Highly efficient recyclable heterogeneous palladium catalyst for C–C coupling, amination and cyanation reactions

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ABSTRACT

An inexpensive, air–moisture stable and reusable PS–Pd(II)–anthra complex was synthesized by reacting chloro-methylated polystyrene with anthranilic acid to get polymer anchored ligand which was then reacted with PdCl$_2$ to get polymer anchored complex. This complex was characterized by different spectroscopic and elemental analyses. The activity of the Pd-complex as catalyst was tested for the Suzuki, Heck, Sonogashira cross-coupling and also for amination and cyanation reactions under various conditions. The catalyst exhibits high catalytic activities for the coupling of various aryl halides with organoboronic acid, alkene, alkyne and amine along with the cyanation of aryl halides providing excellent yields of desired product. Further, the catalyst can be easily recovered quantitatively by simple filtration and reused up to five times without sufficient loss of its catalytic activity.

1. Introduction

Transition metal-catalyzed carbon–carbon and carbon–nitrogen coupling reactions are probably among the most frequently employed methods of C–C and C–N bond formation in organic synthesis [1–6]. They have been applied to the synthesis of many organic compounds, especially those of complex natural products, supramolecular chemistry, and engineering materials such as conducting polymers, molecular wires, and liquid crystals [7–10]. With various metals being employed in coupling reactions, palladium probably is the most versatile metal in promoting or catalyzing reactions involving C–C and C–N bond formation due to its excellent catalytic efficiency in this type of reactions [11–14]. In recent years, various homogeneous palladium–phosphine catalysts [15–18] have been developed for the efficient cross-coupling reactions. However, these catalysts usually need to be handled under inert atmosphere or dry conditions. In addition, they sometimes suffer from significant P–C bond degradation at elevated temperatures, which leads to palladium aggregation and eventually affects the overall catalytic performance. Supported metal complexes continuously attract the interest of a growing part of the scientific community for the advantages that they offer with

respect to their soluble counterpart. The use of heterogeneous catalysts in organic synthesis has now become a common practice [19–22], especially following the rapid development of combinatorial chemistry. Solid-supported palladium complexes having high activity and selectivity, offer several significant practical advantages in synthetic and industrial chemistry; among those, the ease of separation of the catalyst from the desired reaction products and the ease of recovery and re-use of the catalyst are most important. A large number of materials have been used to support, including activated carbon, silica gel, polymers containing covalently bound ligands, metal oxides, porous aluminosilicates, clays and other inorganic materials, and microporous and mesoporous supports [23–29].

Polystyrene is one of the most widely studied heterogeneous supports due to its environmental stability and good catalytic activity. Polymer-supported palladium catalysts derived from chloro-methyl polystyrene resin have been employed in various coupling reactions [30–38], and have shown lower leaching of palladium during cross-coupling. Suzuka et al. have reported PS–PEG resin-bound palladium complex for Sonogashira reaction [39]. Linear polystyrene-supported Pd nanoparticle was developed by Ohtaka et al. for the Suzuki–Miyaura cross-coupling reaction in water medium [40]. These results encouraged us to investigate the anthranilic acid-functionalized polystyrene resin-supported Pd(II) complex, PS–Pd(II)–anthra, for the coupling and cyanation reactions. We have already reported the use of an

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polystyrene anchored Pd(II) complexes as an air-stable, active, and reusable catalyst in C–C coupling reactions [41–43].

In the present work, we have prepared heterogeneous Pd(II) catalyst on polystyrene and used it in the Suzuki, Heck, Sonogashira, amination and cyanation reactions of aryl halides in the presence of inorganic or organic bases. The catalyst was characterized by various physicochemical and spectroscopic techniques. The effects of the various reaction parameters on the catalytic activity were studied. The key features of the catalyst include rapid reactions with excellent conversion without the use of phosphine ligands and total stability under the reaction conditions. Further this polymer-supported catalyst demonstrated outstanding reusability for these reactions.

2. Experimental

All the reagents were analytical grade and used as such without further purification. Solvents were purified and dried according to standard procedures. Chloro-methylated polystyrene was purchased from Aldrich and $PdCl_2$ was procured from Arora Matthey. Other reagents were purchased from Merck.

The palladium content was determined by Varian, USA, AA240 atomic absorption spectrophotometer (AAS). A Perkin–Elmer, USA, 2400C elemental analyzer was used to collect microanalytical data (C, H and N). Surface morphology of functionalized polystyrene ligand and metal complex were analyzed using a scanning electron microscope (ZEISS EVO40, England) equipped with EDX facility. Fourier transform infrared (FTIR) spectra for the catalyst and its precursors were recorded on a Perkin–Elmer, USA, FTIR 783 spectrophotometer using KBr pellets. UV–vis spectrum was taken using a Shimadzu, Japan, UV-2401PC double beam spectrophotometer having an integrating sphere attachment for solid samples. The thermal stability of the immobilized catalyst was determined using a Mettler Toledo, Switzerland, TGA/DTA 851e instrument. The reaction products were analyzed using a Varian, USA, 3400 gas chromatograph equipped with a 30 m CP-SIL8CB capillary column and a flame ionization detector. All reaction products were identified by using an Agilent, USA, GC–MS (QP-5050) equipped with a 30 m HP-5ms capillary column.

2.1. General experimental procedure for Suzuki coupling reaction

A mixture of aryl halide (1.0 mmol), arylboronic acid (1.2 mmol), K_2CO_3 (2.0 mmol), DMF (6 mL), n-dodecane (15–20 mg) as an internal GC standard and 0.5 mol% of catalyst was stirred at 70 °C in air. Progress of the reaction was monitored by withdrawing the reaction mixtures periodically and analyzed by GC/GC–MS. GC yields were based on the amount of aryl halide employed. At the end of the reaction, the catalyst was separated by simple filtration. Filtrate was dried over Na_2SO_4, filtered, concentrated and the residue was purified by flash column chromatography on silica gel. The product was analyzed by GC–MS. All the prepared compounds are known and compared with authentic sample.

