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A new polymer anchored Pd(II) complex has been synthesized and characterized. The catalytic performance of this complex has been tested for thioesters synthesis *via* carbonylation of aryl halides and thiols under phosphine free condition. This catalyst showed excellent catalytic activity, recyclability and reused more than five times without appreciable loss of its initial activity.

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Abstract

A new polymer supported phosphine free Pd(II) complex has been synthesized and characterized. The catalytic performance of the complex has been tested for the carbonylation of aryl halides into aryl thioesters under mild reaction conditions. Thioesters were obtained in excellent yields from various aryl iodides and thiols in the presence of carbon monoxide and polymer supported palladium catalyst. The effects of solvents, bases, reaction time and catalyst amount for the thioesters synthesis were reported. This catalyst showed excellent catalytic activity and recyclability. The polymer supported Pd(II) catalyst could be easily recovered by filtration and reused more than five times without appreciable loss of its initial activity.

Key words: Supported catalyst, Palladium, Carbonylation, Aryl halides, Thiols, Thioesters.

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Introduction

Palladium-catalyzed cross-coupling reaction for the formation of carbon–carbon bonds is a dynamic method in organic synthesis. The palladium-catalyzed coupling of an aryl halide with aryl boronic acid (Suzuki coupling) or terminal alkyne (Sonogashira coupling) is recognized as the most successful method for forming a $C(sp^2)$–$C(sp^2)$ and $C(sp)$–$C(sp^2)$ carbon–carbon bond, respectively. These reactions have been widely employed in the synthesis of natural products, biologically active molecules and materials science.[1]

On the other hand, palladium-catalyzed carbonylation of aryl halides have become a powerful tool in organic synthesis.[2] As an inexpensive and readily available C_1 source, carbon monoxide can be used to synthesize various carbonyl products, such as aldehydes, ketones, carboxylic acids, esters, and amides.[3] Among the different types of carbonylation reactions, palladium-catalyzed coupling carbonylation reaction of aromatic halides has been one of the most important methodologies for the synthesis of valuable carbonyl containing compounds both from academic and industrial perspectives.[4] Palladium catalyzed carbonylations serves as powerful tools for the conversion of aryl halides to carboxylic acid derivatives.[5] Thioesters are activated carboxylic acid derivatives which exhibit acylating properties similar to those of acid anhydrides.[6-11] Thioesters are becoming increasingly important compounds due to their distinctive chemical properties; the reduced electron delocalization provides for the enhanced reactivity compared to oxoesters.[12] The importance of thioesters in the cell is well established; biological systems use their relative reactivity in many enzymatic reactions by employing, for example, acetyl coenzyme A, cysteine proteases or polyketide and fatty acid synthases.[13] Also, thioesters have distinct chemical properties compared to ordinary esters and their enhanced reactivity has been employed successfully in a wide range of synthetic organic reactions.[14-15] Therefore, developing a simple and versatile method for the preparation of thioester is still a challenge in organic synthesis.

Recently, several methods have been reported in the literature for the synthesis of thioesters.[16-18] However, these methods require prolonged reaction time and exotic reaction condition. Alper's group has developed a number of other Pd-catalyzed thiocarbonylation reactions.[19] All of these reported protocols used homogeneous catalysts. Homogeneous catalysts have some disadvantages, such as they may easily be destroyed during the course of the reaction and they cannot be easily recovered after the reaction for reuse.[20] To get rid of these serious issues, we have synthesized and reported several supported metal catalysts[21] and we focused our effort to develop an efficient methodology for palladium-catalyzed thiocarbonylation reaction.

Pd-catalyzed thiocarbonylation of aryl halides are less well-known. Two previous reports in the literature have demonstrated the feasibility of this transformation with aryl iodides. In 2008, Alper and co-workers reported the Pd-catalyzed thiocarbonylation of aryl iodides using a phosphonium salt-based ionic liquid solvent in combination with 14 atm of CO pressure. Later, Lei et al. in mechanistic studies on Pd-catalyzed carbonylation reactions demonstrated that the same transformation could be carried out using a sodium thiolate in a thiol/THF solvent mixture and CO pressure of 10 atm.[22-24] Thus, the development of a new method for the synthesis of thioester derivatives from aryl halides would be highly desirable. At the same time, only a few examples have been reported for the use of supported counterparts of the homogeneous palladium catalysts for the carbonylation reactions of aryl halides.[25-31] To the best of our knowledge, there is only one report of reusable palladium-catalyzed thiocarbonylation reaction of aryl halides and thiols.[18]

We are the first to report the polymer supported palladium-catalyzed thiocarbonylation of aryl iodides with thiols. Herein, we report the synthesis and characterization of a polymer supported palladium catalyst and illustrate its application for the synthesis of aryl thioesters *via* carbonylation of aryl iodides under mild reaction

conditions. This polymer supported Pd(II) catalyst could be easily separated from the reaction mixture by simple filtration and can be reused more than five times without appreciable loss of its activity.

