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Facile Microwave-Assisted Synthetic Approach to Palladium Nanoparticles Supported on Copper Oxide as an Efficient Catalyst for Heck and Sonogashira Cross-Coupling Reactions

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A simple green one-step method for the synthesis of highly active palladium nanoparticles embedded on copper oxide as an efficient catalyst for ligand-free Heck and Sonogashira cross-coupling reactions has been developed. The synthetic approach is based on Microwave (MW)-assisted simultaneous chemical reduction of an aqueous solution of palladium and copper salts using hydrazine hydrate as the reducing agent. Selected characterization of the catalyst with transmission electron microscope (TEM), X-ray photoelectron spectroscopy (XPS) and X-ray diffraction spectroscopy (XRD) reveal a size range of $25 \pm 2\,\mathrm{nm}$ for the generated catalyst nanoparticles with the highest catalytic activity. The use of the generated Pd/CuO nanoparticles is highly advantageous due to the use of ethanol/water as an environmentally green solvent under mild reaction conditions. Furthermore, the synthesized Pd/CuO nanoparticles catalyst can be recycled and re-used up to five times with negligible effect on the efficiency having turnover number up to 6000 and turnover frequency reaching $72\,000\,\mathrm{h}^{-1}$ for 20 wt.% Pd loaded catalyst at $150°\mathrm{C}$.

Keywords: Heck cross-coupling; copper oxide; Pd nanoparticles; hydrazine hydrate; microwave heating; catalysis.

1. Introduction

Transition metals in the nanometer size range have been utilized in catalyzing a lot of reactions due to their superior catalytic properties.[1,2] Recently, a major role in several synthetic applications was played by a variety of nanostructured materials especially in the area of heterogeneous catalysis.[3–5] One of the features that steers the nanoparticles

catalytic activity and their chemical as well as physical behavior is the particle size distribution of such catalysts and their precise control which is considered as a challenging task.[6,7] Among several transition metals, palladium-based nanoparticles and copper derived catalysts have attracted more attention due to their versatile synthetic and catalytic applications. Palladium metal has been extensively used to catalyze several chemical reaction transformations under both homogeneous and heterogeneous reaction media.[8,9] Also, the design of bimetallic Pd-based nanoparticles by combination of palladium with other transition metals like Ni, Au, Pt, Ag, Co and Cu have shown to have diverse applications in organic synthesis.[10] Among several bimetallic nanoparticles, copper oxide-supported transition metal catalysts showed good catalytic activities. Copper is considered as a promising transition metal due to many advantages such as abundant reserve, low cost, versatility, less harmful to the environment and wide use in different applications. In addition, using copper oxide as a solid support for palladium catalysts is highly advantageous by preventing the potential agglomeration of palladium nanoparticles and hence, enhancing the catalytic activity.[11,12] The nanosized Pd particles increase the exposed surface area of the active component of the catalyst to the substrate and consequently, the contact between reactants and catalyst is enormously increased like the case of homogeneous catalysts. Cross-coupling reactions, such as Heck and Sonogashira reactions play a crucial role in pharmaceutical and organic synthesis.[13,14] The possibility of using microwave heating for various reactions using nanocatalysis is a convenient synthetic route to green chemistry.[15] Many reactions such as cross-coupling reactions used for C–C bond formation are now relevant processes in chemical transformations and can be applied in many scientific areas including pharmacy, natural products, agriculture and cosmetics.[16,17]

There is some limitations for using homogeneous metal catalysts including catalyst recovery, leaching issues and recyclability. In this research paper, we report on a fast, mild, green and efficient method to prepare highly active copper oxide-embedded palladium nanoparticles using microwave heating as a heterogeneous catalyst that can overcome most of the disadvantages associated with using homogenous catalyst. Also, we examined the catalyzing efficiency and recyclability of the prepared catalyst nanoparticles in Heck and Sonogashira cross-coupling reactions using a series of different substrates.

