



Magnesium oxide supported bimetallic Pd/Cu nanoparticles as an efficient catalyst for Sonogashira reaction



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ABSTRACT

PdCu bimetallic nanoparticles with a diameter of about 3 nm are prepared and supported on a polymeric vinylimidazole ligand modified magnesium oxide. This new material is characterized using different analysis such as XRD, XPS, CHNS, TEM, SEM, and EDX-mapping. PdCu supported on MgO (MgO@PdCu) exhibits high catalytic activity in the Sonogashira coupling reaction of aryl iodides, bromides and chlorides with low Pd loading (0.05–0.2 mol%). This catalyst is recovered and recycled for 11 consecutive runs preserving its catalytic activity in the model reaction of iodobenzene with phenylacetylene for at least 8 cycles. Reused catalyst is characterized with TEM, XPS and EDX showing preservation of the catalyst structure. Using hot filtration and PVP poisoning tests, the catalyst shows a heterogeneous behavior for the model reaction.

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1. Introduction

The Sonogashira-Hagihara reaction is one of the most important methodology for the bond formation between sp carbon and sp^2 carbon atoms forming substituted aryl-alkynes and conjugated enynes through the coupling of aryl and vinyl halides or triflates with terminal alkynes, respectively, by palladium catalysis and in the presence of copper(I) as co-catalyst [1–11]. The obtained products from the Sonogashira reaction have wide utility in modern organic chemistry and have been extensively applied in the synthesis of natural products and pharmaceuticals, as well as in material science [12–14]. In recent years, different copper-free Sonogashira protocols (the original Cassar–Heck version of this reaction) have been reported [15–19]. However, it has been proved that in many cases, this cross-coupling reaction could be accelerated in the presence of copper under oxygen free conditions to prevent the formation of diynes as homo-coupling products [1–11].

Recently, an increasing attention has been paid to the application of bimetallic catalysts in different organic transformations. Due to new electronic and chemical properties of bimetallic catalysts compared to the monometallic systems, high catalytic activity and selectivity are expected for target products in these bimetallic

catalyzed reactions [20–22]. Among the different bimetallic catalysts, Pd/Cu catalysts have attracted great attentions in different organic transformations [23–43]. Along this line, some efforts have been recently paid to use homogeneous or heterogeneous PdCu bimetallic catalysts in various organic transformations particular in Sonogashira reaction under efficient and enhanced catalytic activity conditions [44–67]. Due to the expensive price and toxicity of Pd, many efforts have been recently devoted to develop very efficient heterogeneous and recyclable palladium catalysts in different organic reactions [1,68–74], especially in the synthesis of pharmaceuticals in which allowable content of Pd is <5 ppm [75]. For this purpose, different solid supports such as polymers [76], silica [77,78], and naturally occurring polysaccharides [79] have been used for stabilization of Pd nanoparticles in different coupling reactions.

Concerning solid supports, metal oxides have received much attention as resourceful materials for design of new heterogeneous catalysts [80,81]. Along this line, MgO an organic ceramic material with different properties such as high concentration of reactive surface ions acting as Lewis acids, lattice bound and isolated hydroxyl groups and anionic and cationic vacancies, is considered as a promising support for the preparation of heterogeneous Pd catalysts [82–103]. For instance, nanocrystalline MgO supported palladium nanoparticles [NAP–Mg–Pd(0)] has been used as catalyst for the selective reduction of nitro compounds [89], Heck reaction of heteroaryl bromides [90], and oxidative coupling between

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N-aryl-2-aminopyridines and alkynes in the presence of copper(II) chloride as additive [91]. In addition, Pd NPs supported on MgO have been used for the regio selective hydrogenation of quinolines, alkenes, and biodiesel under mild reaction conditions [92]. However, to the best of our knowledge there is no report on using MgO as support for the stabilization of bimetallic PdCu nanoparticles in any organic transformations. In this work, we introduce imidazole as a simple nitrogen ligand modified MgO as an excellent support for PdCu nanoparticles stabilization and the application of this new material as a simple and efficient catalyst for Sonogashira coupling reactions of aryl halides with terminal alkynes under efficient and phosphine-free conditions.

2. Experimental

2.1. Synthesis of MgO particles

In a 250 mL flask, $\text{Mg}(\text{NO}_3)_2$ (3 g) was dissolved in distilled water (100 mL) and an aqueous solution of Na_2CO_3 (1.6 g in 100 mL) was added slowly. The obtained mixture was then stirred vigorously for 12 h at room temperature. After centrifugation, the resulting solid was isolated and dried at 100 °C. For achieving the fine powder of MgO, the obtained solid was calcinated at 400 °C for 2 h.

2.2. Synthesis of imidazole functionalized MgO

Acryloyl chloride (5 mmol, 0.4 mL) and Et_3N (8 mmol, 1.1 mL) were added to the synthesized MgO (1g), which was sonicated in THF (15 mL), at 0 °C under an argon atmosphere. Then, the mixture was subjected to centrifugation and the obtained isolated solid was washed with distilled water (2×15 mL) and ethanol (2×15 mL) and then dried in an oven at 70 °C. For introducing the imidazole group, MgO (1 g) was dissolved in EtOH (20 mL) and the mixture was deoxygenated by bubbling argon for 5 min. Then, *N*-vinylimidazole (5 mmol, 0.45 mL) and benzoyl peroxide (6 mg) were added to the previously achieved mixture and the nit was

