



Polymer supported triazine based palladium complex catalyzed double carbonylation reaction of halo aryl compounds for the synthesis of α -ketoamides

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ABSTRACT

Novel polystyrene incorporated Palladium (II) catalyst was developed and well characterized. The efficiency of the supported Pd(II) catalytic material was checked for double carbonylation reaction of 2° amines and aryl iodides to their corresponding α -ketoamides under high pressure reaction conditions. The reaction was carried out in 60 psi carbon monoxide pressure. An extensive variety of aryl iodides in combination with 2° amines in presence of carbon monoxide can produce the respective α -ketoamides with superb chemoselectivity. Effect of solvents, bases, time and amount of catalyst for the production of α -ketoamides were reported. This supported Pd(II) complex was highly catalytically active and recyclable. The developed catalytic material was regenerated by filtration. It could be recycled further six times with no such profound loss in its activity.

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1. Introduction

α -Ketoamides are essential building blocks in synthetic drugs, biologically active molecules, and pharmaceutical compounds [1–6]. In addition these compounds are used as important fragments for the conversion of vary functional group [7–14]. α -Ketoamides can also plays as an important role to formation of medicinally active molecules for example tetrasubstituted 2-oxazolidin-4-one and 2-oxindoles [15–19]. Hence, establishing a common, realistic, and efficient pathway to synthesis α -ketoamides having different functional groups is of meaningful.

For homogeneous catalytic reactions, there are various methodologies have been invented to overcome the problems like metal-contaminated crude products, recycling and catalyst recovery [20,21]. Metal supported heterogeneous catalysts have several advantages such as increasing the stability of the organic moieties, easy separation process; catalyst recovery as well as heterogeneous Pd catalysts improved the efficiency of carbonylation reactions [22].

Pd catalysts in different supported material are extensively used in double carbonylation reaction of various aromatic halides with CO (carbon monoxide) [23–29]. CO is used for synthesis of different carbonyl substances like amides, carboxylic acids, aldehydes and ketones since it is easily available and low-cost C₁ source [30–40]. Amidst diverse CO insertion processes, Pd catalyzed double carbonylation of aryl halides is a valuable strategy in producing vital carbonyl substances [41,42].

In the literature numerous techniques have been recorded to reach their synthesis [43–48] from which the catalysis of transition metal approaches have confirmed to the desired compounds in great selectivity and very well yields. Although, a few number of examples have been reported on the formation of α -ketoamides from aromatic halides and amines in presence of pressurized carbon monoxide gas [49–55].

For double carbonylation reaction there were numerous number of catalytic system was reported such as Pd/C/PPh₃ catalyst system [56], silica-incorporated polytriazane-palladium (Ti–N–Pd) compound [57] and mesoporous silica supported palladium complexes [58]. However, some of the strategies in our excellence of knowledge have been reported for the synthesis of α -ketoamides. Uozumi and co-workers [59] used Pd/PPh₃ catalyst in presence of a base,

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DABCO (1,4-diazabicyclo[2.2.2]octane) in preparing α -ketoamides under atmospheric CO pressure. However, the procedure is only valid to those aryl iodide compounds without electron-withdrawing (EW) groups. Recently, Kondo and co-workers developed an efficient Pd/PtBu₃ catalyst system using DBU as base, for the production of α -ketoamides with tremendous chemoselectivity [60]. However, the using basic ligand is frequently an issue when this ligand is used to a large scale development. In addition this, there has been numerous disadvantage for the use of ambient pressure of CO for the synthesis of α -ketoamides, likely due to poor reactivity of CO and less chemoselectivity [61]. Thus, the progress of a fresh process in preparing α -ketoamides would be highly desirable. To get rid from these serious issues heterogeneous palladium catalyst may be used. Heterogeneous catalysts are commonly used in industrial process as they, can be purified from the mixture simple technique, have a excellent thermal strength, and can be often reused and regenerated.

Herein we report a new methodologies for the synthesis of a polymer supported Pd(II) catalyst that exhibits excellent activity for the synthesis of α -Ketoamide type compounds with superb yields and high selectivities via twice carbonylation reaction of aryl iodides and amines with carbon monoxide.

2. Experimental

2.1. Preparation of catalyst

The preparation technique followed to get the Pd(II) complex is shown in Scheme 1. The polymer complex was synthesised in three step process. At first in 5 ml toluene imidazole (6.8 gm) and potassium iodide (0.1 gm) were dissolved in N₂ atmosphere after that the reaction mixture was heated to 40 °C. Then CH₃ONa (5.4 gm) in methanol (10 ml) was added drop by drop with continuous stirring for about 30 min to form imidazole salt. The chloromethylated polystyrene (1.8 gm) in 15 ml acetonitrile was mixed to sodium imidazole solution. Then the solution was continuously stirred at 65 °C for a time period of 48 h. The imidazole functionalised polystyrene beads was washed by ethanol and dried at 40 °C.

