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PAPER
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The role of atropisomers on the photo-reactivity and fatigue of diarylethene-based metal–organic frameworks

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Polymer incarcerated Palladium catalyzed facile *in situ* carbonylation for the synthesis of aryl aldehydes and diaryl ketones using CO surrogates at ambient conditions

Tusar Kanto Dey[a], Priyanka Basu[a‡], Sk Riyajuddin[b‡], Aniruddha Ghosh[a‡], Kaushik Ghosh[b], and Sk. Manirul Islam[a*]

Abstract

In this existing work an efficient polymer supported palladium catalyst furfurylamine functionalized Merrifield complex of palladium, [Pd@(Merf-FA)] is synthesized and characterized, which showed excellent catalytic activity towards in situ carbonylation reactions using carbon monoxide surrogates like formic acid and chloroform. Here, we examined catalytic activity of Pd@(Merf-FA) catalyst for the formylation of aryl iodides and cabonylative Suzuki-Miyaura coupling reactions. Pd@(Merf-FA) catalyst was systematically characterized by several techniques like HRTEM, elemental mapping, PXRD, TGA-DTA, FESEM, UV-Vis, EDAX, CHN and AAS analysis. The catalyst is highly recyclable up to six times without showing any significant decrease in catalytic activity. The [Pd@(Merf-FA)] catalyst was proved more efficient compared to the corresponding homomogeneous palladium catalyst. In addition the leaching experiment of the synthesized catalyst is studied which showed that leaching of metal is very low from polymeric support.

Introduction

Carbon monoxide is a well known molecule since its immense potential for construction of C1 building units throughout synthesizing valuable organic compounds. In practical sense, treatment of CO gas for laboratory research purpose is not only challenging but also hazardous experience due to its poisonous nature. In fact CO is considered to be the most air polluting gas and its regular exposure can cause severe damage to the ecosystem. By taking into account these facts; researchers have developed some innovative strategies to save our environment from the hazardous effects of carbon monoxide. Modern era is now dealing with the well accepted in situ carbonylation pathway by utilizing CO as C1 building blocks.[1] In this context several CO molecule sources like metal carbonyl complexes[2], oxalyl chloride[3], formylsaccharin[4] etc are being widely used in commercial purpose. Remarkably these CO sources are not only sufficient to perform the carbonylation reaction but also they are inexpensive, nontoxic, and green sources of CO incorporation.

Preparation of aromatic aldehydes through in situ carbonylation process has drawn our attention from the perspective of green methodology. Aromatic aldehydes are susceptible to form bio active molecules accordingly, they are very important chemical intermediates in industry as well as in research laboratories[5], synthesizing artificial flavors, artificial sweetening agent, and pesticides[6] etc. Several methods are being used for the synthesis of aromatic aldehydes since its development in preparation method. Conventional methodologies involved acylation of aromatic ring concerned with two mechanistic pathways. Out of which, one pathway involves C-C bond construction and then oxidation is performed. For example Casiraghi reaction[7] and Duff reaction[8] follows this type of mechanism. Another approach for aromatic aldehyde synthesis involves the direct insertion of formyl group. Gattermann-Koch and Reimer-Tiemann reactions[9] follow the latter mechanistic pathway. Aromatic aldehydes could also be prepared by the oxidation of benzyl alcohols, but the main obstruction in this reaction is the necessity of harsh conditions. Nevertheless, in situ carbonylation of aromatic halides leads to the formation of aromatic aldehyde. This methodology is relatively more acceptable due to green reaction conditions than any other processes.

At a glance the synthesis of diaryl ketones and heteroaryl ketones have drawn extensive interest in industry because of their recent applications in synthetic organic chemistry. They are widely used in the synthesis of biologically active compounds, pharmaceutical compounds, building blocks of many natural products, cosmetics etc.[10] Generally diaryl ketones can be synthesized by Friedel-Crafts acylation with acyl halides.[11] But this methodology has several limitations *e.g.* it is not consistent with numerous functional groups and the regio selectivity restricted to para position etc. Suzuki et al. first established a synthetic pathway for the production of diaryl ketones using a combination of CO, aryl halide and aryl boronic acid using Pd-catalyst in 1993.[12] Successive works on Pd catalyzed carbonylative S-M coupling reaction have been reported by many research groups.[13] But earlier reports have many limitations such as expensive catalyst, high CO pressure, drastic reaction conditions, generation of large amount of byproducts, separation problems etc. In this condition in situ source of CO is the alternative choice to overcome this problem. In a different green and economically cheap method, relatively non toxic $CHCl_3$ can be used as a CO source in presence of a base like KOH to synthesize of diaryl ketone.

Palladium metal is widely accepted in the field of catalysis due to its versatile uses in many organic reactions. It can be easily grafted, embedded and/or incorporated as nanoparticle or as in ionic state

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into different polymeric matrix. Earlier many research groups have reported different palladium catalyzed reactions like Suzuki reactions, Heck reactions, Sonogashira reactions, Ullmann reactions.[14] Palladium catalysts are very effective in both the synthesis of aromatic aldehydes and diaryl ketones.[13b,15] Many of the reported catalysts are very expensive and few of them are non reusable because of the homogeneous in nature. In accordance with the fact the designing of a new heterogeneous, non toxic, reusable catalyst is very convenient to perform the carbonylative reactions using CO surrogates. Polymer supports are very well-known for heterogeneous catalysis because of its superior reusability and strong binding ability.[16] There are many earlier reports on palladium embedded Merrifield resin.[17] But low binding ability, less stability, high production cost limits their applications in large scale industrial process. Consequently in this work we have attempted to expand a cost effective, thermally stable Merrifield resin supported palladium catalyst for the synthesis of some valuable organic products. An easy synthetic route of our reported catalyst makes it widely acceptable in industry as well as in research laboratories than previous developed methods. The current article reports the synthesis of polymer supported palladium catalyst for the production of aryl aldehydes and diaryl ketones by in situ carbonylation. The proposed pathways are convenient, green and economically cheap than any other reported systems previously.

Experimental

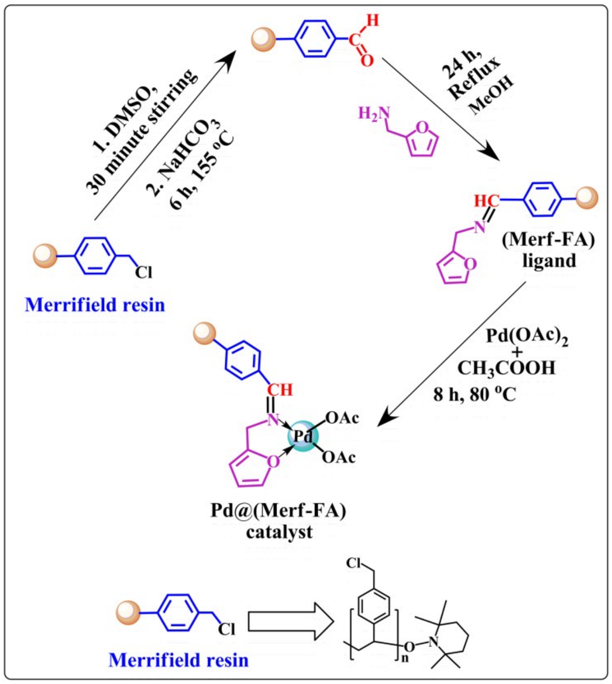
Materials and reagents

Merrifield with 5% crosslink, furfurylamine, and palladium acetate were purchased from Sigma-Aldrich, India. The required solvents and other lab reagents were obtained from Merck, India and used as received. Aryl iodides, boronic acids etc were purchased from Sigma-Aldrich, India.

Synthesis of Pd@(Merf-FA) catalyst

The schematic diagram for the synthesis of polymeric furfurylamine functionalized Merrifield complex of palladium Pd@(Merf-FA) catalyst is represented in Scheme 1.

