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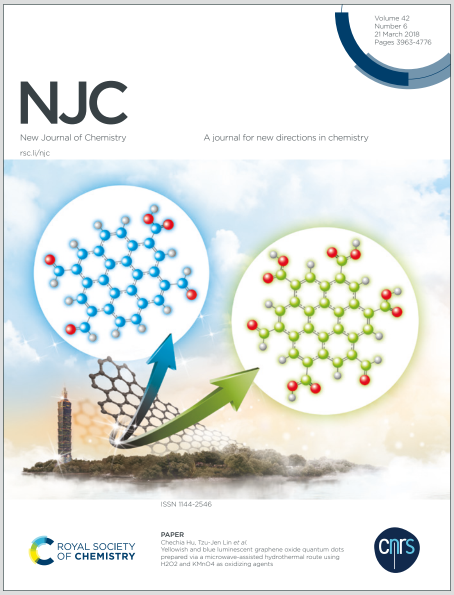

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Journal Name

ARTICLE

POP-Pd(II) catalyzed easy and safe *in-situ* carbonylation towards the synthesis of α-ketoamides from secondary cyclic amines utilizing $CHCl_3$ as the carbon monoxide surrogate

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A novel complex catalyst, POP-Palladium(II)has been synthesized. The developed catalyst has been characterized by XRD, EDX, Scanning electron micrographs (FE-SEM), HR-TEM, FTIR spectra, UV-Vis spectra, TGA and BET isotherm. The reactivity of the incorporated Palladium(II) catalyst was tested for the *in situ* carbonylation of aryl iodides and secondary cyclic amine to the respective α-ketoamides at 80 ˚C. A large number of aryl iodides combined with CO followed by 2˚ amines can generate the corresponding α-ketoamides with high selectivity. This Pd(II)complex catalyst exhibits superb catalytic activities and can also be easily recovered after the reaction by easy filtration method. The catalyst could be reused up to six consecutive cycles without much loss in its activity.

Introduction

α-Ketoamides plays an important role in the preparation of natural products.[1,2] Several biologically active molecules, synthetic drugs and pharmaceutical compounds were synthesized from α-Ketoamides and their derivatives[2-9](Figure 1). Further these molecules are utilized as valuable intermediates for the transformation of different functional group.[10-17]α-ketoamides have also been explored for the production of heterocyclic skeleton such as oxindoles, indoles, quinolines and β-lactams etc.[18-21]Hence, developing an efficient and realistic approach towards the generation of α-ketoamides having versatile functional groups is of immense significance.

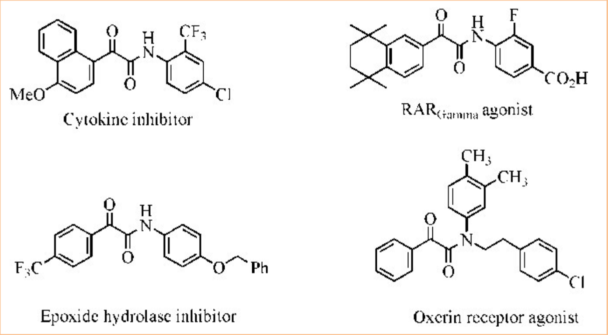

Figure 1: α-Ketoamide containing biologically active compounds

One strategy for synthesizing carbonyl compounds is the transition-metal catalyzed C=O group insertion directly into an organic compound.[22]In many cases, carbon monoxide is used as a source of carbonyl installation. Because of the very toxic nature of CO and its commercial availability in highly pressurized cylinders, safe handling of carbon monoxide is quite the challenge. Thus, alternative CO surrogates such as transition metal carbonyl complexes,[23]formic acid,[24] acid chlorides,[25]silacarboxylic acids,[26] and others have been developed to avoid its direct use. Although, every source of carbon monoxide surrogates has its own competence but still it is important to find out other inexpensive CO sources which are easily available, less toxic, and involve simple reaction set up. Recently, $CHCl_3$ based carbonylation has shown great potential due to its cost effectiveness, ready availability, and easy handling process. A well-known synthetic approach for the generation of CO gas is hydrolysis of chloroform under strongly basic aqueous hydroxide solution.[27] There are some reported works in which CO generated from chloroform has been used for aminocarbonylations,[28] Pd-catalyzed carboxylation,[29] carbonylative Sonogashira coupling[30] and Heck-type domino cyclization.[31]

Various supported Palladium catalyzed carbonylation reaction of aromatic halides is an important and effective method to synthesize ketoamide in presence of CO.[32,33] Several examples of α-ketoamides formation under pressurized CO gas have been reported.[34-40] But, now a day, numerous examples of double carbonylation has been recorded under an atmospheric CO pressure.[41-45]