In CH₃CN (ACN) solvent, the imidazole salt of chloromethylated

polystyrene (0.5 gm) and cyanuric chloride (0.184 gm, 1 mmol) were heated for 2.5 h at 110 °C. The solid product was obtained, washed by ACN and methanol respectively. Then the solid dried at 40 °C under vacuum.

This Polymer supported PlmdCC-ligand (0.5 gm) and ^tBuONa (2.2 mmol) in THF (15 mL) was treated with 9 wt % palladium acetate for 40 min under continuous stirring. After that solution was heated to reflux at 80 °C for 1 day. Thus, the palladium (II) catalyst (PlmdCC@Pd) was formed, filtered followed by washed with CH₃OH and dried at a temperature of 40 °C under vacuum.

2.2. General procedure for double carbonylation of aryl iodides with amine

In a high-pressure reactor, aryl iodides (0.5 mmol), morpholine (0.5 mmol), K₂CO₃ (1 mmol), PlmdCC@Pd catalyst (50 mg) were mixed in 10 ml of toluene and then mixture was purged with CO (60 Psi) before heating at 55 °C for 5 h. After that the reactor was cool to RT, the excess carbon monoxide was release from the high pressure chamber. Then the reaction mixture was extracted with aqueous sodium chloride (15 mL) and ethyl acetate (45 mL). The organic compounds were mixed with EtOAc, and the solvent was removed by a rotary evaporator. The desired compound was isolated. By column chromatography the crude product was purified and yield was identified by ¹H and ¹³C NMR.

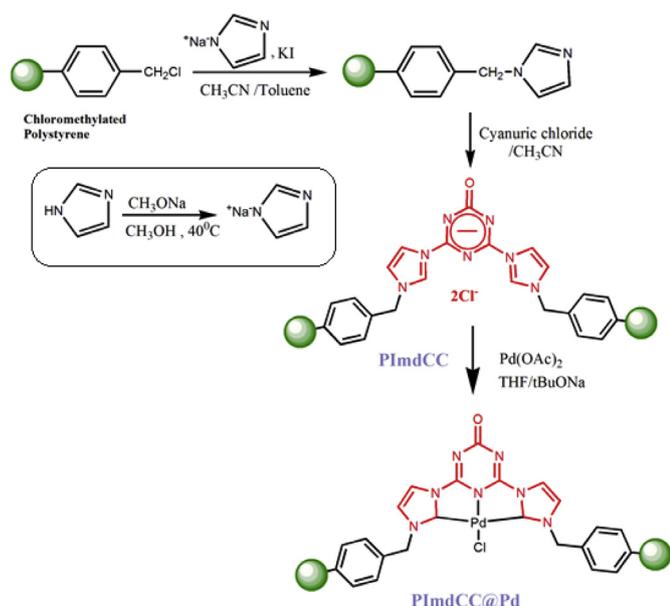
3. Results and discussion

3.1. Characterization of the PlmdCC@Pd catalyst

Because of insoluble nature of supported palladium catalyst in all the commercially available organic solvents, its study of structural examination was limited to its chemical analysis, SEM-EDX, TGA, physicochemical properties, IR and UV–vis spectroscopic data. The elemental data analysis of polymer support and the Pd bind catalyst was shown in Table 1. By AAS, Pd content in the polymeric catalyst was estimated which suggests that 4.56 wt% of Pd present in the catalyst.

The attachment modes of palladium metal onto the supported complex were established by assessment of the Fourier-transform infrared spectroscopic data (Fig. 1) of the palladium incorporated catalyst on the polymer complex in several steps of its preparation method. For PlmdCC@Pd catalyst, the characteristic peaks of the C–H stretching vibration of aromatic ring, symmetric and asymmetric of methylene at 3023 cm⁻¹ and 2852 cm⁻¹ and 2922 cm⁻¹ [62], respectively. In polymeric complex, the bands at ~1094 and ~3415 cm⁻¹ have been shown to the frequency of C–N and N–H stretching respectively which is slightly differ from ligand. The spectra of the PlmdCC@Pd shows one average to intense band around at ~1658 cm⁻¹, that may be assigned to the vibration of stretching of C=O attached with the polymer. The distinct bands observed at 1560 cm⁻¹ and 1447 cm⁻¹ due to presence of triazine ring in the PlmdCC complex. Therefore, it is rather difficult to making accurate assignments to stretching frequency N–Pd in far IR region.