At first Merrifield (1 g) was added in 15 ml DMSO under constant stirring for 30 minutes, and then 0.425 g of $NaHCO_3$ was added. The resultant reaction mixture was refluxed at 155 ^oC temperature for 6 hour. After that it was cooled to room temperature, filtered under suction pump with a Buchner funnel, and finally washed with a mixture of dioxane to water in 2:1 ratio for 3 times. Finally it was again washed with ethanol, dried under vacuum. Then 1 g of -CHO functionalized polymer was swelled in 30 mL methanol for 30 minutes and then 0.5 g of furfurylamine was introduced in the reaction mixture. It was refluxed for 24 hour under inert conditions. The resultant product was filtered out and denoted as furfurylamine functionalized Merrifield ligand (Merf-FA). 0.05 g palladium acetate was dissolved in 10 mL acetic acid and then 0.5 g of Merf-FA was introduced. The resultant mixture was refluxed for 8 hour under 80 ^oC temperature with constant stirring. Then it was filtered out, washed several times by hot methanol and the resulting furfurylamine functionalized Merrifield complex of palladium [Pd@(Merf-FA)] was obtained.



Scheme 1 Synthesis of furfurylamine functionalized Merrifield complex of palladium, Pd@(Merf-FA).

General procedure for the synthesis of aryl aldehydes from aryl iodides

3 mL of toluene was taken in a screw cap reaction tube and tiphenylphosphine (1.95 mmol), iodine (1.8 mmol), were introduced in it. The reaction mixture was stirred by a magnetic stirrer for 8 minutes at room temperature. Then 1.5 mL of DCM was purged in it. After it aryl iodide (1.5 mmol), triethylamine (10 mmol), and 25 mg of Pd@(Merf-FA) catalyst were introduced in this tube. It was again stirred for another 5 minutes under room temperature. Finally formic acid (10 mmol) was added drop wise in the reaction mixture and the tube was sealed tightly by its screw cap. The reaction was continued for 90 minutes under 70 ^oC temperature with vigorous stirring conditions. After completion of the reaction it was cooled to room temperature and extracted with ethyl acetate and water. Column chromatography was performed to get pure products and confirmed by analyzing ^{1}HNMR spectroscopy and FTIR spectroscopy.

General procedure for the synthesis of aryl benzophenone from aryl iodides

In a screw capped 25 mL reaction vessel 5 mL of toluene was introduced and then aryl iodide (1.5 mmol) and aryl boronic acid (2 mmol) were added. Then KOH (8 mmol) and $CHCl_3$ (4 mmol) were introduced on the same reaction vessel. After that, 27 mg of Pd@(Merf-FA) catalyst was added and the cap of the vessel was closed tightly. The reaction vessel was heated at 60 ^oC in an oil bath and the reaction was continued for 8h. After completion of the reaction it was cooled to room temperature and extracted by ethyl acetate and water for three times. Column chromatography was performed to get the pure products and analyzed by ^{1}HNMR spectroscopy and FTIR spectroscopy.

Results and discussion

Characterization:

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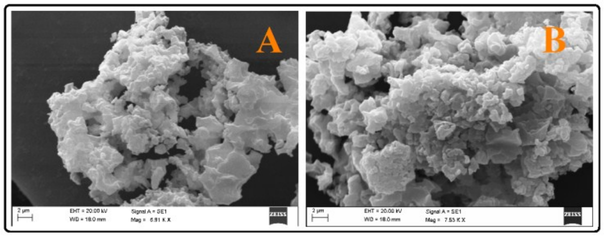

Fig. 1 FE-SEM image of (A) Merf-FA ligand, (B) Pd@(Merf-FA) catalyst.

The morphological study of the synthesized Merf-FA, and Pd@(Merf-FA) polymeric materials were recorded by field emission scanning electron microscopy (model no. ZEISS EVO40, England) attached with EDAX facility and represented in Fig. 1. From Fig. 1A it is apparent to mention that furfurylamine functionalized Merrifield polymeric complex acquires sheet type structure. A good aggregation of polymeric complex was also observed in this image. After loading of palladium salt on Merf-FA ligand, slightly rough surface was observed but sheet like structure predominates in Fig. 1B. Actually SEM analysis only provides information about the surface morphology of the material only, further loading of palladium was confirmed by EDAX facility associated with SEM instrument.

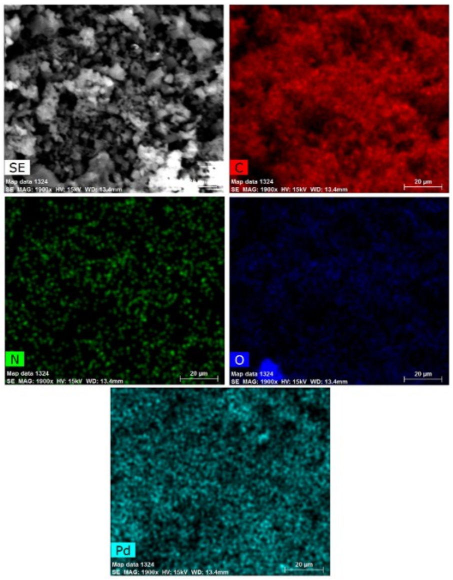

Fig. 2 Elemental mapping of Pd@(Merf-FA) catalyst.

The elemental mapping of synthesized Pd@(Merf-FA) catalyst has been also carried out to obtain a preliminary idea about the composition of different elements present in the synthesized material. The mapping image is represented in Fig. 2. The study of the elemental image concludes that the concentration of oxygen is higher than nitrogen. Besides that the image exhibits a good loading of palladium throughout the surface of polymeric ligand.

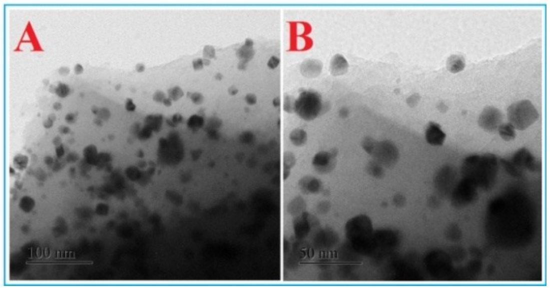

Fig. 3 HRTEM image of Pd@(Merf-FA) catalyst at different magnification (A and B).

High resolution TEM images of synthesized Pd@(Merf-FA) was also carried out to visualize the morphology of Pd@(Merf-FA) catalyst more specifically. The HRTEM images are represented in Fig. 3 and the images are taken in two different magnifications. The morphology of these specimens exhibits that a number of black spots are spread over the whole polymeric surface. This black spot confirms the attachment of Pd in the polymer supported ligand.[13d] Greyish area appears beyond the black spot is due to the Merrifield polymeric support.

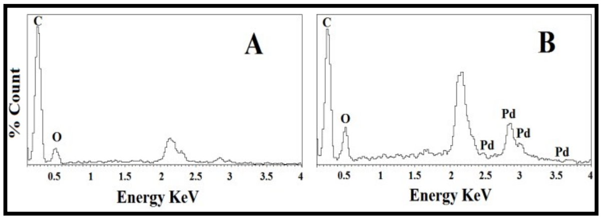

Fig. 4 EDAX spectrum of (A) Merf-FA ligand, (B) Pd@(Merf-FA) catalyst.

EDAX analysis was additionally carried out for both of Merf-FA ligand and Pd@(Merf-FA) catalyst to confirm successful loading of palladium with the polymeric support. From Fig. 4B it is clear that palladium ion has successfully bound with Merf-FA polymeric complex as palladium observed on that figure but not on Fig. 4A. Other elements were also represented on both the Fig. A and B. So, it is another confirmatory analysis indicating the formation of palladium catalyst.

Table 1 Elemental analysis

Compound	C^a %	H^a %	N^a %	Pd^b %
Merf-FA	79.26	5.59	7.78	-
Pd@(Merf-FA)	72.38	5.72	6.23	5.74

[a] Conducted by CHN analysis; [b] Conducted by AAS analysis

Chemical composition analysis of synthesized Merf-FA (polymeric ligand support) and Pd@(Merf-FA) catalyst were conducted to find out the composition of different elements present in our synthesized material. The percentage of carbon, hydrogen and nitrogen were calculated with the help of CHN analyzer and the percentage of palladium content was confirmed by AAS study. The results are represented in Table 1. AAS study shows that the palladium content of synthesized Pd@(Merf-FA) catalyst is 5.74 %. The result obtained from AAS analysis suggests that good loading of palladium occurred in the surface of polymeric support.