Only a few techniques were developed where CO generated from $CHCl_3$ precursor, was used in carbonylation reaction.[46,47]In a current publication by Jain et al., a palladium catalyzedcarbonylation reaction was reported for the synthesis of arylestersand arylketones

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involving $CHCl_3$ as source of CO.[48] In a previous communication from our group, synthesis of aryl aldehydes and diaryl ketones was described using $CHCl_3$ as CO surrogates under palladium-catalyzed carbonylation reaction.[49] Among various CO insertion techniques for the synthesis of carbonyl substances from aryl halides, phosphine free palladium catalyzed double carbonylation is a significant approach.[50] A report by Han et al. highlighted Pd-catalyzed double carbonylation for α-ketoamides synthesis under atmospheric CO at room temperature fromaryl iodides and amines with PEG-400 solvent.[51] This homogeneous methodology motivated us to develop a novel heterogeneous Pd catalyst and explore its application towards the synthesis of α-ketoamides using $CHCl_3$ as carbon monoxide precursor. The developed protocol displayed excellent activity with splendid yields without the use of any external additive.

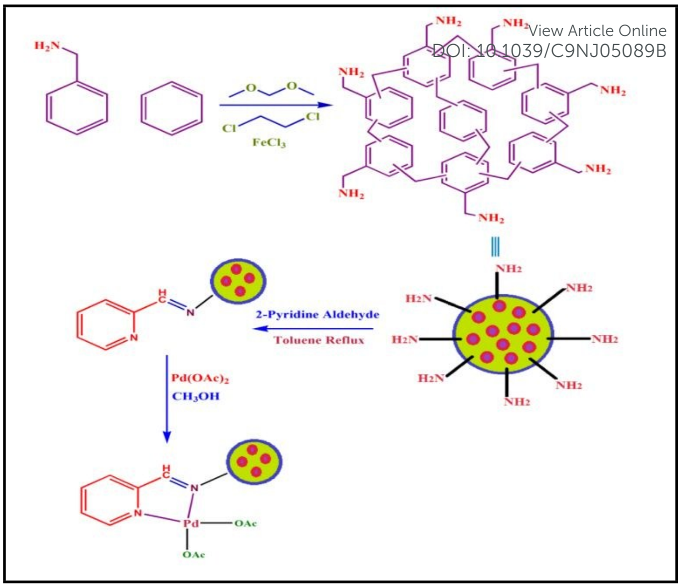
Experimental

Preparation of catalyst

In a 250 ml RB, 15 ml dry DCE was taken followed by addition of benzyl amine (0.321 g, 3 mmol) and benzene (0.234 g, 3 mmol). Then formaldehyde dimethyl acetal (0.912 g, 12 mmol) and anhydrous iron(III) chloride (1.947 g, 12 mmol) was added respectively to the solution. Under a N_2 atmosphere the reaction mixture was heated to 80 ˚C for 18 h. Then the RB containing reaction mixture was allowed to cool to RT. Next reaction mixture was filtered and washed thoroughly with CH_3OH until the filtrate part became colourless. The residue was dried at 80 ˚C for another 20 h. Then, by Soxhlet apparatus, the solid part was washed with methanol for 48 h to deliver a chocolate brown material. This chocolate brown porous organic polymer material was named as POP-1.

In a 100 ml RB, the chocolate brown material (POP-1, 1.5 gm) was taken in 20 ml of toluene and then 2-Formylpyridine (0.8 ml) was added drop by drop wise into the stirring solution. Next the resulting mixture was refluxed for 20 hours. Then, the reaction mixture was allowed to settle to achieve RT; the porous polymeric ligand was filtered, thoroughly washed with toluene followed by CH_3OH. Ultimately, the polymer ligand was dehydrated under vacuum for 24 hours. The porous ligand as well as the final Schiff base was designated as POP-2.

This POP-2 ligand (0.5 gm) and ^tBuONa (2.2 mmol) dissolved in methanol (15 mL) was treated with 0.05 gm of $Pd(OAc)_2$ and the resulting mixture was stirred for 40 min. Then the reaction mixture was refluxed at 80 ˚C for 24 hours. Finally, the Pd(II) catalyst (Pd@POP-2) was filtered, washed carefully with methanol, and dried at 40°-50°C under vacuum. The chocolate brown catalyst was named as Pd@POP-2 (Scheme 1).



Scheme 1. Synthesis of POP supported Pd(II) catalyst

Typical procedure for the synthesis of α-ketoamides

In a 25 ml sealed tube, aryl iodides (1 mmol), morpholine (1.2 mmol), $CHCl_3$ (6 mmol) and KOH (12 mmol) were taken. Then Pd@POP-2 catalyst (50 mg/2.3 mol %) was mixed in 4 ml of polyethylene glycol and resulting solution was heated at 80 °C for a time period of 16 h. After the reaction was complete, the reaction mixture was settled down to RT and opened up the sealed tube. Then the mixture was extracted with ethyl acetate and washed with H_2O as well as brine solution. The organic part was dried over Na_2SO_4 and concentrated with rotary vapour under pressure. Finally the product was purified by column chromatography (using ethyl acetate and petroleum ether solvent).