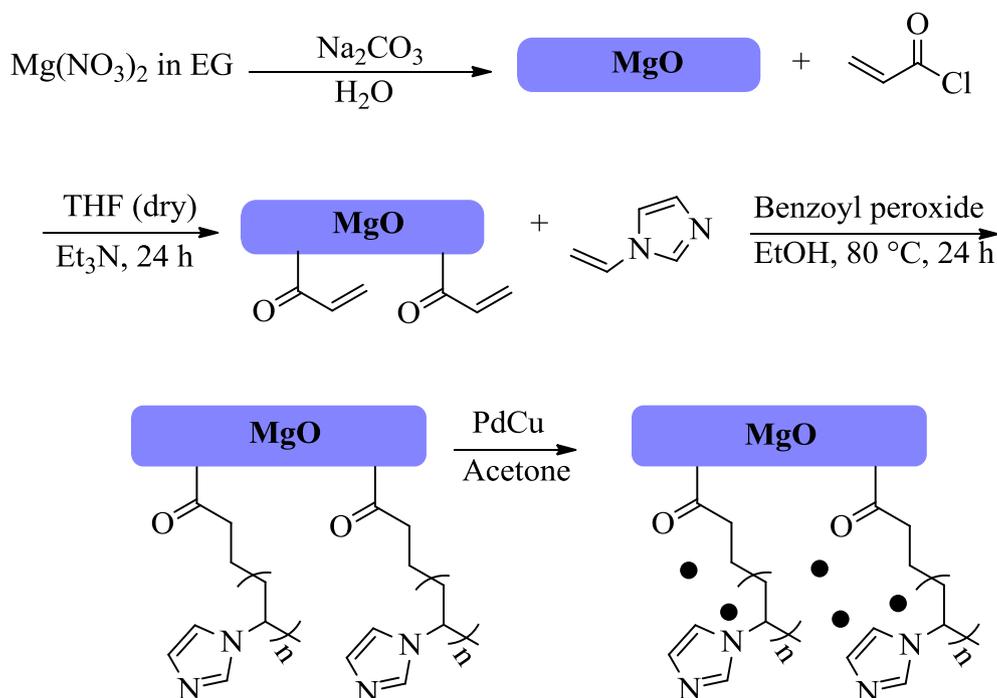
refluxed at 80 °C for 24 h. After centrifugation, the obtained solid was washed with water (15 mL) and dichloromethane (3×15 mL) and dried at 60 °C.

2.3. Synthesis of bimetallic MgO@PdCu

$\text{CuSO}_4 \cdot 5\text{H}_2\text{O}$ (18 mg, 0.07 mmol) was dissolved in a solution of ethylene glycol (5 mL) and polyvinylpyrrolidone (200 mg) and the mixture was stirred for 2 h at 80 °C under an argon atmosphere. In another flask, $\text{Pd}(\text{OAc})_2$ (32 mg, 0.16 mmol) and polyvinylpyrrolidone (400 mg) were dissolved in dioxane (5 mL) and stirred for 2 h at room temperature under argon atmosphere. The obtained solution was mixed with the $\text{CuSO}_4 \cdot 5\text{H}_2\text{O}$ solution and mechanically stirred under an argon atmosphere. During the stirring, a solution of NaOH (1 mol L^{-1}) was added upon reaching pH to 9–10 and the obtained mixture was stirred for 2 h at 100 °C. Then, the reaction mixture was cooled to room temperature and the resulting suspension was concentrated to 5 mL by centrifugation (10000 rpm, 10 min). The obtained suspension was diluted with acetone (5 mL) and the mixture was added to the prepared imidazole functionalized MgO (1 g), which was previously sonicated in acetone (10 mL). The mixture was stirred at room temperature for 24 h under argon atmosphere and subjected to centrifugation. The resulting solid was washed with water (3×10 mL) and dichloromethane (3×10 mL) and dried at 100 °C affording MgO@PdCu.

2.4. General procedure for Sonogashira reaction

To a 5 mL flask, the catalyst MgO@PdCu (10 mg for ArI or 40 mg for ArBr and ArCl), ArX (1 mmol), DABCO (168 mg, 1.5 mmol), and TBAB (322 mg, 1 mmol), for aryl chloride and DMF (2 mL) were added under argon atmosphere. The alkyne (1.5 mmol) was also added and the resulting mixture was stirred at 60–120 °C for appropriate reaction times (see Tables). Progress of reactions was followed by GC. Then, the reaction mixture was cooled down to room temperature and extracted with ethyl acetate (3×5 mL),



Scheme 1. Synthetic steps for the preparation of MgO@PdCu.

the organic phase was washed with H₂O (10 mL), dried and evaporated. The resulting residue was purified by column or plate chromatography using hexane and ethyl acetate as eluents.

2.5. Typical procedure for recycling of the catalyst for the reaction of iodobenzene and phenyl acetylene

After stirring the reaction in each run for 24 h and studying of GC yield, the reaction mixture was centrifuged and the obtained solid was washed with ethyl acetate and dried. The resulting solid was used for another batch of reaction under the optimized reac-

tion conditions. This process was repeated for 11 consecutive runs (see, Fig. 9).

3. Results and discussion

3.1. Materials and characterization

The preparation of MgO@PdCu is summarized in Scheme 1. MgO was prepared by treatment of Mg(NO₃)₂ with Na₂CO₃ in H₂O and further calcination at 400 °C. Then, acryloyl chloride was added in dry THF and the resulting solid was allowed to react with vinylimidazole in the presence of benzoyl peroxide. To this MgO bonded to the polymer containing imidazole, was added the bimetallic PdCu nanoparticles in acetone.

In the first step, the formation of MgO was confirmed using X-ray powder diffraction (XRD) showing related peaks to MgO in $2\theta = 37, 43.1, 62.4, 75.1, 78.7$ [104] and small peaks in $2\theta = 30.3$ and 38.2 correspond to Na₂CO₃ [105] and Mg(OH)₂ [106] impurities (Fig. 1).

Then, the acryloyl functionalized MgO was polymerized with vinyl imidazole to introduce nitrogen ligands on MgO. Because imidazole is considered as excellent ligand for coordination and stabilization of different transition metals [107], vinylimidazole was added for copolymerization with the acryloyl unit. After addition of fresh prepared bimetallic PdCu nanoparticles, MgO@PdCu was obtained containing 0.05 and 0.01 mmol g⁻¹ Pd and Cu, respectively, which has been determined by atomic absorption spectroscopy. Elemental analysis of MgO@PdCu showed a nitrogen

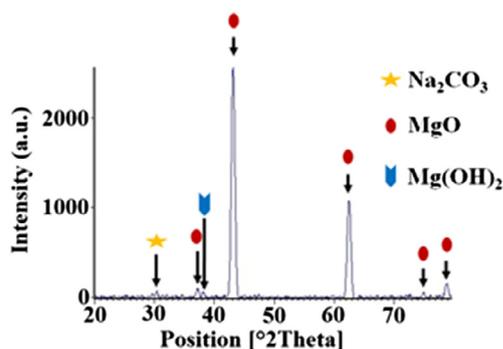


Fig. 1. XRD pattern of prepared MgO.