2.2. General experimental procedure for Heck reaction

A mixture of aryl halide (1.0 mmol), styrene (2.0 mmol), K_2CO_3 (2.0 mmol), DMF (6 mL) n-dodecane (15–20 mg) and 0.5 mol% of catalyst was stirred at 90 °C under air. To study the progress of the reaction, the reaction mixtures were collected at different time interval and quantified by GC analysis. At the end of the reaction, the catalyst was separated by simple filtration. Filtrate was dried over Na_2SO_4, filtered, concentrated and the residue was purified by flash column chromatography on silica gel. The product was

analyzed by GC–MS. All the prepared compounds are known and compared with authentic sample.

2.3. General experimental procedure for Sonogashira reaction

A round-bottomed flask was charged with aryl iodide (1.0 mmol), phenylacetylene (1.5 mmol), catalyst (1.0 mol% Pd), triethylamine (2.0 mmol) and DMF (6 mL) and n-dodecane (15–20 mg) as an internal GC standard. The resulting mixture was stirred at the appropriate temperature (90 °C). The reaction mixtures were withdrawn periodically and analyzed by GC/GC–MS. GC yields are based on the amount of aryl halide employed. Upon completion of the reaction, the reaction mixture was cooled and filtered to remove the catalyst which could be used for further reaction. The filtrate obtained was purified by flash column chromatography on silica gel to afford the desired product, which was confirmed by GC–MS. All the prepared compounds are known and compared with authentic sample.

2.4. General experimental procedure for amination reaction

A mixture of aryl halide (1.0 mmol), amine (1.0 mmol), KO^tBu (1.5 mmol), toluene (6 mL) n-dodecane (15–20 mg) and 1.0 mol% Pd of catalyst was stirred at 120 °C under nitrogen atmosphere. To study the progress of the reaction, the reaction mixtures were collected at different time interval and quantified by GC analysis. At the end of the reaction, the catalyst was separated by simple filtration. Filtrate was dried over Na_2SO_4, filtered, concentrated and the residue was purified by flash column chromatography on silica gel. The product was analyzed by GC–MS. All the prepared compounds are known and compared with authentic sample.

2.5. General experimental procedure for cyanation reaction

A mixture of $K_4Fe(CN)_6$ (1.0 mmol), aryl halides (1.5 mmol), catalyst (1.0 mol% Pd), triethylamine (2.0 mmol) and DMF (6 mL) was stirred for 24 h under air at 100 °C. The progress of reaction was monitored by gas chromatography. After completion, the reaction mixture was cooled and filtered to remove the catalyst which could be used for further reaction. The filtrate obtained was purified by flash column chromatography on silica gel to afford the desired product, which was confirmed by GC–MS. All the prepared compounds are known and compared with authentic sample.

2.6. Synthesis of catalyst

The synthetic procedure of polymer anchored palladium complex is illustrated in Scheme 1. The complex was prepared according to the literature procedure [44]. Firstly, the chloromethylated polystyrene (**1**) (1 g) was reacted with anthranilic acid (500 mg) in DMF (10 mL) under reflux condition for 36 h to afford polymer anchored ligand (**2**). This polymer anchored anthranilic acid ligand (1 g) subsequently reacted with palladium chloride (0.1 g) in methanol (10 mL) at 80 °C for 10 h to generate the corresponding polymer anchored Pd(II) complex (**3**).

3. Results and discussions

3.1. Characterization of the PS–Pd(II)–anthra complex

Due to insolubility of the polymer anchored Pd(II) complex in all common organic solvents, its structural investigations were limited only to its physicochemical properties, SEM–EDX, TGA–DTA, IR and UV–vis spectral data. The complete incorporation of the organic substructure in the material was confirmed by elemental analysis.
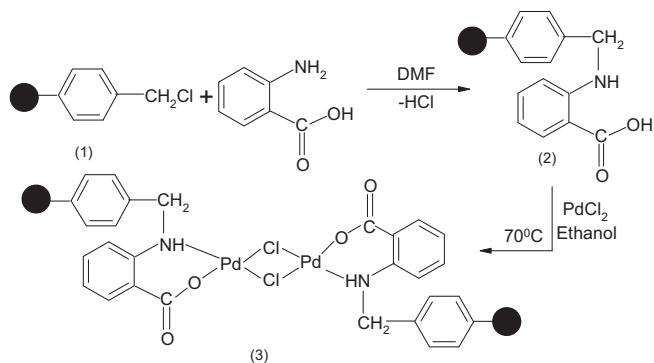
Scheme 1. Synthesis of PS–Pd(II)–anthra complex.

Fig. 2. EDX spectra of PS–anthra ligand (A) and PS–Pd(II)–anthra complex (B).

Pure chloro-methyl polystyrene group contained 19.18 wt% of Cl per gram of resin (5.5 mmol Cl per gram of resin).The remaining chloride content of 1.86% in polymer anchored ligand suggested nearly 89% conversion of the available chloro-methyl group to the corresponding polymer anchored ligand. The metal content of polymer anchored Pd(II) complex determined by AAS suggested 5.28 wt% metal loading in the immobilized palladium complex (degree of loading of palladium is 0.49 mmol/g of resin). The SEM images of polymer anchored ligand and metal complex clearly show the morphological change which occurred on the surface of the polymer matrix after loading of the metal (Fig. 1). EDX data also supports the metal attachment on the surface of polymer matrix (Fig. 2).

Thermogravimetric analyses of supported catalyst and its precursor, polymer anchored anthranilic acid, were taken in air atmosphere at a heating rate of $10\,°C\,min^{-1}$. The polymer anchored palladium complex is stable upto $385\,°C$ whereas polymer anchored ligand decomposes at $360\,°C$ (Fig. 3). After complexation with metal, the thermal stability of the ligand is slightly improved. DTA study reveals that the decomposition stages are exothermic in nature (not shown).