Results and discussion

Characterization of the Pd@POP-2 Catalyst

The evaluation of Pd loading in Pd@POP-2has been conducted by AAS and the loading of palladium in Pd@POP-2 was 4.86 %. Also performed CHN analysis,the data of the analysis shown C= 73.56, H= 6.24 and N= 4.12 % in the catalystPd@POP-2.

In Figure 2, the X-ray diffraction pattern of the Pd@POP-2 catalyst is shown. The XRD pattern of Pd@POP-2 exhibits a broad intense diffraction peak at 2θ value (~17°) indicating porous nature of the material.[52] In the X-ray diffraction pattern of the Pd@POP-2, no intense diffraction peaks was observed except a hump around 41^0.TheXRD analysis indicating the Pd(II) species present in catalyst.These data iscomparable with previous reported works to confirm the of Pd(II).[53]

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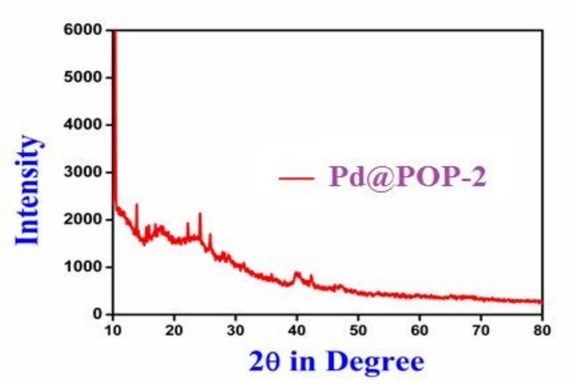

Figure 2:XRD pattern of Pd@POP-2 material

Fourier-transform infrared spectra of POP-2 and Pd@POP-2 materials are depicted in the Figure 3. The absorption peak was observed at 3370 and 3420 cm^{-1} due to the -NH groups present in the porous polymer POP-2 and the Pd@POP-2 materials. The absorption bands near 1603 cm^{-1} and 1430 cm^{-1} corresponds to the stretching vibrations of the C=C bonds in the benzene rings . The peaks of sp^3 C-H bonds in Pd@POP-2 and POP-2 materials was found at 2910 cm^{-1} and 2909 cm^{-1}.The absorption band near ~1070-1075 cm^{-1} indicates that the C-N bond present in the materials.

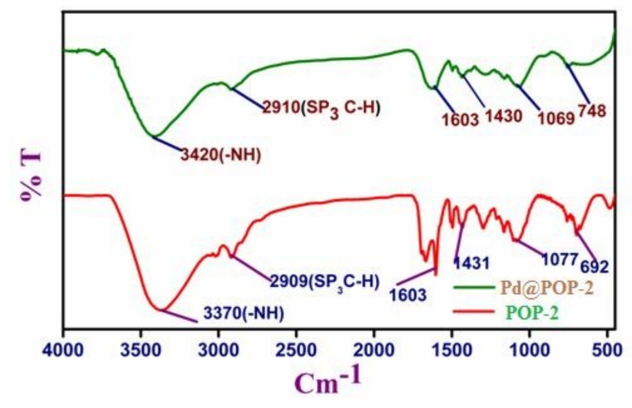

Figure 3:FT-IR spectra of POP-2 and Pd@POP-2

UV-Vis absorbance spectra of POP-2 and Pd@POP-2 were investigated in Figure 4.In case of POP-2, the electronic absorption spectrum exhibits two peak near 218 nm and 272 nm due to n→π* and π→π* transitions, respectively. A visible change was found in absorption spectrum of Pd@POP-2 material. This synthesized complex shows fresh absorption peaks at 295 nm and 350 nm. It can be ascribed to the CT between the central palladium atom and coordinated atoms.[54]