2. Experimental Methods

All chemicals were purchased and used as received without further purifications. Absolute ethanol (99.9%), deionized water (D.I. H_2O) were used for all experiments. A mixture of ethanol/deionized water was used for the Suzuki cross-coupling reactions. Palladium nitrate (10 wt.% in 10 wt.% HNO_3, 99.999%), copper (II) nitrate hemipentahydrate, hydrazine hydrate (80%), bromobenzene, all other aryl halides, and potassium carbonate were obtained from Sigma Aldrich. GC–MS analyses were performed on an Agilent 6890 gas chromatograph equipped with an Agilent 5973 mass selective detector. A CEM Discover microwave instrument was used for cross-coupling reactions. The reactions were performed at operator selectable power output of 250 W.

2.1. *Synthesis of Pd, CuO nanoparticles, and Pd supported on CuO nanoparticles*

2.1.1. *Synthesis of Pd supported on CuO nanoparticles*

A series of four catalysts with various weight percents of palladium loading on copper oxide (5 wt.%, 10 wt.%, 20 wt.%, 30 wt.%) were prepared. 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 placed in a 150 mL beaker then sonicated at room temperature for 1 h. To the previously sonicated solution, the relevant volumes of palladium nitrate solution corresponding to the above loading percents (97 µL, 194 µL, 388 µL, 582 µL, respectively) were added and stirring was continued for another 1 h. Hydrazine hydrate (1200 µL) was added at room temperature to the solution turned to reddish-brown and the suspension was heated in microwave for 30 s (intervals) to afford the black product. Finally, the catalyst was dried in oven at 80°C till constant weight of catalyst.

2.1.2. *Synthesis of Pd nanoparticles*

A solution containing palladium nitrate (1940 µL) in 20 mL deionized water was sonicated at room

temperature for 1 h then stirred for another 1 h. Hydrazine hydrate (1200 μL) was added to the mixture and the mixture was heated in a microwave oven for 30 s (intervals), filtered, washed with deionized water (2–3 times), ethanol (2–3 times) then dried in oven at 80°C till constant catalyst weight.

2.1.3. *Synthesis of copper oxide nanoparticles*

A solution of 366 mg of copper (II) nitrate hemi-pentahydrate $Cu(NO_3)_2.2.5H_2O$ in 20 mL deionized water was sonicated for 1 h stirred for another 1 h at room temperature. After stirring process is finished; 1200 μL hydrazine hydrate was added to the mixture and the mixture was heated in a microwave oven for 30 s (intervals). The mixture was then filtered, washed with hot deionized water (2–3 times), then ethanol (2–3 times), dried in an oven at 80°C till constant catalyst weight.

2.2. *Characterization of catalyst*

The X-ray photoelectron spectroscopy (XPS) analysis was performed on a Thermo Fisher Scientific ESCALAB 250 using a monochromatic Al KR X-ray. The X-ray diffraction patterns were measured at room temperature using an X'Pert PRO PAN analytical X-ray diffraction unit. A JEOL JEM-1230 electron microscope operated at 120 kV and equipped with a Gatan UltraScan 4000SP 4K X 4K CCD camera was used to obtain TEM images. TEM samples were prepared by placing a droplet of the prepared catalyst dissolved in ethanol on a 300-mesh copper grid (Ted Pella) which was then left to evaporate in air at room temperature. GC-MS analyses were performed on an Agilent gas chromatograph equipped with an Agilent mass selective detector.

2.3. *General procedure for Heck cross-coupling reaction*

A solution of aryl bromide (0.32 mmol, 1 eq.) dissolved in a mixture of 4 mL H_2O:EtOH (1:1) was placed in a 10 mL microwave tube. The alkene (0.64 mmol, 2 eq.), potassium carbonate (0.96 mmol, 3 eq.) and palladium/CuO catalyst (2 mol%) were then added, and the tube was sealed, and heated under microwave irradiation (250 W, 2.45 MHz) at 150°C for 10 min. The reaction mixture was

extracted and the collected organic layers were dried over anhydrous sodium sulfate, and filtered. The solvent in the filtrate was removed under reduced pressure to give a solid product which was further purified.