The mode of attachment of anthranilic acid and metal onto the polymeric support is confirmed by IR spectral data both in the mid $(4000–400\,cm^{-1})$ and far $(600–50\,cm^{-1})$ IR regions. The pure chloro-methylated polysterene beads show a sharp characteristic IR peak at $1260\,cm^{-1}$ (ν –CH_2-Cl group in polymer). Disappearance

of ν (–C-Cl) band and appearance of a strong band at $3455\,cm^{-1}$ (ν –NH, secondary amine) on anchoring with anthranilic acid suggests the covalent bond formation through nitrogen atom [45]. Other characteristic peaks at 3448 (ν –OH), 1706 (ν C=O), 1589 (ν_{asym} COO) and 1422 (ν_{sym} COO) also supports the formation of ligand [46]. After metal loading, shifting of these bands toward lower frequency regions (3280 ν N–H, 1555 ν_{asym} –COO and 1410 ν_{sym} –COO) suggests the involvement of the amine and carboxylic groups of the anthranilic acid in complex formation. More conclusive information on the coordination of the ligand to the central metal ion comes from the new bands due to ν (Pd–N) $450\,cm^{-1}$ [47], ν (Pd–Cl, bridged) $332\,cm^{-1}$ [48] and ν (Pd–O, bridged) $358\,cm^{-1}$ [49].
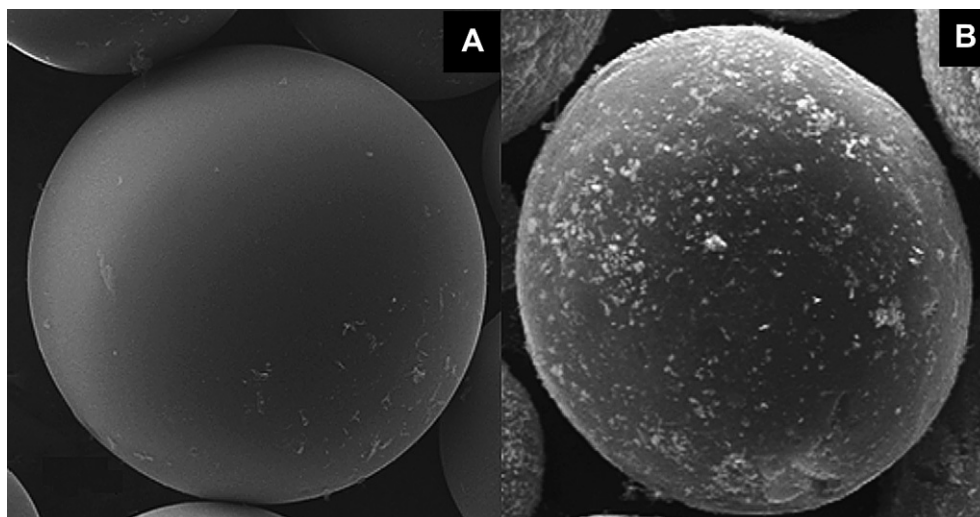

Fig. 1. FE-SEM images of PS–anthra ligand (A) and PS–Pd(II)–anthra complex (B) respectively.
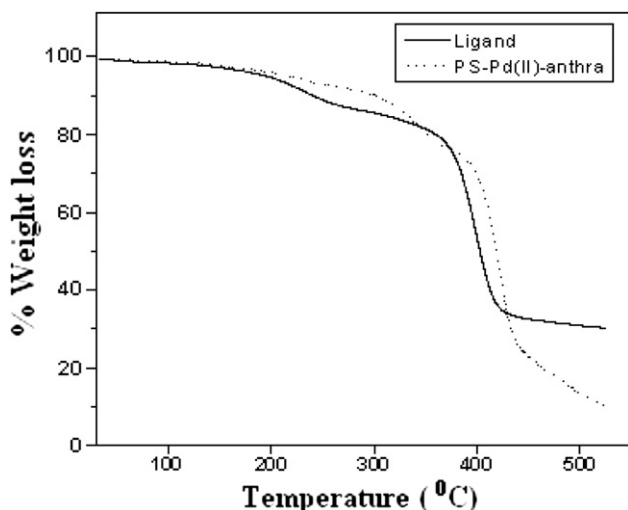
Fig. 3. Thermogravimetric weight loss plots for PS–anthra ligand and PS–Pd(II)–anthra complex, respectively.
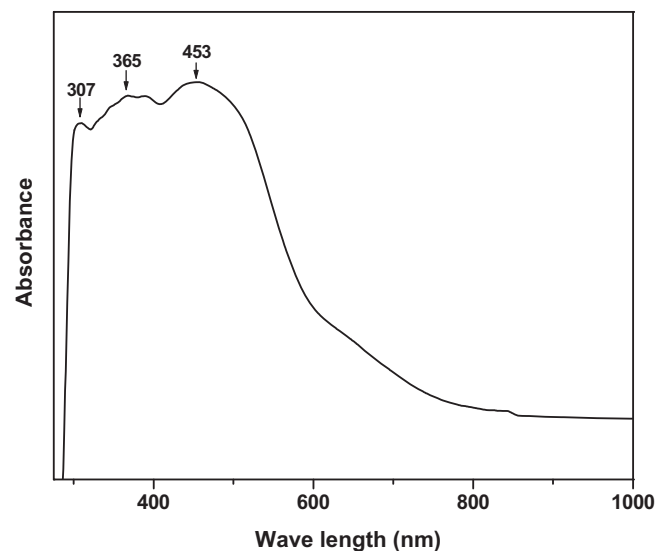

Fig. 4. UV–vis spectrum for PS–Pd(II)–anthra complex.