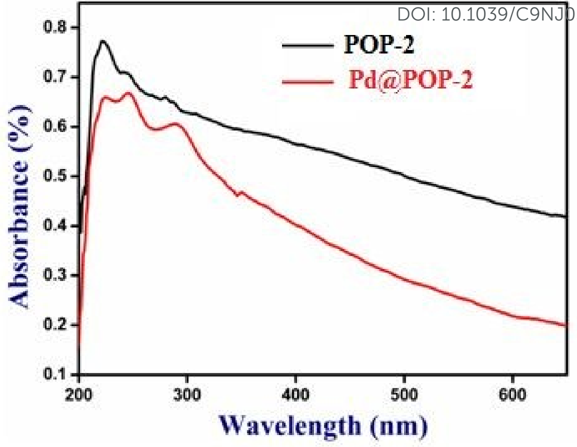

Figure 4:UV-Vis spectra of mesoporous POP-2 and Pd@POP-2

Figure 5 demonstrates N_2 adsorption/desorption isotherm of the complexes Pd@POP-2. According to IUPAC, the adsorption isotherm showed the type IV isotherms for Pd@POP-2 catalyst with a H_2 hysteresis loop in the high pressure region[55] of 0.4-0.8 relative pressure (P/P_0) of N_2. The catalyst Pd@POP-2 showed steady increase in N_2 adsorption with a hysteresis and next rise in the high relative pressure region indicating that the complex consists of mesopores.[56]The Brunauer-Emmett-Teller (BET) surface area of the new Pd@POP-2 material is 652.558 m^2/g.By employing the non-local density functional theory (NLDFT) the pore size distributions of the sample have been drawn from the adsorption isotherm. Peak pore of dimensions ca. 2.0 nm indicates that the sample is mesoporous in nature.

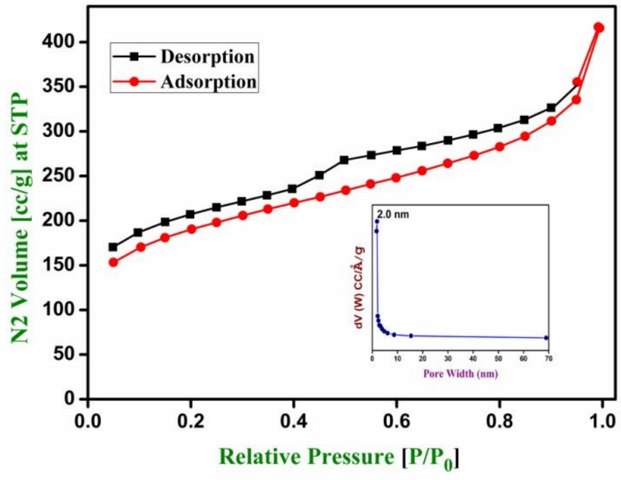

Figure 5: The N_2 adsorption/desorption isotherm of Pd@POP-2.The plot of pore size distributions employing NLDFT method is shown in the inset.

To examine the structural morphology of Pd@POP-2 complex field emission scanning electron microscopy (FE-SEM) has been performed (Figure 6). Different images demonstrate different magnifications. Pd@POP-2 displayed stone like particle morphology with some mesopores present in this complex which could be responsible for inter-particle porosity as seen from the BET adsorption analysis. Energy dispersive spectroscopy analysis of X-rays (EDAX) data of the Pd@POP-2 also signifies the presence of palladium particles over the surface of the polymer material.

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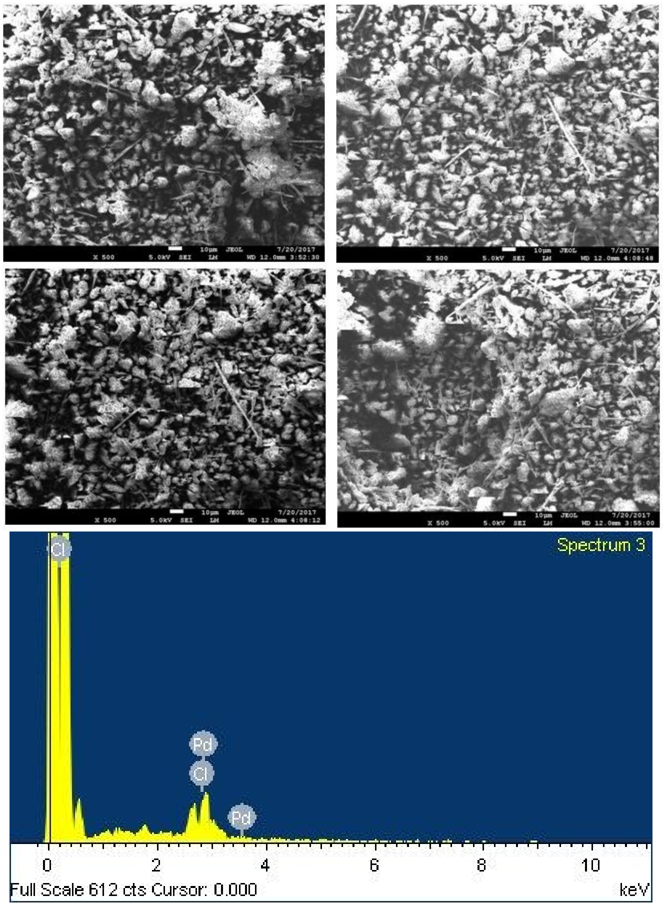

Figure 6: FE-SEM image and EDAX of Pd@POP-2 material

The TEM images of Pd@POP-2 catalyst are presented in Figure 7.The images of the catalyst specify that it is porous material and Palladium metal is dispersed on the outer surface of the porous organic polymer. Besides that, no agglomeration of Pd metal is observed in the entire sample grid. From Figure 7 it is clear that uniform anchoring of Pd(II) metal at the surface of POP-2 complex. Dark spots in the TEM images indicated the existence of Pd metal throughout the sample and diameter of the palladium particles is about 5-10 nm.TEM image indicated that the shape of palladium particles is spherical shape.