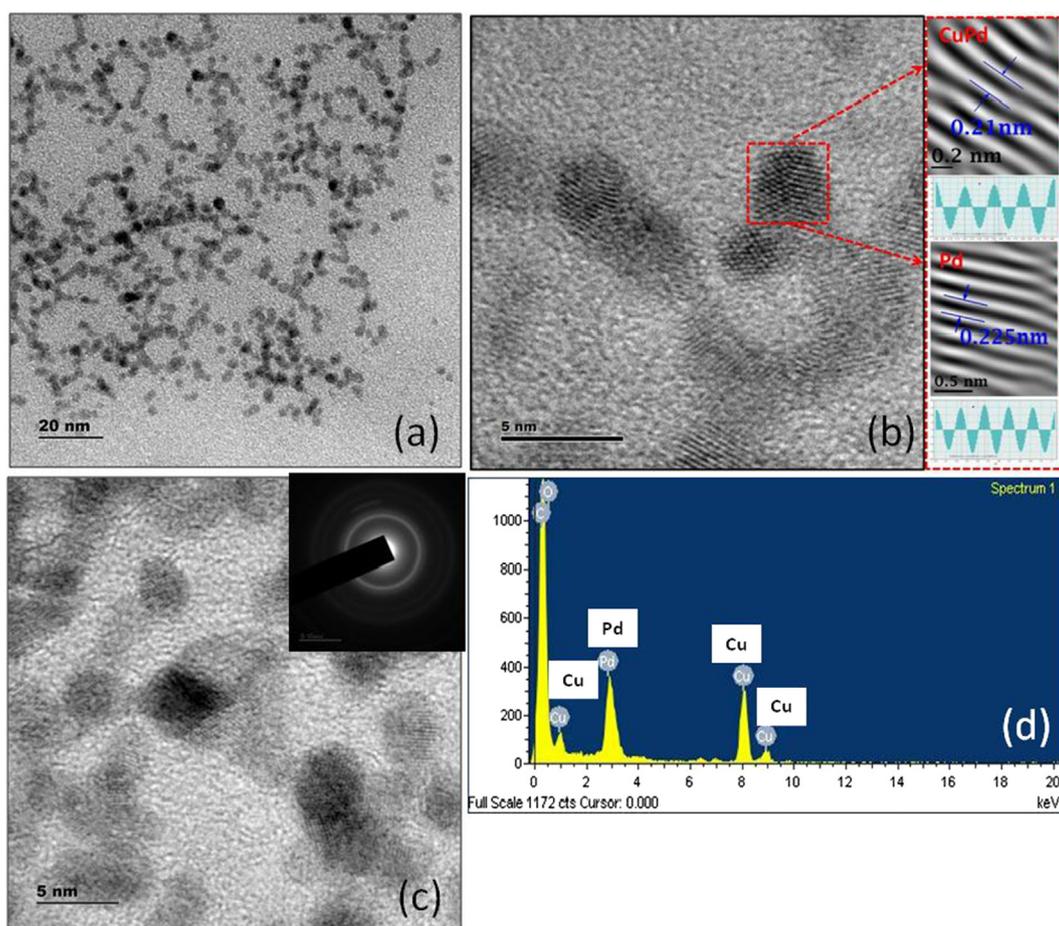


Fig. 2. (a–c) Representative TEM and HRTEM images, (insets in (b) shows the inverse FFT patterns of the selected area and (c) shows the corresponding SAED pattern) and (d) corresponding EDS spectrum of unsupported PdCu nanoparticles.

content of 1.85%. According to this result the degree of introduced imidazole in the MgO support was calculated to be 0.65 mmol g^{-1} .

Fig. 2(a)–(d) shows the TEM image analysis of PdCu nanoparticles before anchoring onto MgO nanosheet supports. The HR-TEM analysis (Fig. 2(b)–(c)) shows the presence of lattice fringes with a d-spacing value of 0.225 nm and 0.21 nm corresponding to the (1 1 1) plane of Pd and (1 1 1) plane of CuPd. Fig. 2b represents the inverse FFT of the selected area which indicated two distinguishable periodic lattice fringes, corresponding to CuPd and Pd and clearly validates the formation of PdCu bimetallic nanoparticles. According to first principles studies, during the formation of PdCu bimetallic nanoparticles, the electron donor atom, such as Cu and an electron acceptor, such as Pd, the d-band of Pd is lowered and the local electronic properties will be more similar to Pt and such

materials, composed of electron donor and acceptor metals, can exhibit desirable catalytic properties [108].

However, TEM images of PdCu nanoparticles before addition to MgO nanosheets, showed slightly aggregated chain-like structure confirming the effect of imidazole modified MgO in stabilization of PdCu nanoparticles (Fig. 3). Fig. 3(a)–(d) reveals the effective anchoring of PdCu particles on the surface of MgO nanosheets. It is interesting to note that the PdCu nanoparticles were found to be highly uniform, monodispersed with particle size in the range of 3–4 nm after anchoring onto MgO nanosheets. Fig. 3f shows the selected area diffraction pattern (SAED) analysis with prominent ring patterns corresponding to the fcc CuPd structure (JCPDS no. 48-1551) and cubic MgO (JCPDS no. 75-1585). The diffraction pattern shows prominent rings with interplanar spacing of