Experimental Section

Materials

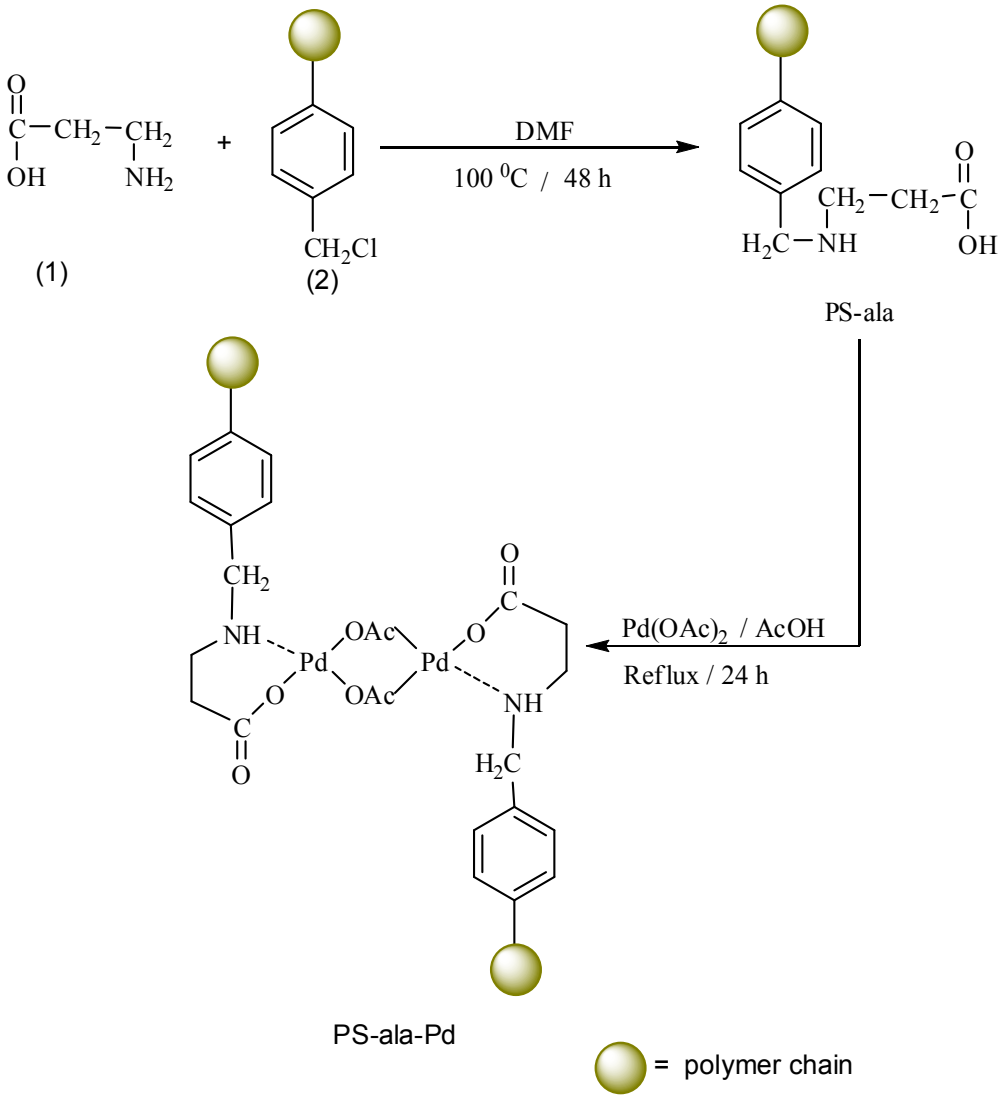
Analytical grade reagents and freshly distilled solvents were used throughout. All reagents and substrates were purchased from Merck. Liquid substrates were predistilled and dried by molecular sieve and solid substrates were recrystallized before use. Distillation, purification of the solvents and substrate were done by standard procedures.[31] 5.5% crosslinked chloromethylated polystyrene and Palladium acetate were purchased from Aldrich Chemical Company; U.S.A. and used without further purification.

Physical measurements

NMR spectra were recorded on a Bruker DPX-400 NMR spectrometer (^{1}H NMR at 400 MHz and ^{13}C NMR at 100 MHz) in pure deuterated solvents with TMS as internal standard. The FT-IR spectra of the samples were recorded from 450 to 4000 cm^{-1} on a Perkine Elmer FT-IR 783 spectrophotometer using KBr pellets. UV-Vis spectra were taken using a Shimadzu UV-2401PC doubled beam spectrophotometer having an integrating sphere attachment for solid samples. Thermogravimetric analysis (TGA) was carried out using a Mettler Toledo TGA/DTA 851e. Surface morphology of the samples was measured using a scanning electron microscope (SEM) (ZEISS EVO40, England) equipped with EDX facility. Palladium content in the catalyst was determined using a Varian AA240 atomic absorption spectrophotometer (AAS).

Synthesis of the metal complex

The synthesis of the immobilized polymer supported palladium(II) catalyst illustrated in Scheme 1. It was readily prepared through a two-step procedure. In Step I, 0.2 g of chloromethylated polystyrene (5.5 mmol Cl/g of resin) (**2**) was treated with 0.979 g of β-alanine (**1**) in *N,N'*-dimethylformamide (DMF) to produce the corresponding white coloured polymer supported ligand (PS-ala). The polymer was washed thoroughly with DMF to remove excess β-alanine. Finally, it was washed with double distilled water, dried and stored at room temperature for further use. In Step II, the polymer supported β-alanine ligand (1 g) in acetic acid (20 mL) was treated with 5 mL 1% (w/v) AcOH solution of $Pd(OAc)_2$ over a period of nearly 30 minutes under constant stirring. Then the reaction mixture was refluxed for 24 h. The brown coloured paladium complex thus formed was filtered and washed thoroughly with ethanol and dried at room temperature under vacuum.



Scheme 1 Synthesis of the polymer supported Pd(II) catalyst

General procedure for the synthesis of thioester

A 50 mL high-pressure reactor was charged with dimethoxyethane (DME) (5.0 mL, 4.35 mol), NaOAc (22.6 mg, 0.275 mmol), aryl iodide (0.25 mmol), palladium catalyst (25 μmol) and CO (1 atm) before heating at 85 ^{0}C for 16 h. After cooling the reactor, the CO was vented from the reactor and the desired compound was purified by chromatography on silica

gel using a pentane/CH_2Cl_2 eluent system. All the prepared compounds were confirmed by ^1H and ^{13}C NMR spectra.

Results and Discussion

Characterization of the polymer supported Pd catalyst

Due to insolubilities of the polymer supported palladium catalyst in all common organic solvents, its structural investigation was limited to its physicochemical properties, chemical analysis, SEM-EDX, TGA, IR and solid UV-Vis spectroscopic data. Table 1 provides the data of elemental analysis of polymer supported ligand and the polymer supported palladium catalyst. Palladium content in the catalyst determined by AAS suggests 9.08 wt% Pd in the catalyst.

Table 1 Chemical composition of polymer anchored ligand and polymer supported catalyst.

Compound	Colour	C %	H %	Cl %	N %	Metal %
PS-ala	white	72.04	5.87	6.10	2.41	-
PS-ala-Pd	Deep grey	64.15	5.07	4.33	1.40	9.08

Various frameworks bonding present in the polymer supported metal catalyst were obtained from the FT-IR spectra (Figure 1). A new strong band appeared at 3436 cm^{-1} showed the presence of a secondary (-NH-) amine group in the ligand. The (C=O), ν_{asym} (COO) and ν_{sym} (COO) stretching vibrations are observed at 1733, 1675 and 1513 cm^{-1} for polymer anchored ligand[30] and this ligand is bidentate ligand and bound to the central metal ion through the carboxylic OH and the secondary amino group; (-NH-). The bands at 1675 and 1513 cm^{-1}, due to ν_{asym} (COO) and ν_{sym} (COO) of the amino acids, appear in the complex at 1670 and 1510 cm^{-1}. The shift of these two bands suggests the involvement of the carboxylic groups of the polymer supported ligand in complex formation. The decrease in the intensity of N-H stretching frequency of the secondary amine group in the complex indicates

that the 'N' of amino group may be coordinated to the metal. Weak bands in the far IR region at ~340-360 cm^{-1} and ~440-450 cm^{-1} have been assigned to ν_{Pd-O} and ν_{Pd-N} vibrations.[33-35] Thus, making precise assignments to distinguish Pd-O from Pd-N bands in the far IR region is rather difficult.