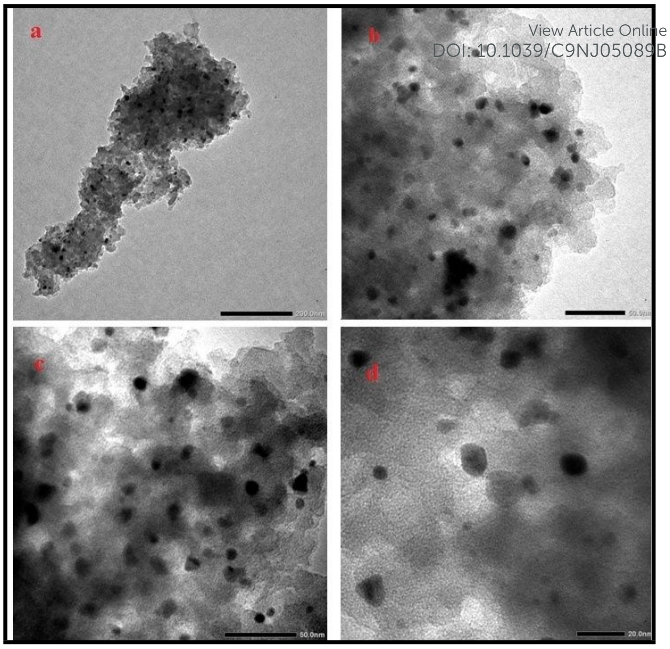

Figure 7: The TEM images of Pd@POP-2 at different scales (a) 200 nm, (b) 50 nm, (c) 50 nm and (d) 20 nm respectively

The thermal stability of the complex Pd@POP-2 was studiedusing TGA-DTA at a heating rate of 10 °C/min over a temp range of 0-700 °C. The thermo gravimetric analysis curve of the mesoporous polymer anchored Pd@POP-2 catalyst is provided in Figure 8. The palladium complex was stable up to approx. 350 °C, after that the catalyst degraded. After 350 °C, there was a gradual decrease in weight.The thermal analysis data suggests that polymer incorporated Pd complex decomposed completely approx. 550 °C.

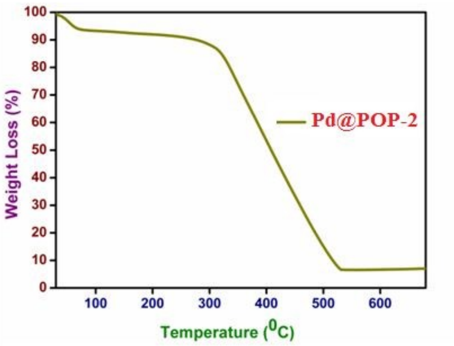

Figure 8:TGA plot of the Pd@POP-2 material

Catalytic Activity

Synthesis of α-ketoamides over Pd@POP-2 through in situ carbonylation

As palladium incorporated complex catalysts illustrate outstanding catalytic activity in variety of important industrial processes as well as extensively applied for C-C coupling,[57] we also endeavored to explore the catalytic activity of the Pd@POP-2 catalyst in the *in situ* carbonylation reaction and eventually succeeded in obtaining the product α-ketoamides from aryl iodides substrates (Scheme 2).

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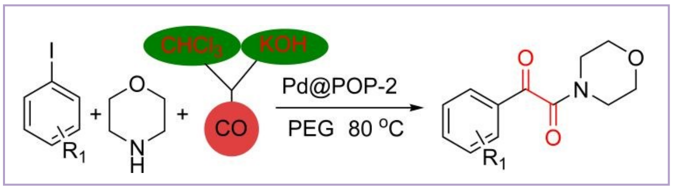
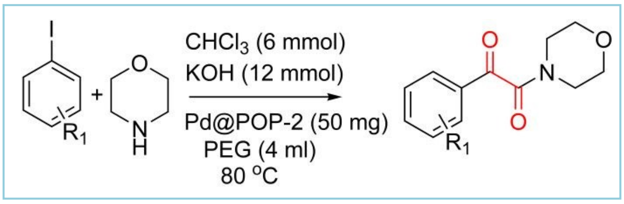
Initial studies were focused on the practical application of the catalytic actions and to standardize the conditions of the reaction for the generalized synthesis of α-ketoamides.

