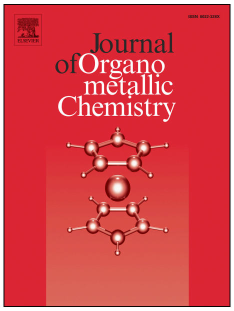

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Graphical Abstract

Synthesis and architecture of polystyrene-supported Schiff base-Palladium complex: Catalytic features and functions in diaryl urea preparation in conjunction with Suzuki-Miyaura cross-coupling reaction by reductive carbonylation

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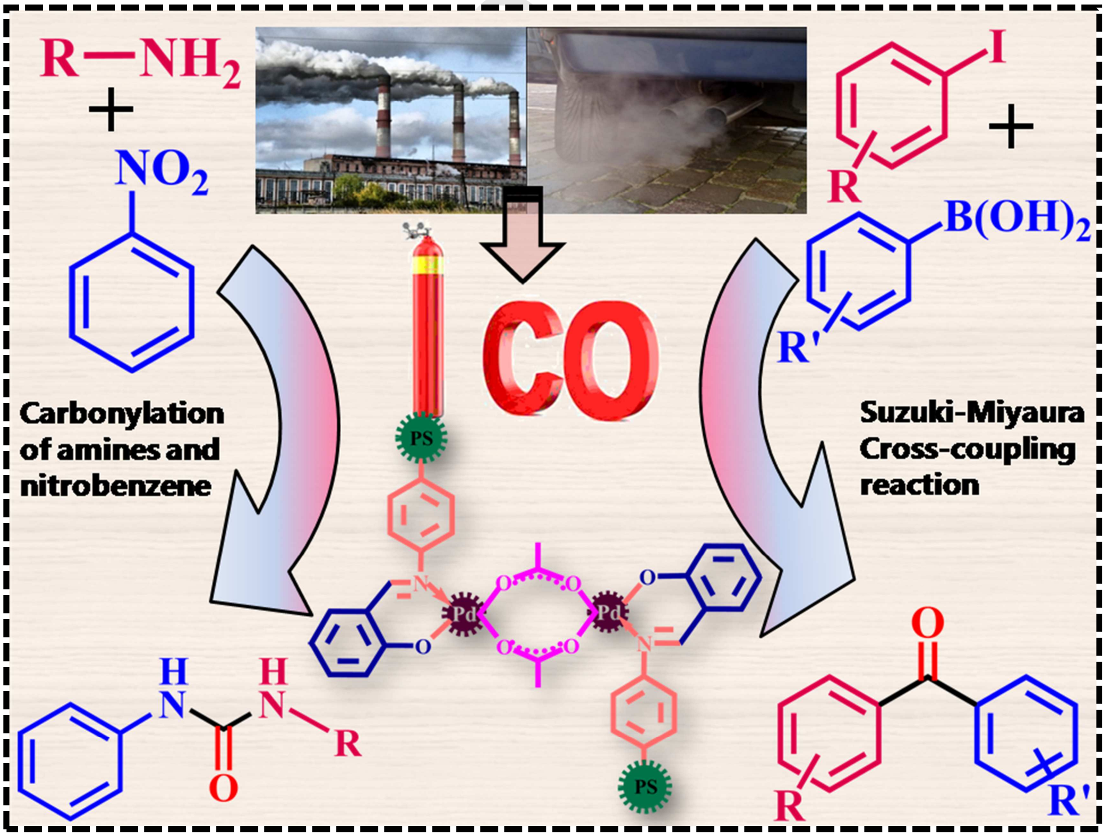

Synthesis and architecture of polystyrene-supported Schiff base-Palladium complex: Catalytic features and functions in diaryl urea preparation in conjunction with Suzuki-Miyaura cross-coupling reaction by reductive carbonylation

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Abstract

This work represents an efficient and unique phosphine-free approach for the polystyrene embedded Schiff-base palladium catalyzed diaryl urea synthesis and Suzuki-Miyaura cross-coupling reaction by reductive carbonylation process. The careful instrumental investigations with FE-SEM, EDAX, TGA, UV-Vis, FTIR, AAS, and elemental analysis precisely characterized the developed heterogeneous catalyst. Reaction parameters, like catalytic natures, starting materials, reaction environment, and solvent were examined sequentially. The present work has been adequately addressed to account for the generation and characterization of a new polymer bound Pd-catalyst and using it in the synthesis of diaryl ureas and diaryl ketones, with no substantial decay of catalytic activity.

Keywords: Suzuki-Miyaura cross-coupling; Diaryl urea; Biaryl ketone; Palladium; Salicylaldehyde; Schiff base.

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Introduction

The increasing worldwide demand for bulk chemicals and materials required strong investigation to discover novel manufacturing procedures from unconventional resources. As necessary raw materials for the chemical manufacturing plant, the C1 compounds: CO and CO_2 can be obtained on a huge scale including renewable. Specifically, CO is a most versatile and cost-effective chemical building block and is easily produced from naturally occurring gas, coal, biomass and so on [1].

Transition metal catalyzed carbonyl conversions have been a centre of attraction among organic chemists for developing environmentally sustaining protocols for synthesizing a variety of medicinal and industrial compounds [2,3]. N,N′-diaryl ureas are one such established biologically active molecules of enormous significance predominantly in medicinal fields [4]. In addition it has several impacts on materials science [5] and catalytic fields [6,7]. Simultaneously, urea has been used as a precursor for synthesizing amines, isocyanates, carbamates and imides and so on [2,3]. The diphenyl urea production from a combination of aniline and nitrobenzene under polystyrene attached Ru(II) catalysis is one of the established methods for oxidative >C=O conversions [8]. At present, the commercial synthesis of N,N′-diaryl urea involves the extremely lethal raw substance phosgene, from which corrosive HCl is liberated, as a by-product. Incidentally, the N,N′-diaryl urea could be prepared in an alternate process, involving the reaction of amine and nitrobenzene with CO in presence of palladium catalyst [9]. Immobilization of palladium metal on the various polymer supports has drawn great attention to the research scientists for its successful functions in multiple and distinct carbonylation reactions [10]. Present approach demonstrates how the surface group of polymer support influences on the stability and the catalytic function of PS-Pd-Schiff base complex. It proved successful for disubstituted urea synthesis from a wide extent of substituted aryl amines and nitrobenzenes. A rational illustration on the heterogeneous Pd-catalyzed synthesis of N,N′-diaryl urea by the use of CO is inadequate. The designing of simple, generous and efficient supported catalyst is the main target for many researchers due to its great potential in catalyzing organic transformations [11].

Palladium catalysts with varieties of ligands [12-14] attached onto polystyrene surface has attracted huge concentration for making C-C bond in organic synthesis. Pd catalyzed carbonylative Suzuki-Miyaura is one such type of C-C coupling reaction and a momentous system for the insertion of CO in both academia and industries. The Pd catalyst containing phosphine-based ligands reported for S-M coupling reaction have adverse hazardous effects, air-sensitivity and high economic resist their widespread applications in catalytic chemistry. Currently multiple examples of phosphine free ligands such as, macromolecular polymers [15,16], mesoporous molecular sieve [17,18], graphene oxide [19,20] are employed to assist the palladium incorporated Schiff base catalyst.

Solid supported Pd complex (such as polymers, graphene, silicate and zeolite) improves facile isolation process alongside enormous catalytic efficiency in Suzuki cross-coupling for synthesizing biaryl ketones [21]. Sufficient attempts have been reached for diaryl ketone preparation concerning their huge involvement in cosmetics [22], biological sensitive compounds [23, 24], pharmaceuticals [25, 26, 27], and in other functional materials [28-30]. The anti-inflammatory drug, S-ketoprofen was derived from diaryl ketone [28,29]. Another derivative of diaryl ketone is fenofibric acid, a regulating agent for lipid substance and is utilized for the medication of high cholesterol in addition to blood triglyceride levels [31]. Evidently from earlier reports the designed polystyrene grafted Pd Schiff base complex has not been employed as a catalyst for carbonylative Suzuki-Miyaura cross-coupling reaction along with diaryl urea synthesis. The current work elucidates the efficient, innovative synthetic routes for the production of diaryl urea from polymer supported heterogeneous Pd catalyzed conversion of aryl amine and nitrobenzene using economically cheaper reagents.

Experimental Section

Materials

5.5 % crosslinked polystyrene, conc. nitric acid were collected from Sigma-Alrich Co.; U.S.A and used without purification. Predistillation was performed for the liquid substrates and dried using specific process. Palladium acetate, salicylaldehyde, nitrobenzene, amine derivatives, phenyl boronic acid and iodobenzene derivatives were purchased from Alfa-Aesar. DMF, ferric chloride, anisole, potassium carbonate were acquired from Merck and used without refinement.

