxic, expensive and moisture-sensitive phosphine ligands and in the presence of a stoichiometric amount of base under inert conditions, which were economically and environmentally malignant. However, these methods suffer from one or more drawbacks such as the use of hazardous organic solvents, use of expensive ligands, low yields, tedious work-up, difficulties in isolation of

catalyst, highest catalyst loading, and difficulties associated with catalyst-product separation thereby, limiting their general applications [1–3]. In addition, most of the current methods were focused on the homogeneous palladium catalysts. While homogeneous Pd catalysts are not used in industrial application due to the difficulty in separating and recycling, low catalytic efficiency, the high leaching of metal species and might result in unacceptable palladium contamination of the product. Hence the development of newer, efficient and convenient techniques for the ligand-free Heck coupling reaction under heterogeneous conditions is very much needed.

In recent years, the synthesis of metal nanoparticles is of much interest because of their electronic, optical, magnetic and biomedical properties and they can also cause specific catalytic activities in organic reactions [4]. Among various metallic catalysts, palladium (Pd) is able to catalyze a wide variety of chemical reactions under homogeneous and heterogeneous conditions [5]. The purification of the product and the reuse of catalyst are quite difficult when a homogeneous catalyst is used. In this context, heterogeneous metal catalysts are emerging as an alternative to the homogeneous ones that suffer various limitations both commercial and environmental.

Due to a higher available catalytic surface, heterogeneous catalysts are more and more used in the form of nanoparticles. Thus, we decided to concentrate on developing an efficient and heterogeneous Pd nanocatalyst that is air and moisture stable and

highly active. We have recently developed synthesis of various metallic and bimetallic nanoparticles (NPs) [6–15] which promote various catalytic transformations under heterogeneous conditions. Immobilization of metallic nanoparticles on solid supports is one of the best methods to improve the efficiency and recovery of catalysts. To prevent the agglomeration of Pd NPs, several materials such as polymer, Fe_3O_4, CuO, TiO_2, perlite have been used as a support for metal NPs [6–8,10,11,16]. Among various metal oxide nanoparticles, CuO NPs have received considerable attention because of their unusual properties and used widely as efficient support and catalysts in organic reactions due to their high catalytic activity, ease of handling, reusability, and benign character [17,18]. CuO NPs, in particular, being cheap, are less harmful to the environment than any other metals in cross-coupling reactions [8,18]. As a result, we decided to design and prepare the Pd/CuO NPs and explore their catalytic ability for the phosphine-free Heck coupling reaction under aerobic conditions. This method provides an improvement on our previous reported protocols for the phosphine-free Heck coupling reaction [8–10].

An advantage of the Pd/CuO NPs catalyst was that its synthesis was very simple. In the present study, high-quality Cu nanoparticles were synthesized without the use of vacuum equipment. The nanoparticles were obtained in the form of dispersed particles in the water by high current electrical arc discharge between two copper electrodes which were submerged in deionized (DI) water. To the best of our knowledge, there are no reports on the fabrication of copper nanoparticles by the electrical arc discharge method. In general, electrical arc discharge in water has the advantage in this regard as it produces self-crystallized nanoparticles due to the high temperature caused by Joule heating. Moreover, compared with other techniques, electrical arc discharge in water is an attractive method because of the simplicity of the experimental set-up, the lack of complicated equipment, low impurity and less production steps leading to a high-throughput and cost-effective procedure to generate high yields of nanoparticles.