2.4. *General procedure for Sonogashira cross-coupling reaction*

A solution of aryl bromide (0.32 mmol, 1 eq.) was dissolved in a mixture of 4 mL H_2O:EtOH (1:1) as an environmentally benign solvent system and was placed in a 10 mL microwave tube. The alkyne (0.64 mmol, 2 eq.), and potassium carbonate (0.96 mmol, 3 eq.) were added to this mixture. Then palladium-CuO catalyst (2 mol%) was then added, the tube was sealed, and heated under microwave irradiation (250 W, 2.45 MHz) at 150°C for 10 min. The progress of the reaction was monitored using GC-MS analysis to an aliquot of the reaction mixture. After the reaction was completed, the reaction mixture was extracted and the collected organic layers were combined, dried over anhydrous sodium sulfate and filtered. The solvent in the filtrate was removed under vacuum reduced pressure to give a solid product which was further purified.

2.5. *General procedure for catalyst recycling*

Aryl bromide (0.32 mmol, 1 eq.) was dissolved in a mixture of 4 mL H_2O:EtOH (1:1) and placed in a 10 mL microwave tube. To this were added the alkene (0.64 mmol, 2 eq.) and Potassium carbonate (0.96 mmol, 3 eq.) and finally the palladium-copper oxide nanoparticles (Pd/CuO) were then added. Then, the reaction tube was sealed with cap and heated at the assigned temperature and time. The progress of the reaction was monitored using GC-MS analysis to an aliquot of the reaction mixture. After the reaction was completed, the reaction mixture was extracted and the collected organic layers were combined, dried over anhydrous sodium sulfate, and filtered. The solvent in the filtrate was removed under vacuum reduced pressure to give a solid product which was further purified.

Ethanol washing for the catalyst was repeated for five times to make sure that all products were removed from catalyst surface. The catalyst was then transferred directly to another microwave tube and fresh reagents were added for the next run. This procedure of recycling the catalyst was

repeated for every run, the GC-MS was used to determine the conversion percentage of the product.

3. Results and Discussion

The Heck cross-coupling reaction of bromobenzene and the alkene in 1:1 mixture of water and ethanol as an environmentally benign solvent system under various reaction conditions was investigated. In order to study the effect of temperature on the catalytic activity, the cross-coupling reaction was carried out at constant reaction time (10 min) and different temperatures (80°C, 120°C, 150°C) using the synthesized Pd/CuO catalysts (2 mol%).

As seen in Table 1, the conversion percentage of the reaction is highly dependent on temperature. Increasing the temperature of the reaction mixture favors higher conversion to the product with maximum conversion obtained at 150°C. This tendency was similar for all prepared Pd/CuO catalysts with different Pd loading percent on the solid support (5 wt.%, 10 wt.% and 20 wt.%).

Also, increasing the catalyst weight percent on the solid support from 5–10 wt.% to 20 wt.%, enhances product conversion (at all studied temperatures) with maximum product conversion reaching 93% for 20 wt.% Pd loaded catalyst at 150°C. Unexpectedly, increasing the Pd content on the solid support to reach 30 wt.% led to sharp drop in the catalytic performance and lower conversion

Table 1. Conversion percentage for Heck reaction at different ratios of Pd/CuO.*

Catalysts	Temp (°C)	Conversion%**
5 wt.% Pd/CuO	80°C	35
	120°C	64
	150°C	**72**
10 wt.% Pd/CuO	80°C	47
	120°C	58
	150°C	**84**
20 wt.% Pd/CuO	80°C	53
	120°C	66
	150°C	**93**
30 wt.% Pd/CuO	150°C	45
Pd nanoparticles	150°C	< 30
CuO nanoparticles	150°C	< 30

Notes: *Aryl bromide (0.32 mmol), alkene (0.64 mmol), potassium carbonate (0.96 mmol), and Pd/CuO (2 mol%) in 4 mL (H₂O:EtOH) (1:1) were heated at (MWI) for 10 min.
**Conversions were determined by GC-MS.