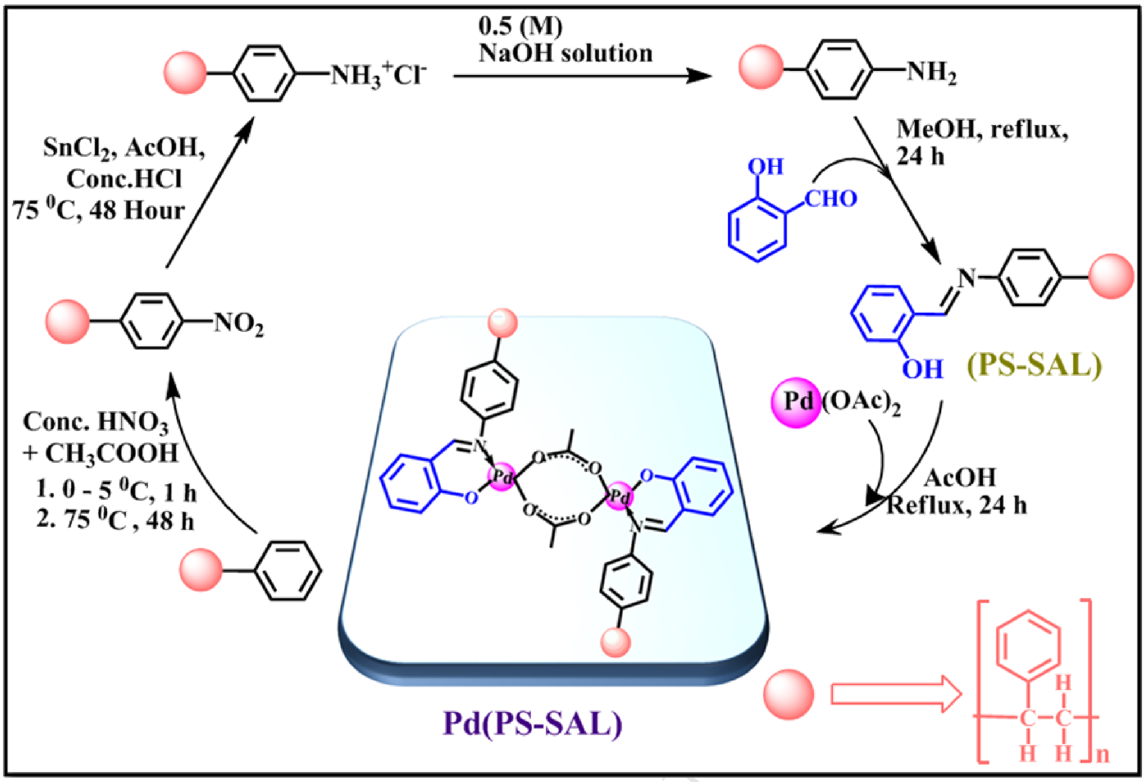
Physical and spectroscopic instruments

FTIR spectra for the respective samples were obtained by placing KBr disc inside a Perkine Elmer FTIR 783 spectrophotometer within range of 400 to 4000 cm^{-1}. The Mettler Toledo TGA/DTA 851e equipment was helpful to analyze the thermogravimetry of the samples. The UV-Vis band of solid samples were obtained by Shimadzu UV-2401PC doubled beam spectrophotometer associated with an integrating sphere counterpart. The surface morphology of the samples was specifically observed with SEM, ZEISS EVO40, England instrument having EDX advantage. The morphological analysis of our synthesized Pd(PS-SAL) complex catalyst was carried out by transmission electron microscopy (TEM) (JEOL JEM 2100) operated at 200 kV. Atomic absorption spectrophotometer (Model Varian AA240) was used to realize the % content of palladium in the palladium loaded material. High pressure reactions were performed with the help of a high pressure reactor containing a magnetic stirrer attached with an autoclave (AmAr Equipment, model no.SE-1TAP-II).

Fig. 1 High Pressure Reactor.

Preparation of catalyst [Pd(PS-SAL)]

The desired catalyst was prepared cautiously by following two-step strategies. Initially the preparatory method of p-aminopolystyrene was performed by means of the previously reports [32]. Secondly, 2 g of p-aminopolystyrene was taken in a 250 mL round bottom flux and swirled for 5 min with 10 mL methanol to prepare polymer anchored salicylaldehyde complex. Methanolic solution (10 mL) of salicylaldehyde (0.8 mL) was added immediately after to it and kept for reflux for 24 h. The colour of the solution was changed from pale yellow to green. Then greenish type solid solution was filtered and washed with methanol. Freshly prepared polymer anchored Schiff base complex (500 mg) was taken in 100 mL rb and settled it with refluxing condition after 10 min mixing of 0.1 g of palladium acetate in 10 mL acetic acid. The reflux was continued for 10 h. The resultant mixture was filtered, washed concomitantly with methanol for 8 to 10 times to remove impure component absolutely and dried in vacuum. Preparation scheme of the polymer supported Schiff base-palladium compound is outlined in Scheme 1.



Scheme 1. Synthesis of polymer anchored Schiff base-palladium catalyst Pd(PS-SAL).

General procedure for synthesis of diaryl ureas

Each of derivatives of amine (6 mmol) was introduced with 6 mL DMF, 6 mL methanol and 2.5 mmol (0.405 g) of ferric chloride and followed by nitrobenzene 3 mmol in a 100 mL glass-lined stainless steel autoclave fitted with a magnetic stirrer (Fig. 1). Then 20 mg (0.013 mmol based on Pd active centre) of polystyrene anchored salicylaldehyde palladium catalyst was added by exerting 80 psi of carbon monoxide. The reaction temperature was fixed at 75 ^{o}C. The used catalyst was collected after 6 h completion of reaction. Later, the rest of the mixture was allowed to work up for 3 times using ethyl acetate and organic part was dried over sodium sulfate. The solid product was analyzed by proton NMR spectroscopy (supporting information).

Procedure of carbonylative Suzuki-Miyaura cross coupling catalysed by Pd(PS-SAL)

In a 100 mL, autoclave equipped with magnetic stirrer (Fig. 1), phenyl boronic acid (1 mmol), iodobenzene (1 mmol), potassium carbonate (3 equiv.), anisole (5 mL) and Pd(PS-

SAL) catalyst (15 mg, 0.01 mmol based on Pd active centre) were added. Then it was purged three times with carbon monoxide (65 psi) and after closing the autoclave tightly, it was heated at 90 ^{o}C. The reaction was continued for 8 h, cooled at room temperature then Pd(PS-SAL) catalyst was removed from the reaction system and washed down with methanol. The organic content was dried out absolutely with sodium sulfate after work up it with ethyl acetate (3×10 mL) followed by water. The unstable components were allowed to evaporate through a rotary evaporator. The solid product was analyzed by ^{1}H NMR spectroscopy (supporting information).

Characterization of catalyst

In this context it is noteworthy to mention that the prepared polystyrene embedded Pd catalyst has some boundaries to investigate and characterize only to their physicochemical properties, SEM, TEM, EDX, TGA-DTA, FTIR, and UV-Vis spectral data. The complete integration of the organic substructure in the substance was established by elemental analysis.

Scanning electron micrographs (SEM) and energy dispersive X-ray analyses (EDX)

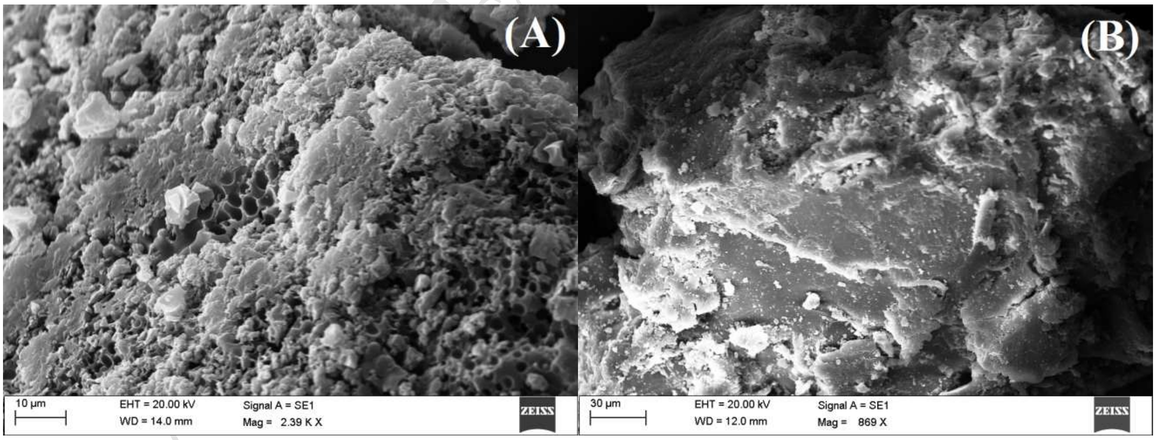


Fig. 2 SEM images of (A) polymer-supported Schiff base ligand (PS-SAL) and (B) the fresh palladium catalyst Pd(PS-SAL).

SEM pictures in Fig. 2 represent the polymer bound Schiff-base ligand (A) and the coordinated Pd-complex on tailored polystyrene (B). The observed SEM images demonstrate the morphological and characteristic distinct vision between the metal free PS-SAL ligand

and the metal loaded catalyst. The presence of Pd caused changes, demonstrated by disappearing of the extent of porosity and roughness of the -OH functionalized polymeric material surface.

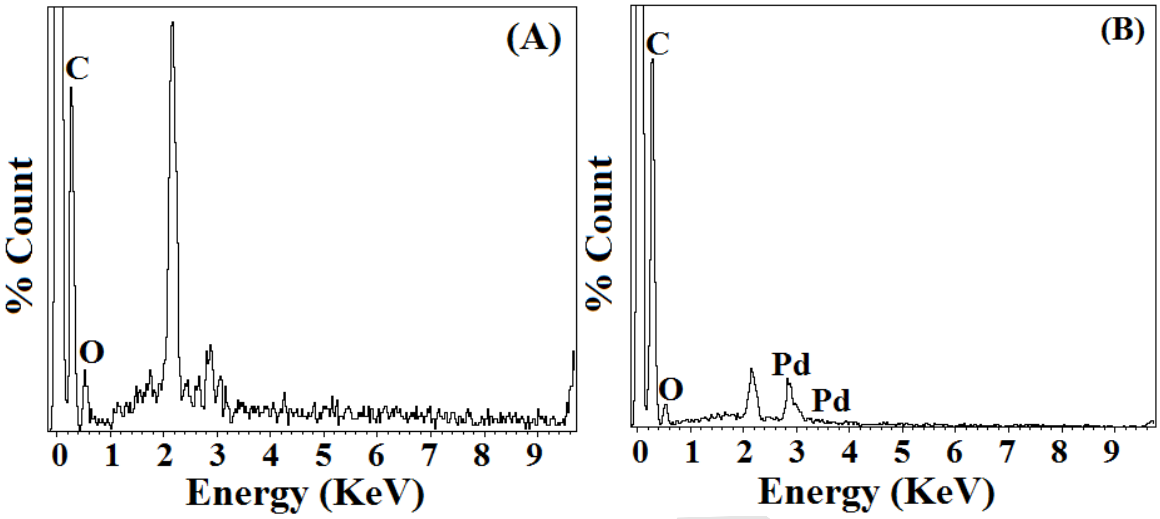


Fig. 3 EDX spectrum of (A) PS-SAL and (B) Pd(PS-SAL).