2. Experimental

2.1. Instruments and reagents

High-purity chemical reagents were purchased from the Merck and Aldrich chemical companies. All materials were of commercial reagent grade. Melting points were determined in open capillaries using a BUCHI 510 melting point apparatus and are uncorrected. ^1H NMR and ^{13}C NMR spectra were recorded on a Bruker Avance DRX-400 spectrometer at 400 and 100 MHz, respectively. FT-IR spectra were recorded on a Nicolet 370 FT/IR spectrometer (Thermo Nicolet, USA) using pressed KBr pellets. The element analyses (C, H, N) were obtained from a Carlo ERBA Model EA 1108 analyzer carried out on Perkin-Elmer 240C analyzer. X-ray diffraction (XRD) measurements were carried out using a Philips powder diffractometer type PW 1373 goniometer (Cu $K\alpha = 1.5406$ Å). The scanning rate was $2°/min$ in the 2θ range from 10 to 80°. Scanning electron microscopy (SEM) was performed on a Cam scan MV2300. EDS using EDS (S3700N) was utilized for chemical analysis of prepared nanostructures. Transmission electron microscopy (TEM) was recorded on a Philips EM208 microscope operating at an accelerating voltage of 90 kV.

2.2. Preparation of Pd/CuO nanoparticles

The setup for synthesis of Cu comprises contains DC power supply and a reactor including two electrodes and a glass chamber filled by water. The cathode and anode are both pure copper rods.

The current in the discharge process is maintained at 15 A. As the rods are brought close together, discharge occurs resulting in the formation of plasma. As more copper was ablated from the anode, the plasma expands, pushing the liquid away, and a gaseous bubble forms. Melted species can react with plasma and then condense into the liquid. It is worth noting that during the process, as the anode is consumed, the rods are kept at a constant distant from each other of about 1–2 mm. The Cu nanoparticles solution was added to a solution containing $PdCl_2$ prepared by ultrasonic dissolving 0.02 g (0.005 or 0.01 g) of $PdCl_2$ powder (5 N), 99.9 mL DI water and 0.1 mL HCl. Then, samples were heated at 90 °C for 1 h. In order to extract the dispersed nanoparticles, the solution was dried at a pressure of 10^{-1} Torr and centrifuged several times and then dispersed on a glass substrate.

2.3. General procedure for the photochemical Heck cross-coupling reaction

A mixture of styrene or olefin (1.5 mmol), aryl halide (1.0 mmol), Et_3N (2.0 mmol), DMF (4.0 mL) and the catalyst (3.0 mol%) was stirred in an oil bath at 110 °C for 20 h. The progress of the reaction was monitored by thin layer chromatography (TLC) and on completion, the reaction mixture was cooled to room temperature and the catalyst was separated from the reaction mixture by centrifugation. The remaining solution was diluted with water and the products were extracted using ether, dried over Na_2SO_4 and purified by using column chromatography. All products are known in the literature and the physical data of the products were found to be identical with those reported in the literature [8–10,19,20].

3. Results and discussion

3.1. Characterization of catalyst

Pd/CuO NPs were characterized using the powder XRD, FE-SEM and EDS. Fig. 1 shows XRD patterns of the three films (the $PdCl_2$ is equal to $a = 0.005$, $b = 0.01$, $c = 0.02$ g). Pd/CuO NPs exhibited Bragg diffractions corresponding to the cupric oxide (CuO) and palladium (Pd).

FE-SEM, TEM and EDS were carried out for study of morphology, size and composition of nanostructures. Typical FE-SEM and TEM images of Pd/CuO NPs ($PdCl_2 = 0.02$ g) are shown in Figs. 2 and 3, respectively. As it is clear, Pd/CuO NPs show morphology like rectangular structures. According to FE-SEM analysis, the average length, width and height of this rectangular are about 70, 70 and 250 nm, respectively. We used EDS to determine chemical
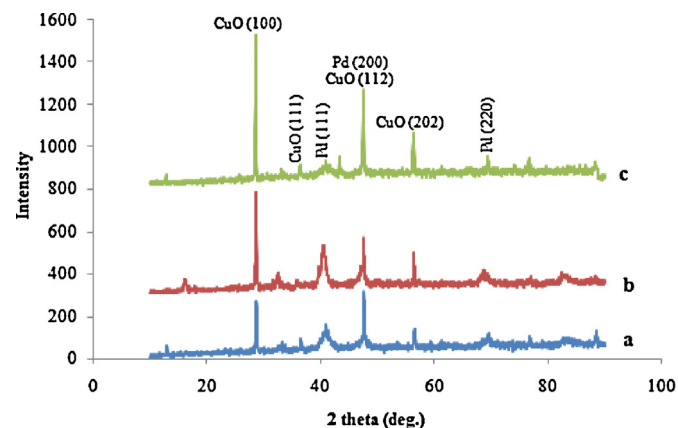