The UV–vis spectra 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 307 nm, 365 nm and 453 nm, which may be designated as $^1A_{1g} \rightarrow {}^1E_g$, $^1A_{1g} \rightarrow {}^1B_{1g}$ and $^1A_{1g} \rightarrow {}^1A_{2g}$ transitions respectively [50,51] (Fig. 4). The room-temperature magnetic moment of the polymeric Pd(II) complex has been found to be diamagnetic due to spin paired d^8 system [52]. This diamagnetic nature supports the formation of a low-spin square-planar geometry around Pd(II). Based on the above results of elemental analysis, IR, electronic spectra, magnetic moment measurements and thermal analysis, the structure of the Pd(II) complex is suggested and are given in Scheme 1.

3.2. Catalytic activities

3.2.1. Suzuki cross-coupling reaction

Suzuki cross-coupling reaction represents a powerful method for the C–C bond formation [53–55]. Construction of biaryl compounds via the palladium-catalyzed Suzuki reaction is an interesting area in organic synthesis. The importance of biaryl units as molecular components in pharmaceuticals, herbicides and natural products, as well as in engineering materials such as conducting polymers, molecular wires and liquid crystals, has attracted enormous interest [56–58]. The reaction represents an attractive alternative over other methods using organometallics because organoboranes are air- and moisture-stable with relatively low toxicity.

We started our investigation for Suzuki reaction (Scheme 2) with the coupling of 4-bromoacetophenone and phenylboronic acid as model reaction. The performance of a palladium-catalyzed Suzuki reaction is known to be governed by the number of factors such as the bases, solvents, reaction temperatures etc. To verify the solvent effect in Suzuki cross-coupling reactions, a series of reactions were investigated by taking the model reaction in different solvents. The reaction conducted in polar solvent medium like DMF and DMSO, were found to be most effective. The use of THF, MeOH and ACN as solvents led to slower reactions and no desired cross-coupling products were observed while reactions were carried out in nonpolar solvents like toluene and dichloromethane. Consequently, DMF was chosen as the medium of choice for this coupling. This coupling reaction was found to be highly sensitive to the reaction temperature. At lower temperatures (30–50 °C) only low to moderate yield was obtained. A reaction temperature of 70 °C was found to be optimal for the model reaction. The influence of base on the catalytic performance of this system was investigated by employing various bases. Comparison of inorganic bases utilized showed that carbonate bases were more stable than the other ones. Within a short time the reaction proceeded in high yield in presence of Na_2CO_3 or K_2CO_3. We found that using K_2CO_3 as base in DMF at 70 °C gave the coupled product in 99% yields. The other inorganic bases such as NaOH, K_3PO_4, NaOAc and organic bases like Et_3N were not as effective as K_2CO_3, only affords moderate to low yields of coupling products. The quantity of K_2CO_3 was also found to be important. The base–substrate molar ratio of 2:1 was found to be ideal for present catalytic system.

To examine the scope of this coupling reaction, a variety of aryl halides were coupled with different phenylboronic acids in DMF in the presence of a catalytic amount of PS–Pd(II)–anthra using K_2CO_3

X = Cl, Br, I
R_1 = H, CH_3, OMe, COMe, NO_2,
R_2 = H, CH_3, COMe
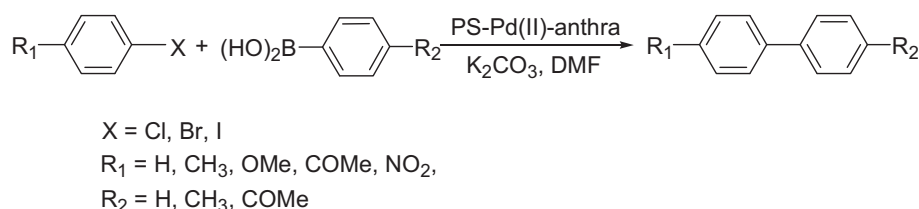
Scheme 2. Suzuki cross-coupling reaction.

Table 1
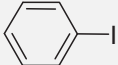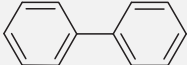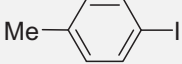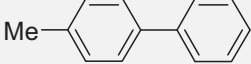Suzuki cross-coupling reaction of aryl halides and arylboronic acids using PS–Pd(II)–anthra.[a]
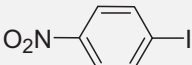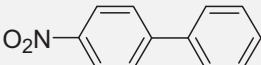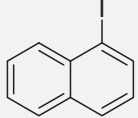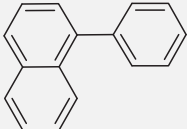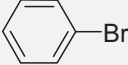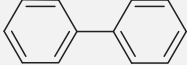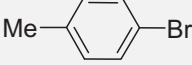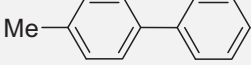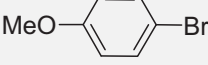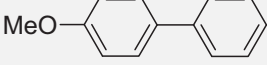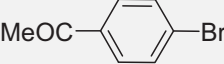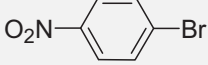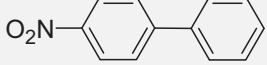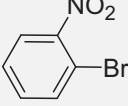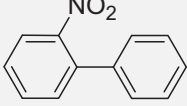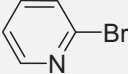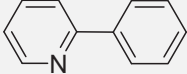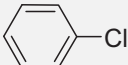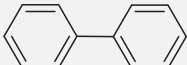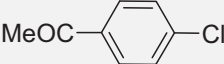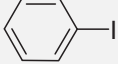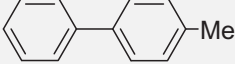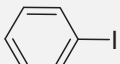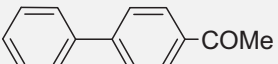
Entry	ArX	Product[b]	Time	Yield[c] (%)
1			5	100
2			5	98
3			5	100
4			6	93
5			6	97
6			8	98
7			8	95
8			6	99
9			6	99
10			8	89
11			6	94
12			12	72
13			12	83
14			8	98

Table 1 (*continued*)

Entry	ArX	Product[b]	Time	Yield[c] (%)
15	(phenyl)–I	(biphenyl)–COMe	8	99

[a] Reaction conditions: ArX (1.0 mmol), ArB(OH)$_2$ (1.2 mmol), K$_2$CO$_3$ (2.0 mmol), DMF (6 mL), catalyst (0.5 mol% of Pd); All the reactions were carried out in air.