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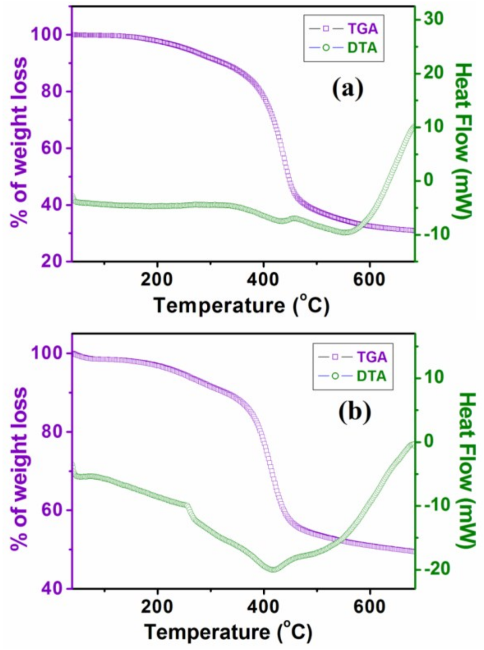

Fig. 5 TGA/DTA plot of (a) Merf-FA ligand and (b) Pd@(Merf-FA) catalyst.

Thermal stability of the synthesized Pd@(Merf-FA) was measured by Mettler Toledo TGA/DTA 851 instrument. It is an essential tool for characterization of polymeric materials to know about the thermal stability of the synthesized material (Fig. 5). TGA analysis was carried out for Merf-FA ligand and Pd@(Merf-FA) catalyst under nitrogen atmosphere with constant heating rate of 10 ^{o}C/minute ranging from 30 ^{o}C-700 ^{o}C temperature. For Merf-FA weight loss occurred in the range of 320 ^{o}C to 465 ^{o}C due to decomposition of the components present in the polymeric material. Where the weight loss for Pd@(Merf-FA) occurred in the range of 345 ^{o}C-455 ^{o}C. So our synthesized Pd@(Merf-FA) polymeric catalyst is thermally stable up to 345 ^{o}C.

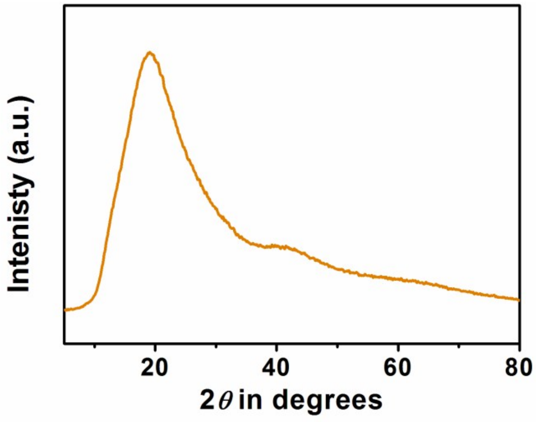

Fig. 6 Wide angle PXRD pattern of functionalized polymeric ligand Merf-FA.

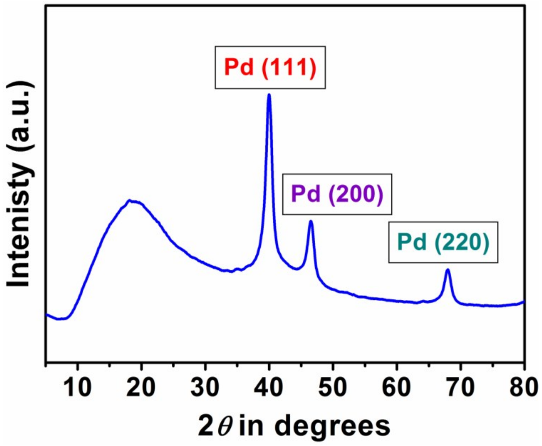

Fig. 7 Wide angle PXRD pattern of Pd@(Merf-FA) catalyst.

The wide angle PXRD pattern of functionalized polymeric ligand Merf-FA and polymeric catalyst Pd@(Merf-FA) were recorded in the range of $10 \leq 2\theta \leq 80$ and represented in Fig. 6 and Fig. 7. A broad intense peak was observed at the 2θ angles between 18-19^{o} in both of the Merf-FA and Pd@(Merf-FA) which corresponds to existence of the polymeric nature in the Merf-FA and Pd@(Merf-FA). At 2θ angles of 40.04, 46.47 and 67.87 degree three intense sharp peak appeared in Fig. 7 due to different plane of Pd present in Pd@(Merf-FA) catalyst. These characteristic diffraction peaks are assigned as the (111), (200), and (220) reflection planes of Pd respectively. These data is compared with other reported works to confirm the reflection planes of Pd.[18]

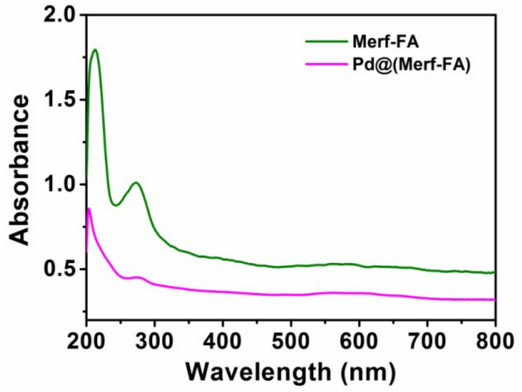

Fig. 8 UV-Vis spectra of (A) Merf-FA ligand (green color) and (B) Pd@(Merf-FA) catalyst (magenta color).

The UV-Visible reflectance spectrum of the Merrifield supported Schiff base ligand (Merf-FA) and the catalytic material Pd@(Merf-FA), have been monitored in the solid state diffuse reflectance spectrum mode using BaSO$_4$ disc. UV-Vis absorbance spectra of Merf-FA ligand reveals two broad peaks at 260 and 280 to 320 nm due to $\pi\rightarrow\pi^*$ and n–π^* transitions, respectively. The spectra reflect the appearance of broad absorbance peaks around 280 to 320 nm for both the catalyst and complex (Fig. 8). These absorption bands may be attributed to $\pi\rightarrow\pi^*$ transition in phenyl ring present both in the Schiff base ligand and its palladium complex. The absorption spectra of the ligand upon complexation with Pd metal exhibited slight alteration in the absorption bands corresponding to $\pi\rightarrow\pi^*$ and n–π^* transitions. The broad band arises at around 320-360 nm in the electronic spectrum of Pd@(Merf-FA), substantiates the

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LMCT from ligand (HOMO) to palladium (LUMO). Another broad band appears in the region 530-700 nm in the Pd@(Merf-FA) complex due to the d-d electronic transitions.

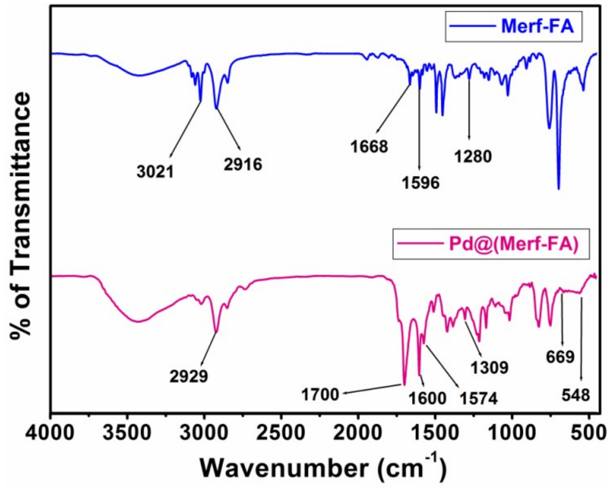


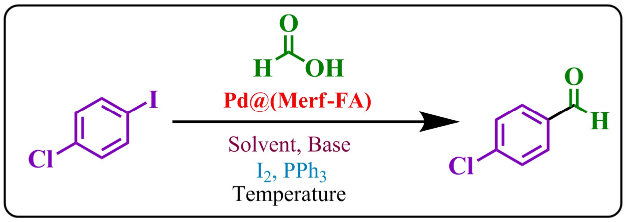
Fig. 9 FTIR spectra of (A) Merf-FA ligand (blue color) and (B) Pd@(Merf-FA) catalyst (pink colour).