Fig. 1. XRD patterns of the three films (the $PdCl_2$ is equal to $a = 0.005$, $b = 0.01$, $c = 0.02$ g).
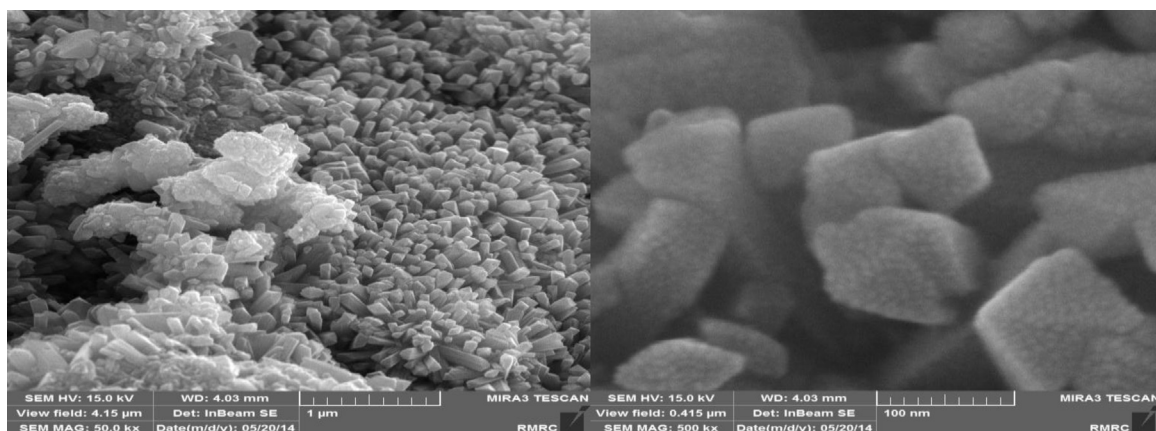
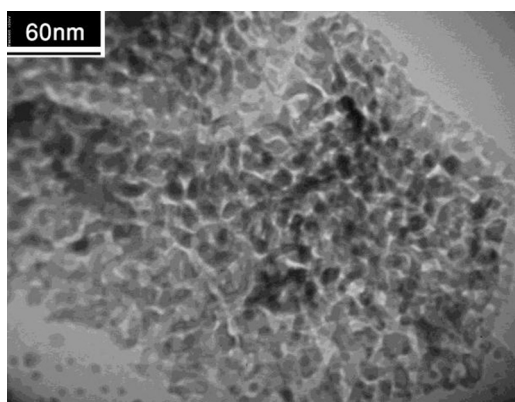**Fig. 2.** FE-SEM images of Pd/CuO thin films on glass substrates.

Fig. 3. TEM image of Pd/CuO NPs.

composition of nanostructures. EDS results show that Cu, Pd and oxygen concentrations are about 35%, 38% and 24%, respectively. It is worth noting that some of the oxygen content may be related to oxidation of copper nanoparticles to CuO or Cu_2O during the heating or discharge process and the excess oxygen is due to physical absorption of oxygen from environment during sample preparation.

3.2. Catalytic activity of Pd/CuO NPs for the Heck cross-coupling reactions of aryl halides with substituted styrenes or olefins