[b] Products were identified by comparison of their IR, GC–MS and ^{1}HNMR spectral data those reported in the literature.

[c] Yield of product was determined by GC and GC–MS analysis using dodecane as internal standard.

as base. The experimental results are summarized in Table 1. A control experiment indicated that the coupling reaction did not occur in the absence of catalyst. Aryl halides bearing either electron-donating or electron-withdrawing substituents in the *para* positions, afforded the corresponding biphenyls in good to excellent yields. Heteroarylbromide, 2-bromopyridine, was coupled efficiently with phenylboronic acid to give the desired product in excellent yield (Table 1, entry 11). The cross-coupling of sterically hindered aryl halides, 1-iodonaphhalene and 2-nitrobromo benzene also proceed quite well (Table 1, entries 4, 10). The reaction of 4-methyl or 4-acetyl boronic acid with iodobenzene provided the corresponding biaryls in high yields (Table 1, entries 14, 15). The coupling reaction of chloroarenes also took place under similar reaction conditions, though the reactivity was lower than their iodo and bromo counterpart (Table 1, entries 12, 13).

3.2.2. Heck cross-coupling reaction

The Heck cross-coupling reaction, the palladium-catalyzed coupling of aryl halides with alkenes, is an extremely valuable method for carbon–carbon bond formation [59–62]. It is now widely used in the special chemical and pharmaceutical manufacturing industries, because it is simple, versatile, and relatively mild. Our catalyst was next tested for the Heck coupling reaction (Scheme 3). Initial catalytic studies with 0.5 mol% of catalyst were performed on the Heck cross-coupling of bromobenzene with styrene as a model reaction in different temperature, solvents and bases under air atmosphere. The reaction was conveniently carried out at 90 °C. At lower temperature, incomplete conversion of bromobenzene was obtained. Several organic and inorganic bases were screened and it was observed that the potassium carbonate was the most efficient base for present catalytic reaction. Other bases were significantly less effective and gave moderate yield. The influence of solvents on Heck coupling reaction was also examined in different polar and non-polar solvents. Among different polar solvents, such as DMF, DMSO, NMP, high catalytic activity was observed in DMF medium. Non-polar solvents were not favorable for the Heck coupling reaction under present reaction condition. In the absence of catalyst, the reaction did not proceed.

With these optimized reaction conditions, the reaction of various substituted and non-substituted aryl halides with styrene were examined to explore the scope and generality of this catalyst for the synthesis of various aryl-alkenes and the results are summarized in Table 2. As shown in Table 2, the substituent groups on the aromatic ring of the aryl halides had a significant effect on the yields. It was observed that aryl halides with electron-withdrawing functionality undergo Heck coupling reaction efficiently to afford the corresponding products in excellent yields. Aryl halides with electron donating functionality gave moderate to good yields of coupled product. Iodobenzene gave excellent yield of coupled product (Table 2, entry 1). Compared with substituted aryl bromides, the reaction of bromobenzene with styrene gave slight lower product yield (Table 2, entry 6). Sterically hindered 1-iodonaphthalene also coupled with styrene to give desired product in good yield (Table 2, entry 5). The entire coupled products showed *E*-stereochemistry. These results showed that the scope of the reaction is quite broad and the conditions are tolerant of various functional groups of substituted on aryl bromides and iodides with an extremely good selectivity to the *trans*-isomer. However no coupling product was obtained in the reaction of less reactive chlorobenzene (Table 2, entry 11).

3.2.3. Sonogashira cross-coupling reaction

The present palladium catalyst was then tested another most important C–C bond forming process in synthetic organic chemistry, known as Sonogashira coupling reaction, the palladium-catalyzed coupling of aryl halides with terminal alkynes [63–65]. To survey the reaction parameters for the Sonogashira reaction, we chose to examine K$_2$CO$_3$, NaOH, Cs$_2$CO$_3$, Et$_3$N and piperidine as base and DMF, DMSO, toluene and DCM as the solvent. It was found that the reaction performed in DMF with Et$_3$N as base at 90 °C showed the best performances (Scheme 4).

Under optimized reaction conditions, the efficiency of this catalyst was studied for Sonogashira coupling reaction of various aryl halides and the results are summarized in Table 3. A control experiment indicated that the coupling reaction did not occur in the absence of catalyst. Iodobenzene efficiently reacted with the phenylacetylene to yield coupled product in good yield (Table 3, entry 1). Aryl iodides with electron donating group such as methyl (Table 3, entry 2) and electron-withdrawing groups such as nitro and acetyl (Table 3, entries 3, 4) were well tolerated under the present catalytic system. Sterically hindered 1-iodonaphthalene was also found to react smoothly under present reaction conditions (Table 3, entry 5). Very small amount homocoupled product was detected during the reaction. Using aryl bromide instead of aryl iodide yielded only a small amount of coupled derivatives under the conditions employed for iodides (Table 3, entry 6). 4-Acetyl-bromobenzene gave moderate yield of coupled product (Table 3, entry 7).
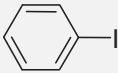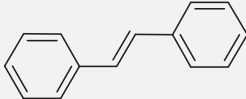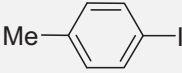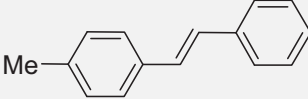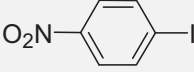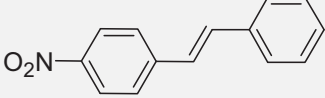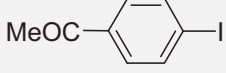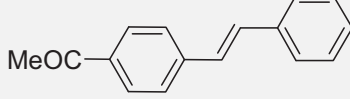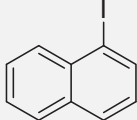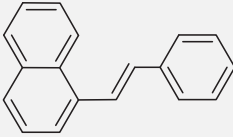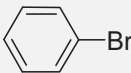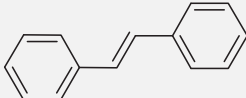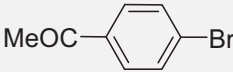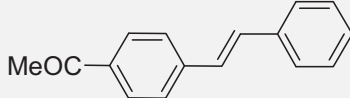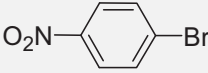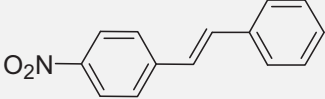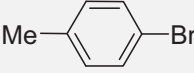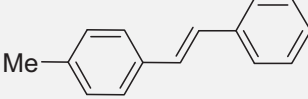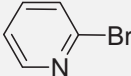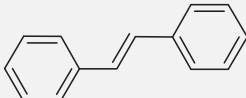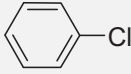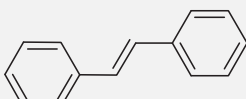
3.2.4. Amination reaction