In the diffuse reflectance method, the electronic spectrum of the polymer supported PlmdCC ligand and the immobilized



Scheme 1. Preparation of polymer incorporated palladium (II) catalyst.

Table 1
Chemical composition of polymeric ligand and polymer incorporated catalyst.

Compound	colour	C%	H%	N%	metal%
PlmdCC	Off white	72.75	5.16	9.44	–
PlmdCC@Pd	Light yellow	69.47	4.67	8.55	4.56

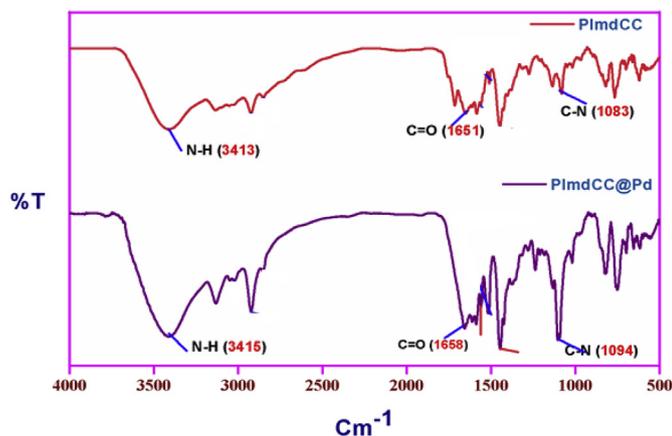


Fig. 1. FT-IR Spectral data of polymer anchored ligand (a) PlmdCC, (b) PlmdCC@Pd complex.

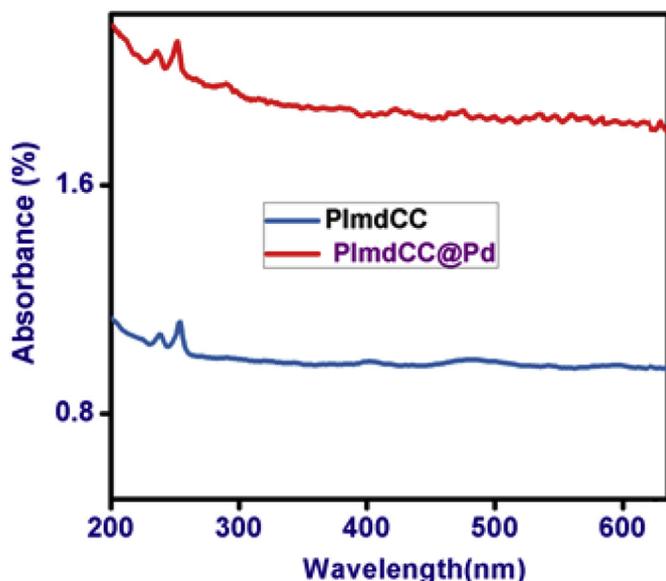


Fig. 2. DRS-UV-visible spectral data of the PlmdCC and PlmdCC@Pd catalyst.

PlmdCC@Pd catalyst has been shown in Fig. 2. Diffuse reflectance ultraviolet–visible spectral data of the PlmdCC and PlmdCC@Pd catalyst was taken from 200 to 800 nm range. The Pd(II) metal complex showed the two absorption due to the transition of $n-\pi^*$ and $\pi-\pi^*$ at 235 nm and 252 nm respectively [63]. The d-d transitions were seen due to the absorption bands around 510 nm is

assigned respectively [64].

The SEM image of PlmdCC (Fig. 3A) and supported PlmdCC@Pd catalyst (Fig. 3B) definitely show changes in morphology which happened on the polymer surface after complexation on it. The EDX analysis of X-rays spectral data for PlmdCC and PlmdCC @Pd catalyst are shown in Fig. 4A and B. The Energy dispersive spectroscopy analysis confirmed that the palladium metal is attached over the polymeric surface.

Thermal strength of the supported complex was examined using TGA over a temperature between 30 and 600 °C at a rate of heating 10 °C/min in N₂ atmosphere. A TGA- plot of the polymer incorporated PlmdCC and PlmdCC @Pd catalyst is shown in Fig. 5. The thermal stability of the PlmdCC@Pd catalyst is higher as compares to PlmdCC ligand obviously shown that the palladium metal loading to the surface of the polymeric complex. The catalyst is stable upto 350 °C temperature. Thermogravimetric analysis proves that the polymer supported PlmdC@Pd catalyst decomposes at slightly higher temperature than the polymeric ligand (PlmdCC). This catalyst and its ligand are rapidly decomposed after 450 °C temperature.