FTIR spectroscopy is a supporting tool for assigning several functional groups or bonds present in Pd@(Merf-FA) catalyst. The FTIR spectroscopy was precisely examined in the range of 4000 cm^{-1} to 450 cm^{-1} using KBr pellet (Fig. 9). The wave number values indicated for both Merf-FA and Pd@(Merf-FA) represent their corresponding stretching frequencies. A sharp medium band at 3021 cm^{-1} appeared in Merf-FA due to the aromatic C-H stretching vibration mode. Aromatic C=C stretching frequency is observed in case of Merf-FA and Pd@(Merf-FA) at 1668 and 1700 cm^{-1} respectively. At 2916 and 2929 cm^{-1} a sharp band appeared in case both of Merf-FA and Pd@(Merf-FA) respectively due to the stretching vibration of =C-H bond. Presence of C=N functional group in the synthesized ligand and catalyst is confirmed due to the appearance of a peak at 1596 and 1600 cm^{-1}. C-O bond stretching frequency of the furfuryl ring was found at 1280 and 1309 cm^{-1} respectively for both the polymeric ligand and catalyst. A small band appeared at 669 cm^{-1} is assigned for the Pd-N bond present in the Pd@(Merf-FA) catalyst. In addition, Pd-O stretching vibration was observed in Pd@(Merf-FA) catalyst at 548 cm^{-1}.

Catalytic activity

In situ carbonylative formylation of aryl iodides

Carbonylative formylation of aryl iodides were conducted using formic acid as C1 source in presence of Pd@(Merf-FA) catalyst. Before entering into the deep study of tolerance of different functional groups attached with iodobenzene, different parameters are checked during the course of reaction. Several parameters like effect of solvent, catalyst amount, reaction temperature, reaction time, effect of base etc are studied to establish a well defined reaction condition by conducting the reaction of 4-chloroiodobenzene with formic acid (Scheme 2).



Scheme 2 Synthesis of 4-chlorobenzaldeyde by in situ carbonylative formylation of 4-chloroiodobenzene.

Table 2 Effect of solvent and co-solvent on in situ 4-chlorobenzaldehyde synthesis[a]

Entry	Solvent	Co-solvent	Ratio	Yield (%)[b]
1.	DMF	DCM	1:1	56
2.	THF	DCM	1:1	60
3.	Acetonitrile	DMF	1:1	63
4.	Toluene	DMF	1:1	85
5.	Toluene	DCM	1:1	92
6.	**Toluene**	**DCM**	**2:1**	**98**
7.	Toluene	DCM	1:2	86
8.	Toluene	-	-	81
9.	DCM	-	-	78

[a]Reaction Conditions: 4-chloroiodobenzene (1.5 mmol), Formic acid (10 mmol), Et_3N (10 mmol), I_2 (1.8 mmol), PPh_3 (1.95 mmol), 70 °C, 25 mg of Pd@(Merf-FA) catalyst, 90 minute. [b]isolated yield.

The formylation reaction of aryl iodides was performed in the presence of a suitable solvent and co-solvent by maintaining a particular ratio. Several solvents and co-solvents were used to screen the effect of different solvents in this in situ carbonylation reaction (Table 2). DMF, DCM, acetonitrile, toluene, etc were used with different ratios and surprisingly it was observed that in 2:1 toluene and DCM (V/V) ratio best yield was obtained than any other combinations. The reason behind is that 2:1 mixture of toluene and DCM maintains a particular polarity of the reaction medium and this incident facilitates the reaction to produce a high yield of the respective product and maximum conversion of the substrate occurs. When only toluene was used without addition of DCM, the yield of isolated product was decreased to 81% because toluene is an aprotic non-polar solvent, while DCM is moderately polar. This interesting result can be justified as the polarity index of solvent plays a crucial role in this carbonylative formylation reaction in presence of Pd@(Merf-FA) catalyst.

Effect of I_2/PPh_3 molar ratio

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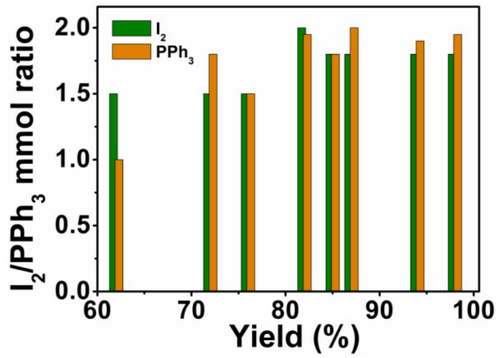

Fig. 10 Effect of I_2/PPh_3 molar ratio on formylation of 4-chloroiodobenzene. Reaction Conditions: 4-chloroiodobenzene (1.5 mmol), Formic acid (10 mmol), Et_3N (10 mmol), Toluene:DCM (3mL:1.5mL), 70 ^oC temperature, 25 mg of Pd@(Merf-FA), 90 minute.

I_2 and PPh_3 here help to generate CO from formic acid and leads to the formation of formylated products. I_2 and PPh_3 act as a trigger of this formylation or in situ carbonylation reaction. At first I_2 and PPh_3 both react with each other to form a conjugate complex which further releases CO from formic acid. So the amount of I_2 and PPh_3 would be strictly maintained. For this purpose, we had conducted a set of experiments using different amount of I_2 and PPh_3. The results are represented in Fig. 10. This result shows that when I_2 and PPh_3 are taken in 1.8 and 1.95 mmol respectively maximum yield (98%) of isolated product was observed. Further change in concentration of I_2 and PPh_3 suppresses the yield of reaction.

Table 3 Screening of different bases on in situ carbonylative formylation of 4-chloroiodobenzene[a]

Entry	Base	Amount of base (mmol)	Yield (%)[b]
1.	K_2CO_3	10	13
2.	**Et_3N**	**10**	**98**
3.	DBU	10	68
4.	DABCO	10	Trace
5.	Cs_2CO_3	10	14
6.	Et_3N	8	86
7.	Et_3N	12	98
8.	Et_3N	14	98

[a]Reaction Conditions: 4-chloroiodobenzene (1.5 mmol), Formic acid (10 mmol), I_2 (1.8 mmol), PPh_3 (1.95 mmol), Toluene:DCM (3mL: 1.5 mL), 70 ^oC, 25 mg of Pd@(Merf-FA) catalyst, 90 minute. [b]isolated yield.

In this formylation reaction of 4-chloroiodobenzene, different types of bases were screened and the results are represented in Table 3. Among them, triethylamine (Et_3N) showed maximum efficiency when it was used in 10 mmol amount than any other bases. K_2CO_3 which is commercially available almost failed in this reaction. DBU showed some better result than others, but its yield on usage is low than that of Et_3N. Lowering of Et_3N amount than 10 mmol, yield of isolated products also gets suppressed, but increasing its quantity beyond 10 mmol has no effect in the reported reaction. So, triethylamine (Et_3N) is the best choice as a base in this formylation reaction.

Effect of reaction temperature

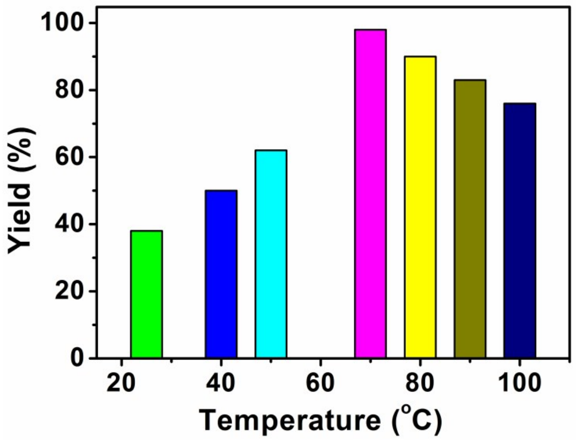

Fig. 11 Effect of reaction temperature on formylation of 4-chloroiodobenzene. Reaction Conditions: 4-chloroiodobenzene (1.5 mmol), Formic acid (10 mmol), Et_3N (10 mmol), I_2 (1.8 mmol), PPh_3 (1.95 mmol), Toluene:DCM (3mL:1.5 mL), Pd@(Merf-FA) catalyst = 25 mg, Time = 90 minute.

Pd@(Merf-FA) catalyzed synthesis of 4-chlorobenzaldehyde from 4-chloroiodobenzene by formylation reaction using formic acid, temperature plays a critical role. Because bellow and above the optimized temperature level the isolated yield was obtained in a lower amount. To find out the best optimized temperature in this reaction a set of experiments were performed varying temperature from 25 ^oC to 100 ^oC (Fig. 11). From this study, it was found that at 70 ^oC maximum yield of product obtained. After this temperature, the yield gradually decreases due to oxidation of 4-chlorobenzaldehyde to 4-chlorocarboxylic acid. Also below of 70 ^oC temperature the isolated yield of formylated product is low.