Table 2. Optimizing the reaction conditions for Heck reaction at different ratios of Pd/CuO.*

Catalysts	mol%	Conversion%**
5 wt.% Pd/CuO	1	22
	2	72
	3	65
10 wt.% Pd/CuO	1	35
	2	**84**
	3	71
20 wt.% Pd/CuO	1	86
	2	**93**
	3	88

*Aryl bromide (0.32 mmol), alkene (0.64 mmol), potassium carbonate (0.96 mmol), and Pd/CuO in 4 mL (H₂O:EtOH) (1:1) were heated at 150°C (MWI) for 10 min.
**Conversions were determined by GC-MS.

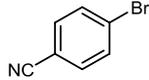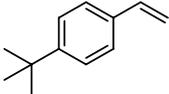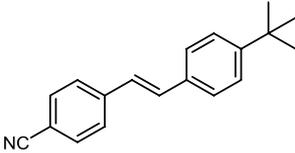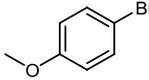(about 45%) to the desired product was observed (Table 1).

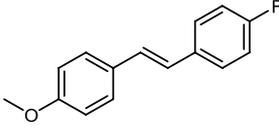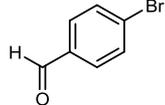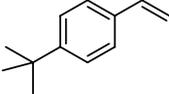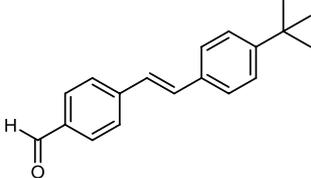Carrying out the Heck reaction using different Pd/CuO catalysts percents at a reaction temperature of 150°C and a reaction time of 10 min revealed that using 2 mol% corresponds to the highest conversion values compared to 1 mol% and 3 mol% (Table 2).
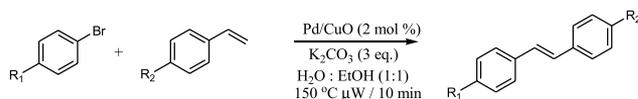
The effect of palladium nanoparticles distribution on the surface of CuO solid support was studied as it has a great impact on the catalytic performance and this can be explained by comparing the TEM images of the freshly prepared catalyst versus the recycled catalyst after the fifth run. As seen in Fig. 1(a), for 20 wt.% Pd/CuO catalyst, the palladium nanoparticles of size was measured using XRD and it shows that the particle size is about 25 ± 2 nm so, the palladium nanoparticles are well dispersed within the CuO matrix which is consistent with the experimental results of higher catalytic activity when compared with the same catalyst after the fifth run which is probably due to the severe agglomeration of the particles that took place after reaction as shown in Fig. 1(b).

Figure 2(a) displays the XRD pattern of palladium supported on copper oxide (CuO) that was prepared by microwave method.

Table 3.   Diversity of the Heck coupling reactions using Pd/CuO catalyst.*

Entry	Aryl halide	Alkene	Product	Yield (%)**
1				87%
2				90%
3				93%
4				88%
5				75%
6				82%
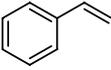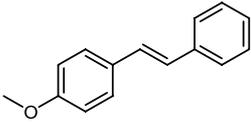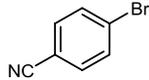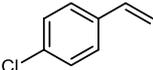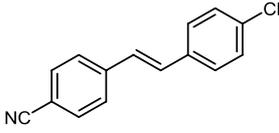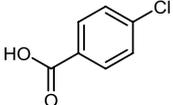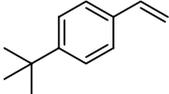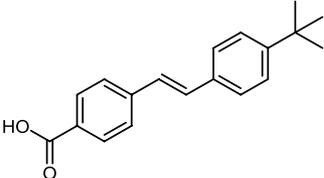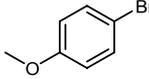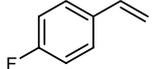
Notes: *Aryl bromide (0.32 mmol), alkene (0.64 mmol), potassium carbonate (0.96 mmol), and Pd/CuO (2 mol%) in 4 mL (H$_2$O:EtOH) (1:1) were heated at 150°C (MWI) for 10 min. *Conversions were determined by GC-MS.
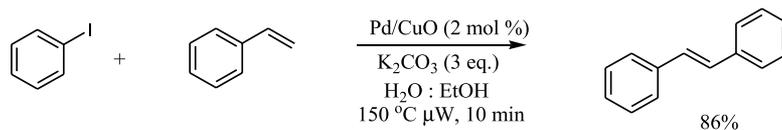
Scheme 1.   Reactivity of Pd/CuO catalyst towards Heck coupling reactions.
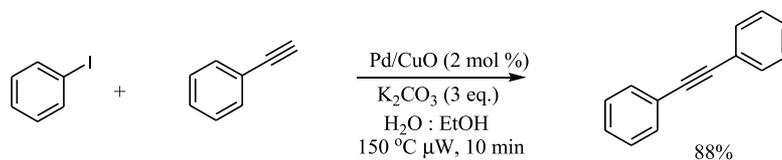
Scheme 2.   Reactivity of Pd/CuO catalyst towards Sonogashira coupling reactions.