Moreover the EDX analysis supports the metal attachment on the polymer matrix (Fig. 3). The interaction of the Pd metal onto the polystyrene anchored ligand causes a small extent of smoothening on the surface layer, which probably due to metal ion and ligand interaction and orienting a specific geometry of the complex. From this spectroscopic analysis (EDX analysis) of the metal complex confirms the metal attachment along with C and O and recommends the construction of the metal complex Pd(PS-SAL) containing polystyrene anchored ligand. SEM and EDX analysis confirmed the palladium attachment onto the polymer matrix.

Transmission electron microscopy (TEM)

Image 4(a) and 4(b) represents the TEM images of nitro and amino polystyrene respectively. These two images suggest that there is no distinct change in morphology when nitro polystyrene converts to amino polystyrene. From TEM image 4(c) of PS-SAL ligand, the black spot strike the attachment of salicyladehyde on the surface of amino polystyrene. Image

4(d) and 4(e) are the TEM images of Pd(PS-SAL) complex catalyst in two different magnification, where black spherical balls are spread over the whole specimen. These black balls confirm coordination of Pd with polymer supported ligand.

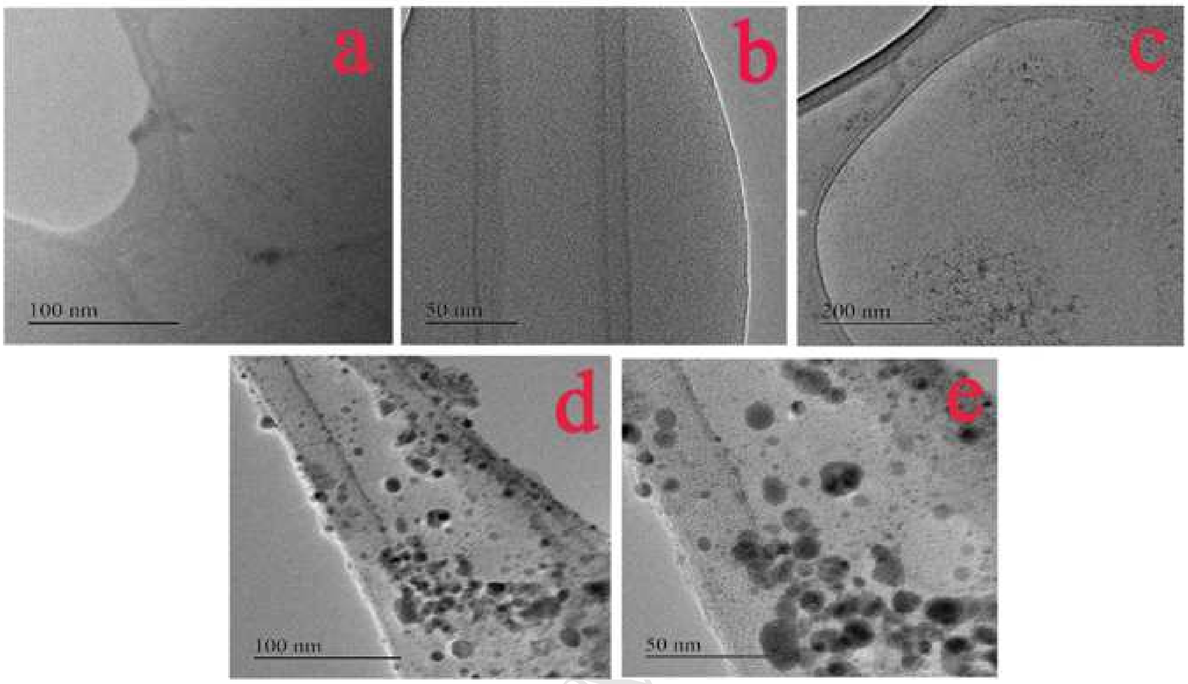
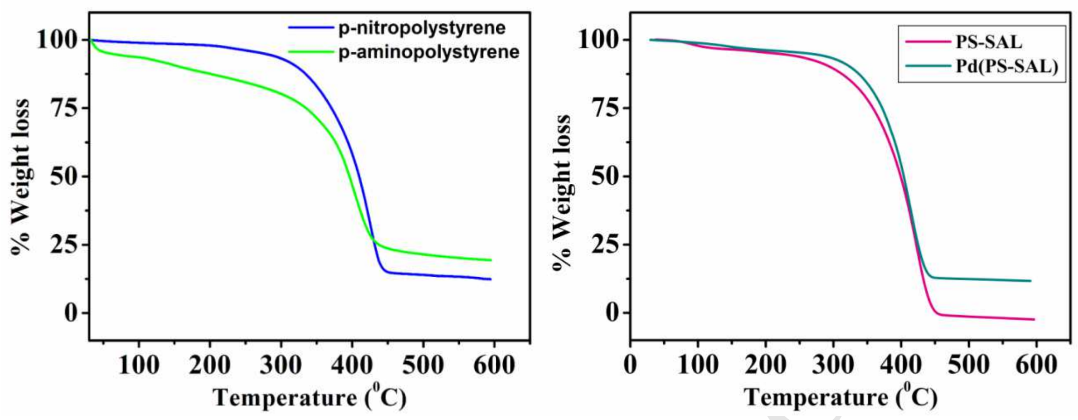


Fig. 4 TEM images of (a) p-nitro polystyrene; (b) p-amino polystyrene; (c) polymer-supported Schiff base ligand (PS-SAL); (d) and (e) polymer anchored Schiff base-palladium complex catalyst Pd(PS-SAL) in two different magnification.

Thermogravimetric analysis

Thermogravimetric analysis (TGA) was carried out to predict the thermal stability of p-nitropolystyrene, p-aminopolystyrene, polymer surrounded Schiff base ligand and the Pd-complex (Fig. 5) respectively. Thermal stability analyses of the synthesized materials were conducted in N_2 atmosphere with 10 ^{o}C/minute heating rate at the temperature measured from 30-600 ^{o}C. p-Nitropolystyrene starts to decompose in the range of 290-300^{o}C, where p-aminopolystyrene starts to decompose from 313 ^{o}C (Fig. 5A). The weight reduction of polymeric ligand varies from 320 ^{o}C to 450 ^{o}C, where the maximum weight loss of metal loaded polymeric catalyst arises from 340 ^{o}C to 458 ^{o}C (Fig. 5B). The loss of weight in this region comes out due to the disintegration of the component in the polymeric matrix. Hence the prepared polymeric supported catalyst is capable to execute its catalytic activities up to 340 ^{o}C without any loss of weight.



(A) **(B)**

Fig. 5 TGA plot of (A) p-nitropolystyrene and p-aminopolystyrene, (B) PS-SAL and Pd(PS-SAL).

FTIR spectroscopy

The attachment of salicylaldehyde and palladium metal onto the amino functionalized polymeric support was confirmed by IR spectral bands (Fig. 6).

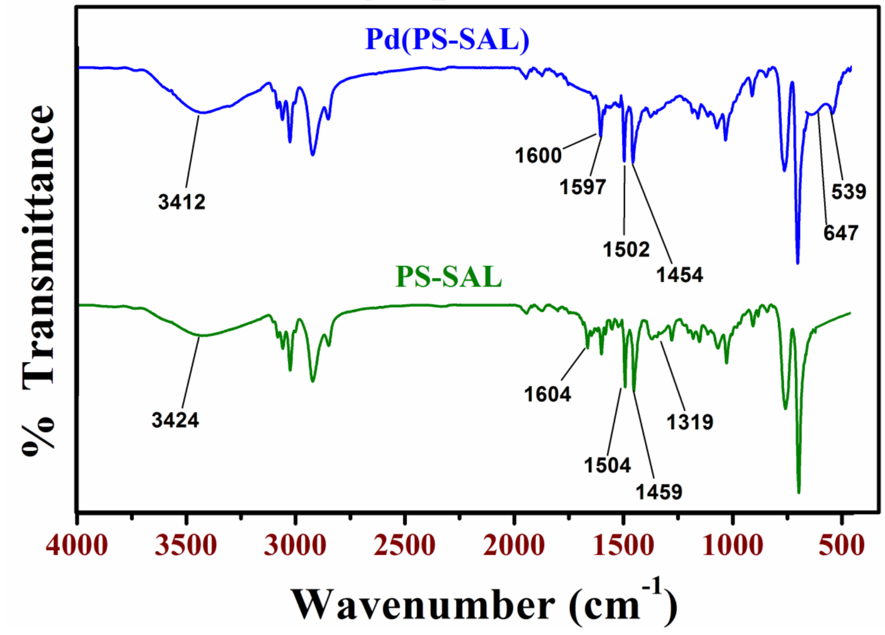


Fig. 6 FTIR spectra of PS-SAL and Pd(PS-SAL).

The formation of p-nitro polystyrene and p-amino polystyrene were recognised by FTIR spectroscopy (supporting information). Usually the Schiff base type ligands and its metal coordinated complexes are fundamentally recognized by the FTIR analysis due to different stretching vibrations of PS-SAL appeared at the expected positions. The range of 1600-1500 cm^{-1} corresponds to the $\upsilon_{(C\text{-}C)}$ and $\upsilon_{(C=N)}$ stretch of aromatic rings. C-O stretching furnishes its characteristic vibrations at 1319 cm^{-1}. Formation of the PS-SAL is indicated from strong IR band appeared at 1604 cm^{-1} due to the C=N azomethyne nitrogen stretching. The C=C stretching frequencies for the polymer supported free ligand was appeared around 1504 cm^{-1} accordingly [33,34]. The stretching vibration at 3424 cm^{-1} has been assigned to the corresponding hydrogen bonded phenolic -OH group present in the polymer bound Schiff base ligand.

