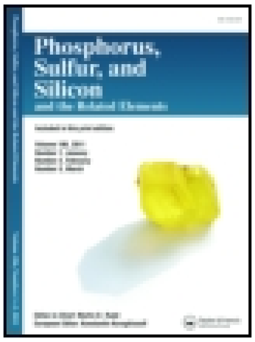

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Polymeric PCP Pd catalyst for cyanation reaction

Modified Merrifield resin-supported PCP pincer palladium nanoparticles as a new polymeric catalyst for cyanation of aryl iodides

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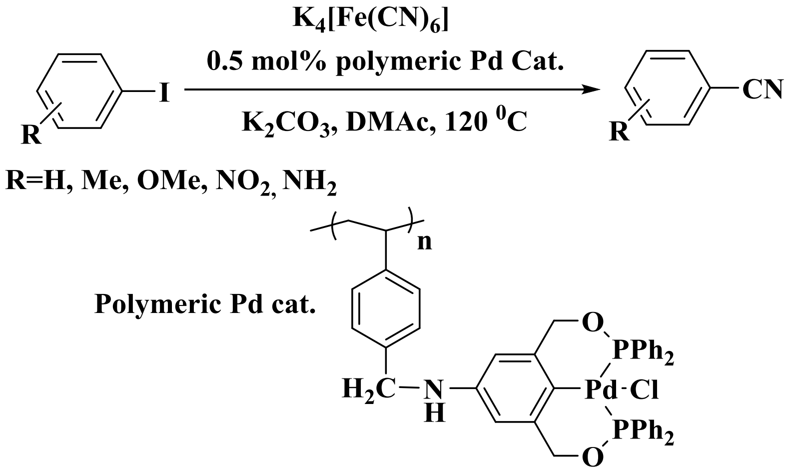
Abstract

A new tridentate PCP pincer palladium complex based on cross-linked Merrifield resin containing phosphinite ligand was synthesized and characterized. This polymeric catalyst was used in preparation of benzonitriles from different aryl iodides using potassium hexacyanoferrate (II) as a cyanide source. The presence of active metallic palladium in the catalyst was verified by X-ray power diffraction (XRD) and X-ray photoelectron spectroscopy (XPS) techniques. Transmission electron microscopy (TEM) showed good dispersion of catalytic sites in the range of 30-50 nm. The catalyst is easily separated from reaction mixture and can be used several times in repeating cycles without considerable loss in its activity. The leaching of Pd from the support is negligible which was confirmed by ICP-OES and hot filtration test.



Keywords

Merrifield resin, pincer palladium complex, cyanation.

Introduction

Aryl nitriles play crucial role in organic synthesis [1]. Products containing the nitrile group are biologically important [2,3] and can be easily transformed into various classes of compounds such as nitrogen containing heterocycles, aldehydes, amines, tetrazoles, acids, and acid derivatives [4,5]. Many synthetic methodologies are reported in the literature for the synthesis of benzonitriles [6,7].The traditional method for preparing aromatic nitriles from the corresponding aryl halides is Rosemund-Von Braun reaction [8,9] which requires stoichiometric amount of copper (I) cyanide at elevated temperatures. This approach produces equimolar amounts of heavy metal waste. Of numerous recently reported methods, transitional metal-catalyzed cyanation of aryl halides is one of the most convenient ones. In this regard, transition metal complex of palladium [10-21], nickel [22] and copper [23-25] have been introduced. Among them, Pd complexes are useful catalysts due to the tolerance to a variety of functional groups and less sensitivity to air and humidity. In spite of the fact that many homogeneous active Pd catalysts have been reported successfully for cyanation of aryl halides [10-21], immobilizations of these catalysts on insoluble support can facilitate the recovery and reuse of the metal complexes. There are, however, only few examples of heterogeneous palladium catalysts for the cyanation of aryl halides [26-29].

In continuation of our previous studies on the introduction of heterogeneous palladium catalysts based on polyacrylamide support [30] and polymer grafted silica, [31-33] recently we disclosed the preparation of an active heterogeneous PCP-pincer palladium catalyst containing phosphinite ligand based on Merrifield resin for carbon-carbon coupling reactions [34]. Herein, we reveal new application of this efficient catalyst in cyanation reaction of aryl iodides using commercially available potassium hexacyanoferrate (II) as a cyanide source.