Effect of catalyst amount

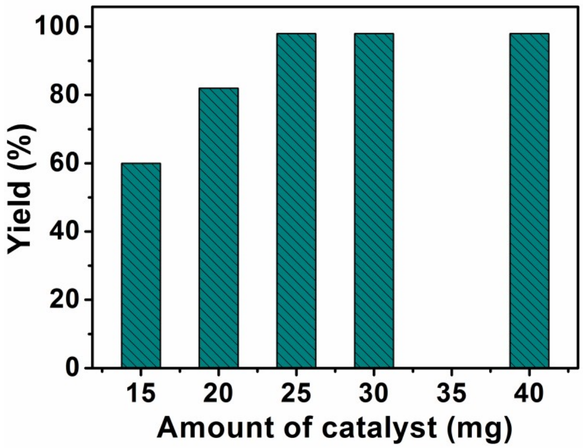

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Fig. 12 Effect of catalyst amount on formylation of 4-chloroiodobenzene. Reaction Conditions: 4-chloroiodobenzene (1.5 mmol), Formic acid (10 mmol), Et_3N (10 mmol), I_2 (1.8 mmol), PPh_3 (1.95 mmol), Toluene:DCM (3mL:1.5 mL), 70 °C temperature, time = 90 minute.

In addition to solvent and temperature effect, the role of catalyst amount was studied to achieve maximum efficiency of catalyst. An exact catalyst amount can control the complete conversion of substrates. So to study the minimum amount of catalyst that should give maximum yield, different amount of catalyst was used in a set of reactions, and the results are represented by Fig. 12. The result can be interpreted from this graph and it shows that only 25 mg of catalyst is sufficient to carry out the reaction with maximum yield. Above this value of catalyst amount, no increase in yield of product was observed and this indicates that maximum conversion of substrates takes place.

Reaction time profile diagram

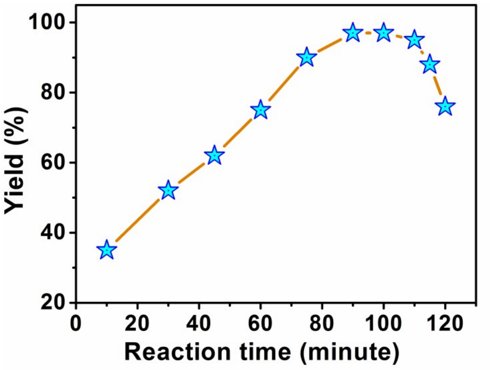
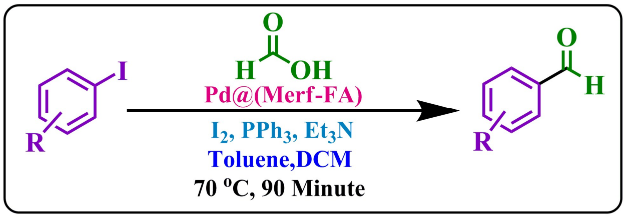
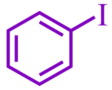
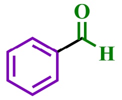
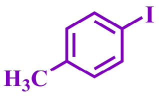
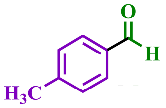
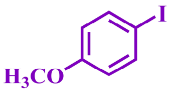
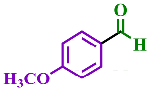
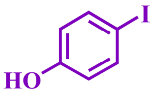
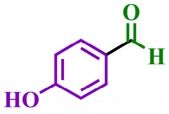
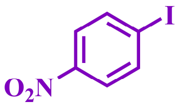
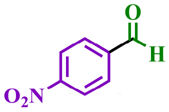
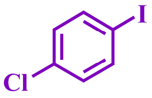
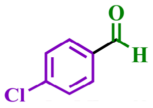
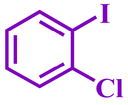
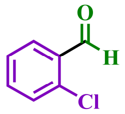
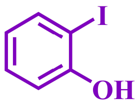
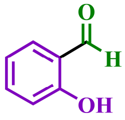
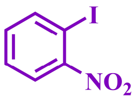
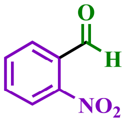
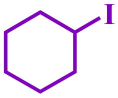
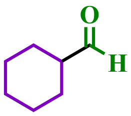
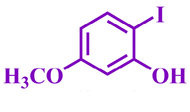
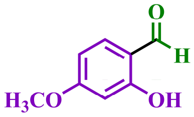


Fig. 13 Effect of reaction time on 4-chlorobenzaldehyde synthesis catalyzed by Pd@(Merf-FA). Reaction Conditions: 4-chloroiodobenzene (1.5 mmol), Formic acid (10 mmol), Et_3N (10 mmol), I_2 (1.8 mmol), PPh_3 (1.95 mmol), Toluene:DCM (3mL:1.5 mL), temperature = 70 °C, 25 mg of Pd@(Merf-FA) catalyst.

Like other parameters reaction time profile diagram was also studied for this formylation reaction because it can control the course of the reaction. The reaction time was varied from 10 to 120 minutes and the results are represented in Fig. 13. From this result, it can be concluded that when the reaction time was increased to 90 minutes from 10 minutes the yield of respective product also increases regularly. But above 90 minutes reaction time yield of the product remains unchanged up to 100 minutes and above this time limit the yield of product decreases indicating the desired product gets oxidized and converted to the respective carboxylic acid.

Table 4 Synthesis of aryl aldehydes from different aryl iodides by in situ carbonylative formylation[a]



Entry	Aryl Iodides	Product	Yield[b] (%)
1.			95
2.			91
3.			94
4.			91
5.			76
6.			98
7.			88
8.			82
9.			22
10.			89
11.			91

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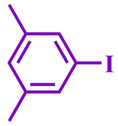
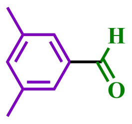
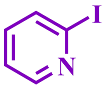
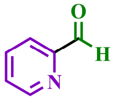
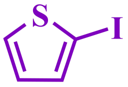
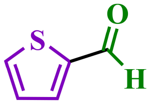
12.			83
13.			80
14.			76

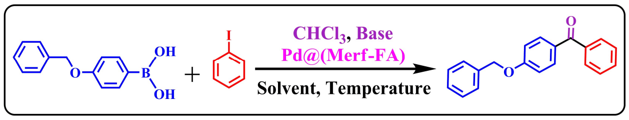
[a] Reaction Conditions: Aryl iodide (1.5 mmol), Formic acid (10 mmol), Et_3N (10 mmol), I_2 (1.8 mmol), PPh_3 (1.95 mmol), Toluene:DCM (3mL:1.5 mL), temperature = 70 ^oC, time = 90 minute, 25 mg of Pd@(Merf-FA) catalyst. [b] isolated yield.

To find out the tolerance of different functional groups present in aryl iodides for in situ carbonylative formylation reaction catalyzed by Pd@(Merf-FA) different derivatives of iodobenzene were used. Starting this reaction with iodobenzene (Table 4, Entry 1) excellent yield of respective product was observed during course of the reaction. But when +I category group was introduced in para position (Table 4, Entries 2,3) yield of the product slightly diminished. But methoxy group showed moderately higher yield than methyl group due to the presence of electron withdrawing capacity of oxygen atom in methoxy group. As nitro is a highly deactivating group, using it in para position (Table 4, Entry 5) decreases yield of the product. Also owing to its bulky nature when we used ortho substituent of nitro (Table 4, Entry 9) the yield of product was found extremely low as expected. A surprising result was found when -I category group like -OH, -Cl, etc were used in para position (Table 4, Entries 4,6). The yield of the respective products was found in a good range and chloro group showed better yield than any other functional groups. So the presence of electron donating or electron withdrawing groups does not extremely influence the course of reaction. Presence of functional groups in ortho position (Table 4, Entries 7,8,11) gives considerably low yield than para position due to the appearance of steric hindrance in some extent. Among them, 2-iodo-5-methoxyphenol (Table 4, Entry 11) offered some better yield than other ortho substituents due to the presence of +I category group in its para position. Also, nonaromatic cyclohexaldehyde (Table 4, Entry 10) showed slightly lower yield than benzaldehyde may be due to absence of ring current. When 3,5-dimethyliodobenzene (Table 4, Entry 12) was used the yield of the desired product slightly decreased than benzaldehyde. Using of the heterocyclic compounds instead of regular aryl iodides for carbonylative aldehyde synthesis, offers moderately good yield (Table 4, Entries 13,14).