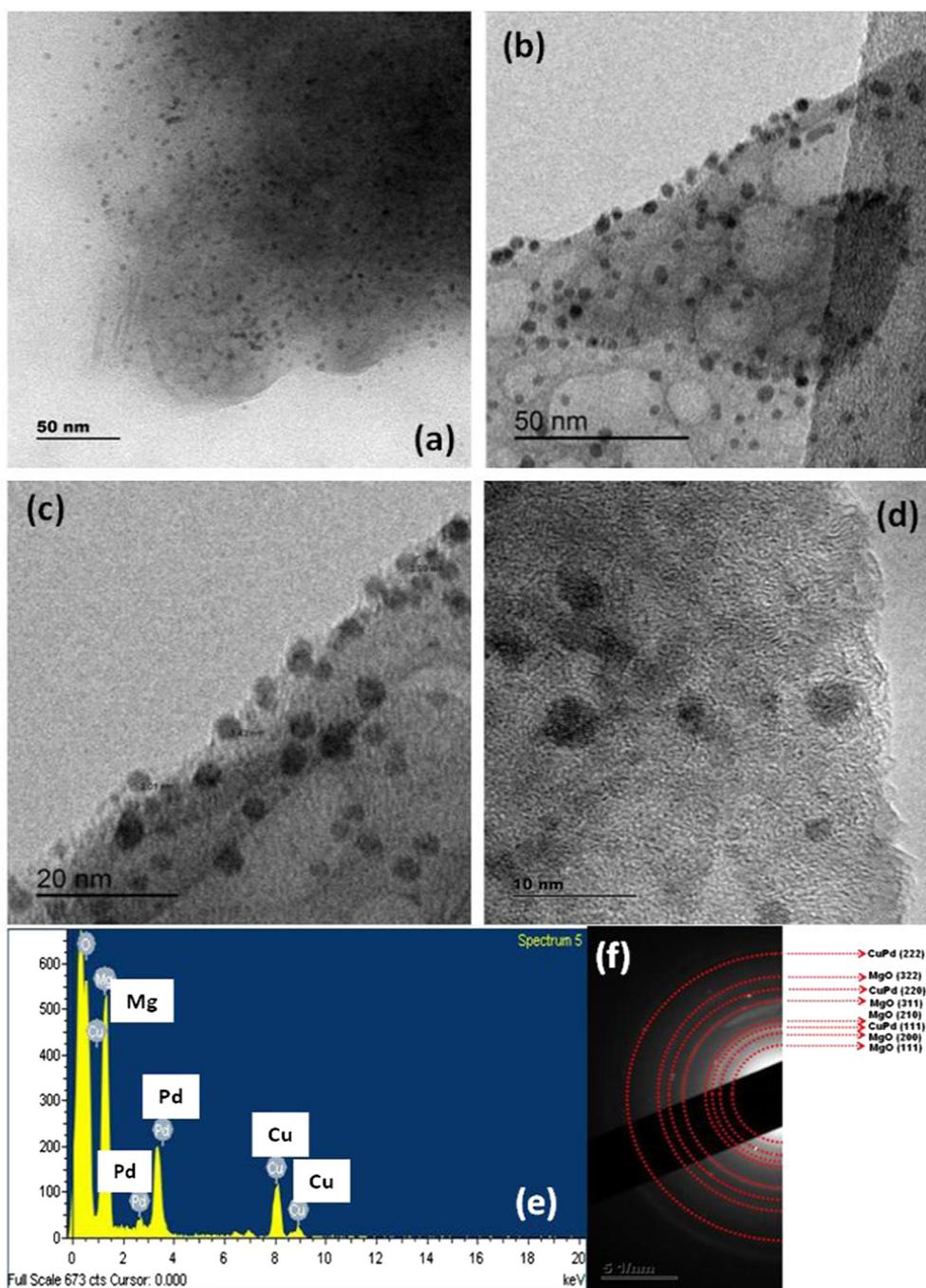


Fig. 3. (a–d) Representative TEM and HRTEM images, (e) corresponding EDS spectrum and (f) SAED pattern of MgO@PdCu.

0.275 nm, 0.235 nm and 0.146 nm corresponding to the (1 1 1), (2 0 0) and (3 1 1) of MgO and interplanar spacing of 0.211 nm, 0.133 nm and 0.100 nm corresponding to the (1 1 1) of CuPd. The (1 1 1)

plane of CuPd and (1 1 1) plane of Pd [JCPDS No: 46-1043] matched well with the SAED pattern revealing the existence of PdCu bimetallic nanoparticles on MgO. The preferential growth plane

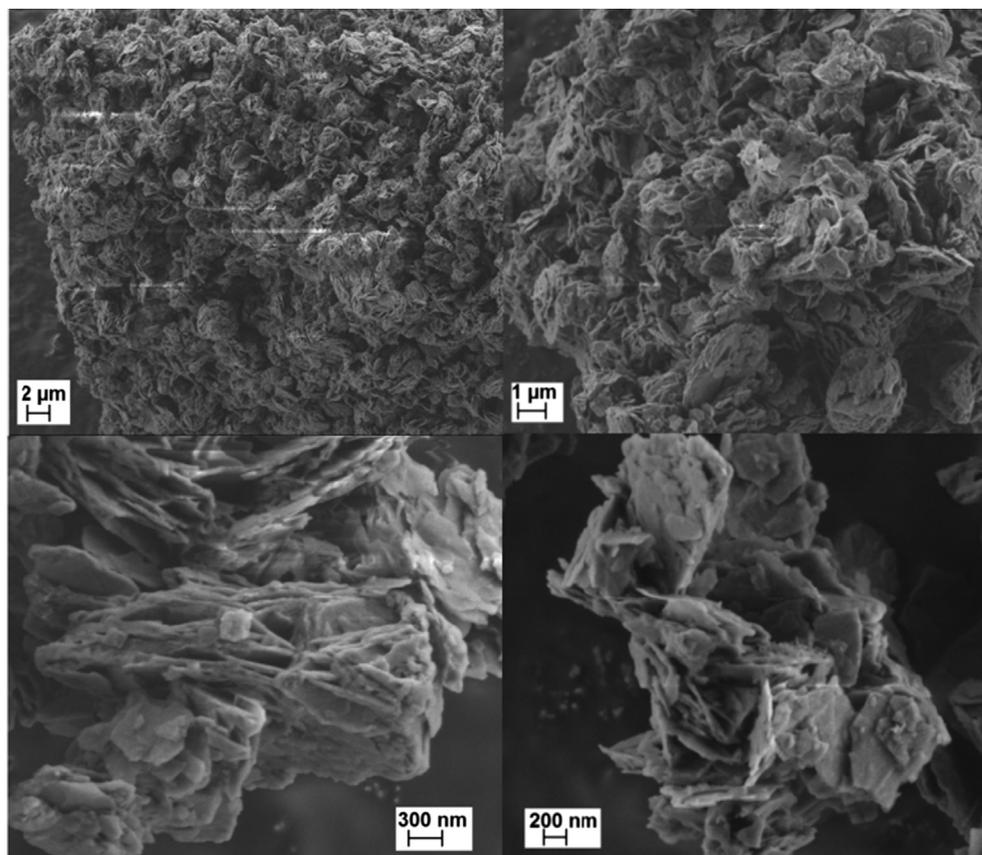


Fig. 4. SEM images of MgO@PdCu in different magnifications.