(a)   (b)

Fig. 1.   TEM — images of Pd/CuO (a) before the reaction and (b) after fifth run of catalyst recycling.
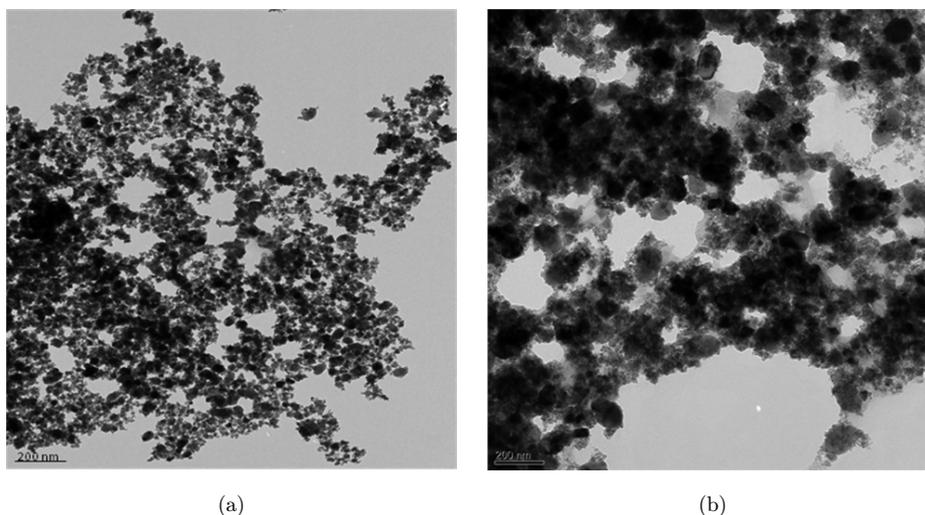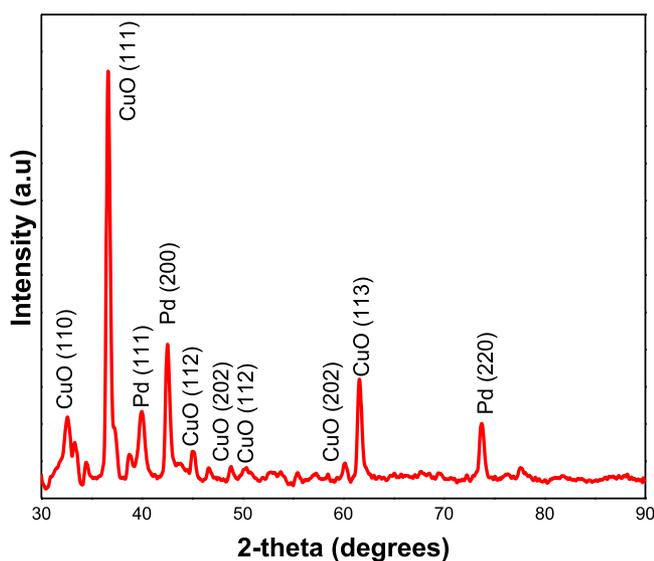

Fig. 2.   XRD pattern of Pd/CuO nanoparticles.