The C=N and C=C stretching frequencies for the polymer supported Pd-Schiff base complex were observed at 1600 cm^{-1} and 1502 cm^{-1} respectively. The Pd(PS-SAL) complex shows asymmetric and symmetric stretching vibrations of corresponding COO for bridging bidentate acetate groups at 1597 cm^{-1} and 1454 cm^{-1} respectively. The band appeared near 647 cm^{-1} is assigned for the stretching vibration of Pd-N present in the metal incorporated polymeric complex. Pd-O stretching was also inferred by the observed weak absorption peak at 539 cm^{-1}. The polymer bound palladium-Schiff base complex Pd(PS-SAL) exhibits a broad band at 3412 cm^{-1} correspond to the stretching vibrations of deprotonated phenolic -OH group coordinated with palladium. In the polymer-anchored Pd-complex, both $\upsilon_{Ar\text{–}O\text{–}C}$ and $\upsilon_{C=N}$ experience a small shift highlighting the Pd is chelated with the nitrogen and oxygen atom.

Chemical analysis

After metal ion incorporation the resulting material in solution phase was analyzed with AAS instrument which offered a view about the complexation of palladium metal onto the polymer anchored Schiff base. Present of metal in the polymer anchored Schiff-base Pd catalyst was ascertained quantitatively with AAS expressing 7.05% Pd loading in the polymer matrix. However, the elemental composition of Pd(PS-SAL) revealed Schiff base complex formation.

The elemental analysis of the polymer embedded Schiff base ligand and its palladium complex (Table 1) substantiate to the prediction of the complex as proposed. This implies that polystyrene was embedded on the surface of the Pd-Schiff base complex. The ICP-AES was also performed to analyze the entire palladium content of the synthesized Pd(PS-SAL) catalyst. Elemental analysis of catalyst by ICP spectroscopy provided a palladium loading of 7.03 wt% (Table 1). Table 1 presents the C, H and N elemental analysis data of PS-SAL and Pd(PS-SAL) catalyst. The comparative analytical data provided from elemental experiment (C, H, N), ICP-AES and EDX analysis facilitates to determine the composition of ligand and Pd supported material consistent with the proposed structure.

Table 1. Elemental analysis of the polymer anchored ligand and polymer anchored palladium catalyst

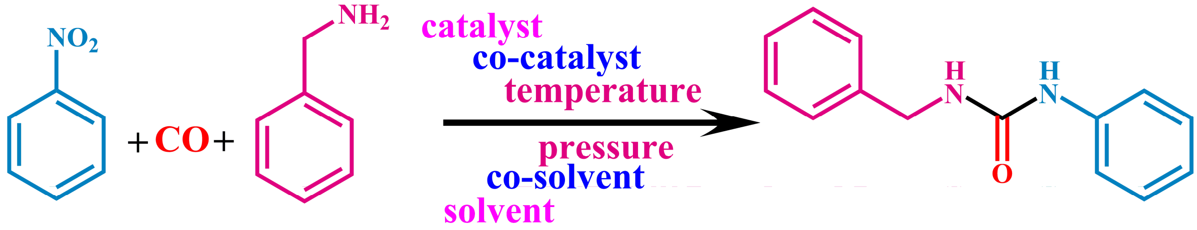
Compound	C %	H%	N%	Pd %
PS-SAL	79.78	5.11	7.15	-
Pd(PS-SAL)	72.12	4.8	5.6	7.05[a] 7.03[b]

[a]determined by AAS, [b]determined by ICP-AES

Results and discussion

Activity of catalyst

Activity of polymer supported palladium Schiff-base catalyst has a vital role in various industrial applications. The possible activity of the synthesized palladium catalyst was investigated by altering different experimental conditions like temperature, pressure, solvent, amount of co-solvent and catalyst used.



Scheme 2. Carbonylation reaction of nitrobenzene and phenylmethanamine in the presence of Catalyst.

Effect of solvent in the presence of methanol

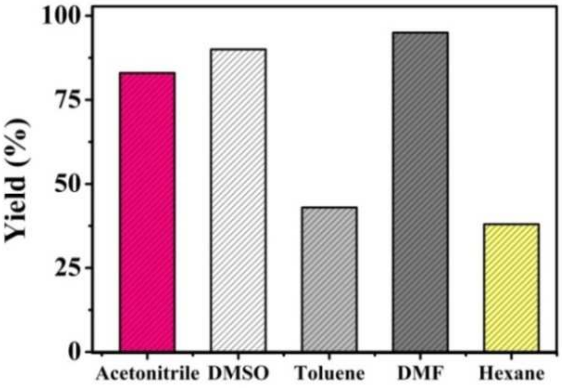
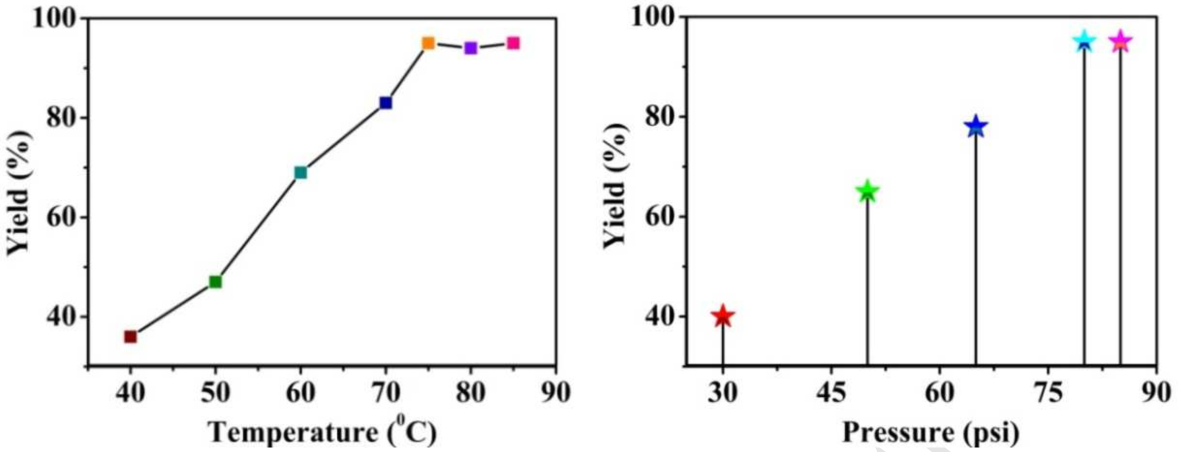


Fig. 7 Effect of solvent on polymer anchored Schiff base-palladium catalyzed 1-benzyl-3-phenylurea production. Reaction condition: nitrobenzene (3 mmol), benzyl amine (6 mmol), Catalyst (20 mg, 0.013 mmol based on Pd active centre), $FeCl_3$ (2.5 mmol), MeOH (6 mL), temperature (75 ^{o}C), time (6 h), P_{CO}=80 psi.

The formation of carbonylative product 1-benzyl-3-phenylurea was developed with the catalyst Pd(PS-SAL) and co-solvent methanol. Optimizing the reaction condition with various solvent the most suitable one was chosen for 1-benzyl-3-phenylurea formation. The polar aprotic solvent dimethyl formamide (DMF) is a solvent of highest priority with respect to the yield of 1-benzyl-3-phenylurea production as rationalized from above Fig. 7. The polar aprotic solvent like DMSO and acetonitrile were also effective but provided low yield for 1-benzyl-3-phenylurea production. Non polar solvents like hexane, toluene contribute an insignificant yield to the product formation. The 95% yield was observed for using DMF solvent. So, aprotic solvent with polar nature has been found more appropriate than only aprotic one for 1-benzyl-3-phenylurea formations.

Effect of temperature and pressure on 1-benzyl-3-phenylurea production



(A) **(B)**

Fig. 8 Effect of (A) temperature and (B) pressure for 1-benzyl-3-phenylurea production catalysed by Pd(PS-SAL). Reaction condition: nitrobenzene (3 mmol), benzylamine (6 mmol), Catalyst (20 mg), $FeCl_3$ (2.5 mmol), DMF (6 mL), methanol (6 mL), time (6 h).

The yield of 1-benzyl-3-phenylurea was varies with carbon monoxide pressure and also with temperature on the carbonylation of nitrobenzene and benzylamine. Moreover the optimization of temperature and pressure on 1-benzyl-3-phenylurea production was studied. The temperature of reaction medium was increased gradually from 40 ^{o}C to 70 ^{o}C and at final temperature 1-benzyl-3-phenylurea yield was 83%. In addition the present reaction was set to undergo at 75 ^{o}C and the significant yield obtained 95% (Fig. 8A). Even in the presence of methanol no yield of product isolated although the reaction proceed in room temperature. At low carbon monoxide pressure (< 30 psi) no trace of product was found since the amount of reactants remains unchanged. Whereas an outstanding performance was present at 80 psi of CO pressure providing 95% yield (Fig. 8B). As the reaction pressure was boosted from 30 psi to 85 psi progressively increases of % yield of 1-benzyl-3-phenylurea from 40% to 95%. At comparatively low temperature and CO pressure no development of product detected but highest (95%) yield was obtained at 75 ^{o}C and 80 psi pressure.

Table 2. Optimization of amount of catalyst for 1-benzyl-3-phenylurea production^{a}

Entry	**Time (h)**	**Amount of catalyst (mg)**	**Yield (%)^{b}**

1.	2	20	24
2.	3.5	20	45
3.	5	20	72
4.	**6**	**20**	**95**
5.	6.5	20	91
6.	6	15	76
7.	6	25	95

[a]Reaction condition: nitrobenzene (3 mmol), phenylmethanamine (6 mmol), $FeCl_3$ (2.5 mmol), DMF (6 mL), MeOH (6 mL), temperature (75 ^oC), P_{CO} (80 psi). [b]Isolated yield.