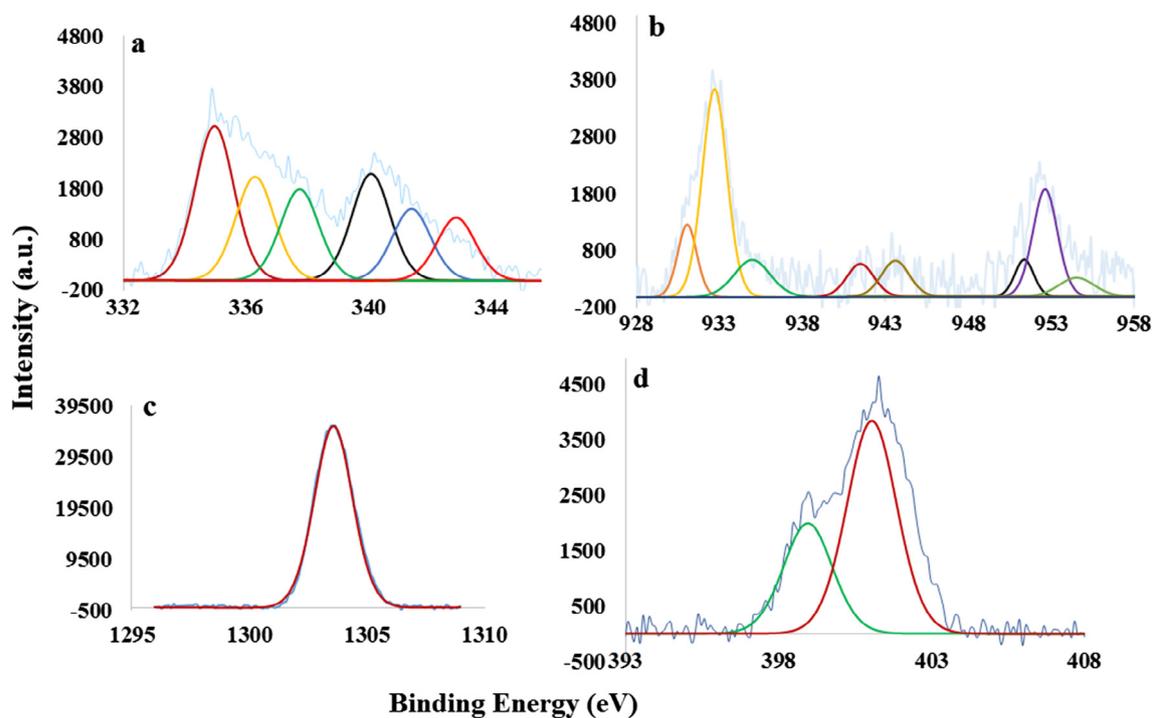


Fig. 5. XPS spectra of MgO@PdCu in (a) Pd 3d, (b) Cu 2p, (c) Mg 1s and (d) N 1s regions.

of MgO was found to be (1 1 1) as confirmed from SAED. EDS spectra of the unsupported (Fig. 2d) and MgO supported (Fig. 3e) PdCu bimetallic nanoparticles clearly give evidence for the presence of Cu, Pd and MgO in the samples.

EDS mapping images of the material MgO@PdCu was also studied (Fig. 1, ESI). It can be seen that both Pd and Cu are mostly distributed evenly throughout each PdCu species, suggesting an alloy structure [64,109,110]. Furthermore, energy-dispersive X-ray spectroscopy (EDS) analysis of MgO@PdCu confirmed the presence of Pd, Cu, Mg and N species (Fig. 2, ESI).

In order to investigate the oxidation states of Pd and Cu in the solid support, X-ray photoelectron spectroscopy (XPS) of the MgO@PdCu was performed (Fig. 5). High resolution XPS analysis of Pd region showed three doublets between 335 and 343 eV. An intense doublets at 335 and 340 eV were related to Pd(0) and a doublet peak at 336.5 and 341.6 eV related to Pd(II) in PdO form.

A doublet peak in higher binding energy at 338 and 343 eV could be assigned to the Pd(IV) species in PdO₂ form (Fig. 5a) [111–113]. These results indicated that 44% of Pd are in Pd(0) oxidation state, 32% as PdO and 24% as PdO₂ form. Formation of Pd(0) may result from the addition of concentrate electron rich polyethylene glycol and polyvinylpyrrolidone and oxidized palladium are the results of the reaction with sodium hydroxide at high temperatures under the catalyst preparation steps.

XPS spectra of Cu 2p region showed two peaks centered at 932.8 and 952.9 eV which were assigned to Cu 2p_{3/2} and Cu 2p_{1/2} of CuO, respectively [113–115] (Fig. 5b). The small peak at the binding energy of 935.1 was assigned to the presence of Cu(OH)₂ species [116]. Apart from the main peaks of CuO, three extra shake-up satellite peaks were observed in higher binding energies at 941.7, 943.8, 954.8 which can be attributed to Cu(II) states in CuO and Cu(OH)₂ [114–117]. The spectra also showed two smaller peaks at 931.5 and 951.5 which correspond to Cu₂O or Cu species. Since binding energies of Cu(0) and Cu₂O are very close and are different by only 0.1 eV, detection of true species by using this region of binding energy is very difficult [114–117]. Therefore, we studied it by LMM auger transition spectroscopy in the XPS spectra and it was found out to be 568 eV for Cu(0) and 570 eV for Cu₂O species [118,119]. Fitting of these XPS data in this region showed appearance of a peak at 570 eV confirming the peak in 931.5 eV is related to Cu₂O species (Fig. 3, ESI). XPS studies of Mg [120] region confirmed the presence of Mg by showing related peaks to MgO at 1304 eV (Fig. 5c). Furthermore, XPS analysis in N1s region confirm the presence of imidazole by two peaks at 398.9 and 401.02 eV which can be attributed to the C=N and C–N bonds of the imidazole (Fig. 5d) [121,122].

XRD pattern of the PdCu suspensions before stabilization on MgO were also studied (Fig. 6). The XRD diffractogram of MgO@PdCu showed related peaks to MgO at 36.7, 42.9, 62.2, 74.5 and 78.5 [104] and a peak at 34.3 which is related to formation of perovskite structure (Mg₇O₄C₄₋₀₀O_{20,00}) [123] (Fig. 6a). However, this diffractogram did not show any significant peaks for Cu and Pd due to low loading weight of them and the overlap of MgO peaks

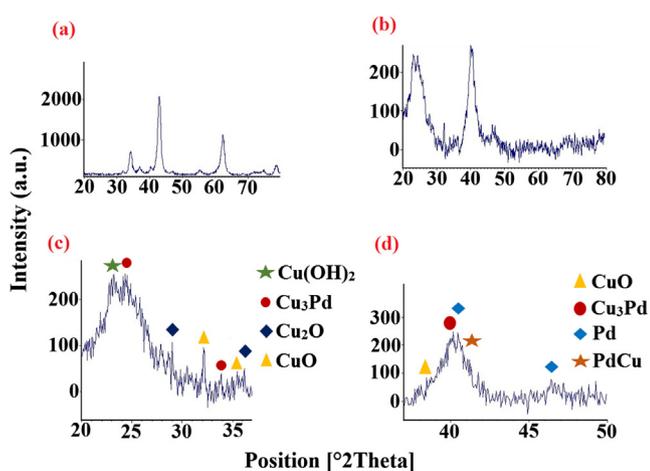
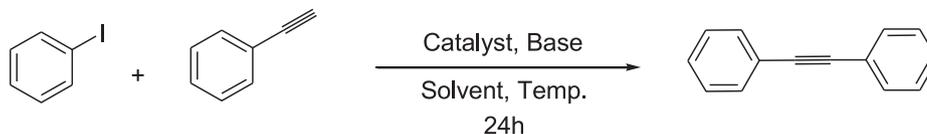


Fig. 6. XRD spectra of: (a) MgO@PdCu, (b) PdCu suspension in 2θ: 20–80, (c) PdCu suspension in 2θ: 20–37, (d) PdCu suspension in 2θ: 37–50.