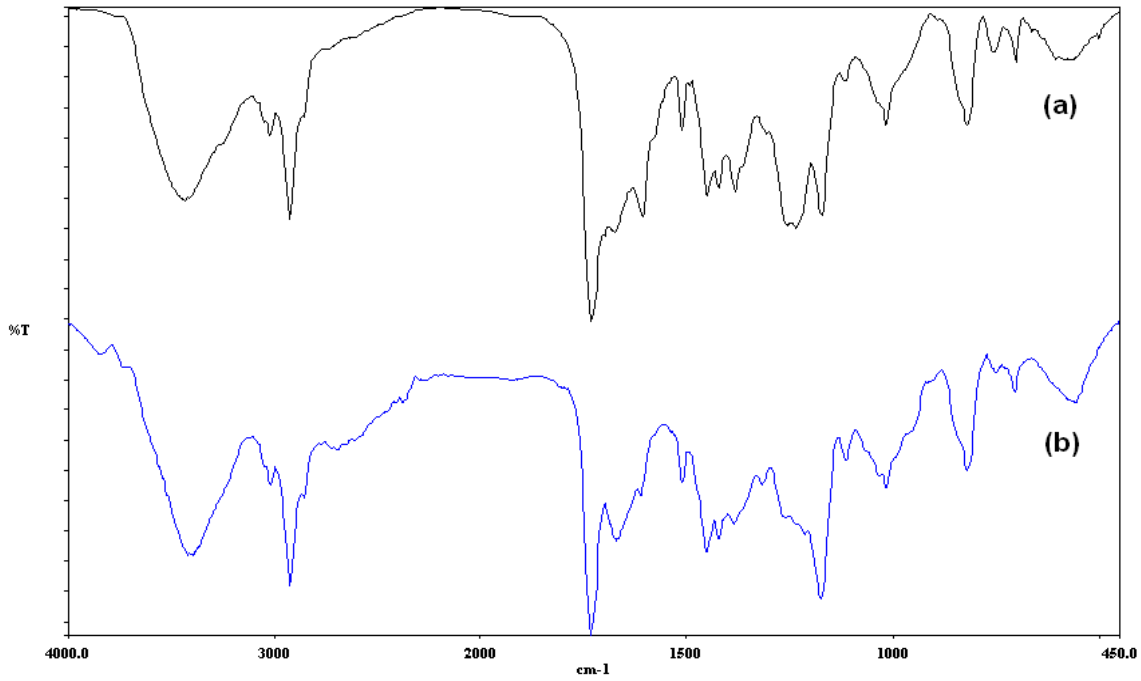


Figure 1. FT-IR Spectra of polymer anchored ligand PS-ala (a), PS-ala-Pd complex (b)

The scanning electron micrographs (Figure 2) of the polymer supported ligand and palladium catalyst clearly show the morphological change which occurred on the surface of polystyrene after loading of metal on it. Energy dispersive spectroscopy analysis of X-rays (EDAX) data for the polymer anchored ligand and palladium catalyst are given in (Figure 3). The EDX data also confirm the attachment of metal on the surface of the polymer matrix.

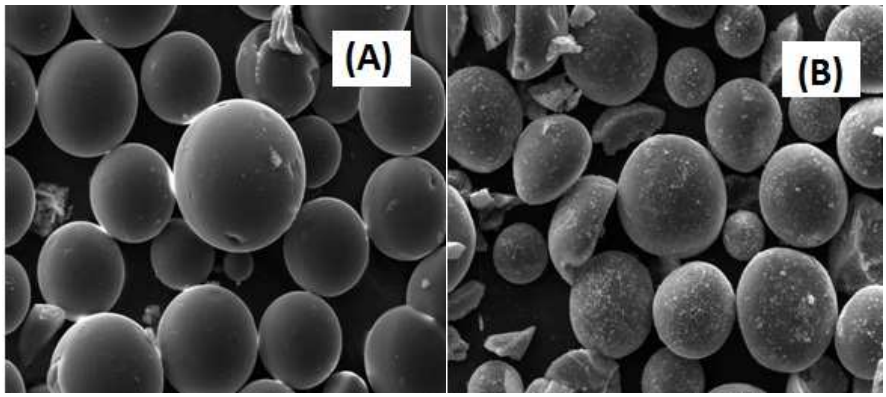


Figure 2. FE-SEM images of polymer anchored ligand (PS-ala) (A), PS-ala-Pd complex (B)