The amount of catalyst also performs as crucial function in current reaction for carbonylative diaryl urea production (Table 2). In above table, the yield of carbonylation reaction was moderate when reaction was simulated in presence of 15 mg of catalyst for 6 h. Increasing catalyst amount from 15 mg to 20 mg for 6 h reaction percent production of product increase but enhancement of time with same amount of catalyst (20 mg) reduce the yield percentage. No yield of product was obtained without addition of Pd(PS-SAL) catalyst. The sample carbonylative reaction was elaborated for 2 to 6 h. When the reaction was progress for 5 h provide moderate yield 72% whereas 2 h reaction offer a lowest yield of product. A rise in the catalyst amount (25 mg) showed no advancement in the model reaction. A preeminent result was found when the model reaction was optimized with 20 mg of catalyst and 6 h.

Table 3. Optimization of co-catalyst for 1-benzyl-3-phenylurea synthesis[a]

Entry	**Co-catalyst**	**Yield (%)[b]**
1.	-	-
2.	$SnCl_4$	91
3.	KOH	30

4.	Et_3N	25
5.	Pyridine	23
6.	**$FeCl_3$**	**95**
7.	p-toluene sulphonic acid	92

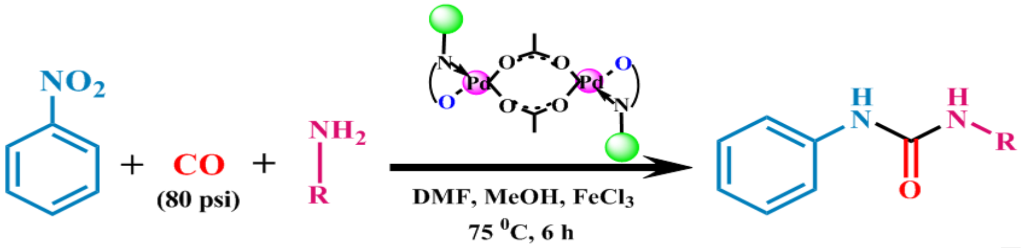
[a]Reaction condition: nitrobenzene (3 mmol), phenylmethanamine (6 mmol), DMF (6 mL), MeOH (6 mL), temperature (75 ^{o}C), P_{CO} (80 psi). [b]Isolated yield.

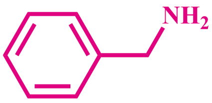
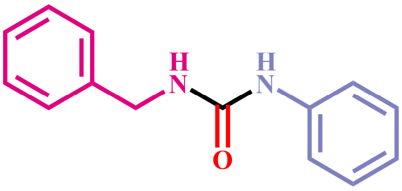
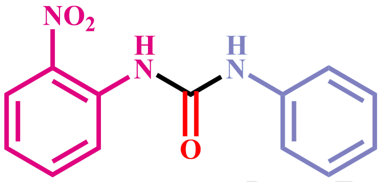
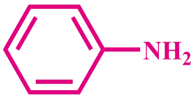
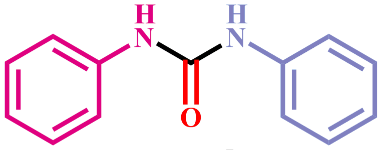
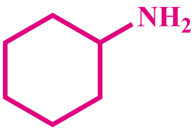
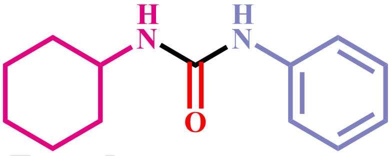
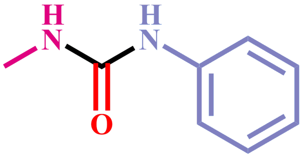
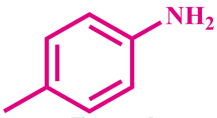
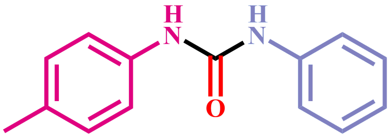
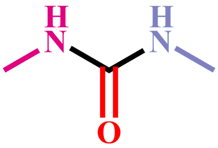
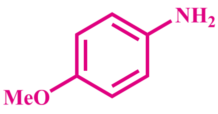
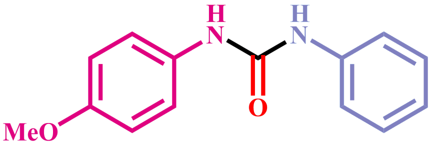
Exploration of optimized condition for co-catalyst having acidic and basic nature was done. The acidic catalyst like $SnCl_4$, $FeCl_3$, p-toluene sulphonic acid (PTSA) was improved the yield of the product maintaining the other optimized condition fixed (Table 3). The mixture of nitrobenzene and benzylamine may undergo carbonylation in the presence of Lewis acidic co-catalyst $FeCl_3$ to afford the corresponding phenyl urea, with almost quantitative yield. But the basic co-catalyst like Et_3N, pyridine provide worst yield of product. Without co-catalyst no existence of product established even at 80 psi CO pressure, 6 mL MeOH and other necessary controlled conditions. The percent yield of product in model reaction will decrease if moisture is in the reaction system. Finally, an excellent yield (95%) was observed. The % yield of product for the reaction between nitrobenzene and benzylamine with co-catalyst was highest for $FeCl_3$. Iron co-catalysis in the above system offers a satisfactory high yield due to development of the catalytic cycles associated with activation of the CO molecule [35].

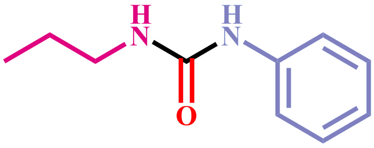
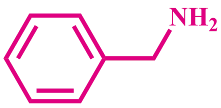
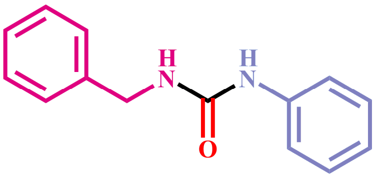
Synthesis of diaryl urea production using different derivatives

The carbonylation of nitrobenzene together with a number of different substituted amines underwent spontaneously under gentle conditions, affording the carbonylative products i.e. diaryl urea in moderate to high yields is outlined in Table 4.

Table 4. Reductive carbonylation of nitrobenzene with different derivative of amines by polymer anchored Schiff base-palladium complex[a]



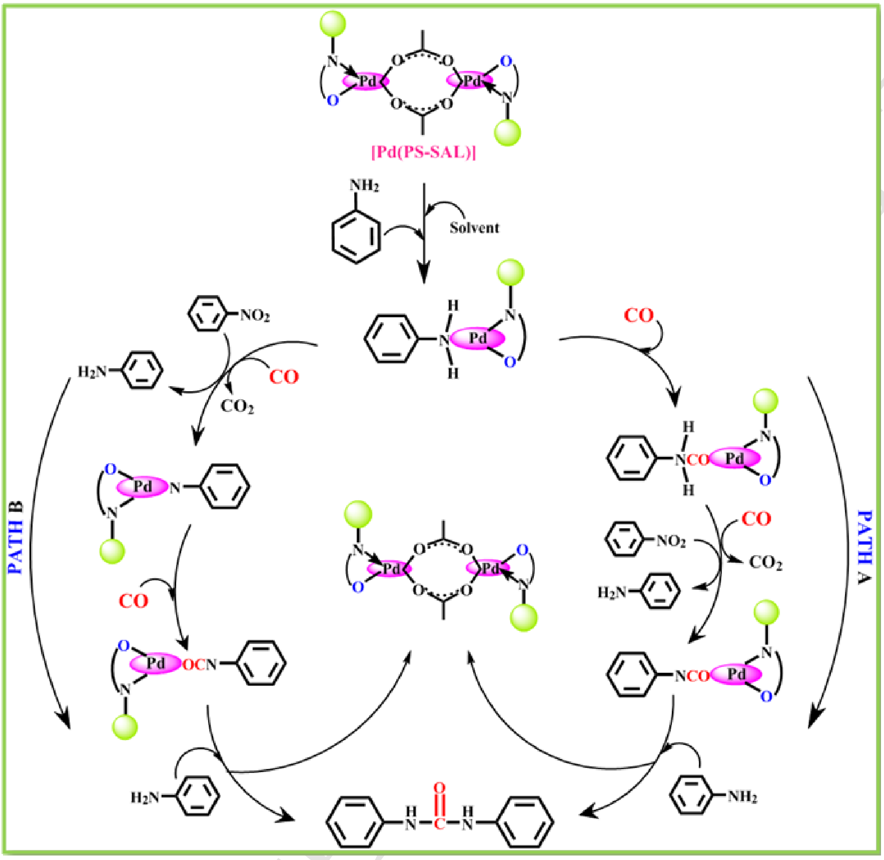
Entry	Amines	Product	Conv. (%)[b]	Yield (%)[c]	TOF (h^{-1})
1.			98	95	37.69
2.			17	Trace	6.53
3.			96	90	36.92
4.			99	96	38.07
5.	$H_3C—NH_2$		95	91	36.53
6.			98	97	37.69
7.	$H_3C—NH_2$		40	32[d]	15.38
8.			100	98	38.46

9.			96	94	36.92
10.			16	Trace[e]	6.15

[a]Reaction condition: nitrobenzene (3 mmol), amine (6 mmol), $FeCl_3$ (2.5 mmol), DMF (6 mL), MeOH (6 mL), Catalyst (20 mg, 0.013 mmol based on Pd active centre), temperature (75 °C), time (6 h), 80 psi CO pressure. [b]GC conversion. [c]Isolated yield. [d]nitromethane used instead of nitrobenzene. [e]without Pd(PS-SAL) catalyst but $FeCl_3$ present.

Under optimized reaction system, the reaction of nitrobenzene and the derivatives of aniline were observed as represented in Table 4. The effectiveness of catalyst was examined with cyclohexylamine, p-toluidine, aniline, benzylamine, 4-methoxyaniline etc. and among their corresponding products 1-(4-methoxyphenyl)-3-phenylurea grant for the highest yield and better conversion (Table 4, Entry 8). Disappointingly, o-nitroaniline provides a negligible yield of urea and lower conversion of amine signifying that $-NO_2$, an electron withdrawing group strictly weaken the $-NH_2$ group activity (Table 4, Entry 2). When aliphatic nitro compound are used instead of aromatic nitro compound the yield is too low with respect to other derivatives (Table 4, Entry 7). But when propylamine treated with nitrobenzene the yield is interestingly high than that of methylamine product (Table 4, Entry 5,9). This is due to more inductive effect of propylamine. Urea of cyclohexylamine, p-toluidine, and aniline led to 96%, 97%, 90% yield respectively with a satisfactory conversion (Table 4, Entries 3,4,6). Hence the group that has electron donating capability give better yield than others. Benzylamine also provide a better result than other aliphatic amines (Table 4, Entry 1). However, without Pd(PS-SAL) catalyst and presence of ferric chloride afford a trace amount of reaction product. $FeCl_3$ provides the definite work in the reaction of which it enhances the yield of the reaction but sufficient amount of Pd(PS-SAL) catalyst ensure better yield of the product.