C–N bond formation by palladium-catalyzed cross-coupling reaction is one of the powerful techniques in synthetic organic chemistry. This method has been widely used in biological, pharmaceutical, and material sciences for various applications [66,67]. To test the further applicability of the PS–Pd(II)–anthra catalyst, we examined the amination reaction (Scheme 5) between aniline with various aryl halides. In the absence of catalyst the reaction did

$$X = Cl, Br, I$$
$$R = H, CH_3, COMe, NO_2$$
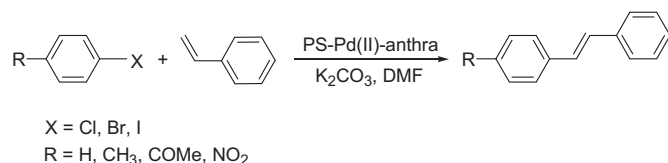
Scheme 3. Heck cross-coupling reaction.

Table 2
Heck cross-coupling reaction of aryl halides and styrene using PS–Pd(II)–anthra.[a]

Entry	ArX	Product[b]	Time	Yield[c] (%)
1			8	95
2			8	89
3			8	97
4			8	97
5			10	92
6			16	84
7			16	90
8			16	92
9			16	86
10			16	81
11			24	No reaction

[a] Reaction conditions: ArX (1.0 mmol), styrene (2.0 mmol), K_2CO_3 (2.0 mmol), DMF (6 mL), catalyst (0.5 mol% of Pd); all the reactions were carried out in air.
[b] Products were identified by comparison of their IR, GC–MS and ^{1}HNMR spectral data those reported in the literature.
[c] Yield of product was determined by GC and GC–MS analysis using dodecane as internal standard. In all the coupling reactions, only *E*-stereochemistry was observed.

X = Br, I
R = H, CH₃, COMe, NO₂,
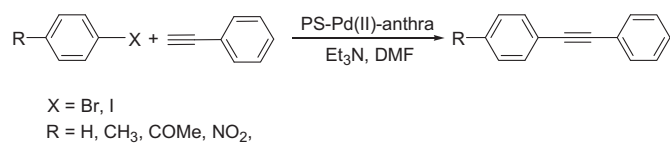
Scheme 4. Sonogashira cross-coupling reaction.

not proceed. Initially we screened typical reaction parameters including solvents and bases and we varied the temperature and time. Bases such as K_2CO_3, Cs_2CO_3, Et_3N, K_3PO_4, NaOMe and KO^{t}Bu are found to facilitate this coupling reaction and among them KO^{t}Bu was the best. Solvents such as DMF, ACN, MeOH, C_6H_6 and toluene were investigated and it was found that nonpolar solvents were more favored. With DMF, ACN, and MeOH, yields were comparatively low. Consequently toluene is chosen as the medium of choice for this coupling as highest conversion was obtained. This arylation is also found to be highly sensitive to reaction temperature and time. At lower temperatures (30 and 60 °C), the reaction totally fails and with lower reaction time (6 and 12 h) only low to moderate yield was obtained. It was found that the reactions performed in toluene medium with KO^{t}Bu at 120 °C for 24 h showed the best performance.

On the basis of the above optimized reaction conditions, the coupling reactions between a variety of aryl halides and amines

were investigated. Representative results are summarized in Table 4. It was observed that the reaction of iodobenzene and aniline proceeded at 120 °C resulting in corresponding coupling product in high yield (Table 4, entry 1). Iodoarenes with electron-withdrawing group (Table 4, entries 2, 3) reacted at a faster rate than iodoarenes with electron donating group (Table 4, entry 4). Morpholene was also coupled with iodobenzene to give the desired aryl amines in good yields (Table 4, entry 6). Substituted anilines coupled with iodobenzene to give the desired product in moderate yield (Table 4, entry 5). Bromobenzene remained inactive in amination reaction under present reaction conditions (Table 4, entry 7). Although increasing the reaction temperature to 140 °C and prolonged the reaction time to 48 h, slight conversion of bromobenzene was obtained (Table 4, entry 8).