Pd incorporated polymer catalyst which has high specific surface area and intrinsic porosity was used for the conversion of aromatic iodides to their respective α-ketoamides under thermal condition. Potassium hydroxide was used as a standard base and polyethelene glycol (600) as a solvent for the *in situ* double carbonylation. Excess amount of $CHCl_3$and base utilized to get the selective α-ketoamides. The heterogeneous reaction was carried out in a sealed tube where $CHCl_3$ was utilized for internal carbon monoxide source under basic condition at 80 ˚C for 16 h.



Scheme 2: POP-Pd(II) catalyzedα-ketoamides synthesis of aryl iodides

In our preliminary attempts, iodobenzene was taken as an ideal substrate for the recognition of the optimum reaction conditions(scheme 3). To monitor the reactivity of the polymer supported Pd@POP-2 catalyst a variety of reaction parameter is checked. Numerous solvents and bases were used to find out the suitable reaction conditions (Table 1). To determine of valuable conditions for the Palladium catalysed carbonylation reaction, the conversion was carried out under several temperatures and time interval (Table 2).



Scheme 3: Pd@POP-2 catalyzedcarbonylation of iodobenzene

Base plays a vital role for this catalytic conversion. Inorganic hydroxides were found to be more effective for this reaction according to the investigational results (Table 1). A variety of bases such as LiOH, NaOH and $Mg(OH)_2$ were examined but in all cases observed yield was lower than that of KOH. KOH was observed to be the most effective base for the transformation in presence of $CHCl_3$ in polyethene glycol medium at 80 ˚C resulting 88% conversion.For study of the effect of solvent, PEG-600 was replaced by DMSO, dioxane, CH_3CN, DMF and water for the carbonylation reaction. Polyethelene glycol turned out to be the most competent solvent giving maximum yield.

Table 1: Effect of base and solvent on carbonylation of iodobenzene

Entry	Base	Solvent	Isolated Yield (%)^a
1	NaOH	Toluene	54
2	LiOH	Toluene	30
3	$Mg(OH)_2$	Toluene	20
4	KOH	Toluene	85
5	KOH	PEG-600	88
6	KOH	DMSO	20
7	KOH	dioxane	55
8	KOH	CH_3CN	30
9	KOH	DMF	25
10	KOH	H_2O	0

Reaction conditions:PhI (1 mmol), morpholine (1.2 mmol), $CHCl_3$ (6 mmol), Base (12 mmol), Pd@POP-2 (50 mg/2.3 mol %), PEG-600 solvent(4 ml), 80 ˚C, 16 h.PPh_3(40 mg)was used for 1 to 10 except 5. ^{a}Isolated yield of α-ketoamides.

Table 2: Effect of reaction temp and time on carbonylation reaction

Entry	Temperature (˚C)	Time (h)	Yield (%)^a
1	40	8	34
2	50	10	44
3	60	12	56
4	70	14	77
5	**80**	**16**	**88**
6	80	18	88
7	80	20	88
8	90	16	86
9	100	16	84
10	100	14	82

Reaction conditions: PhI (1 mmol), morpholine (1.2 mmol), $CHCl_3$ (6 mmol), Base (12 mmol), Pd@POP-2 (50 mg/2.3 mol %), PEG-600 solvent(4 ml), 80 ˚C, 8-20 h.^{a}Isolated yield of α-ketoamides.

The reaction was conducted for several time intervals varying from 8 h to 20 h. The best result was observed at 16 h. Therefore 16 h was chosen as the suitable time for the carbonylation reaction providing upto 88% yield (Table 2). Like other parameter we also checked the temperature at a range of 40 ˚C to 100 ˚C. It was found

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that 80 ˚C was the standardised temperature for the catalytic carbonylation transformation (Table 2). The double carbonylation reaction was carried out in presence of other palladium sources such as $Pd(OAc)_2$, $PdCl_2$, and $PdCl_2(PPh_3)_2$ and the observed yields were found to be 68%,55% and 65% respectively. The reaction was unsuccessful with catalytic Pd/C.Comparatively our catalyst Pd@POP-2 affordedmuch better yield (88%).

The quantitative effect of the Pd@POP-2 was optimized during the phase of the reaction. The yield of the product was also investigated by utilizing the amount of the catalyst (Figure 9).We carried out the catalytic reaction with varying the quantity of Pd@POP-2 from 5 mg to 60 mg. Using 50 mg of catalyst maximum yield of 88% was obtained as amount of active sites increases. Using more than 50 mg (2.3 mol %) Pd@POP-2 catalyst, no further transformation occurred. As a result, 50 mg supported heterogeneous catalyst was selected to be ideal amount for the conversion.