Mechanism of diphenyl urea synthesis in presence of Pd(PS-SAL) catalyst

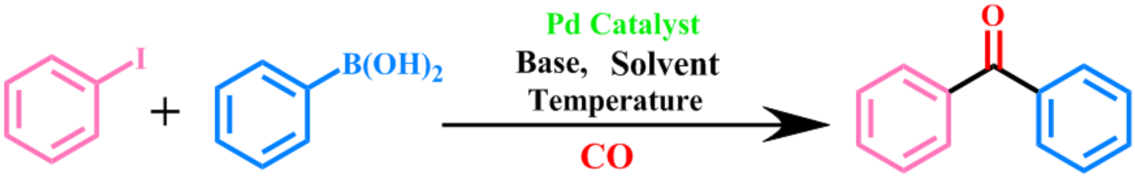


Scheme 3. Plausible mechanistic pathway for polymer supported palladium catalysed diphenyl urea synthesis.

The possible mechanism is suggested on the basic assumption that a Pd-CONHAr complex is formed during carbonylation (Path A, Scheme 3). There are lot of literature examples which proposed the same intermediate [36,37]. Nitrobenzene engaged itself in the mechanism as an oxidant. Nitrobenzene undergoes react with CO molecule and itself reduced to aniline. In this way the carboxylation cycle commences as depicted in Scheme 3. The reaction forwards with involving the catalyst proceeding through carbonylation of aniline-Pd intermediate to generate Pd-carbamoyl complex followed by withdrawal of oxygen atom from $PhNO_2$ by CO molecule. The simultaneous reduction process of $PhNO_2$ to $PhNH_2$ was experienced by the uptake of the H-atom released from aniline molecule [38]. Several authors reported a nitrene mechanism followed for rationalizing the product urea [39,40]. **Path A**, describes a carbamoyl intermediate is generated during the carbonylation reaction between $PhNH_2$ and CO. Next it is proficient to reacts with aniline and nitrobenzene with the subsequent formation of diphenyl urea. Nitrobenzene in this reaction treats as an oxidant through drawing H atom from the carbamoyl complex [36,41].

Likewise additional mechanistic pathway can be considered in Scheme 3 based on the Pd-nitrene intermediate as explored in **Path B**. First, from aniline as the substrate, the feasible Pd-nitrene species is formed simultaneously with the release of CO_2 where aniline is also formed in the reaction system from nitrobenzene reduction. The nitrobenzene reduction by the CO in the presence of Pd(PS-SAL) catalyst occurs at a faster rate. The insertion of CO is next into Pd-nitrene species took place to produce Pd-coordinated isocyanate. Ultimately, amine attacks as a nucleophile to the isocyanate escalated by the palladium complex consequences to the yield of expected unsymmetrical ureas alongside regeneration of Pd catalyst [42]. As represented in Scheme 3, PhNCO[Pd] complex is known to be formed by carbonylation of PhN[Pd] (a nitrene complex), which has been generated by stepwise deoxygenation of nitrobenzene with CO **(Path B)**. The phenyl isocyanate complex is able to react with aniline and gives rise to the targeted N,N'-diphenyl urea [36,43]. The transformation to isocyanate is very rapid since isolation of this intermediate is beyond feasibility [38].

Catalytic Activity of Carbonylative S-M cross coupling reaction



Scheme 4. Carbonylative Suzuki-Miyaura cross coupling reaction of iodobenzene and phenylboronic acid.

Effect of pressure for diphenyl ketone synthesis

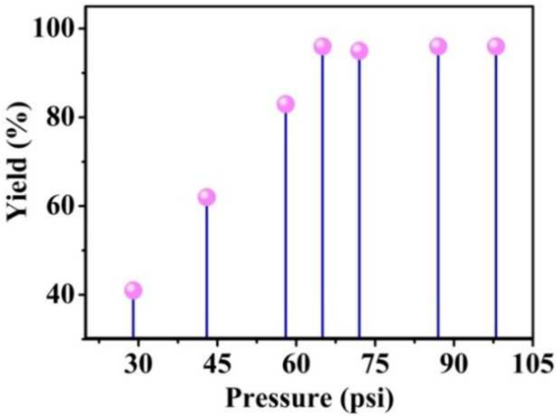


Fig. 9 Pressure effect for diphenyl ketone formation by polystyrene supported Pd catalyst. Reaction condition: Iodobenzene (1 mmol), phenyl boronic acid (1 mmol), K_2CO_3 (3 equiv.), anisole (5 mL), temperature (90 ^oC), time (8 h), catalyst (15 mg, 0.01 mmol based on Pd active centre).

Effect of carbon monoxide pressure on carbonylative Suzuki-Miyaura cross coupling reaction of iodobenzene and phenylboronic acid (a model reaction) illustrated in Fig. 9. Increase of CO pressure from 65 psi, promotion of product yield was not observed which might cause that rising of CO concentration perform a petite role in the cross-coupling reaction. Investigation of pressure over the carbonylative S-M cross-coupling reaction was done from 29 to 98 psi. However, enhance of CO pressure from 29 to 65 psi a continuous increasing of product yield in the model reaction from 41% to 96% respectively. Moreover, maintaining all the optimized condition we find 96% yield at 65 psi carbon monoxide pressure.

Effect of amount of catalyst on cross-coupling product diphenyl ketone synthesis

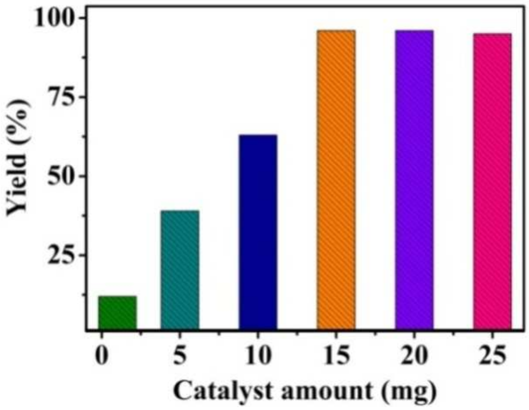


Fig. 10 Effect of amount of catalyst on diphenyl ketone formation by Pd catalyst. Reaction condition: Iodobenzene (1 mmol), phenylboronic acid (1 mmol), K_2CO_3 (3 equiv.), anisole (5 mL), P_{CO}=65 psi, temperature (90 ^oC), time (8h).

The amount of catalyst is another essential part in model reaction for carbonylative cross-couping reaction present in Fig. 10. Elaboration of optimized condition with the quantity of catalyst was done from 1 mg to 25 mg. The low yield of carbonylative product was observed in the model reaction containing low amount of catalyst. The captivating outcome was achieved (96% yield) when 15 mg of catalyst was used. Without catalyst no product was obtained. Increase of catalyst amount in the sample reaction, no reasonable yield of carbonylative product.

Table 5. Benzophenone synthesis using different solvent and base[a]

Entry	**Base**	**Solvent**	**Yield (%)[b]**
1.	K_2CO_3	EtOH	0
2.	K_2CO_3	DMSO	37
3.	**K_2CO_3**	**Anisole**	**96**
4.	K_2CO_3	-	0
5.	Cs_2CO_3	Anisole	65
6.	-	Anisole	0
7.	Et_3N	Anisole	trace
8.	KOH	Anisole	42
9.	K_3PO_4	Anisole	51
10.	K_2CO_3	Toluene	69
11.	K_2CO_3	H_2O	0
12.	K_2CO_3	DMF	62
13.	K_2CO_3	Anisole	72[c]
14.	K_2CO_3	Anisole	88[d]
15.	Na_2CO_3	Anisole	93

[a]Reaction condition: Iodobenzene (1 mmol), phenylboronic acid (1 mmol), P_{CO}=65 psi, temperature =90 °C, [c]temperature =80 °C, [d]temperature =100 °C, time (8 h), catalyst (15 mg, 0.01 mmol based on Pd active centre). [b]Isolated yield.

Maintaining the other optimized condition unaltered for the reaction between phenylboronic acid and iodobenzenes in the presence of polystyrene supported palladium catalyst was also selected for optimization with various base and solvent. The impact of different organic/inorganic bases and protic/aprotic solvents are represented in Table 5, Entries 1-14. According to the observation it is proved that polar aprotic solvent is more reliable for better yield formation than polar protic solvent. When the model Suzuki-Miyaura cross coupling reaction was optimized with ethanol, water (polar protic) (Table 5, Entries 1,11) no desired product was found. But for nonpolar protic solvent toluene product contribution was 69% (Table 5, Entry 10). However, the percentage yield of cross-coupling reaction product was moderately good for DMF, DMSO, anisole (polar aprotic) (Table 5, Entries 2,12,13). Afterwards a satisfactory result was obtained where anisole was used as a solvent. The maximum yield 96% (Table 5, Entry 3) was obtained for polar aprotic solvent anisole keeping the other optimized parameter same.

As base also acts a reasonable role in the model reaction has endured a variety of organic and inorganic bases (Table 5, Entries 1-14). The result of optimizing base parameter indicates that bases of inorganic origin like K_2CO_3, Cs_2CO_3, K_3PO_4 provide a better result than organic bases like Et_3N. The excellent report was inferred for K_2CO_3 base while the reaction was executed under 15 mg of Pd catalyst and 65 psi of CO pressure. But temperature has an effect on reaction condition when other conditions are optimized. When sample reaction temperature was reached to its upper limit 90 °C excellent yield of product (Table 5, Entry 3) but extending this temperature to 100 °C lower the yield of carbonylative product. So, it is concluded that to achieve a marvelous result in terms of % of yield a base K_2CO_3, solvent anisole and heating under 90 °C temperature is necessary with other optimized parameter.