3.2.5. Cyanation reaction

Cyanation of aryl halides is a common and useful transformation in organic synthesis as aryl cyanides constitute building blocks for the synthesis of fine chemicals [68,69] and are integral parts of several dyes, natural products, herbicides, agrochemicals, and pharmaceuticals. In this reaction traditionally used cyanide sources are KCN, Me₃SiCN, NaCN and Zn(CN)₂ [70–72]. It is evident that the utilization of these cyanide sources is connected with a numerous drawbacks. They are highly poisonous and may contaminate in the product mixture. Recently, $K_4[Fe(CN)_6]$ has been shown to be

Table 3
Sonogashira cross-coupling reaction of aryl halides and phenylacetylene using PS–Pd(II)–anthra.[a]

Entry	ArX	Product[b]	Time	Yield[c] (%)
1			12	94
2			12	85
3			12	96
4			12	96
5			12	87
6			24	14
7			24	45

[a] Reaction conditions: ArX (1.0 mmol), phenylacetylene (1.5 mmol), Et₃N (2.0 mmol), DMF (6 mL), catalyst (1.0 mol% of Pd); all the reactions were carried out in air.
[b] Products were identified by comparison of their IR, GC–MS and ¹HNMR spectral data those reported in the literature.
[c] Yield of product was determined by GC and GC–MS analysis using dodecane as internal standard.
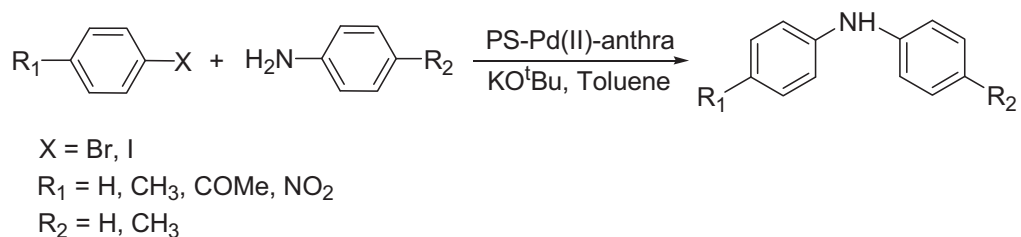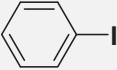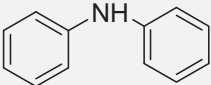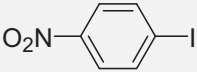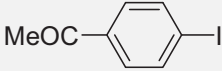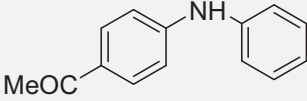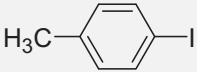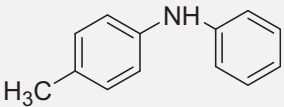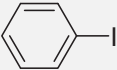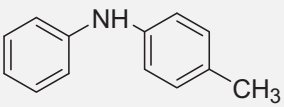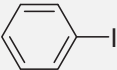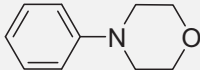
Scheme 5. Amination reaction.

Table 4
Amination reaction of aryl halides using PS–Pd(II)–anthra.[a]

Entry	ArX	Product[b]	Time	Yield[c] (%)
1			24	83
2			24	85
3			24	83
4			24	74
5			24	76
6			24	84
7			24	No reaction
8			48	26[d]

[a] Reaction conditions: ArX (1.0 mmol), amine (2.0 mmol), KO^{t}Bu (2.0 mmol), toluene (6 mL), catalyst (1.0 mol% of Pd); all the reactions were carried out in nitrogen atmosphere.
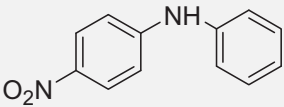[b] Products were identified by comparison of their IR, GC–MS and ^{1}HNMR spectral data those reported in the literature.
[c] Yield of product was determined by GC and GC–MS analysis using dodecane as internal standard.
[d] Temperature = 140 °C.

Scheme 6. Cyanation reaction.

effective as a source of cyanide since it is nontoxic, commercially available, cheaper and easily handled [73–75].

We finally explored the utility of this PS–Pd(II)–anthra catalytic system for cyanation reaction of aryl halides (Scheme 6). After screening a range of usual inorganic and organic bases and exploring the scope of various solvents, it was found that this catalyst is most efficient for the cyanation reaction in the presence of Et_3N as base and DMF as solvent at 100 °C. The control experiments showed that the coupling reaction did not occur in the absence of the catalyst or base. Iodobenzene efficiently reacted with $K_4[Fe(CN)_6]$ to yield the nitrile product in excellent yields (Table 5, entry 1). Substituted aryl iodides also provided good yield of nitrile products (Table 5, entries 2–4). 1-iodonaphthalene also underwent smooth reaction providing 85% yield (Table 5, entry 5). The results are presented in Table 4. Only aryl iodides are reactive and other halides remained inert under present reaction conditions (Table 5, entry 6).

3.3. Comparison with other reported system

Table 6 provides a comparison of the results obtained for our present catalytic system with those reported in the literature. From Table 6, it is seen that present catalyst exhibited higher conversions and yields compared to the other reported system [76–81]. Reactions conducted at lower temperature and shorter reaction time was required for these reactions using present catalyst.

3.4. 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 and the palladium leaching of this catalyst were examined by the "hot-filtration test" and "solid phase poisoning test" for the Suzuki coupling reaction of 4-bromoanisole and phenylboronic acid.

3.4.1. Hot-filtration test

Hot-filtration test was performed in the Heck cross-coupling reaction of 4-bromoanisole with phenylboronic acid to investigate whether the reaction proceeded in a heterogeneous or a homogeneous fashion. After continuing the reaction for 3 h, the catalyst was removed by filtration and the determined conversion was 46%. The resulting filtrate was subjected to heating for further 6 h. From GC result it reveals 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. Further, no evidence for leaching of palladium or decomposition of the complex catalyst was observed during the catalytic reaction and no palladium could be detected by atomic absorption spectroscopic measurement of the filtrate after removal of catalyst. These studies clearly demonstrated that palladium was intact to a considerable extent with the heterogeneous support, and there is no significant amount of leaching occurred during reaction.