3.2. Catalytic activity of the PlmdCC @Pd catalyst

Since palladium supported catalysts show superb catalytic reactivity in a variety of the important industrial processes and have been widely considered for C-C coupling [65], therefore we determined to examine the reactivity of the PlmdCC @Pd in the field of double carbonylation of aryl iodides to α -Ketoamides. Preliminary studies paying attention on probing the practicability of the catalytic reactions and to optimize the reaction conditions, it could be applicable to a various aryl halides.

In order to verify the action of the PlmdCC @Pd, the double carbonylation of aromatic iodides and morpholine in carbon monoxide atmosphere described in Scheme 2 was performed. In this conversion aryl iodides were changes to α -Ketoamides under the reaction conditions. Quantitative transformation of aryl iodide to α -Ketoamides was performed by utilizing Pd supported polymeric catalyst (PlmdCC @Pd). The double carbonylation reaction of aryl iodide and morpholine was done in the toluene solvent medium using K₂CO₃ as the base. The reaction was done in a 50-ml high pressure autoclave at 55 °C under 60 psi of carbon monoxide pressure for 5 h reaction time.

Preliminary analysis was carried out with iodobenzene as model substrate (Scheme 3) for the identification of the optimization conditions. The activity of palladium-catalyst towards carbonylation reaction is monitored by a number of reaction parameters. Various bases and solvents were checked to discover the suitable conditions of reaction (Table 2). So as to recognize valuable reaction conditions for the promotion of Pd catalyzed carbonylation, the

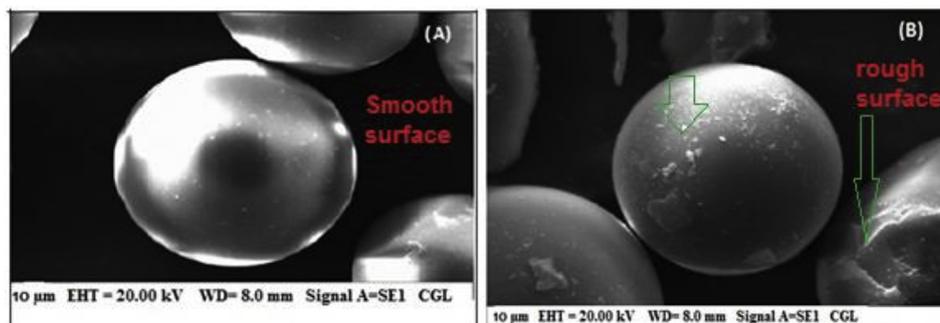


Fig. 3. SEM images of polymer supported ligand (A) PlmdCC, (B) PlmdCC @Pd complex.