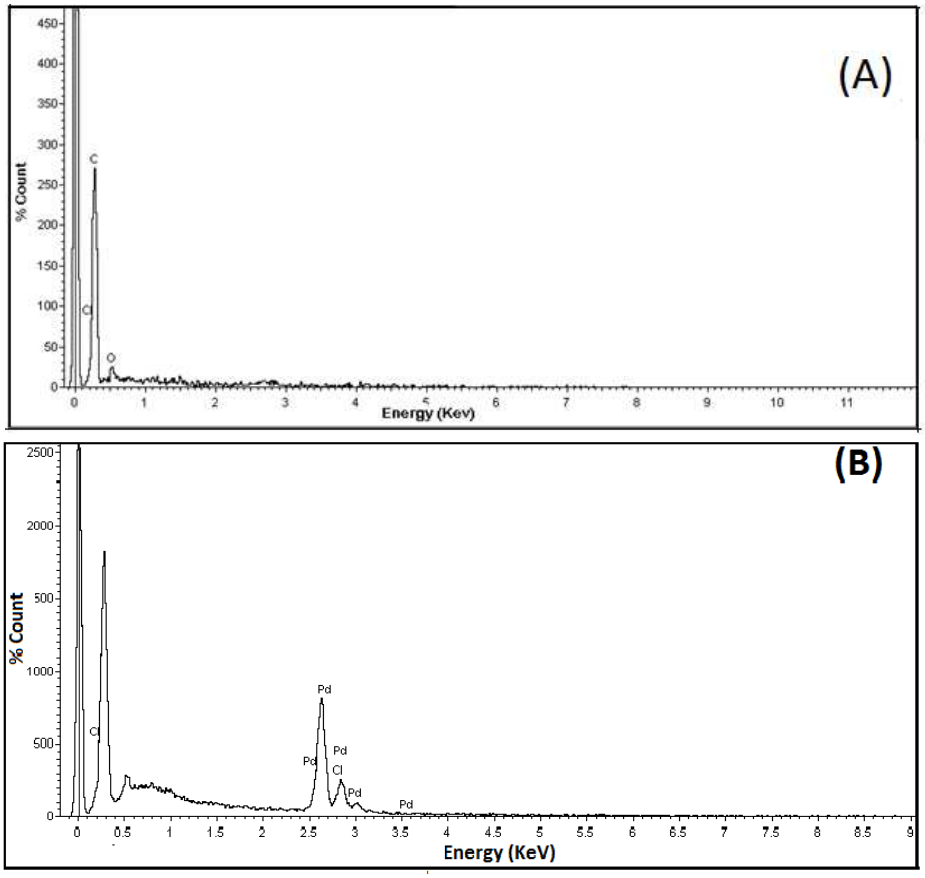


Figure 3. EDAX data of polymer supported ligand (PS-ala) (A) and PS-ala-Pd complex (B)

The UV-vis spectra (Figure 4) provided further evidence for the presence of palladium on polymer support. The electronic spectra of the polymeric Pd(II) catalyst has been recorded in diffuse reflectance spectrum mode as $BaSO_4$ disc due to its solubility

limitations in common organic solvents. The low-spin Pd(II) complex may exhibit three spin-allowed d-d transitions from lower lying d orbital to higher empty $d_{x^2-y^2}$ orbital. The bands are observed at 305 nm, 365 nm and 420 nm which may be designated as $^1A_{1g}/^1Eg$, $^1A_{1g}/^1B_{1g}$ and $^1A_{1g}/^1A_{2g}$ transitions respectively.[36-37]

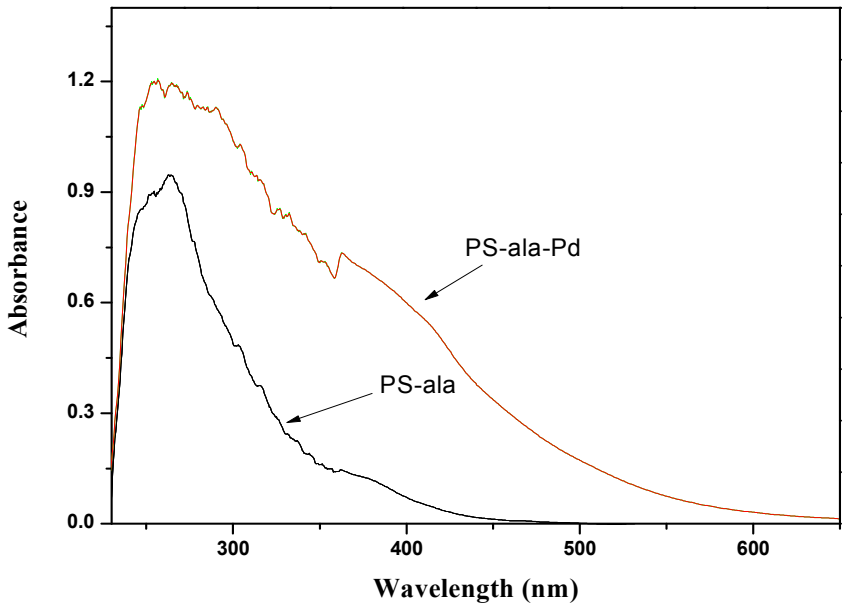


Figure 4. DRS-UV-visible absorption spectra of the polymer supported ligand and palladium catalyst.

Thermal stability of the complex was investigated using TGA at a heating rate of 10 ^{0}C/ min in air over a temperature range of 30-600 ^{0}C. TGA curve of the polymer supported palladium catalyst is shown in Figure 5. The palladium complex was stable up to 320-350 ^{0}C and above this temperature it decomposed. Thermogravimetric study suggests that the polymer supported palladium complex degrade at considerably higher temperature.

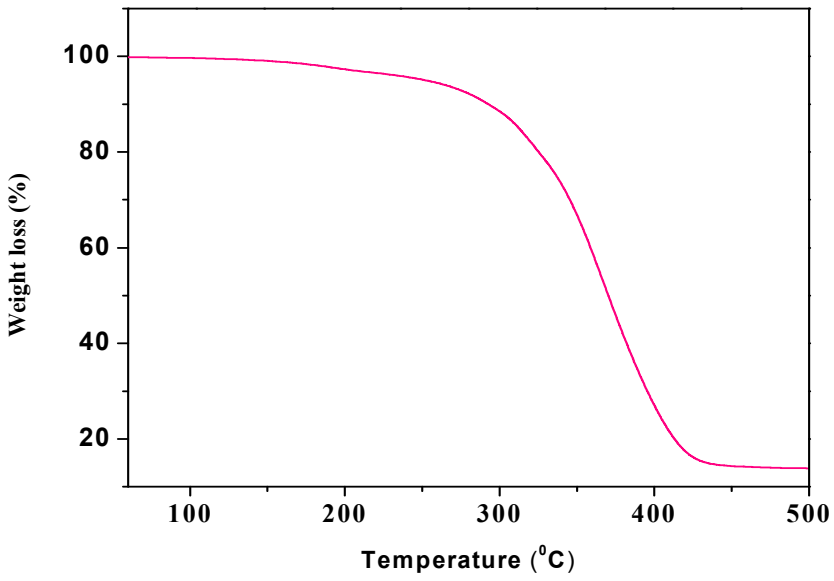
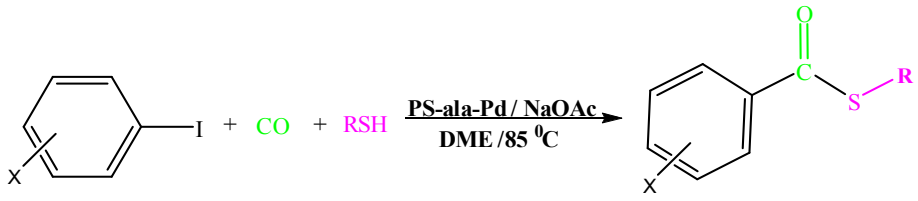


Figure 5. Thermogravimetric weight loss plot for the polymer supported catalyst PS-ala-Pd complex.