Table 5
Cyanation reaction of aryl halides and $K_4Fe(CN)_6$ using PS–Pd(II)–anthra.[a]

Entry	ArX	Product[b]	Time	Yield[c] (%)
1			18	98
2			18	91
3			18	98
4			18	97
5			24	85
6			24	No reaction

[a] Reaction conditions: $K_4Fe(CN)_6$ (1 mmol), aryl halide (1.5 mmol), catalyst (1.0 mol% Pd), Et_3N (2.0 mmol), DMF (6 mL), 100 °C.
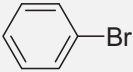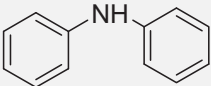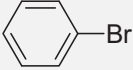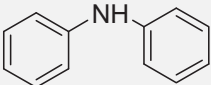[b] Products were identified by comparison of their IR, GC–MS and ^{1}HNMR spectral data those reported in the literature.
[c] Yield determined by GC and GC–MS analysis using dodecane as internal standard.

Table 6
Comparison of catalytic activity of the present catalyst in the cross-coupling and cyanation reactions with other related reported systems.

Reaction	Catalyst	Reaction conditions	Yield%	Reference
Suzuki reaction: (bromobenzene + Phenylboronic acid)	PS–Pd(II)–anthra	K_2CO_3, DMF, 0.5 mol% catalyst, 70 °C, 6 h	97	Present
	CuO/Pd-3	K_2CO_3, DMF, 110 °C, 10 h	80	[76]
	Pd^{2+} sepiolite	K_2CO_3, DMF, 0.5 μmol of Pd catalyst, 100 °C, 8 h	81	[77]
Heck reaction: (bromobenzene + styrene)	PS–Pd(II)–anthra	K_2CO_3, DMF, 0.5 mol% catalyst, 90 °C, 16 h	84	Present
	Catalyst 2	Na_2CO_3, DMF, 0.5 mol% catalyst, 140 °C, 7 h	78	[78]
	Si–As–Pd(0)	Bu_3N, p-xylene, 0.03 mmol Pd catalyst, 140 °C, 12 h	54	[79]
Sonogashira reaction: (iodobenzene + phenylacetylene)	PS–Pd(II)–anthra	Et_3N, DMF, 1.0 mol% catalyst, 90 °C, 12 h	94	Present
	I-Pd	Et_3N, ACN, 500 mg cat. (0.1 mmol as $Pd(OAc)_2$), reflux	80	[80]
Amination reaction: (iodobenzene + aniline)	PS–Pd(II)–anthra	KO^tBu, DMF, 1.0 mol% catalyst, 120 °C, 24 h	83	Present
	Pd (DPPE)	NaOMe, toluene, 0.05 mmol $Pd(OAc)_2$, 110 °C, 24 h	82	[81]
Cyanation reaction: (iodobenzene)	PS–Pd(II)–anthra	Et_3N, DMF, $K_4Fe(CN)_6$, 1.0 mol% catalyst, 100 °C, 10 h	98	Present
	CuO/Pd-3	DMF, $K_4Fe(CN)_6$, 120 °C, 10 h	60	[76]

3.4.2. Solid phase poisoning test

Further the heterogeneous nature of the catalyst was checked by the solid phase poisoning test. This test was performed for the Suzuki coupling reaction of 4-bromoanisole. We used commercially available 3-mercaptopropyl-functionalized silica as effective palladium scavenger which selectively coordinates and deactivates the leached out palladium. For Suzuki reaction, a mixture of 4-bromoanisole (1.0 mmol), phenylboronic acid (1.2 mmol), K_2CO_3 (2.0 mmol), DMF (6 mL), 0.005 g 3-mercaptopropyl-functionalized silica and 0.5 mol% of Pd catalyst was stirred at 70 °C for 8 h. In this case no change in conversion was observed which suggests that the catalyst is heterogeneous in nature since 3-mercaptopropyl-functionalized silica form a complex with the leached palladium and there by deactivate the catalyst. From this result we may conclude that no leaching of palladium is occurred during Suzuki coupling reaction.

3.5. Catalyst reusability

Recovery and catalyst reuse are important issues in the coupling 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 Heck cross-coupling reaction taking the reaction of 4-bromoanisole and phenylboronic acid (Fig. 5). 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 °C. The recovered catalyst was employed in the next run with further addition of substrates in appropriate amount under optimum reaction
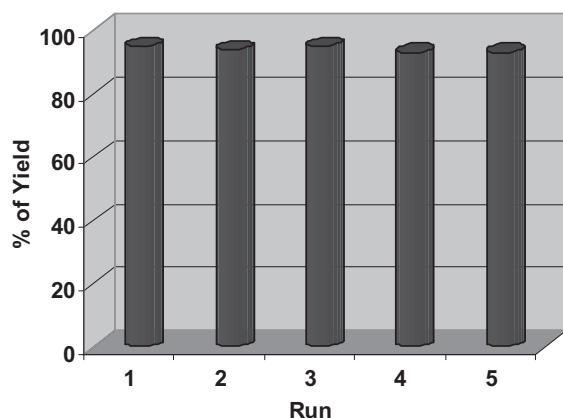
conditions. The catalyst shows unchanged catalytic activity up to five reaction cycles. No catalyst deterioration was observed, confirming the high stability of the heterogeneous catalyst under the reaction conditions.

4. Conclusions

In conclusion, we have reported the simple preparation of polystyrene-supported Pd(II) complex and its successful application for the coupling and cyanation reactions of aryl halides under air atmosphere using DMF as solvent. The present system is highly air and moisture stable and the catalyst can be synthesized readily from inexpensive and commercially available starting materials. The system works equally well for wide variety of aryl halides, alkenes, alkynes, amines and organoboronic acid and tolerates a variety of functional groups. Moreover the catalyst was reused for five consecutive cycles with consistent catalytic activity. Further work is in progress to broaden the scope of this catalytic system for other organic transformation.

Fig. 5. Recycling efficiency of PS–Pd(II)–anthra complex catalyst for the Suzuki cross-coupling reaction of 4-bromoanisole.

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