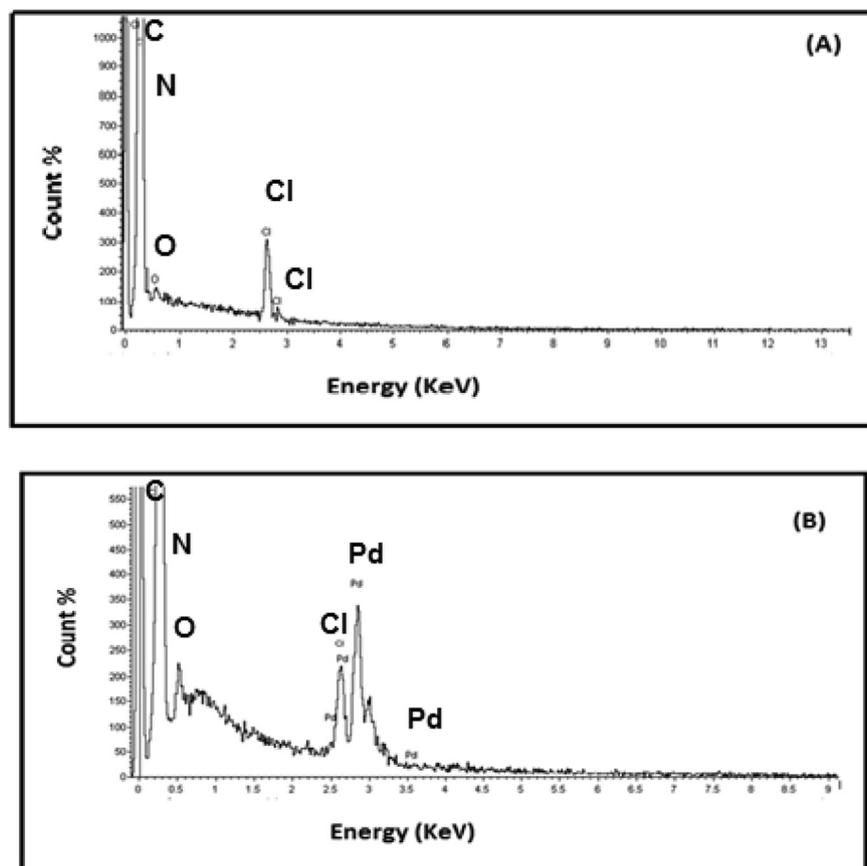


Fig. 4. Energy Dispersive Spectroscopy data of polymeric ligand (PlmdCC) (A) and PlmdCC @Pd complex (B).

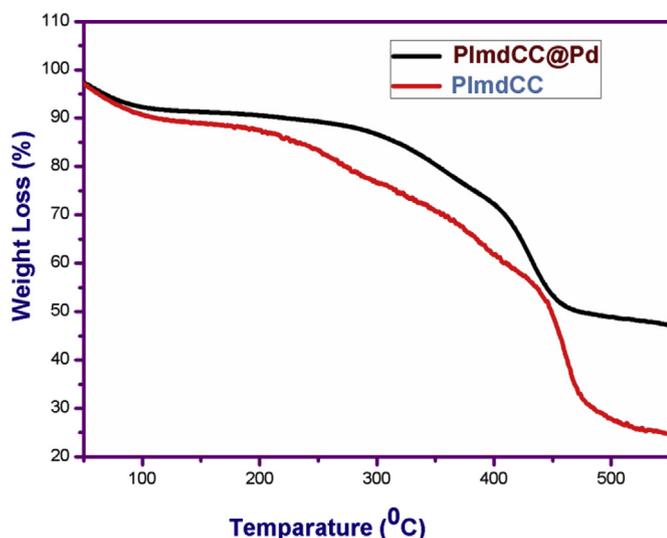


Fig. 5. TGA plots of the PlmdCC and PlmdCC @Pd complex.

transformation was checked under different time interval and temperatures (Table 3).

To examine the importance of base for this catalytic transformation, a variety of bases were screened (Table 2). Experimental results exhibit that inorganic bases are highly active for the reaction. In a short time period, in presence of K_2CO_3 the reaction gives high yield. We established that utilizing K_2CO_3 as base in toluene medium at $55^\circ C$ gave 94% conversion. The other bases like, Na_2CO_3

and EtONa were less effective compared to K_2CO_3 , and only afforded medium to moderate yield. To examine the effect of solvent and different organic solvents were also checked for the carbonylation reaction of iodobenzene. The reaction carried out in less polar aprotic solvent, toluene gives a maximum yield and shows the most efficient solvent. With the utilization of other polar solvents like, dioxane and DMF gave lesser yield. Therefore, toluene was taken as the solvent medium for this carbonylation reaction.

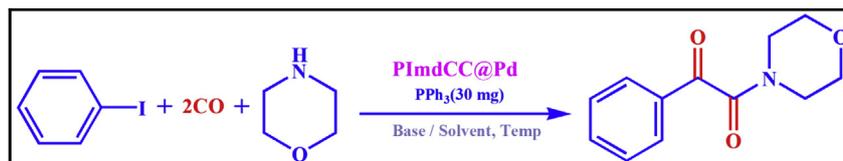
It has been found that this carbonylation reaction was very sensitive to temperature of the reaction medium. At temperature range $45^\circ C$ to $85^\circ C$ was applied for this reaction but it has also been found that the temperature of $55^\circ C$ was the ideal temperature for the novel reaction (Table 3). The catalytic transformation was also done for various time interval, ranging from 2 h to 7 h and it showed that at 5 h the conversion was 94% under the given reaction condition (Table 3).

The effect of quantity of the PlmdCC@Pd catalyst on the production of yield for this reaction was also examined (Fig. 6). The catalyst amount was increased from 10 mg to 60 mg in the reaction settled under optimization. The yield of the reaction increases as the amount of active sites increases and maximum yield of 94% was obtained for 50 mg palladium catalyst. Beyond 50 mg of catalyst loading to the reaction no such further conversion was observed. Therefore, 50 mg of catalyst loading is the optimum amount of catalyst for the conversion of the desired product.

With help of this optimization, different derivatives of aryl iodide were transformed to their corresponding α -ketoamides. In Table 4 the various substrate were tested and results are summarized. To explore the substrate scope with different aryl iodides and amines these protocol is very much important. As shown in Scheme



Scheme 2. Pd(II) catalyzed carbonylation reaction of aryl iodides.