Result and discussion

The design of the Pd catalyst is shown in Scheme 1.

Chloromethylated polystyrene (2% crosslinked) **(1)** was reacted with excess 5-amino-isophthalic acid dimethyl ester **(2)** to form its corresponding ester modified polymer **(3)**. The ester groups reduced to their corresponding hydroxyl groups with $LiAlH_4$ in dry THF to produce polymer **(4)**. The FT-IR spectrum of this modified polymer showed a broad band at 3388 cm^{-1} due to overlapping of stretching frequencies of OH and NH groups (Figure 1). The polymeric phosphinite ligand **(5)** was then prepared by the reaction of polymer **(4)** with $ClPPh_2$ in THF. FT-IR spectrum of this modified polymer showed no broad band of hydroxyl groups (Figure 1). Finally, palladium pincer complex **(6)** was obtained by mixing polymer **(5)** with $PdCl_2$ in presence of cesium carbonate as a base in DMF. Determination of Pd content was carried out by digestion of the catalyst with concentrated H_2SO_4 and HCl (1/1) followed by ICP analysis using calibration curve method. ICP analysis revealed that polymer **(6)** contained an average of 0.36 mmol/g of Pd.

According to the previous studies in the literature [35-37], Pd (II) pincer complexes are simply precatalysts that decompose under reaction conditions; often basic conditions at elevated temperatures and releasing colloidal Pd (0) nanoparticles that act as catalytically active species. Formation of Pd (0) nanoparticles on the catalytic system can be proven using various techniques such as XRD, XPS and TEM [34]. The XRD patterns for the Pd catalyst **(6)** showed the expected crystallinity of Pd (0) nanoparticles. The XPS spectrum showed the binding energy appearing in 344 and 349 eV for 3d5/2 and 3d3/2 respectively. The separation of the two peaks to be 5 eV is assigned to Pd (0) [38]. Furthermore, TEM image clearly showed that Pd nanoparticles were dispersed well in the polymer matrix with a size in the range of 30–50 nm [34].

Thermogravimetric analysis (TGA) of **(6)** was carried out to investigate the thermal stability of the polymer-supported pincer Pd complex (Figure 2). The weight loss of **(6)** on heating up to 200 °C is negligible and might be attributed to the release of loosely bound volatiles on the surface. Thermal degradation of **(6)** started mostly after ~250 °C with three stages of decomposition and the most weight loss occurred after ~400 °C. The 5.7% decomposition at temperature range of 250-350 °C could be assign to the loss of organic moiety tethered to Merrifield resin which loading calculated to be 0.26 mmol/g. Another considerably weight loss occurred at 350-470 °C which is due to polystyrene backbone decomposition. Lastly, a minor decomposition at 470-600 °C is assigned to Pd loss and the capacity determined to be 0.31 mmol/g.

The patentability of this polymeric Pd catalyst was checked for the cyanation reaction of different aryl iodides. To optimize reaction condition, iodobenzene was chosen. Different cyanide sources such as potassium hexacyanoferrate (II), alkali and transition metal cyanides, trimethylsilyl cyanide and acetone cyanohydrins are reported in the literature [10-29]. Among theses we select commercially available potassium hexacyanoferrate $K_4[Fe(CN)_6]$ as a source of cyanide which combines excellent efficiency with low palladium catalyst loadings. It is non-toxic and has a low price. Furthermore it is soluble in polar solvents which are suitable for cyanation reactions. We used different solvents and bases for the cyanation of iodobenzene (Table 1). Among them DMAc and K_2CO_3 was the best option. Under this reaction condition, 100% conversion of iodobenzene to cyanobenzene was achieved within 135 min using 0.5 mol% of Pd catalyst (Table 1, entry 3).