To investigate the catalyst activity of Pd/CuO NPs catalyst, we have chosen the Heck cross-coupling reaction of aryl halides with substituted styrenes. Our initial investigation was directed toward exploring the reaction conditions for the model cross-coupling of bromobenzene with styrene. The reaction was carried at 110 °C for 20 h. A series of experiments were performed to optimize the various reaction parameters such as effect of catalyst loading, base and solvents. The results are summarized in Table 1. We performed an experiment in the absence of catalyst, in which no cross-coupling product was observed, which confirmed the necessity of catalyst for the Heck cross-coupling (Table 1, entry 1). The results for various solvents indicated that yield of product in polar solvent (DMF) is high (Table 1, entry 2). After choosing DMF as the best solvent, the effect of base and the amount of catalyst on the reaction was investigated. As seen from Table 1, with the decrease of catalyst amount from 3.0 mol% to 1.0 mol%, the yield of reaction decreased from 90% to 67% (Table 1, entries 2 and 9). Thus, we performed the reaction in the presence of 3.0 mol% catalyst to get the highest yield. Further increase in catalyst did not show any

appreciable increase in product yield (Table 1, entry 10). Also, it was observed that the yield of product was decreased when the ratio of Pd:Cu was decreased (Table 1, entries 2, 11 and 12). As shown in Table 1, among the various Pd sources tested, sample c (the $PdCl_2$ is equal to 0.02 g) led to significant conversion (Table 1, entry 2). Due to the sensitivity of Heck reactions to the base used, the effects of NaOH, K_2CO_3, KOAc, Na_2CO_3, Cs_2CO_3, $NaPO_4$, and Et_3N were investigated. Inorganic bases gave low yields (entries 13,16–18) and NaOH gave a lower yield (entry 14). When organic base K_2CO_3 was used, the moderate product yield (70%) was obtained (entry 15). Gratifyingly, the use of organic base Et_3N dramatically improved the yield (90%) (entry 2). The main reason for this is that the solubility of the inorganic bases in the reaction system was very poor, while Et_3N is soluble with the substrates. This indicates that the solubility of the bases in the reaction mixture is crucial for the Heck reaction. Model reaction was carried out by using various bases with optimized catalyst concentration as 3.0 mol% and Et_3N gave maximum yield of desired product (Table 1, entry 2), it was used for further study.

After obtaining the optimal reaction conditions, we then examined the applicability of the present catalytic system to the

Table 1
Pd/CuO NPs catalyzed Heck cross-coupling reaction of bromobenzene with styrene.[a]

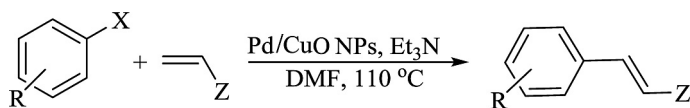| Entry	Pd/CuO NPs (mol%)	Solvent	Base	Yield (%)[b]
1	0	DMF	Et_3N	0
2	3.0[c]	DMF	Et_3N	90
3	3.0[c]	DMF	–	Trace
4	3.0[c]	n-Hexane	Et_3N	N.R.
5	3.0[c]	DMSO	Et_3N	15
6	3.0[c]	Toluene	Et_3N	37
7	3.0[c]	THF	Et_3N	21
8	3.0[c]	CH_3CN	Et_3N	9
9	1.0[c]	DMF	Et_3N	67
10	5.0[c]	DMF	Et_3N	90
11	3.0[d]	DMF	Et_3N	69
12	3.0[e]	DMF	Et_3N	50
13	3.0[c]	DMF	Na_2CO_3	33
14	3.0[c]	DMF	NaOH	8
15	3.0[c]	DMF	K_2CO_3	70
16	3.0[c]	DMF	KOAC	13
17	3.0[c]	DMF	$NaPO_4$	34
18	3.0[c]	DMF	Cs_2CO_3	27

[a] Reaction conditions: bromobenzene (1.0 mmol), styrene (1.5 mmol), solvent (4 mL), base (2.0 mmol) at 110 °C, 20 h, aerobic conditions.
[b] Yield of isolated products.
[c] Sample c: the $PdCl_2$ is equal to 0.02 g.
[d] Sample b: the $PdCl_2$ is equal to 0.01 g.
[e] Sample a: the $PdCl_2$ is equal to 0.005 g.