Scheme 3. Pd(II) supported polymer catalyzed carbonylation of iodobenzene.

Table 2
Effect of solvent and base on carbonylation of iodobenzene.

Entry	Base	Solvent	GC Yield (%)
1	EtONa	Dimethylformamide	72
2	Na ₂ CO ₃	Dimethylformamide	52
3	K ₂ CO ₃	Dimethylformamide	59
4	EtONa	dioxane	62
5	Na ₂ CO ₃	dioxane	73
6	K ₂ CO ₃	Toluene	94
7	EtONa	Toluene	44
8	Na ₂ CO ₃	PEG-600	57
9	K ₂ CO ₃	PEG-600	78
10 ^a	K ₂ CO ₃	Toluene	trace

Reaction conditions: PhI (0.5 mmol), morpholine(0.5 mmol), Base (1.0 mmol), CO (60 psi), PImdCC @Pd (50 mg), PPh₃(30 mg), solvent (3.0 mL), 55 °C, 5 h.

^a Absence of PPh₃.

Table 3
Effect of time and reaction temperature on double carbonylation.

Entry	Temperature (°C)	Time(h)	Yield (%)
1	45	5	84
2	55	5	94
3	65	5	94
4	85	2	65
5	85	7	90

Reaction conditions: PhI (0.5 mmol), morpholine (0.5 mmol), K₂CO₃ (1.0 mmol), CO (60 psi), PImdCC @Pd (50 mg), PPh₃(30 mg), Toluene (3.0 mL).

2, double carbonylation of various substituents aryl iodides and amines were carried out in the optimized condition and all the reactant delivers well to excellent yields. The different position of reactants slightly influences the double carbonylation reaction: *p*-iodotoluene (Table 4, entries 2-3, 7-8). Comparatively lower yields for 1-bromo-4-iodobenzene were found due to mixture of products due to formation small amount amide side product (Table 4, entry 6, 10). The substitutions on the aromatic ring of aryl iodides, which may either electron rich or electron deficient moiety shows significant effect on the result of the catalytic reaction. Aryl halides contain electron-withdrawing and electron-donating substituents, transformed to the respective α -ketoamides with superb yields. Aryl iodides containing strong electron-releasing moiety such as methyl and methoxy, produced in higher yields than 1-bromo-4-iodobenzene due to presence of reactive bromide attached para to the iodide of the phenyl ring (Table 4, entries 2-5 and 7-9). Reaction pathway may be similar to previous literature report (55, 66-67). Palladium metal is very stabilized by nitrogen enrich PImdCC

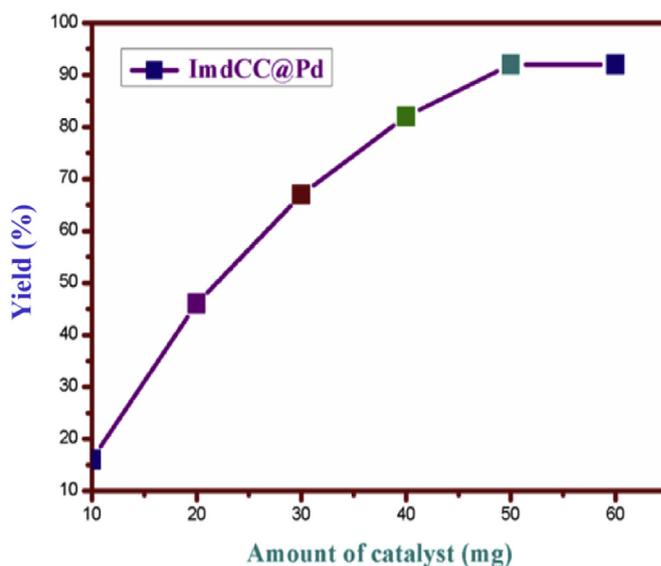


Fig. 6. Effect of catalyst loading on carbonylation of iodobenzene.

support. These supported Pd material is contain of active sites which are responsible for the double carbonylation reactions. It is usually found that by oxidative addition of an aryl halide to the Pd(0) complex gives an organopalladium halide species. After that the process will give an acylpalladium halide, involves migratory insertion of a coordinated CO. It is observed that in presence of CO (60 Psi) pressure the acylpalladium halide complex reacts with an amine (nucleophile) and a base to give α -ketoamides.