Catalytic activity

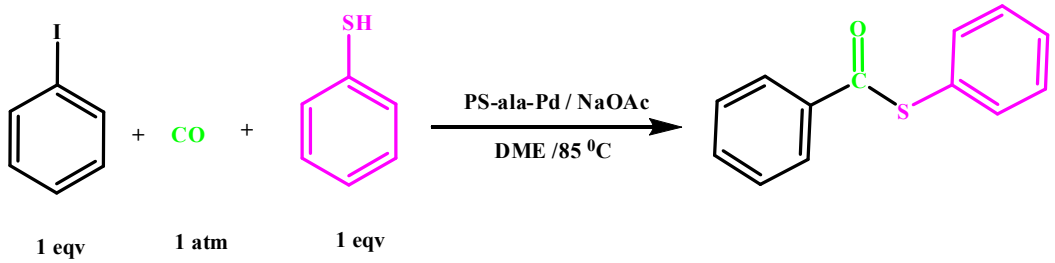
Since supported palladium catalyst exhibits high catalytic activity in a wide range of industrially important processes and have been extensively studied for C-C coupling, we decided to investigate the catalytic activity of the PS-ala-Pd in the field of carbonylation. Initial studies focused on examining the feasibility of the thiocarbonylation reactions and optimizing reaction conditions that could be applied to a variety of thiols and aryl halides.



Scheme 2 Palladium catalyzed carbonylation of aryl iodides

To test the catalytic activity of the present catalyst, the carbonylation of aryl iodides and thiols were performed as illustrated in Scheme 2. In this reaction aryl halide was

converted to aryl thioester under 1 atm CO pressure. Quantitative conversion of aryl halide to aryl thioester can be achieved by using the polymer supported Pd catalyst (PS-ala-Pd). The carbonylation reaction of aryl iodide was carried out by using sodium acetate as the base in the DME solvent medium. The reaction was run in a 50-mL autoclave at 85 ^{0}C under carbon monoxide atmosphere for 16 h. In our initial studies, the iodobenzene was chosen as the reactant for the optimization of the carbonylation reaction (Scheme 3). The performance of palladium-catalyzed carbonylation reaction is known to be governed by a number of reaction parameters. To find the appropriate reaction conditions various bases and solvents were screened (Table 2). In order to identify effective conditions for promoting the Pd-thiocarbonylation, the reaction was carried out under various temperature and reaction time (Table 3).



Scheme 3 Palladium catalyzed carbonylation of of iodobenzene and thiophenol

The influence of base on the catalytic performance of this system was investigated by employing various bases. Comparison of inorganic bases utilized, showed that inorganic bases are more effective than organic bases like pyridine and Et_3N. Within a short time the reaction proceeded with high yield in presence of NaOAc or K_2CO_3 (Table 2, entries 4 and 7). We found that using NaOAc as base in DME at 85 ^{0}C gave 85% conversion. Other inorganic bases such as K_3PO_4, $NaHCO_3$ and organic bases like Et_3N were not as effective as NaOAc, only afforded moderate to low yields of coupling products (Table 2, entries 2, 3, 5 and 6).

Table 2 Effect of bases on the carbonylation of iodobenzene and thiophenol

Entry	Base	Conversion (%)
1	NaO^tBu	62
2	Et_3N	28
3	K_3PO_4	37
4	K_2CO_3	52
5	Pyridine	22
6	$NaHCO_3$	26
7	NaOAc	85
8	NaOAc	56
9	NaOAc	72
10	NaOAc	68

Reaction conditions: thiophenol (0.30 mmol), iodobenzene (0.30 mmol), DME (5 mL), CO (1 atm), PS-ala-Pd (25 μmol), time (16 h) and temperature (85 ^{0}C).

To verify the solvent effect, a series of solvents were investigated by taking the carbonylation of iodobenzene as the model reaction. The reactions were that conducted in polar solvent medium, like DME and Propionitrile, were found to be most effective (Table 3, entries 1 and 3). The use of toluene, dioxane as solvents led to slower reactions (Table 3, entries 2 and 4). Consequently, DME was chosen as the medium of choice for this carbonylation.

Table 3 Effect of solvents on the carbonylation of iodobenzene and thiophenol

Entry	Solvent	Conversion (%)
1	DME	85
2	Toluene	56

3	Propionitrile	72
4	Dioxane	68

Reaction conditions: thiophenol (0.30 mmol), iodobenzene (0.30 mmol), NaOAc (0.275 mmol), CO (1 atm), PS-ala-Pd (25 μmol), time (16 h) and temperature (85 ^{0}C).

This coupling reaction was found to be highly sensitive to the reaction temperature. At lower temperatures (45-65 ^{0}C) only low to moderate yield was obtained (Table 4, entries 1-3). A reaction temperature of 85 ^{0}C was found to be optimal for the model reaction (Table 4, entry 5). Also the reaction was carried out for different time ranging from 10 h to 18 h and it was found that at 16 h the conversion was 85% at given conditions (Table 4, entries 5 and 7-10).

Table 4 Effect of temperature and reaction time on carbonylation reaction

Entry	Temperature (^{0}C)	Time (h)	Conversion (%)
1	45	16	29
2	55	16	43
3	65	16	57
4	75	16	71
5	85	16	85
6	95	16	85
7	85	10	38
8	85	12	51
9	85	14	69
10	85	18	85

Reaction conditions: Thiophenol (0.30 mmol), iodobenzene (0.30 mmol), CO (1 atm) PS-ala-Pd (25 μmol), NaOAc (0.28 mmol), DME (5.0 mL).

The influence of amount of catalyst on the yield was also investigated (Figure 6). An increase in the catalyst amount from 10 μmol to 25 μmol resulted in an increase in the yield up to 85%. Further increase in catalyst amount had no profound effect on the yield of the desired product.