The exact palladium content in microwave synthesized Pd/CuO catalysts prepared with different palladium loading weight percent was determined by means of inductively coupled plasma-optical emission spectroscopy (ICP-OES) and it was found to be 3.5 wt.%, 6.5 wt.%, 10 wt.%, 18 wt.% Pd corresponding to prepared 5 wt.%, 10 wt.%, 20 wt.%, 30 wt.% of Pd/CuO catalysts, respectively. Further characterization of the microwave synthesized palladium supported on copper oxide catalyst (Pd/CuO) was achieved by using XRD pattern of catalyst sample as seen in Fig. 2. The sharp diffraction peak at $2\theta = 40°$ is the characteristic peak of palladium. The XRD reflections of CuO match that of JCPDS No. 48-1548 corresponding to monoclinic structure.[18,19] The diffraction peaks are ascribed to the (110), (111), (112), (202), (112) and (113) planed of copper oxide NPs as shown in Fig. 2.[3,4,7]

The XPS technique is widely used as a more sensitive technique for the analysis of surface oxides than XRD.[20–23] To characterize the surface composition of the supported nanocatalysts, XPS measurements were carried out as shown in Fig. 3 for the 20 wt.% Pd/CuO catalyst. All the samples had a C1s binding energy around 284.5 eV derived from the carbon contamination in the analysis. In Figs. 3(a) and 3(b), samples reveal the existence of copper oxide. The XPS show that the binding energy of Cu $2P^{3/2}$ was located at 933.1 eV and the binding energy of Cu $2P^{1/2}$ was located at 953.1 eV, indicating that Copper was present as Cu^{2+}. There is also shake-up satellite peaks located at 941.9 eV and 961.7 eV. Also, the binding energy of Pd $3d^{5/2}$ was 334.8 eV, and Pd $3d^{3/2}$ was 340.1 eV indicating that the Pd was present as Pd^0. Similarly, the binding energy of Pd $3d^{3/2}$ was 341.38 eV, and Pd $3d^{5/2}$ was 336.23 eV indicating that the Pd was present as PdO (Pd^{2+}).[3,4,7]

It was also found as in Table 4, that catalyst shows a high catalytic activity. As in case of using catalyst with 2 mol% it could be recycled up to five times with nearly 90% conversion as shown in Fig. 4 which represents an evidence for the high catalytic activity of the prepared catalyst; while by increasing the mole percentage to 3 mol%, the catalyst could be recycled up to five times with conversion 88%.

TEM images of Pd/CuO can be used as an evidence for the deactivation process that happens to
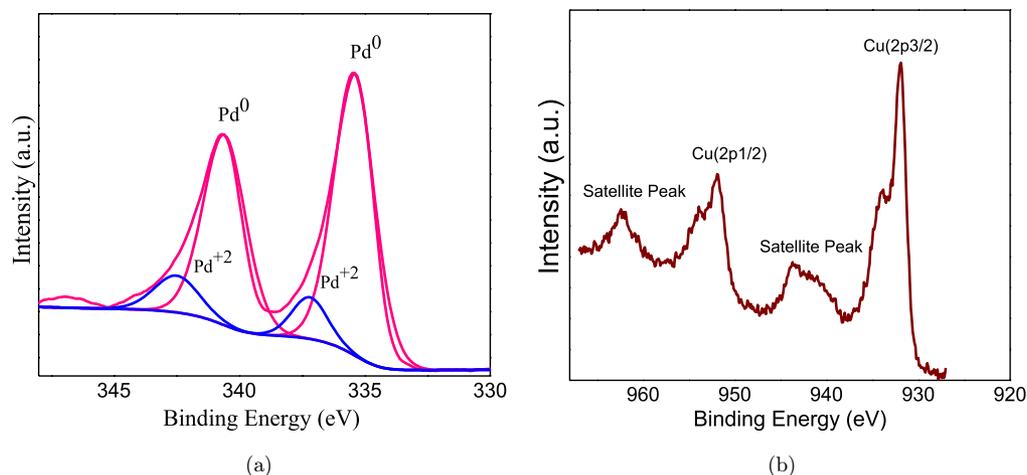
Fig. 3.　(a) XPS (Pd3d) and (b) XPS (Cu2p) of Pd/CuO.