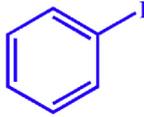
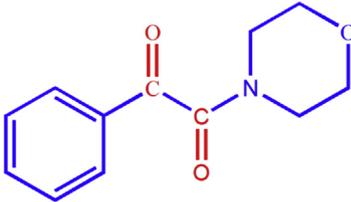
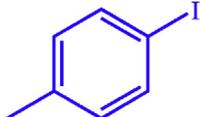
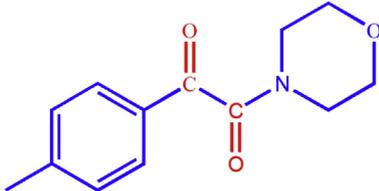
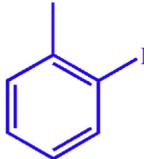
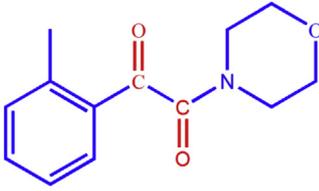
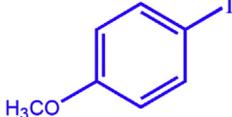
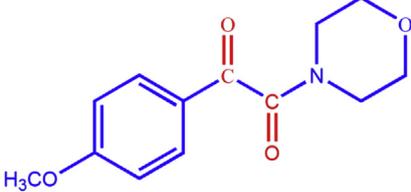
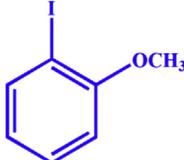
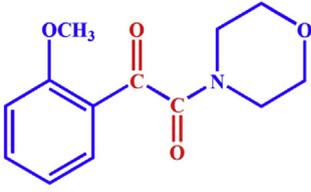
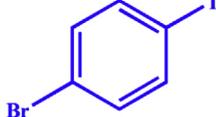
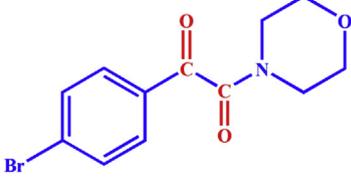
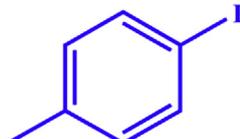
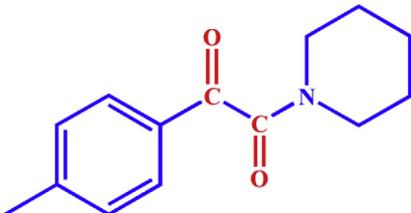
3.2.1. Comparison with other reported catalytic system

The activity of the PImdCC@Pd(II) catalyst was shown outstanding performance in case of carbonylation of iodobenzene and its derivatives. A relative study is shown in Table 5. This polymer-anchored complex plays a significant role in this superb activity.

3.2.1.1. Heterogeneity test

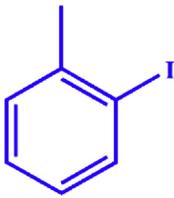
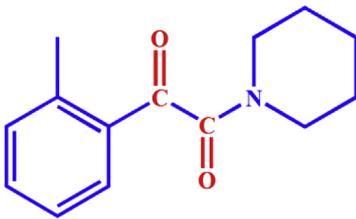
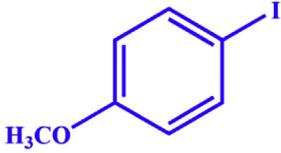
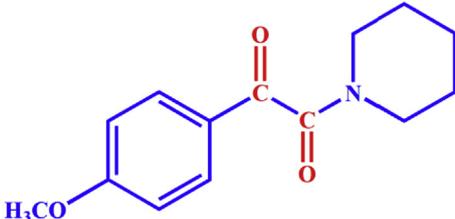
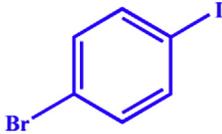
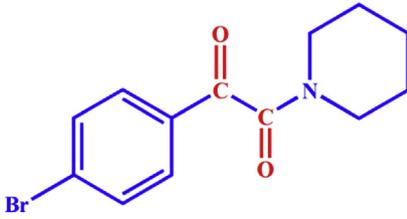
3.2.1.1.1. Hot-filtration test. To examine whether the catalytic reaction go through in a homogeneous or a heterogeneous mode, hot-filtration method was applied in the double carbonylation of aryl iodide. By simple filtration, the solid catalyst was separated after proceed the reaction mixture (Scheme 3) for 2 h, and the

Table 4
Polymer supported palladium (II) catalyzed carbonylation of aryl iodides.