In situ carbonylative Suzuki-Miyaura cross coupling reaction

Optimization of reaction conditions

Maximum efficiency of any catalyst can be achieved by selecting perfect reaction conditions, such as reaction temperature, reaction time, solvent, catalyst amount etc. The in situ carbonylative Suzuki-Miyaura cross-coupling reaction between aryl iodide and aryl boronic acid in presence of Pd@(Merf-FA) provides a maximum yield of isolated product when different controlling parameters are varied. Iodobenzene and 4-(benzyloxy)phenylboronic acid (Scheme 3) is taken as model substrate and several parameters are varied as follows.



Scheme 3 In situ carbonylation of iodobenzene and 4-(benzyloxy)phenylboronic acid by Pd@(Merf-FA) catalysis.

Table 5 Screening of solvents on synthesis of 4-benzyloxybenzophenone[a]

Entry	Solvent	Base	Yield (%)[b]
1.	H_2O	KOH	trace
2.	methanol	KOH	22
3.	DMSO	KOH	32
4.	THF	KOH	74
5.	**Toluene**	**KOH**	**97**
6.	dioxan	KOH	68
7.	DMF	KOH	36
8.	CH_3CN	KOH	29
9.	Toluene	NaOH	90
10.	Toluene	Cs_2CO_3	89
11.	Toluene	Morpholine	Trace
12.	Toluene	K_2CO_3	92

[a] Reaction Conditions: Iodobenzene (1.5 mmol), 4-(benzyloxy)phenylboronic acid (2 mmol), solvent (5 mL), $CHCl_3$:base (4 mmol:8 mmol), temperature = 60 ^oC, 27 mg of Pd@(Merf-FA) catalyst, time = 8 h. [b] isolated yield.

Carbonylative Suzuki-Miyaura coupling reaction using CO surrogates like $CHCl_3$ in presence of a base is by some means dependent on the polarity of solvent. Actually, Suzuki Miyaura cross-coupling reaction is performed in nonpolar solvents like toluene.[19] Most of the reports recommend that toluene is best solvent for this reaction. To confirm the result, a variety of solvents was tested to find out the effect of different solvents in this reaction (Table 5). Protic polar solvents like water, methanol, etc when used as reaction medium low yield of product was isolated. An interesting fact was also observed, as the polarity of solvent decreases, yield of the isolated product increases progressively. This observation leads that nonpolar aprotic solvents are best for this reaction. When we used toluene in combination of potassium hydroxide maximum yield of

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product was observed. Potassium hydroxide (KOH) acts as a perfect base which is used here to liberate CO form chloroform. Other bases like Cs_2CO_3, K_2CO_3, NaOH also provide fine results in this reaction. But organic bases *e.g.* morpholine is not a good choice of candidate because of its poor ability to liberate CO.

Effect of reaction temperature

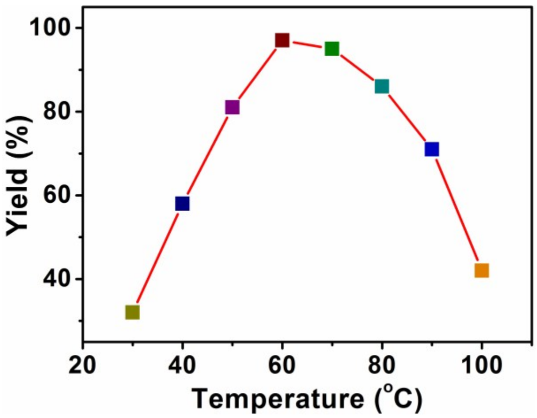

Fig. 14 Effect of reaction temperature on in situ carbonylative S-M coupling reaction. Reaction Conditions: Iodobenzene (1.5 mmol), 4-(benzyloxy)phenylboronic acid (2 mmol), toluene (5 mL), $CHCl_3$:KOH (4 mmol:8 mmol), 27 mg of Pd@(Merf-FA) catalyst, time = 8 h.

Temperature profile diagram of carbonylative S-M cross coupling was conducted by varying the temperature from room temperature to 100 ^oC and a surprising result was observed. The results are represented in Fig. 14. From this analysis, it can be concluded that on increasing the reaction temperature, the yield of product increases but after reaching optimum value i.e. after 60 ^oC the yield of the product decreases steadily. So, 60 ^oC is considered as optimal temperature for this carbonylative S-M coupling reaction and maximum yield is 97%.

Reaction time profile diagram

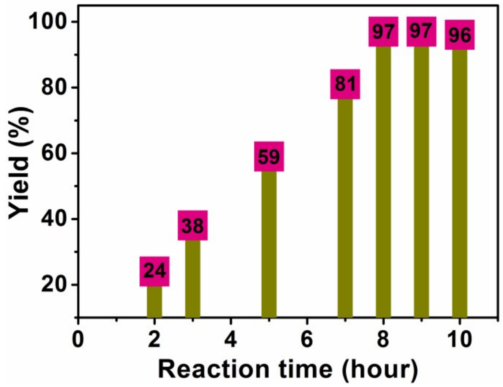

Fig. 15 Effect of reaction time on in situ carbonylative S-M coupling reaction. Reaction Conditions: Iodobenzene (1.5 mmol), 4-(benzyloxy)phenylboronic acid (2 mmol), toluene (5 mL), $CHCl_3$:KOH (4 mmol:8 mmol), temperature = 60 ^oC, Pd@(Merf-FA) catalyst = 27 mg.

Like other parameters, reaction time was also varied for this carbonylative S-M cross-coupling reaction. For this purpose yield of isolated product was observed within a time period of 2 h to 10 h. The results of this experiment are represented in Fig. 15. These results show that at start of the reaction initially the yield of product is very low. At 2 h reaction time yield of product is only 24%. But as the reaction time increases yield of products get promoted and the maximum yield of product was observed at 8 h reaction time which is 97%. After this time period, no noticeable change in yield of product was observed.

Variation of chloroform and potassium hydroxide molar ratio

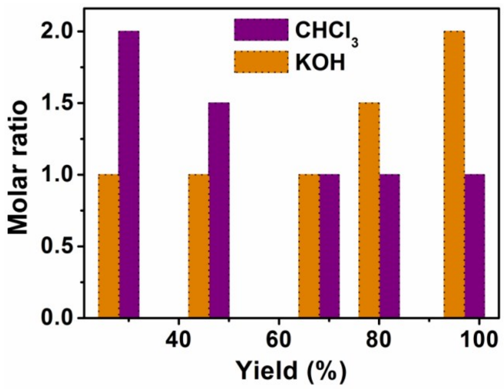

Fig. 16 Effect of $CHCl_3$ and KOH molar ratio on in situ carbonylative S-M coupling reaction. Reaction Conditions: Iodobenzene (1.5 mmol), 4-(benzyloxy)phenylboronic acid (2 mmol), toluene (5 mL), temperature = 60 ^oC, 27 mg of Pd@(Merf-FA) catalyst, time = 8 h.

Effect of $CHCl_3$/KOH molar ratio was examined for carbonylative S-M coupling reaction. In this reaction, both of $CHCl_3$ and KOH plays a major role because $CHCl_3$ acts as CO surrogate and KOH generates CO from $CHCl_3$. So a particular ratio must be maintained between them to supply the required amount of carbon monoxide also to obtain maximum yield of isolated product. We used different $CHCl_3$/KOH molar ratio to find out its role and the results are represented in Fig. 16. Maximum yield (97%) of product was found when the molar ratio is 1:2 ($CHCl_3$: KOH). When we performed this reaction using 2:1 molar ratio low yield of product was isolated. As we increased the molar amount of base i.e. KOH, and decreased the molar amount of chloroform yield of isolated products also goes on increasing. This result suggests that molar amount of chloroform should be less than that of the base because here KOH liberates CO from $CHCl_3$. In this reaction, we maintained $CHCl_3$/KOH molar ratio in 1:2.