Table 4.　Recycling experiments for Pd/CuO catalyst using a concentration of 2 mol% and 3 mol%.[a]

Run	Conversion (%)[b] (2 mol%)	Conversion (%)[b] (3 mol%)
1	93	88
2	90	86
3	90	85
4	89	83
5	88	81
6	80	70

Notes: [a]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. [b]Conversions were determined by GC-MS.
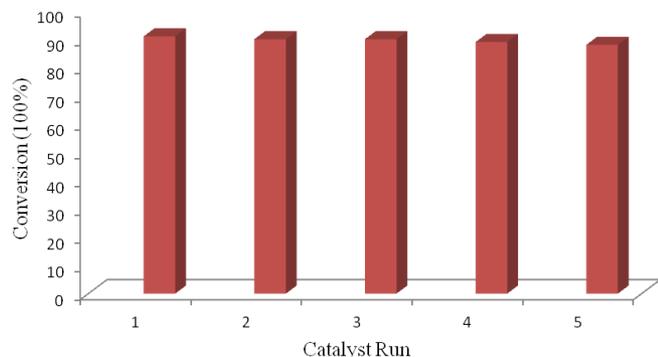

Fig. 4.　Recycling experiments of Pd/CuO catalyst for Heck cross-coupling reaction.

the catalyst after fifth run, which clearly demonstrates the agglomeration and accumulation of Pd nanoparticles on CuO surface as shown in Fig. 1(b). To investigate the extent of Pd leaching from prepared catalyst, the reaction was carried out in the presence of 2 mol% catalyst at 150°C for 10 min

under microwave heating. Upon the completion of the reaction period, the mixture was hot filtered and the Pd content was determined in the filtrate to be 195 ppm based on the ICP-MS analysis. Moreover, the filtrate solution was subjected to the same reaction using fresh reagents, and no further catalytic activity was observed in this solution after heating the fresh reaction mixture to 150°C for 10 min under microwave irradiation. This confirms the lack of residual activity in the reaction mixture after the catalyst removal which is consistent with the very small amount of Pd content in solution determined by ICP-MS.

4. Conclusions

In summary, we have succeeded in development of an efficient procedure to generate highly active palladium based catalysts supported on copper oxide at the nanoscale by applying microwave assisted chemical reduction of an aqueous mixture of a palladium nitrate and copper nitrate. The addition of copper oxide and its potential effect as a support was investigated. The catalysts were prepared by applying a simple green microwave-assisted synthesis approach using Hydrazine hydrate as a strong reducing agent for mixtures of palladium nitrate in combination with copper (ii) nitrate hemipentahydrate $Cu(NO_3)_2 \cdot 2.5H_2O$ that was successfully used as a source of copper. The prepared catalysts showed a remarkable catalytic activity towards Heck and Sonogashira cross-coupling reactions with 93% and 88% conversion for the catalyst first run, respectively. The bimetallic unique structure offers enormous advantages including high reactivity, mild reaction conditions

and short reaction times in an environmentally benign solvent system. This catalyst also provided excellent yields over a broad range of highly functionalized substrates. In conclusion, the palladium bimetallic nanoparticles exhibit superior catalytic activity towards Heck cross-coupling with excellent turnover number (6000) and turnover frequency of $72\,000\,\mathrm{h}^{-1}$ for 20 wt.% Pd loaded catalyst at $150°C$. Furthermore, the prepared catalysts is stable and can be reused showing 93% conversion within 10 min at $150°C$, and could be easily recovered and recycled up to five times with high catalytic activity in case of palladium supported on copper oxide under batch reaction conditions, thus providing high economic viability.

Acknowledgments

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