Effect of time on diphenyl ketone synthesis

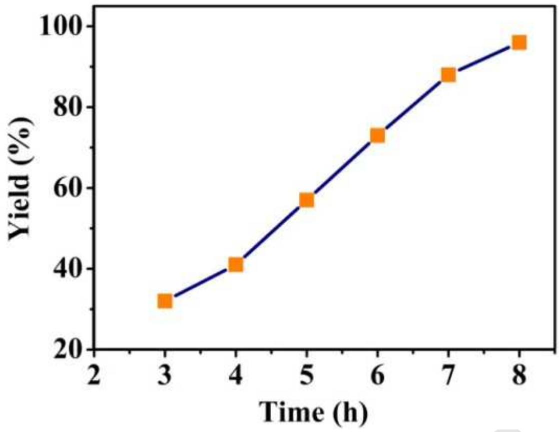


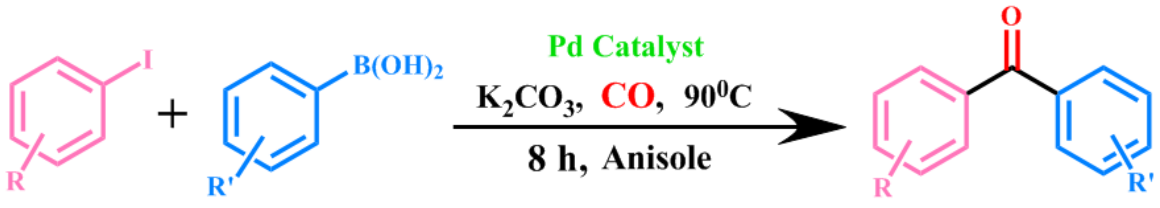
Fig. 11 Effect of time on carbonylative Suzuki-Miyaura reaction catalysed by polystyrene supported Pd catalyst. Reaction condition: Iodobenzene (1 mmol), phenylboronic acid (1 mmol), K_2CO_3 (3 equiv.), anisole (5 mL), P_{CO}=65 psi, temperature (90 °C), catalyst (15 mg, 0.01 mmol based on Pd active centre).

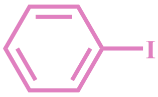
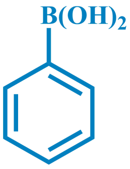
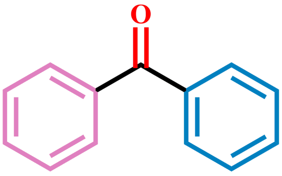
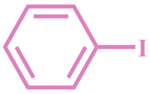
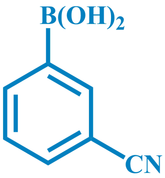
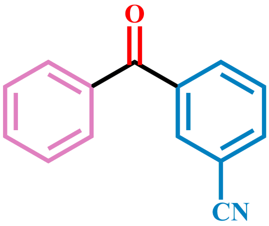
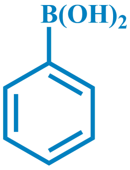
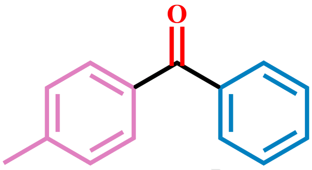
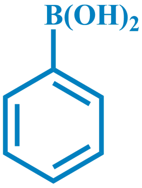
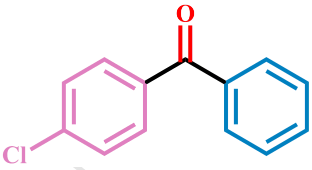
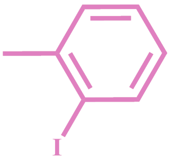
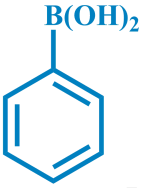
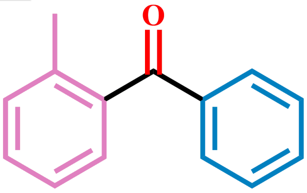
After accomplishment of optimized CO pressure and amount of catalyst now investigate about the effect of time in the model reaction (Fig. 11). The elevation in reaction period from 3 h to 8 h results constant increase of yield of carbonylative product from 36% to 96%. A moderate yield 73% obtained when the reaction time was 6 h. Maximum yield obtained when the same was performed with 15 mg of catalyst, 80 psi of CO pressure, 90 °C temperature and surely 8 h certain reaction time.

Synthesis of diaryl ketone by carbonylative Suzuki-Miyaura reaction

The scope of S-M cross-coupling reaction was investigated by using aryl boronic acids and an extensive class of aryl iodides as starting materials.

Table 6. Carbonylative S-M cross-coupling reaction of aryl iodide with aryl boronic acid catalyzed by polymer anchored Schiff base-palladium catalyst[a]

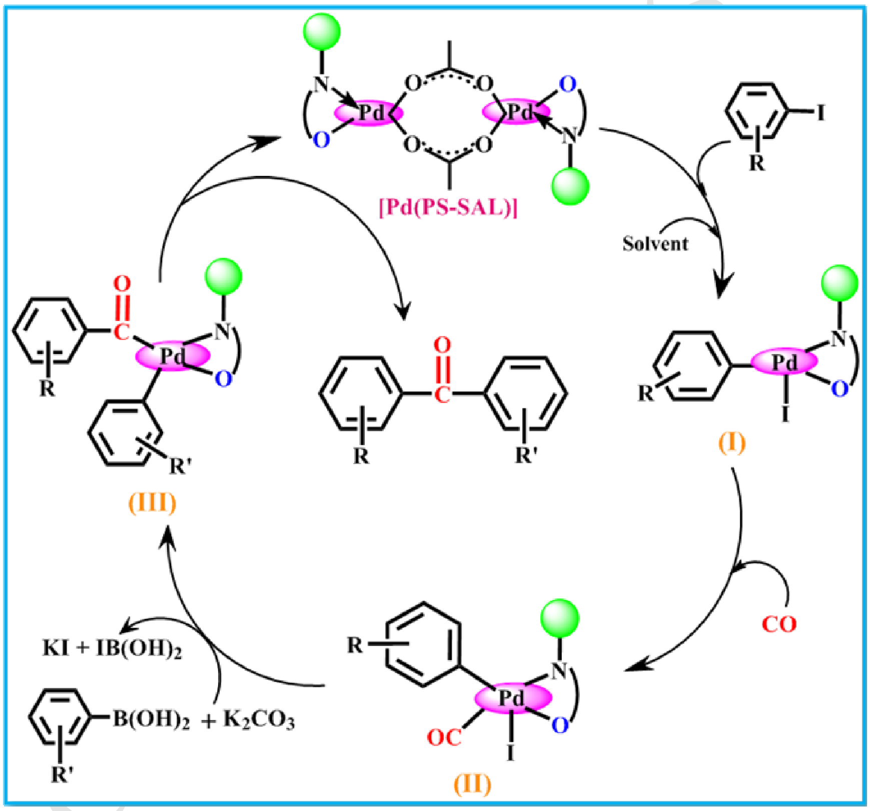


Entry	Aryl iodide	Aryl boronic acid	Product	Conv. (%)^b	Yield (%)^c	TOF (h^{-1})
1.				98	96	12.25
2.				93	87	11.62
3.				95	94	11.87
4.				96	93	12
5.				75	73	9.38

[a] Reaction condition: aryl iodide (1 mmol), aryl boronic acid (1 mmol), K_2CO_3 (3 equiv.), anisole (5 mL), P_{CO}=65 psi ,temperature (90 ^oC), time (8 h), catalyst (15 mg, 0.01 mmol based on Pd active centre). [b] GC conversion. [c] Isolated yield.

With established optimization conditions we expand the cross-coupling with various aryl boronic acid and aryl iodide (Table 6) in the presence of CO have been expanded. Both aryl boronic acids and aryl iodides containing electron releasing and attracting groups are efficiently employed for carbonylative cross-coupling reaction with polystyrene supported Pd catalyst having moderate to excellent yield 73-96%. Phenyl boronic acid without any substituted group is finely tolerated and provide corresponding carbonylative product as maximum yield with 96% and the % conversion is also excellent. Likewise, 4-chloro substituted iodide provide almost 93% yield efficiently with polymer supported palladium catalyst. Iodide containing para substitution having electron releasing -CH_3 group in phenyl ring affording corresponding product yield 94% whereas ortho substituted product give only 73% of yield with relatively low conversion. This low yield happen due to bulky nature of -CH_3 group which may creat steric hinderance. Relatively low yield (87%) of isolated product was obtained for the corresponding reaction of iodobenzene and 3-cyanophenylboronic acid with palladium catalyst.

Mechanism of carbonylative S-M cross-coupling reaction in presence of heterogeneous palladium catalyst



Scheme 5. Plausible mechanism for the carbonylative S-M cross-coupling reaction catalyzed by polymer anchored Schiff base-palladium complex.

The possible mechanistic pathway for cross coupling suggests the catalytically active Pd(PS-SAL) species coordinates to the π-system in the electrophile, followed by the migration of Pd metal to an initially possible species (I). The next step in the carbonylation reaction is the coordination of CO to palladium leading to an intermediate (II) (Scheme 5) followed by the migration of organyl group to the CO carbon that creates an acylpalladium complex (III) [44].

The aryl iodide undergoes oxidative addition to the Pd center to form the aryl palladium intermediate (I). The inserted CO molecule coordinates with the aryl palladium species and later an internal migration process leads to the formation of acyl palladium species. The arylboronic acid undergoes transmetallation with the Pd center in the existence of K_2CO_3 to give PhCO-Pd-Ph species. The subsequent transmetallation between $PhB(OH)_2$ and PhCO-Pd-L offering the PhCO-Pd-Ph molecule, which immediately experiences an elimination to generate the diaryl ketone exclusively accompanied by the release of Pd(PS-SAL) catalyst [45,46].