Table 2

Pd/CuO NPs catalyzed Heck cross-coupling reactions of aryl halides with olefins or substituted styrenes.[a]

Entry	X	R	Z	Yield[b] (%)
1	I	H	Ph	98
2	I	4-Me	Ph	94
3	I	4-NO$_2$	Ph	89
4	I	4-Br	Ph	92
5	Br	H	Ph	90 (90, 90, 89, 87, 95)[c]
6	Br	4-Me	Ph	85
7	Br	4-COMe	Ph	92
8	Br	4-CF$_3$	Ph	92
9	I	H	CO$_2$Et	94
10	I	4-Me	CO$_2$Et	85
11	I	4-OMe	CO$_2$Et	82
12	I	4-Cl	CO$_2$Et	92
13	Br	H	CO$_2$Et	91
14	Cl	H	CO$_2$Et	65
15	Br	H	COMe	90
16	Br	4-OMe	COMe	81
17	Br	3-CHO	COMe	94
18	Br	4-NO$_2$	COMe	95
19	Cl	H	COMe	70
20	Cl	4-NH$_2$	COMe	80
21	Cl	4-COOH	COMe	84
22	I	H	CO$_2{}^n$Bu	95
23	Br	H	CO$_2{}^n$Bu	92
24	Br	4-Me	CO$_2{}^n$Bu	87
25	Br	4-NO$_2$	CO$_2{}^n$Bu	93
26	Br	4-COMe	CO$_2{}^n$Bu	93

[a] Reaction conditions: aryl halide (1 mmol), styrene or olefin (1.5 mmol), Pd/CuO NPs (3.0 mol%, sample c), Et$_3$N (2.0 mmol) in DMF (4.0 mL) at 110 °C, 20 h, aerobic conditions.

[b] Yield of isolated products.

[c] Yield after the fifth cycle.

Heck cross-coupling of various aryl halides with different styrenes and various olefins (Table 2). In all reactions only 3.0 mol% Pd/CuO NPs catalyst (sample c) based on the aryl halides was used. Various aryl halides bearing electron-withdrawing and electron-donating groups react with olefins and different substituted styrenes to afford corresponding cross-coupling products in good to excellent yields at 110 °C. Our results indicate that aryl chlorides could be easily converted to their corresponding cross-coupling products in good yields. As seen from Table 2, aryl iodides and bromides were more reactive than the chlorides. This relates to the strength of the Ar—X bond, which increases: I < Br < Cl. In our study, we found that the reactivity of aryl halides with electron-withdrawing substituents was higher than that of aryl halides with electron-donating substituents.

3.3. Catalyst reusability

We also checked the recyclability of the catalyst. The recycling potential of Pd/CuO NPs catalyst was studied by model Heck coupling reaction for bromobenzene with styrene in five consecutive cycles (Table 2, entry 5). The Pd/CuO NPs could be recycled and reused by separating them from the reaction mixture through centrifugation and frequent washing with water and ethyl acetate. The results show that the yield of product after five runs was only slightly reduced. Thus, the catalyst is stable during the Heck coupling reaction. Another key factor to be investigated is the stability of the Pd/CuO NPs; leaching of active species into the reaction mixture may occur. To investigate the catalyst leaching in these reactions, the filtrate of the reaction between bromobenzene and styrene after completion was analyzed by inductively coupled plasma atomic emission spectroscopy (ICP-AES) technique. The results show that the leaching of Pd/CuO NPs into the solution is very low by ICP-AES. It was shown that less than 0.2% of the total amount of the original palladium species was lost into solution during the course of a reaction.

4. Conclusions

In summary, the phosphine-free Heck coupling reaction was achieved under heterogeneous conditions by use of Pd/CuO NPs as a highly efficient and stable heterogeneous catalyst. The effects of catalyst composition, solvent and bases, aryl halides or olefins species on corresponding products were optimized. The present method has the advantages of readily available starting materials, straightforward and simple work-up procedures, elimination of ligand, copper and homogeneous catalyst, high yields, and tolerance for a wide variety of functionality. The catalyst showed best performance up to five recycles. In general, this catalytic system is nontoxic, thermally stable, reusable, and also makes it possible for the reactions to occur in air.

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