Table 1

Optimization of reaction condition for the coupling of iodobenzene and phenylacetylene catalyzed by MgO@PdCu.^a

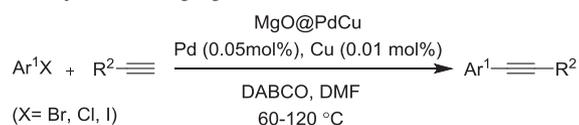


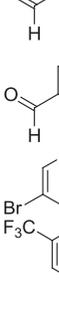
Entry	Cat Pd (mol%)	Cat Cu (mol%)	Base	Solvent	T (°C)	Yield (%) ^b
1	0.1	0.02	DABCO	H ₂ O	50	8
2	0.1	0.02	K ₂ CO ₃	H ₂ O	50	7
3	0.1	0.02	<i>t</i> -BuOK	H ₂ O	50	11
4	0.1	0.02	N(Et) ₃	H ₂ O	50	6
5	0.1	0.02	K ₃ PO ₄ ·3H ₂ O	H ₂ O	50	9
6	0.1	0.02	DABCO	DMF	50	87
7	0.1	0.02	K ₂ CO ₃	DMF	50	2
8	0.1	0.02	<i>t</i> -BuOK	DMF	50	28
9	0.1	0.02	Et ₃ N	DMF	50	36
10	0.1	0.02	K ₃ PO ₄ ·3H ₂ O	DMF	50	7
11	0.1	0.02	DABCO	CH ₃ CN	50	86
12	0.1	0.02	DABCO	EtOH	50	0
13	0.1	0.02	DABCO	Toluene	50	19
14	0.1	0.02	DABCO	DMF	60	98
15	0.05	0.01	DABCO	DMF	60	97
16	0.025	0.005	DABCO	DMF	60	85
17	0.05	–	DABCO	DMF	60	37
18	–	0.01	DABCO	DMF	60	8

^a Reaction conditions: iodobenzene (0.5 mmol), phenylacetylene (0.75 mmol), base (0.75 mmol), solvent (1.5 mL), catalyst (see column).

^b GC yields.

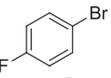
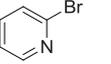
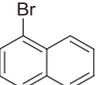
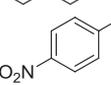
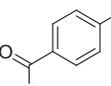
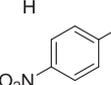
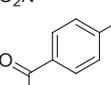
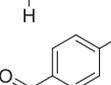
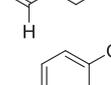
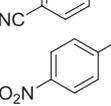
Table 2
Sonogashira-Hagihara reaction of terminal alkynes with aryl halides using MgO@PdCu.^a



Entry	Ar ¹	R ²	Cat (mol%)	t (h)	T (°C)	Yield (%) ^b
1		C ₆ H ₅	0.05	24	60	97 ^c
2		C ₆ H ₅	0.05	15	60	95
3		C ₆ H ₅	0.05	15	60	96
4		C ₆ H ₅	0.05	24	60	94
5		C ₆ H ₅	0.05	15	60	94
6		C ₆ H ₅	0.05	10	60	96 ^c
7		C ₆ H ₅	0.05	24	60	97 ^c
8		C ₆ H ₅	0.05	24	60	82
9		C ₆ H ₅	0.05	24	60	75
10		HOCH ₂ —	0.05	24	60	99 ^c
11		HOCH ₂ —	0.05	24	60	98 ^c
12		HOCH ₂ —	0.05	24	60	90
13		4-MeC ₆ H ₄	0.05	24	60	94
14		C ₆ H ₁₃	0.05	24	60	88
15		C ₆ H ₅	0.02	24	80	83 ^c
16		C ₆ H ₅	0.2	6	60	93
17		C ₆ H ₅	0.2	24	60	70 ^c
18		C ₆ H ₅	0.2	24	80	85
19		C ₆ H ₅	0.2	24	60	88 ^c
20		C ₆ H ₅	0.2	24	60	94

(continued on next page)

Table 2 (continued)

Entry	Ar ¹	R ²	Cat (mol%)	t (h)	T (°C)	Yield (%) ^b
21		C ₆ H ₅	0.2	24	60	95
22		C ₆ H ₅	0.2	24	80	82
23		C ₆ H ₅	0.2	24	80	90
24		C ₆ H ₅	0.2	24	60	55 ^{c,d}
25		C ₆ H ₅	0.2	24	80	25 ^{c,d}
26		C ₆ H ₅	–	24	60	10 ^{c,e}
27		C ₆ H ₅	0.2	48	100	61 ^{c,f}
28		C ₆ H ₅	0.2	24	120	94 ^{c,f}
29		C ₆ H ₅	0.2	24	120	89 ^{c,f}
30		C ₆ H ₅	0.2	24	100	95 ^{b,f}

^a Reaction conditions: ArX (1 mmol), alkyne (1.5 mmol), DABCO (168 mg, 1.5 mmol), catalyst (10–40 mg), DMF (2 mL).

^b Isolated yields.

^c GC yields.

^d Reaction in the absence of Cu using Pd@MgO.

^e Reaction in the absence of Pd using Cu@MgO.

^f Reactions using 1 eq of TBAB.

with PdCu peaks. Therefore, we studied XRD of PdCu suspension before stabilization on MgO support (Fig. 6b).