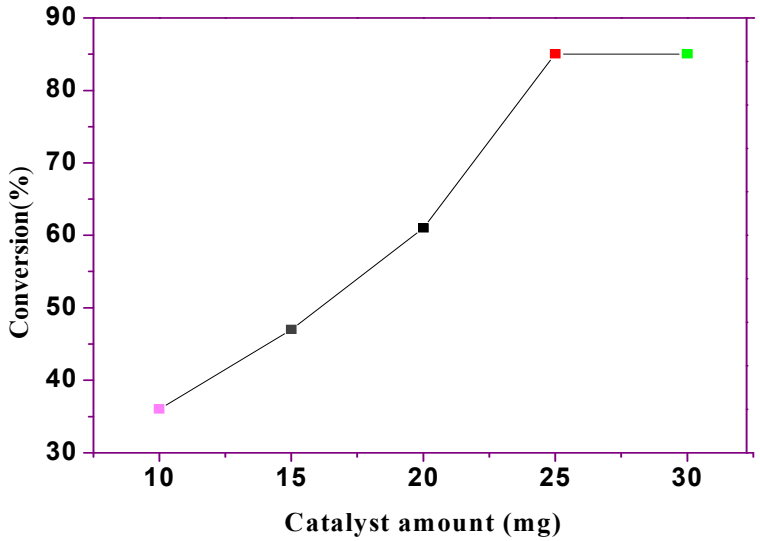


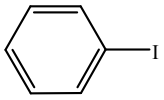
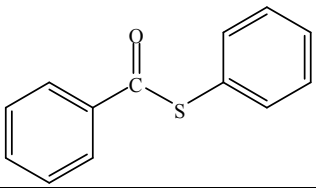
Figure 6. Effect of catalyst amount on carbonylation of iodobenzene

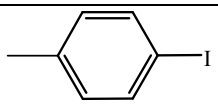
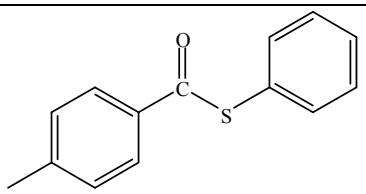
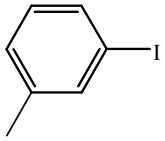
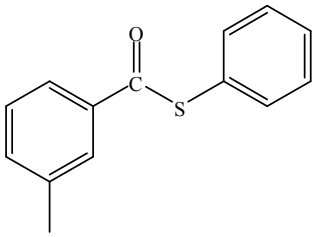
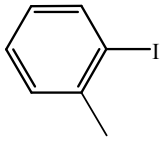
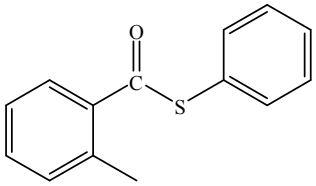
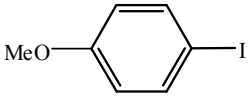
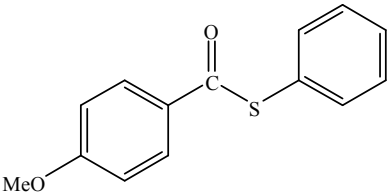
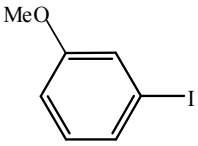
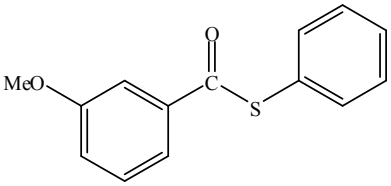
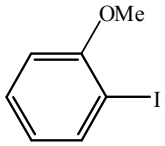
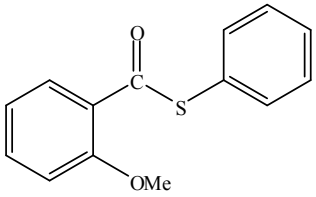
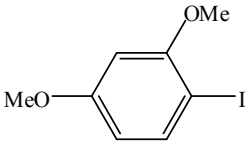
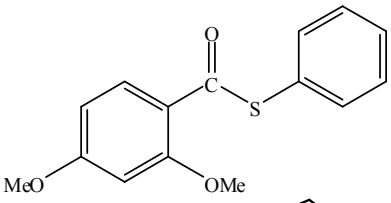
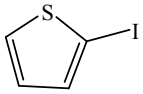
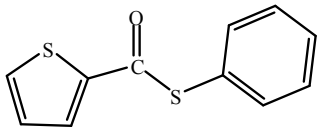
Reaction conditions: thiophenol (0.30 mmol), iodobenzene (0.30 mmol), CO (1 atm), NaOAc (0.28 mmol), DME (5.0 mL), time (16 h), temperature (85 ^{0}C).

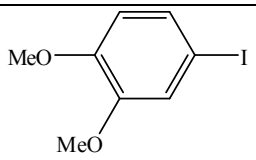
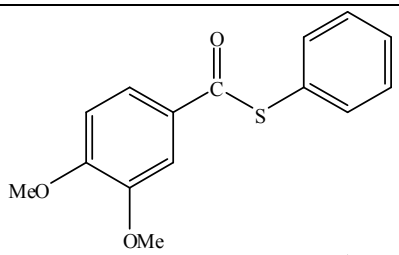
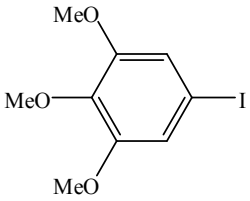
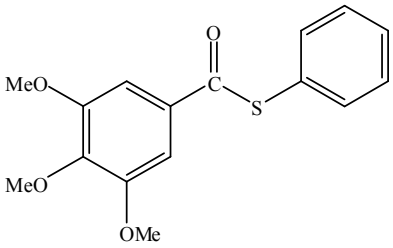
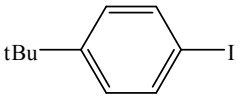
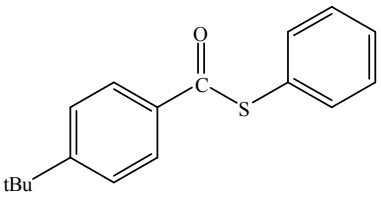
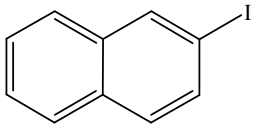
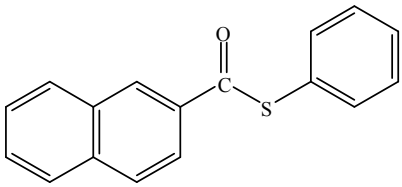
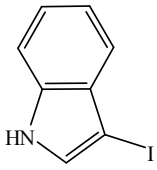
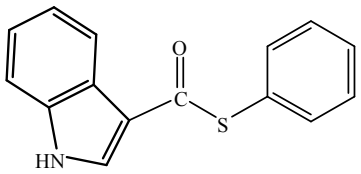
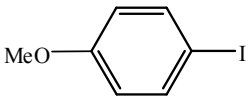
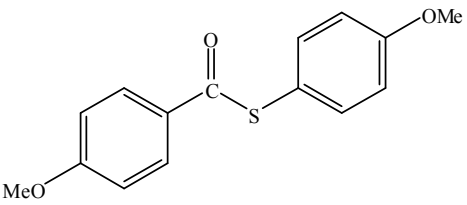
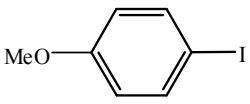
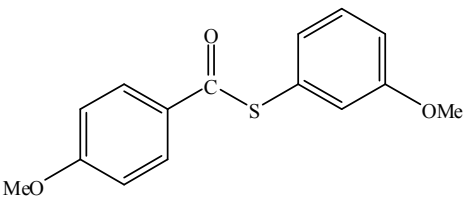
To examine the scope of this carbonylative coupling reaction, a variety of aryl iodides were coupled with different thiophenols in DME in the presence of PS-ala-Pd(II) catalyst. The experimental results are summarized in Table 5. With a defined protocol in hand, the substrate scope with various aryl iodides was explored. As shown in Scheme 2, the protocol well tolerated diverse electronic and steric substituents of the aryl iodides, as well as heterocyclic substrates, all resulting in good to excellent yields. The relative position of substituents had slight impact on the coupling efficiency: *p*-iodotoluene and *p*-iodoanisole