The step following insertion in carbonylative cross-coupling is defined as transmetallation (Scheme 5) and transports the organonucleophile to the Pd center. Attack of base (here K_2CO_3) to aryl boronic acid followed by -Ph group migration delivers the intermediate (III) which undergoes the reductive elimination, to produce the ultimate unsymmetrical diaryl ketones by regenerating the Pd-catalyst (Scheme 5) [47-49].

Heterogeneity test

Heterogeneity test was performed to prove whether Pd(PS-SAL) truly act as heterogeneous or not in carbonylation reaction of nitrobenzene and benzylamine as a model reaction. The reaction was conceded for 4 h firstly then the catalyst was removed. The yield of 1-benzyl-3-phenylurea was 57%. The reaction was performed for another 2 h in absence of catalyst but there was no satisfactory enhancement in the yield of product (Fig. 12).

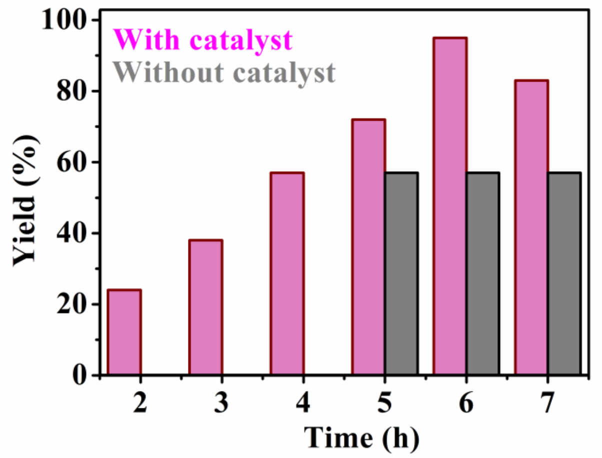


Fig. 12 Heterogeneity test of polymer supported schiff base-Pd catalyst.

The yield of product remains same. The reaction mixture was passed through a filter which upon AAS analyses of the liquid phase confirmed the absence of Pd. These inferred that Pd is not being leached out from the Pd(PS-SAL) catalyst throughout the reaction. Moreover, when a blank reaction (absent of catalyst) was performed no yield of corresponding 1-benzyl-3-phenylurea observed. This outcome suggested the catalytic character of Pd is midpoint in this carbonylation reaction and was heterogeneous in nature.

Recyclability of catalyst

Heterogeneous catalyst has an important character shown through its recyclability and stability. It is pertinent to remove the separation problems and disadvantages through the immobilization via covalent bond with the support to make it heterogeneous. The system becomes more convenient, lucrative over the commonly used incorporation process in terms of diminishing catalyst leaching and next to enhancing stability of Pd-catalyst. The leaching of Pd metal in each run has been given in the following Table 7 indicating that very small amount (almost negligible) of palladium metal was leached out even after 5 times reaction.

Table 7. Leaching studies of the recycled catalyst in each cycle

Entry		No. of cycles	Palladium leaching (ppm)	
			Diaryl urea synthesis	Diaryl ketone synthesis
1.	**Pd(PS-SAL) Catalyst**	1	-	-
2.		2	0.001	0.002
3.		3	0.002	0.003
4.		4	0.006	0.013
5.		5	0.011	0.021

The catalyst Pd(PS-SAL) retains its activity almost intact after recycle and can be easily separated by washing with methanol and dried at 60 ^{o}C for 4 h. In accordance with the optimized reaction conditions both carbonylative urea preparations and cross-coupling reactions were investigated with the recycled catalyst. The heterogeneous catalyst was reused up to 5 times to detect catalyst stability in the optimized reaction condition (Fig. 13). There was no considerable change in yield of 1-benzyl-3-phenylurea which indicated the catalytic activity of catalyst remained constant and steady for repetitive use. The catalyst remains intact after five times recycling which evidenced by SEM, TEM and FTIR analysis (supporting information).

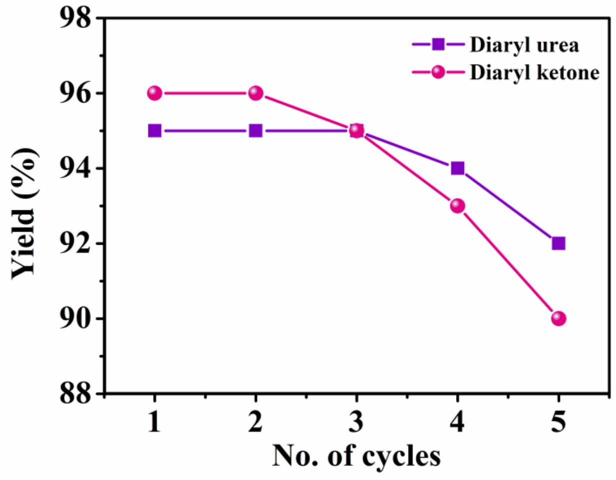


Fig. 13 Recycling efficiency of polystyrene anchored palladium catalyst for both carbonylative diaryl urea and S-M coupling reaction. [Diaryl Urea=1-benzyl-3-phenylurea; Diaryl ketone = benzophenone]

Evaluation of catalytic efficiency of polymer attached palladium catalyst with the former reported systems

Table 8 corresponds to an evaluation of efficiency for the synthesized catalyst with the other established catalyst performed in the present reactions. The following table exhibits that the current developed polymer anchored Pd-catalyst is more fascinating and well competent one than the previous well-known catalyst for the above reactions.

Table 8. Comparision with different catalyst for both diaryl urea and diphenyl ketone synthesis

Reaction	Reported catalyst	Reaction condition	Yield (%)	Ref.
Diaryl urea synthesis	$PdCl_2$ or $PdCl_2(Py)_2/Fe/I_2$	Aniline (54 mM), ethanol (20 mL), catalyst = 0.056/1,2/0,04 mmol, 100 ^oC, 3.6 MPa CO, 0.6 MPa O_2, 60 min.	74	[50]
	$[Ru(PSimd)(CO)_2Cl_2]$	Nitrobenzene (10 mM), amines (20 mM), catalyst = 1.0×10^{-2} mmol, CO (60 atm), $FeCl_3$ (20 mM), methanol (20 mL), 120 ^oC, 5 h.	92	[51]
	$PdCl_2/Fe/I_2/Py$	Aniline (53 mM), P(CO) = 40 bar, Nb (27 mM), catalyst = 1/52/2.3/37 molar ratio, chlorobenzene (20 mL), 180 ^oC, 60 min.	42	[52]
	Pd(PS-SAL)	**Nitrobenzene (3 mM), aniline (6 mM), catalyst = 20 mg, $FeCl_3$ (2.5 mM), DMF (6 mL), MeOH (6 mL), 75 ^oC, 6 h, 80 psi CO pressure**	**90**	**This Study**
Diphenyl ketone synthesis	PS-Pd-NHC	Phenyl iodide (1 mM), phenyl boronic acid (1.2 mM), catalyst = 14.5 μmol K_2CO_3 (3 mM), toluene (10 mL), temp.= 100 ^oC, P(CO) = 100 psi, time = 10 h.	94	[53]
	Pd/C	Phenyl iodide (1 mM), phenyl boronic acid (1.2 mM), 10% Pd/C (2 mol %), CO (200 psi), K_2CO_3 (3 mM), anisole (10 mL), temp.= 100 ^oC, time = 8 h	90	[54]
	P(DVB-NDIIL)-Pd	Phenyl iodide (1 mM), phenyl boronic acid (1.4 mM), catalyst = 1.0 mol%, K_2CO_3 (3 mM), toluene (10 mL), 120 ^oC, 12 h, 30 bar CO	85	[55]

	Pd(PS-SAL)	**Phenyl iodide (1 mM), K_2CO_3 (3 equiv.), phenyl boronic acid (1 mM), catalyst = 15 mg, anisole (5 mL), P_{CO} = 65 psi, 90 ^oC, 8 h.**	**96**	**This Study**

Conclusions

In summary, the present system offers the highly efficient Pd(PS-SAL) catalyzed carbonylative diaryl urea and Suzuki-Miyaura cross coupling reaction by using CO to synthesize diaryl urea and biaryl ketones, respectively. The synthetic chemists are concerned about the development of innovative production methods from alternative and versatile resources having C1 chemical building block such as CO. Selective coupling of CO still have been throwing a serious challenge to the research scientists. The catalyst Pd(PS-SAL) has been found efficient and successful candidate for diaryl urea and biaryl ketone synthesis with extensive conversion and higher yield. It is remarkable to discuss that Pd(PS-SAL) could be used for five reaction cycles without any reduction in the catalytic efficiency. The carbonylated products were achieved in adequate yields in all cycles without too much alter in morphology of catalyst. The S-M carbonylation reaction procedure using CO tolerates different substituent on both coupling partners. The present methodology contributes mild conditions: 80 psi CO pressure and 75 ^oC temperature with a tolerance of different type of substituted groups in the starting amines for diaryl urea synthesis. Production of biaryl ketones form iodobenzenes and phenyl boronic acids at 65 psi CO pressure and 90 ^oC temperature enhances the universal acceptance of the catalytic system. Simultaneously, this work will propagate the researchers to develop new strategies for conversion to C1 chemicals or even higher chemicals.

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Research Highlights

Synthesis and architecture of polystyrene-supported Schiff base-Palladium complex: Catalytic features and functions in diaryl urea preparation in conjunction with Suzuki-Miyaura cross-coupling reaction by reductive carbonylation

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- Polymer anchored Pd(PS-SAL) catalyst uniquely synthesized for impending functioning in carbonylation.
- Pd(PS-SAL) catalyzes diaryl urea and diaryl ketone synthesis without stringent conditions.
- Diaryl urea compounds have miscellaneous bioactivities and medicinal applications.
- Diaryl ketones widely used as natural products, cosmetics, pharmaceuticals and biosynthetic precursors.
- Polymer embedded heterogeneous catalyst is reusable up to five reaction cycles.