Screening of catalyst amount

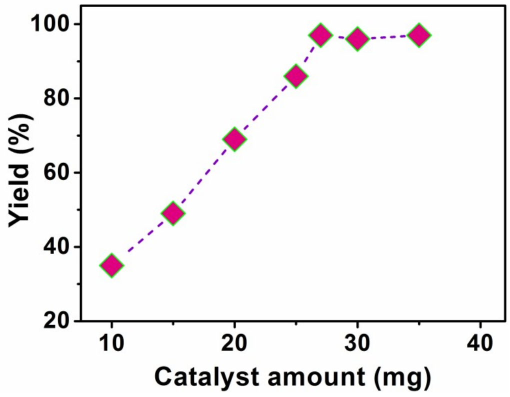

Fig. 17 Effect of catalyst amount on in situ carbonylative S-M coupling reaction. Reaction Conditions: Iodobenzene (1.5 mmol), 4-

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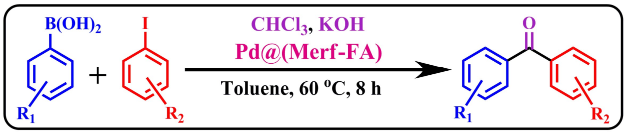
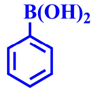
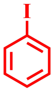
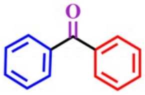
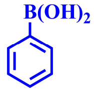
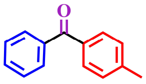
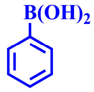
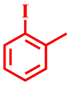
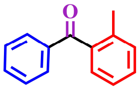
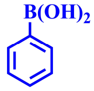
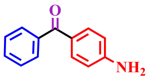
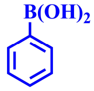
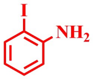
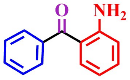
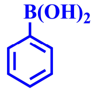
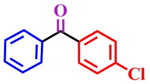
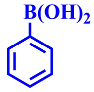
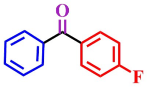
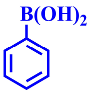
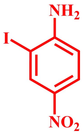
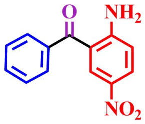
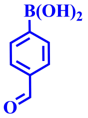
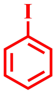
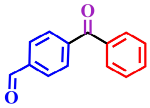
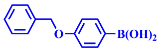
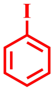
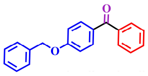
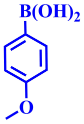
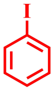
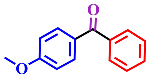
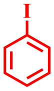
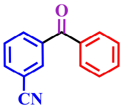
(benzyloxy)phenylboronic acid (2 mmol), toluene (5 mL), $CHCl_3$:KOH (4 mmol:8 mmol), temperature = 60 ^oC, time = 8 h.

The amount of catalyst that would require for carbonylative S-M coupling reaction was studied by using different amount of catalyst and measuring yield of isolated products. The result of this experiment is represented in Fig. 17 which shows that 27 mg of Pd@(Merf-FA) catalyst is required to get maximum yield (97%) of product. Excess catalyst amount has no effect in this reaction.

Table 6 Synthesis of carbonylative S-M coupling product from aryl iodide and boronic acid derivatives using Pd@(Merf-FA) catalyst[a]



Entry	Aryl boronic acid	Aryl iodide	Product	Yield[b] (%)
1.				92
2.				94
3.				84
4.				91
5				87
6.				90
7.				88
8.				76
9.				91
10.				97
11.				94
12.				90

[a] Reaction Conditions: Aryl iodides (1.5 mmol), aryl boronic acids (2 mmol), toluene (5 mL), $CHCl_3$:KOH (4 mmol:8 mmol), 27 mg of Pd@(Merf-FA) catalyst, temperature = 60 ^oC, time = 8 h. [b] isolated yield.

The scope of in situ carbonylative S-M coupling reaction was investigated for its industrial application by using different substrates of aryl boronic acids and aryl iodides. The reactions were performed under the optimized condition to get a maximum amount of product. At first different substrates of aryl iodides (Table 6, Entries 1-8) were used to find out the tolerance of different functional groups present in aryl iodides. It was observed that para substituted iodobenzenes (Table 6, Entries 4,6,7) except 4-methyliodobenzene offered a slightly lower yield of the respective products compared to iodobenzene. The ortho substituted iodobenzenes (Table 6, Entries 3,5) gave quite lower yield than iodobenzene owing to the presence of steric hindrance between the carbonyl group and the ortho functional group. Vastly ring deactivating nitro group present in case of aryl iodides (Table 6, Entry 8) decreases yield of the desired product. Electron donating groups (Table 6, Entries 2,4) and electron withdrawing groups (Table 6, Entries 6,7) present in para position of aryl iodide has no significant effect on the reaction because no large differences in isolated yield of product were observed. This result offers that our synthesized catalyst is far better enough than any other conventional catalysts. After that, we have used different derivatives of aryl boronic acid (Table 6, Entries 9-12). All derivatives of aryl boronic acids showed excellent yield and among all of them (Table 6, Entries 1-12) maximum yield was found in case of 4-(benzyloxy)phenylboronic acid. In case of different substrates of aryl boronic acid, para substituents (Table 6, Entries 9-11) showed a slightly better yield than meta substituents (Table 6, Entry 12). This study concludes that Pd@(Merf-FA) catalyzed carbonylative S-M coupling reaction from aryl boronic acid and aryl iodide offers its efficiency towards its industrial applications.

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Heterogeneity test

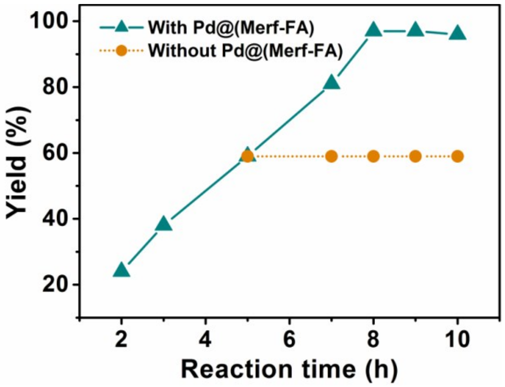

Fig. 18 Heterogeneity test of Pd@(Merf-FA) catalyst. Reaction conditions: Iodobenzene (1.5 mmol), 4-(benzyloxy)phenylboronic acid (2 mmol), toluene (5 mL), $CHCl_3$:KOH (4 mmol:8 mmol), temperature = 60 ^{o}C, 27 mg of Pd@(Merf-FA) catalyst.

Heterogeneity test is very useful to prove that the synthesized catalyst is completely heterogeneous in nature and no leaching of metal is occurring during the course of the reaction. For this purpose, we have performed heterogeneity test of our synthesized Pd@(Merf-FA) catalyst using carbonylative S-M coupling reaction between 4-(benzyloxy)phenylboronic acid and iodobenzene as model reaction. We have conducted this experiment using Pd@(Merf-FA) catalyst, but we removed catalyst after 5 hours from the reaction mixture and the reaction was continued for another 5 h. The results of this heterogeneity test are represented in Fig. 18. This result suggests that when the catalyst was removed from the reaction mixture no increment in yield of product was observed though the reaction further proceeded for 10 h. So there was no apparent leaching of metal occurred from the synthesized catalyst. To confirm this result we performed AAS of reaction mixture and no presence of Pd in reaction mixture was found.

Recyclability test of catalyst

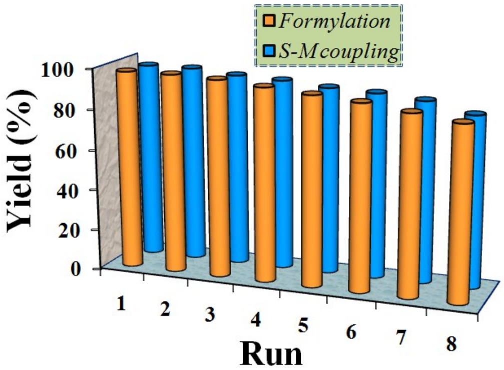

Fig. 19 Recyclability test of Pd@(Merf-FA) catalyst. Reaction conditions: (a) Carbonylative formylation reaction: 4-chloroiodobenzene (1.5 mmol), Formic acid (10 mmol), Et_3N (10 mmol), I_2 (1.8 mmol), PPh_3 (1.95 mmol), Toluene:DCM (3mL:1.5 mL), 70 ^{o}C, 90 minute, 25 mg of Pd@(Merf-FA) catalyst. (b) Carbonylative S-M coupling reaction: iodobenzene (1.5 mmol), 4-(benzyloxy)phenylboronic acid (2 mmol), toluene (5 mL), $CHCl_3$:KOH (4 mmol:8 mmol), temperature = 60 ^{o}C, time = 8 h, 27 mg of Pd@(Merf-FA) catalyst.