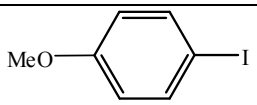
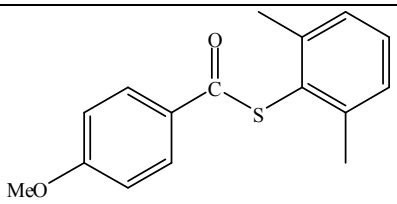
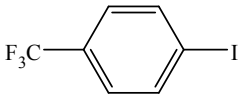
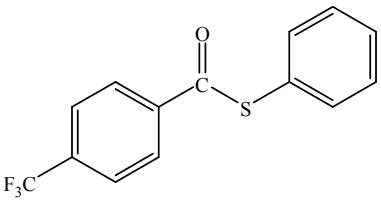
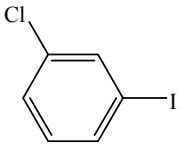
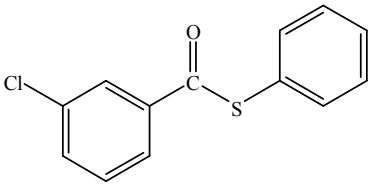
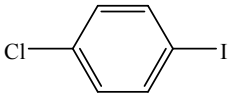
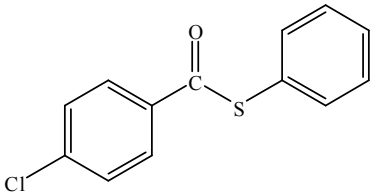
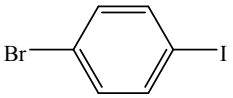
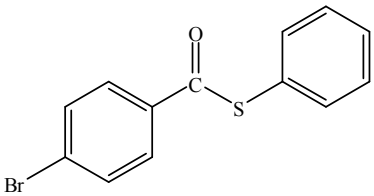
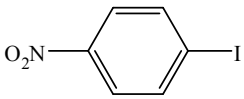
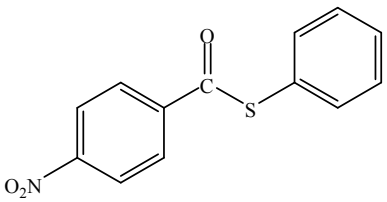
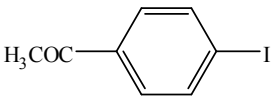
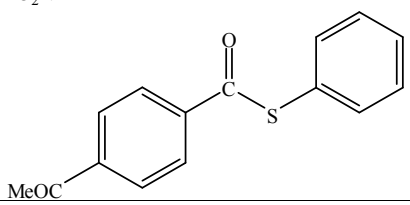
resulted in a higher yield than its *m*- or *o*-analogues (Table 5, entries 2-7). Almost similar yields were obtained with iodobenzene and *p-tert*butyl-iodobenzene (Table 5, entries 1 and 12). The substitution of electron withdrawing and electron donating groups on the phenyl ring of aryl iodides did not have any appreciable influence on the outcome of the reaction (Table 5, entries 2, 5, 12 and 18-22). Aryl iodides bearing either electron-donating or electron-withdrawing substituents, afforded the corresponding cabonylative products in good to excellent yields. Strong electron-donating groups such as methyl and methoxy group containing aryl iodides resulted in slightly more yields than aryl iodides with electron-withdrawing groups, such as chloride and bromide (Table 5, entries 19 and 21). Even heteroaromatic iodides proved effective for these carbonylative couplings as depicted with the indole and thiophene ring system leading to products (Table 5, entries 9 and14). A few other aromatic thiols were also successfully tested as represented by compounds (Table 5, entries 15-17). The di-substituted alkyl thiol was run, providing the functionalized thioester (entry 17) in approximately 74% yield. The scope of the thiocarbonylation procedure with the other electron-poor aryl iodides were also tested (entries 18 and 23). In most cases, good to excellent yields of the thioesters were obtained. Even in the case of the *p*-nitro derivative, the desired compound (entry 22) was formed.

Table 5 Polymer supported palladium(II) catalyzed carbonylation of aryl iodides.

Entry	Aryl halide	Product	Conversion (%)
1			85

2			91
3			88
4			72
5			95
6			68
7			72
8			93
9			83

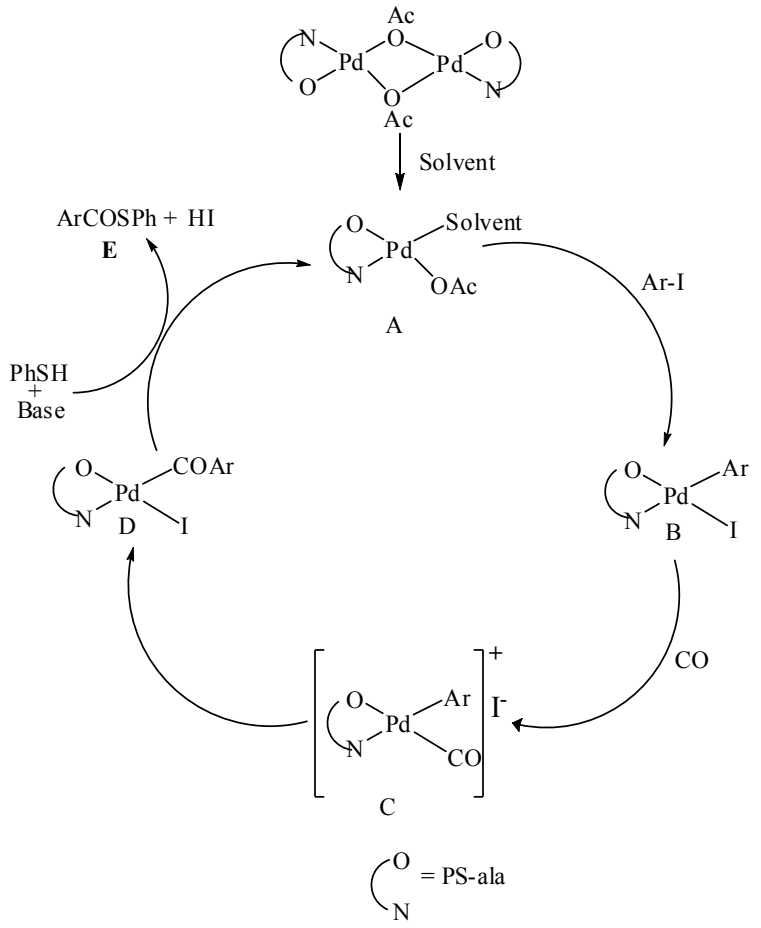
10			81
11			83
12			84
13			74
14			45
15[a]			85
16[b]			83