Expanded XRD of PdCu suspension before stabilization on MgO showed the presence of peaks at 2 theta value of 23.3°, which is matched with (0 2 1) planes of Cu(OH)₂ [124] (Fig. 6c). These spectra also showed the presence of peaks at 24°, 34° and 39.9°, which correspond to the lattice planes of (1 0 1), (1 1 0) and (1 1 0) of Cu₃Pd. (JCPDS no. 07-0138) (Fig. 6c, d). These results indicated the presence of peaks at 29.1° and 36.2°, which are related to the plane (1 1 0) and (1 1 1) of Cu₂O [125] (Fig. 8c). The peaks at 2 theta = 32.2, 35.5 and 38.5 were ascribed to the (1 1 0), (0 0 2), and (2 0 0) reflections of CuO [126] (Fig. 8c,d). In addition, the appearance of a peak at 2theta value of 41.7° is related to the lattice plane (1 1 0) of CuPd (JCPDS no. 48-1551) (Fig. 8d). Furthermore, peaks related to Pd were observed at 2theta value of 40.5° and 46.3°, which correspond to (2 2 0) plane of Pd [127] (Fig. 6c,d).

3.2. Catalytic performance

Catalytic activity of prepared PdCu catalyst was studied in Sonogashira alkylation reaction of aryl halides with terminal alkynes. Initially, for finding optimized reaction conditions, the reaction of iodobenzene with phenylacetylene was selected as a model reaction and effect of different factors such as solvent, reaction temperature and catalyst loading were studied. Using water as

solvent and different bases such as DABCO, K₂CO₃, *t*-BuOK, Et₃N, and K₃PO₄ in the presence of 0.1 mol% Pd loading, gave very low yields for this reaction (Table 1, entries 1–5). By changing the solvent to DMF and using different bases (Table 1, entries 6–10), the yields were improved. The best results were obtained using DABCO as a base (Table 1, entry 6). Using DABCO in other solvents such as CH₃CN, EtOH, or toluene gave lower yields (Table 1, entries 11–13). By increasing the reaction temperature to 60 °C and using DABCO and DMF, yield of this reaction was increased to 98% (Table 1, entry 14). However, in order to insure about Pd loading, this model reaction was performed in the presence of 0.05 and 0.025 mol% of Pd and results indicate the formation of the desired products in 97% and 63% yield, respectively (Table 1, entries 15 and 16). Therefore, we selected 0.05 mol% of Pd, DABCO as a base and DMF as solvent at 60 °C to be most efficient and optimized reaction conditions (Table 1, entry 15). It is worth mentioning that for showing the important effects of the both Cu and Pd in the reaction efficiency, the model reaction in the presence of similar catalyst without Cu and also without Pd were studied. The corresponding results indicated that only 37 and 8% GC yield were obtained, respectively (Table 1, entries 17 and 18).

Using the optimized reaction conditions, the Sonogashira reaction of structurally different aryl halides with alkynes were studied. Under the optimized reaction conditions, alkynylations of aryl iodides containing electron-donating groups such as methyl,

isopropyl and methoxy and electron-withdrawing groups such as NO_2 , Cl, and F as well as the heteroaromatic 2-iodothiophene, proceed very efficiently and produced the desired products in excellent yields (Table 2, entries 1–9). Also, reactions of aryl iodides with other alkynes such as propargyl alcohol and 4-ethynyltoluene, and 1-octyne proceed efficiently affording the corresponding alkynes in high to excellent yields (Table 2, entries 10–14). Furthermore, reactions of different aryl bromides as well as heterocyclic 5-bromopyrimidine and 2-bromopyridine proceed efficiently at 60–80 °C by increasing the loading to 0.2 mol% Pd affording the desired products in high to excellent yields (Table 2, entries 15–23). It should be noted that reactions of 4-nitrobromobenzene and 4-bromobenzaldehyde in the absence

of Cu using Pd@MgO (Table 2, entries 24–25) and also in the absence of Pd using Cu@MgO (Table 2, entry 26) gave very low yields for desired products. Reactions of 4-chlorobenzaldehyde under the optimized reaction conditions was slow, therefore the reaction temperature was increased to 100 °C and TBAB (1 eq) was added to the reaction mixture. Under these reaction conditions, the desired product was obtained in 61% yield (Table 2, entry 27). However, by increasing the temperature to 120 °C, the yield was improved to 94% (Table 2, entry 28). Under this new reaction conditions, other aryl chlorides such as 4-chloronitrobenzene and 4-chlorobenzonitrile proceed well and gave 89–95% yield for the corresponding products, respectively (Table 2, entries 29–30).

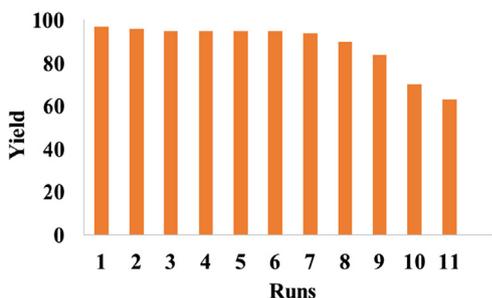


Fig. 7. Recovering and reusing of the catalyst for the reaction of iodobenzene with phenyl acetylene.

3.3. Recycling of the catalyst

Recovering and reusing of heterogeneous catalysts are very essential factors from economical and sustainable chemistry points of view. Along this line, we have studied recyclability of the catalyst for the reaction of iodobenzene and phenylacetylene under the optimized reaction conditions. For this purpose, after 24 h progress of the reaction, the catalyst was separated by centrifugation (6000 rpm), washed with ethyl acetate and after drying reused in another batch of reaction. By using this method, the catalyst was recovered and reused for 8 consecutive runs with very small decreasing in activity (97–90%). However, the yield of the reaction was decreased to 84% in run 9 and to 63% in run 11 (Fig. 7).