Recycling experiment of synthesized Pd@(Merf-FA) catalyst which is heterogeneous in origin, was conducted to find out how much this catalyst is efficient and novel. We conducted recycling experiments for both formylation and carbonylative S-M coupling reactions and the results are represented in Fig. 19. The catalyst was removed from the reaction mixture by filtering through a small funnel and before reusing of this catalyst it was washed with ethanol for several times and dried in vacuum. The catalyst is highly recyclable up to six times without any noticeable loss of catalytic activity and above six times of run yield of the product decreases gradually due to leaching of metal. We have conducted a recycle experiment up to 8 times to confirm the results.

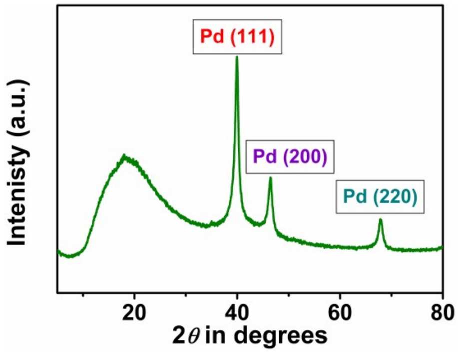

Fig. 20 Wide angle PXRD pattern of sixth times recycled Pd@(Merf-FA) catalyst.

The PXRD pattern of sixth times recycled Pd@(Merf-FA) catalyst is represented in support of the fact that no change was observed in the catalyst structure and composition. The PXRD data of recycled catalyst is shown in Fig. 20. The result indicates that no change in this PXRD pattern as compared to the freshly prepared catalyst. So our synthesized Pd@(Merf-FA) catalyst is highly recyclable and stable for several reaction runs.

Table 7 Comparison of Pd@(Merf-FA) catalyst with other commercially available homogeneous catalysts

Reaction	Catalyst	Yield (%)
Carbonylative Formylation[a]	$Pd(OAc)_2$	78
	$PdCl_2$	73
	Pd@(Merf-FA)	95
Carbonylative S-M coupling[b]	$Pd(OAc)_2$	trace
	$PdCl_2$	trace
	Pd@(Merf-FA)	92

[a] Reaction conditions: Iodobenzene (1.5 mmol), formic acid (10 mmol), Et_3N (10 mmol), I_2 (1.8 mmol), PPh_3 (1.95 mmol), toluene:DCM (3mL:1.5 mL), temperature = 70 ^{o}C, time = 90 minute, 25 mg catalyst.

[b] Reaction conditions: Iodobenzene (1.5 mmol), phenylboronic acid (2 mmol), toluene (5 mL), $CHCl_3$:KOH (4 mmol:8 mmol), 27 mg of Pd@(Merf-FA) catalyst, temperature = 60 ^{o}C, time = 8 h.

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Activity of synthesized Pd@(Merf-FA) catalyst was also compared with some commercially available homogeneous catalysts like $Pd(OAc)_2$ and $PdCl_2$ in both of the reactions. The results are tabulated in Table 7. This result implies that our designed catalyst is highly effective in case of both of the reactions than other homogeneous catalysts. It was also noticed that carbonylative S-M coupling is very inert in presence of $Pd(OAc)_2$ and $PdCl_2$. Also the homogeneous catalysts cannot be recycled further which should increase the production costs of desired products.

Table 8 Comparision with different catalyst for both carbonylative formylation and S-M coupling reaction

Reaction	**Catalyst**	**Reaction condition**	**Yield (%)**	**Ref.**
Carbonylative Formylation	$Pd(DPPP)Cl_2$	Bromobenzene (2 mmol), PMHS (Si-H, 5 mmol), DBU (3 mmol), $Pd(DPPP)Cl_2$ (0.04 mmol), CO_2 (1 MPa), DMF (5 mL), 100 °C.	81	[20]
	Pd/C	Iodobenzene (5 mmol), PMHS (Si-H 15 mmol), DBU (1.1 equiv.), CH_3CN (10 mL), Pd/C (2.5 mol%), 80 °C, CO_2 (1 MPa), 20 h.	77	[15 (a)]
	$Pd(OAc)_2$	Iodobenzene (1.0 mmol), HCOOH (4.5 mmol), acetic anhydride (2.0 mmol), $Pd(OAc)_2$ (3 mol%), PCy_3 (6 mol%), Et_3N (5 equiv), DMF (2 mL), 6 h.	66	[21]
	$Pd(OAc)_2$	Iodobenzene (1.0 mmol), $Pd(OAc)_2$ (3 mol%), PCy_3 (6 mol %), HCOOH (7.0 mmol), DCC (2.0 mmol), Et_3N (2.0 mmol), DMF (2 mL), 80 °C, 10 h,	74	[22]
	Pd@(Merf-FA)	**Iodobenzene (1.5 mmol), Formic acid (10 mmol), Et_3N (10 mmol), I_2 (1.8 mmol), PPh_3 (1.95 mmol), Toluene:DCM (3mL:1.5 mL), 70 °C, 90 minute, 25 mg of Pd@(Merf-FA) catalyst.**	**95**	**Present work**
Carbonylative S-M coupling	P(DVB-NDIIL)-Pd	Phenylboronic acid (1.4 mmol), iodobenzene (1 mmol), toluene (10 mL), K_2CO_3 (3 mmol), catalyst 1 mol%, 120 °C, 12 h, 30 bar CO pressure.	85	[23]
	Pd/C	Phenylboronic acid (1.2 mmol), iodobenzene (1 mmol), anisole (10 mL), K_2CO_3 (3 mmol), Pd/C (2 mol %), 200 psi CO pressure, 100 °C, 8 h.	90	[15b]
	Pd@(Merf-FA)	**Phenylboronic acid (2 mmol), iodobenzene (1.5 mmol), toluene (5 mL), $CHCl_3$:KOH (4 mmol:8 mmol), 60 °C, 8 h, 27 mg of Pd@(Merf-FA) catalyst.**	92	**Present work**

Conclusion

The present work can be summarized as a newly designed polymer supported furfurylamine functionalized palladium incorporated Pd@(Merf-FA) catalyst has been developed. The synthesized catalyst is excellent for the synthesis of aryl aldehydes and diarylketones by in situ carbonylation reaction using CO surrogates. Formic acid was used for aryl aldehydes synthesis and a mixture of chloroform and base KOH was applied for the synthesis of diarylketones as a CO source respectively. The yields of isolated products are satisfactory compared to the other reported systems. The catalyst Pd@(Merf-FA) offered 76-98% yield in case of aryl aldehyde synthesis. In addition the diaryl ketones are synthesized with excellent yield (76-97%) using Pd@(Merf-FA) complex catalyst. It is significant to discuss in this current work that there is no influence of electron donating or electron withdrawing groups in case of diaryl ketone synthesis was observed. Catalytic activity of Pd@(Merf-FA) catalyst was also compared with other commercially available homogeneous catalysts of Pd and surprising elevation of yield of the isolated products was observed especially in case of carbonylative S-M coupling reaction. Our synthesized catalyst is thermally stable up to 345 °C and efficiently enough to be recyclable up to six reaction runs. By taking into account all these facts we can now arrive at the conclusion part that Pd@(Merf-FA) catalyst is potentially an excellent catalytic system for the in situ carbonylation process to synthesize both aryl aldehydes and diaryl ketones with significant yield.

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Polymer incarcerated Palladium catalyzed facile *in situ* carbonylation for the synthesis of aryl aldehydes and diaryl ketones using CO surrogates at ambient conditions

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A palladium incorporated heterogeneous catalyst, Pd@(Merf-FA) is designed for the synthesis of aryl aldehydes and diaryl ketones using carbonylative surrogates.