17[c]			74
18			86
19			81
20			88
21			86
22			61
23			85

Reaction conditions: Thiophenols, (0.30 mmol), aryl iodides (0.30 mmol), CO (1 atm), PS-ala-Pd (25 μmol), NaOAc (0.28 mmol), DME (5.0 mL), time (16 h), temperature (85 ^{0}C). [a]*p*-methoxythiophenol, [b]*m*-methoxythiophenol, [c]2,6-di-methylthiophenol used. All the prepared compounds were confirmed by ^{1}H and ^{13}C NMR.

An interesting observation was made in the reaction of the substituted iodobenzenes with either thiophenol or its derivative. In all cases, the major products resulted from a

thiocarbonylation even though more than 1 atm of CO was applied. The corresponding less expensive aryl bromides or chlorides are more attractive substrates, but the reaction often requires harsher reaction conditions. We have tried to synthesize the aryl thioester from aryl bromide under the optimized reaction conditions but only trace amount of yield was obtained. Aryl chloride did not respond to the reaction under the optimized reaction conditions. Although the exact reaction sequence was not determined, based on our experimental results and former mechanistic studies of palladium-catalyzed carbonylations of aryl halides,[38] the reaction mechanism of this thioester synthesis is proposed in Scheme 4. It is generally accepted that an organopalladium halide (**B**) is produced by oxidative addition of an organic halide to a Pd species (**A**) formed in the catalytic system but the later course of the catalytic reaction may vary depending on the nucleophiles and reaction conditions employed. The most often assumed process involves migratory insertion of a coordinated carbon monoxide in (**C**) to give an acylpalladium halide (**D**), which reacts further with a nucleophile (PhSH) and a base to liberate ArCOSPh.



Scheme 4 Proposed reaction mechanism of palladium catalyzed carbonylation of aryl iodide

Heterogeneity test

An important point concerning the use of heterogeneous catalyst is its lifetime, particularly for industrial and pharmaceutical applications of the coupling reaction. Heterogeneity of this catalyst was examined by the "hotfiltration test" for the carbonylation of iodobenzene.

Hot-filtration test

Hot-filtration test was performed in the carbonylation of iodobenzene to investigate whether the reaction proceeded in a heterogeneous or a homogeneous fashion. After continuing the reaction for 10 h, the catalyst was removed by filtration and the determined conversion was 66%. The resulting filtrate was subjected to heating for further 6 h, it has

been found that after separation of the catalyst no conversion takes place in the filtrate part. This confirms that the reaction did not proceed upon the removal of the solid catalyst. Furthermore, no evidence for leaching of palladium or decomposition of the complex catalyst was observed during the catalytic reaction and no metal could be detected by atomic absorption spectroscopic measurement of the filtrate after removal of catalyst. These studies clearly demonstrated that metal was intact to a considerable extent with the heterogeneous support, and there was no significant amount of leaching during the reaction.

Catalyst reusability

Recovery and catalyst reuse are important issues in the carbonylation reactions. Easy catalyst separation and recycling in successive batch operations, can greatly increase the efficiency of the reaction. We studied the reusability of the present heterogeneous palladium catalyst in the carbonylation of iodobenzene with thiophenol. After completion of the reaction, the catalyst was recovered by simple filtration and washed with ethyl acetate followed by acetone then dried in reduced pressure at 40 ^{0}C. The recovered catalyst was employed in the next run with further addition of substrates in appropriate amount under optimum reaction conditions. The catalyst showed almost the same activity up to six reaction cycles. No catalyst deterioration was observed, thus confirming the high stability of the heterogeneous catalyst under the reaction conditions.

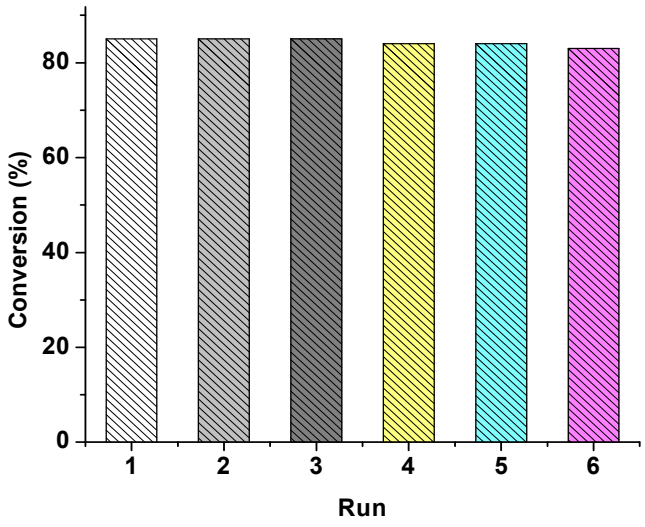


Figure 7. Catalyst reusability test of the polymer supported Pd catalyst.

Conclusions

In conclusion, we have reported the preparation and characterization of polystyrene-supported Pd(II) complex and its successful applications for the thiocarbonylation of aryl iodides with thiols exploiting a simple setup and reaction conditions, which use only 1 atm carbon monoxide. Both electron-rich and electron-deficient aryl iodides could be applied and the nature of the base, temperature and the solvent system proved crucial for the transformation. The present system is highly air and moisture stable and the catalyst can be synthesized readily from inexpensive and commercially available starting materials. Moreover, the catalyst was reused for six consecutive cycles with consistent catalytic activity. Further work is in progress to broaden the scope of this catalytic system for other organic transformation. A protocol, which allows expansion of this chemistry to other aromatic halides and mechanistic pathway of this reaction are currently under investigation.

Acknowledgments

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