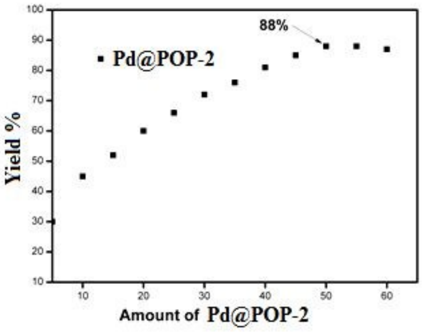
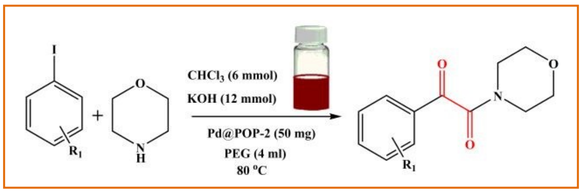
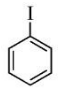
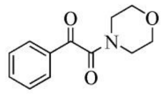
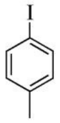
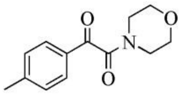
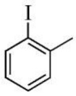
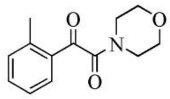
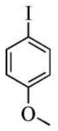
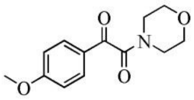
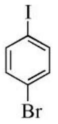
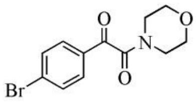
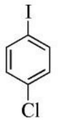
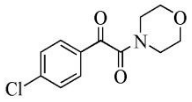
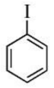
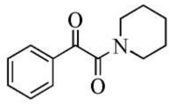
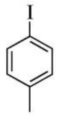
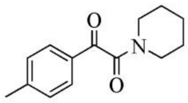
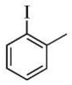
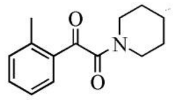
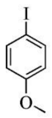
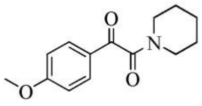


Figure 9: Catalyst loading effect on *in-situ*carbonylation reaction

After several parameter optimizations, a variety of aryl iodide and amines were explored to expand the scope of the reaction (Table 3). Substituted iodobenzene with either electron donor or electron withdrawing moiety under optimum condition converted to their corresponding α-ketoamides with good to excellent yields. Strong electron donating group in the aryl iodides such as methoxy and methyl, resulted in superior yields than 1-bromo-4-iodobenzene (Table 3, entries 2-4 and 8-10).For the catalytic reactions, mainly the yield of the ketoamide product was observed but from the Table 3, only aryl halide containing bromo group in the aryl ring leads to the monocarbonylated side products[51]with yield 6%.We checked the reaction in presence of acyclic secondary amine very poor yield was obatined.

Table 3: POP supported Pd (II) catalyzedcarbonylation of aryl iodides



Entry	Aryl halides	Product	Conversion (%)^a/ Isolated Yield (%)^b	TON
1.			90^a/88^b	39
2.			86^a/84^b	37
3.			81^a/80^b	35
4.			82^a/79^b	36
5.			64^a/62^b	28
6.			76^a/74^b	33
7.			92^a/90^b	40
8.			88^a/86^b	38
9.			82^a/81^b	36
10.			81^a/79^b	35

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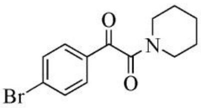
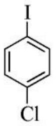
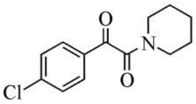
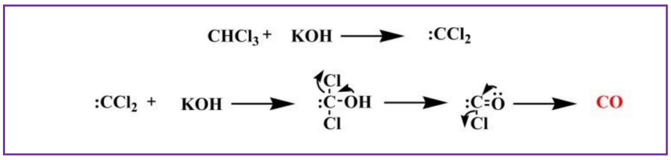
11.			$63^a/61^b$	27
12.			$79^a/76^b$	34

Reaction conditions:aryl iodides (1 mmol), morpholine/piperidine (1.2 mmol), $CHCl_3$ (6 mmol), KOH (12 mmol), Pd@ POP-2 (50 mg/ 2.3 mol %), PEG-600 solvent(4 ml), 80 ˚C, 16 h.

In Scheme 4,at first chloroform in presence of base gives carbene intermediate, which on reaction with excess base, produced carbon monoxide gas. Once the CO is generated then in presence of aryl iodide and amine formed the corresponding α-ketoamides. We have suggested the mechanism of the reaction pathway according to literatures report.[51,59] The nitrogen rich POP-2 support is stabilizing Palladium (0) metal generated from Pd(II).[58]The responsible factor for the carbonylation reaction is the active sites present in the catalyst. Generally, it is postulated that Pd(0) complex forms an organopalladium halide complex by O.A (oxidative addition) of an aryl iodide. Then the process would provide an acylpalladium halide which includes migratory insertion of a coordinated carbon monoxide. The CO coordinated acylpalladium species would combine with a nucleophile to give α-ketoamides.