Entry	Aryl halides	Product	GC Yield (%)
1.			94/92 ^a
2.			90/88 ^a
3.			85/84 ^a
4.			84/82 ^a
5.			80/77 ^a
6.			64/62 ^a
7.			92/90 ^a

(continued on next page)

Table 4 (continued)

Entry	Aryl halides	Product	GC Yield (%)
8.			86/84 ^a
9.			88/85 ^a
10.			62/60 ^a

Reaction conditions: PhI (0.5 mmol), morpholine (0.5 mmol), base (1.0 mmol), CO (60 psi), PlmdCC @Pd (50 mg), PPh₃(30 mg), Toluene (3.0 mL), 55 °C, 5 h

^a Isolated Yield (%).

Table 5

Comparison of catalyst activity of the PlmdCC@Pd catalyst in the formation of α -ketoamides with various reported systems.

Entry	Catalyst	Reaction Conditions	Yield (%)	Ref.
1.	Pd(OAc) ₂	Na ₂ CO ₃ , PEG-400, CO (ballon), RT	94	[61]
2.	Pd-NHC complex II	K ₂ CO ₃ , Dioxane, P(CO 2.0 MPa); 90 °C; 5 h.	99	[66]
3.	PlmdCC@Pd	K ₂ CO ₃ , Toluene, CO (60 psi), PPh ₃ , 55 °C, 5 h.	94	This Study
4.	mPMF-Pd ⁰ Catalyst	K ₃ PO ₄ , CO (20 atm), DMF (5.0 mL) at 90 °C, 12 h.	98	[67]

observed yield was 65%. The liquid reaction mixture part was heating for another 3 h it has been found that no transformation occurs. This ensures that the reaction was not proceeding without the solid catalyst. Moreover, no proof for significant leaching of Pd metal or decomposition of the supported catalyst was shown during the phase of the reaction and no Pd was found by AAS data of the liquid phase of the reaction mixture after elimination of the catalyst. Through the phase of carbonylation, the above study clearly suggests that the Pd was not being leached out from the heterogeneous catalyst.

3.2.1.1.2. Catalyst reusability. Separation process and reusability of the heterogeneous catalyst are very much important in the carbonylation reactions. We checked the recyclability of the palladium supported heterogeneous complex in the carbon monoxide insertion reaction of iodobenzene (Fig. 7). Herein, aryl iodides (0.5 mmol), morpholine (0.5 mmol), K₂CO₃ (1 mmol), PlmdCC@Pd catalyst (50 mg) were mixed in 10 ml of toluene and then mixture was purged with CO (60 Psi). The PlmdCC@Pd catalyst was separated from reaction mixture by centrifuged method after the reaction was completed. Then the catalyst was thoroughly washed with distilled water and subsequently with other solvent like, acetone. The catalyst dried in air at 40 °C. After that, the recovered

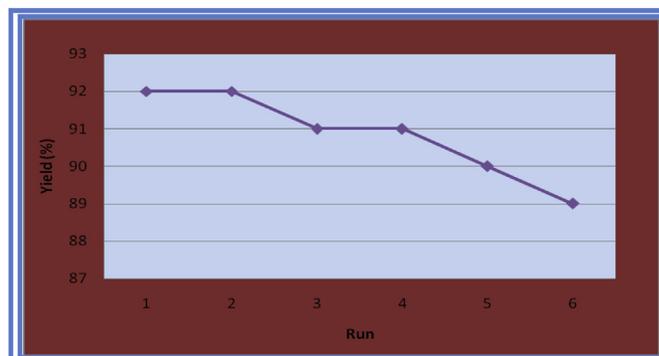


Fig. 7. Reusability test of PlmdCC@Pd catalyst.

catalyst was used in carbonylation reaction under optimal conditions for the next run. The heterogeneous PlmdCC@Pd catalyst was efficiently recycled up to six times with no loss in desired product yield under the same reaction conditions.

4. Conclusions

In conclusion, this work demonstrated that synthesis and characterization of polymer incorporated Pd(II) complex and its successful application towards the synthesis of α - ketoamide. Electron-donating and electron withdrawing containing aryl iodide derivatives can check and also various crucial factors such as temperature, bases and the nature of the solvents are responsible for the transformation. The reaction system is extremely moisture and air stable and the supported Pd₂(dppf)Cl₂ complex was prepared easily from commercially obtainable and low-priced materials as starting. However, with no efficient loss in its catalytic activity the catalyst was reused for six more times. Moreover, this work is used as a strategy to expand the possibility of other various organic conversions.

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Appendix A. Supplementary data

Supplementary data to this article can be found online at <https://doi.org/10.1016/j.jorganchem.2018.12.008>.

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