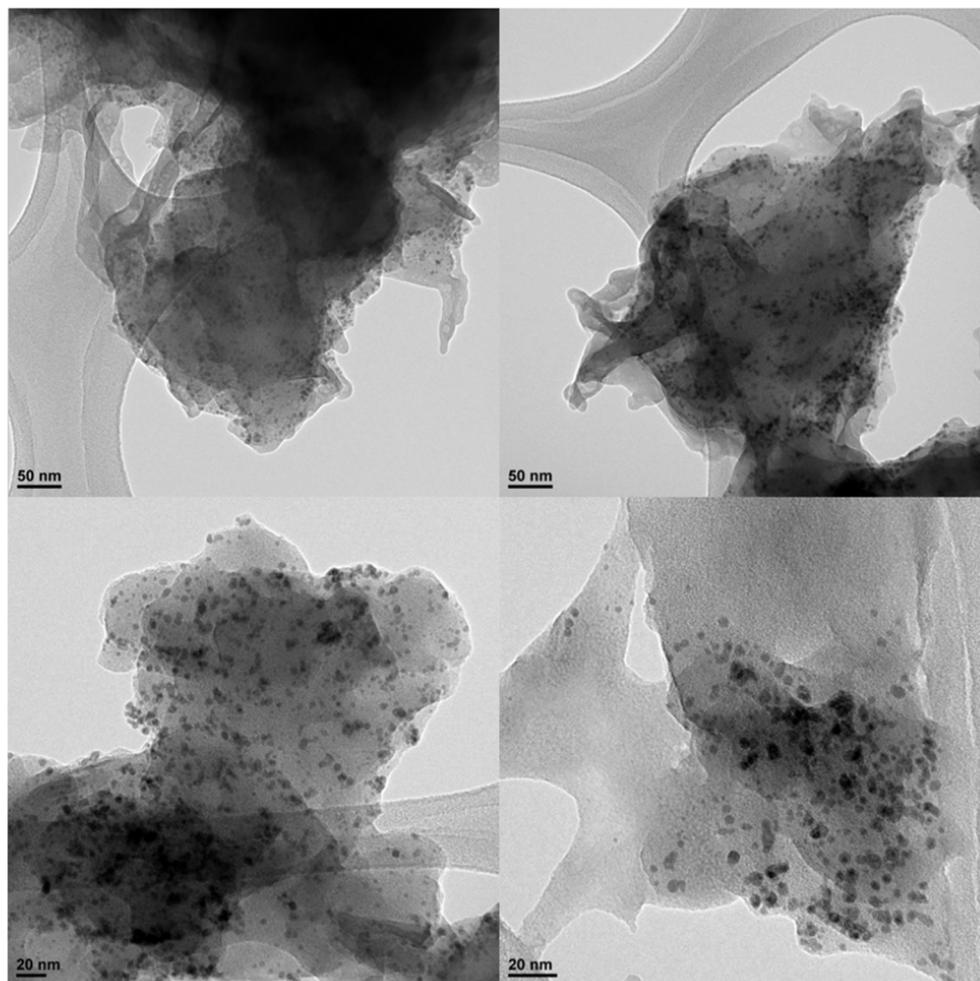


Fig. 8. TEM images of the reused catalyst after the 9 run.

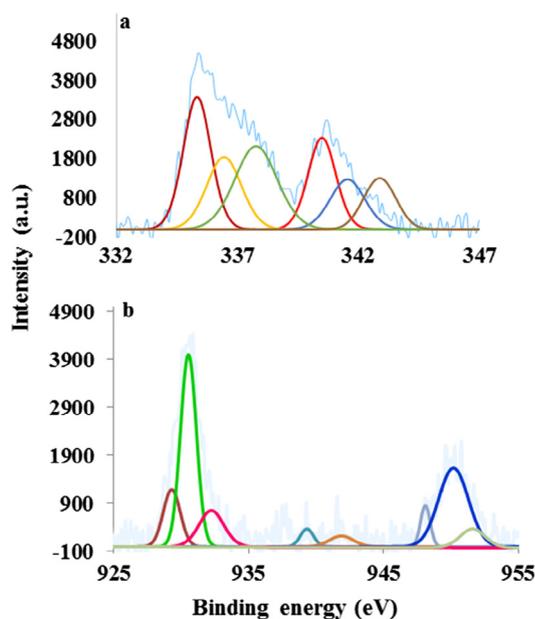


Fig. 9. XPS spectra of reused catalyst after 9 run: (a) Pd 3d and (b) Cu 2p regions.

TEM images of the reused catalyst after 9 runs showed preservation of the catalyst structure and also the presence of nanoparticles with slight aggregation (Fig. 8). Also, XPS analysis of reused catalyst after 9 runs showed in Pd 3d and Cu 2p region showed very similar pattern to fresh catalyst (Fig. 9). In the case of palladium, Pd(0), Pd(II) and Pd(IV) percentage determined to be 38, 26 and 36%, respectively. Furthermore, elemental EDS analyses showed the presence of Pd, Cu, Mg, and N in the structure of the reused catalyst (Fig. 4, ESI).

Finally, in order to find information about heterogeneous or homogeneous nature of the catalyst, two important tests were performed for the reaction of iodobenzene and phenylacetylene under the optimized reaction conditions. Initially, after 2 h stirring of the catalyst in DMF (2 mL) at 60 °C, the catalyst was removed under hot filtration condition and iodobenzene, phenylacetylene and base were added to the obtained solution. The resulting mixture was stirred at 60 °C and GC analysis of the reaction after 24 h showed only 31% conversion of iodobenzene to diphenylacetylene (Fig. 10). It should be noted that despite the fact that positive result of this hot filtration test is a strong proof for leaching or presence of homogeneous catalysis, a negative hot filtration test does not basically identify the presence of heterogeneous catalysis due to possibility of fast deactivation or redeposition of soluble active species. Thus further investigations are required for identifying the nature of true catalyst.

In another test we added polyvinylpyridine (PVP) (molar ratio to [Pd] ~400) as a strong poison for homogeneous Pd species under optimized reaction conditions [128,129]. GC analysis of reaction showed that reaction proceeded well with small interruption and gave 76% yield (Fig. 10).

From the above described experiments, we deduce that the supported material MgO@PdCu catalyzes the Sonogashira reaction mostly under heterogeneous conditions.

4. Conclusion

In conclusion, we prepared new bimetallic PdCu supported on modified MgO catalyst using simple method and characterized by different techniques. This catalyst exhibits good catalytic efficiency in the Sonogashira reaction of aryl halides at 60–120 °C.

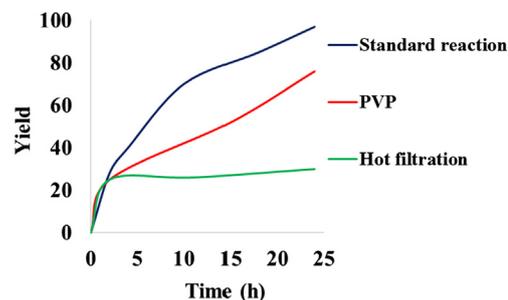


Fig. 10. MgO@PdCu catalyzed reaction of iodobenzene with phenylacetylene in the presence of PVP and hot filtration conditions.

The presence of Cu was demonstrated to be crucial to obtain good yields. The catalyst was recovered and recycled using simple centrifugation and reused for 8 consecutive runs with very small decrease in activity. Heterogeneous properties of the catalyst was confirmed using addition of PVP and hot filtration test.

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Appendix A. Supplementary material

Supplementary data associated with this article can be found, in the online version, at <https://doi.org/10.1016/j.jcat.2018.02.028>.

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