Scheme 4: Proposed mechanism for CO formation

Comparative studies of the Pd@POP-2 with other reported catalytic system

The performance of the catalyst Pd@POP-2 was shown to be excellent towards the carbonylation reaction. The polymer incorporated Pd catalyst plays an important function in this outstanding activity. A comparative study is shown in Table 4.

Table 4: Comparative studies of the Pd@POP-2 catalyst in the synthesis of α-ketoamides with different reported catalytic systems

Reaction	Entry	Catalyst	Reaction Conditions	Yield (%)	Ref.
α-ketoamide synthesis	1.	$Pd(OAc)_2$	Na_2CO_3, PEG-600-400,CO (balloon), RT	94	51
	2.	mPMF–Pd^0 Catalyst	K_3PO_4,CO (20 atm), DMF (5.0 mL) at 90 ˚C, 12 h	98	59
	3.	Pd@POP-2	$CHCl_3$ (6 mmol), KOH (12 mmol), PEG-600 solvent(4 ml), 80 ˚C, 16 h	90	This Study
	4.	$Pd(dba)_2$	$HBF_4P(tBu)_3$, CO generator ,DBU (1mmol), THF (5 mL), RT	68	60
	5.	Pd/CTFs	CO (balloon), K2CO3 (0.4 mmol) in CH3CN (1 mL) at 70 ºC for 24 h	84	61

Heterogeneity test

In order to assess the heterogeneous nature of our designed Pd@POP-2 materials we have performed the hot filtration test under the optimized condition. In the synthesis of α-ketoamide using CO surrogates, the catalyst was separated out from reaction mixture after 10 h under the optimization condition (yield 68 %) and further reaction was continued with the filtrate. It was observed that no further conversion took place after filtration of the catalyst from reaction mixture. Alternatively as measured by AAS analysis, it was also found that the palladium did not leach into the solution. No metal trace was detected in the filtrate and in the catalyst same metal loading was noted as that of fresh catalyst (4.86 %). So, our study clearly demonstrated that our porous Pd@POP-2 catalyst was stable and maintained heterogeneous nature throughout the reaction.

Catalyst reusability

The superb catalytic activity of the catalyst encouraged us to examine its thermal stability, recoverability and reusability which are the main important feature in a heterogeneous catalytic system. In order to investigate the recyclability, this porous material was successfully recycled and used to obtain α-ketoamidesusing CO surrogate chloroform, which are shown in the Figure 10. Once the reaction was complete, 8 ml ethyl acetate and 16 ml H_2O was added to the final reaction mixture. Then workup the reaction mixture by separating funnel and the product was obtained by evaporating the organic layer under reduced pressure.The catalyst was recoveredfrom the remaining aqueous phase through centrifuge, followed by washing with methanol and then dried at 50 ˚C to 60 ˚C.After drying, the recycled catalyst Pd@POP-2 was further utilized under optimal conditions in carbonylation reaction. The Pd@POP-2 catalyst shows excellent catalytic efficiency upto six cycles. The catalytic yield becomes nearly half after twelve cycle. We got only 45% yield after becomes twelve cycle. After eleven cycles, AAS data showed that the Pd@POP-2 catalyst contains 1.24 % of Palladium. This decrease of catalytic efficiency is due to the leaching of metal from support and catalysis poison. After twelve run the catalyst showed very low yield.

Figure 10: Reusability test of Pd@POP-2 catalyst

Conclusions

We successfully established a new Pd(II) grafted onto Porous organic polymer (POP-2) catalyst. The recyclable heterogeneous catalyst has been well characterized and checked its successful application towards the preparation of α-ketoamides by carbonylation reaction. Several electron-deficient and electron-rich aryl iodides can be employed as substrates furnishing products with good to excellent yields. The supported Pd@POP-2 complex was synthesized simply from commercially obtainable and inexpensive materials as starting. The catalysts are reusable with no efficient loss in its catalytic activity. The porous catalyst showed very high recycling efficiency towards the synthesis of α-ketoamide, suggesting huge potential of porous Pd@POP-2 material in sustainable and green heterogeneous catalyst. Moreover, this *in situ* carbonylation strategy can be extensively explored to develop the opportunity of different organic transformations.

Acknowledgments

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POP-Pd(II) catalyzed easy and safe *in-situ* carbonylation towards the synthesis of α-ketoamides from secondary cyclic amines utilizing $CHCl_3$ as the carbon monoxide surrogate

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