The optimized reaction condition was applied in cyanation reaction of different aryl iodides (Scheme 2). Both electron-deficient and electron-rich aryl iodides were transformed to their corresponding cyanides in moderate to high yields (Table 2). As a general trend, electron-deficient aryl iodides are more reactive than electron-rich iodides. Ortho substituent was also tolerated (Table 2, entry 3 and 4).

On the basis of the general mechanism reported earlier in the literature [37, 40, 41], a mechanism for cyanation reaction is outlined in Scheme 3. After formation of colloidal Pd (0) nanoparticles from decomposition of Pd (II) pincer complexes as precatalysts, oxidative addition of the aryl halide to the Pd (0) catalyst gives Pd (II) complex (step 1). Ligand exchange with cyanide ion (step 2) gives complex which undergoes reductive elimination to produce the benzonitrile (step 3).

We investigated the recoverability and reusability of the supported catalyst in the conversion of iodobenzene to the cyanobenzene. The catalyst was recovered and reused for 5 cycles. The Pd catalyst exhibited only a slight loss in its activity and required a bit longer time to achieve full conversion even after 5 cycles. The results are shown in Figure 3. Furthermore, to probe the issue of palladium leaching in our system, the filtrate of the reaction mixture of iodobenzene was analyzed by ICP in 5 repeating cycles. Low palladium contamination was observed during these experiments. Analysis of the crude reaction mixture for the first reaction indicated a leaching of

3.2%. A leaching of 8.8% was observed in total for all 5 runs. Furthermore, hot filtration test proved the heterogeneous character of the catalytically active species [42].

Furthermore, TEM image of the used catalyst after five runs showed the stability of Pd nanoparticles without agglomeration in the surface of the polymer after recycling (Figure 4).

We provide a comparison of the results obtained for our present catalytic system with those limited heterogeneous palladium catalysts reported in the literature. From Table 3, it is seen that present catalyst yielded the cyanation product in a shorter reaction time compared to the other reported systems [26-29]. In other aspects such as solvent, base, cyanide source, amounts of catalyst, temperature and recyclability the heterogeneous catalyst **(6)** is comparable with other reported systems.

Experimental

Materials and techniques

All chemicals were of reagent grade and obtained from Merck, Aldrich and Fluka chemical companies and used without further purification. All products were characterized by FT-IR, ^{1}H-NMR and ^{13}C-NMR spectroscopy. ^{1}H-NMR and ^{13}C-NMR were performed on a Bruker Avance DPX instrument (250 MHz) in $CDCl_3$. FT-IR was performed using a Shimadzu FTIR-8300 spectrophotometer. All yields refer to the isolated products. Progress of reactions was followed by TLC on silica-gel Polygram SIL/UV 254 plates or by GC on a Shimadzu model GC 10-A instrument. The Pd analysis and leaching test was carried out by inductively coupled plasma (ICP) analyzer (Varian, Vista-Pro). TGA thermograms were recorded on an instrument of Perkin Elmer with N_2 carrier gas and the rate of temperature change of 20 °C/min was used. X-ray diffraction data obtained with XRD, D8, Advance, Bruker, axs. X-Ray photoelectron spectroscopy (XPS) was performed with XR3E2 (VG Microtech) twin anode X-ray source using AlKα=1486.6 eV). TEM analysis was performed on a Philips model CM 10 instrument. The Supplemental Materials contains additional characterization of the catalyst (Figures S 1 – S 3) and sample NMR spectra for the known products (Figures S 4 – S 15)

Preparation of polymer supported PCP pincer palladium catalyst

The Pd polymeric catalyst was prepared as described in our previous paper [34]. ICP determination using calibration curve method revealed Pd content of 0.36 mmol/g.

General procedure for cyanation of aryl iodides

To a mixture of aryl iodide (1.0 mmol), $K_4[Fe(CN)_6].3H_2O$ (1.0 mmol), K_2CO_3 (1.0 mmol) and Pd complex (0.5 mol%), DMAc (5 mL) was added. The reaction mixture was stirred at 120 ^{o}C for an appropriate time. On completion of the reaction determined by TLC or GC, the mixture was filtered and the filtrate was poured into water (50 mL) and extracted with EtOAc (3×15 mL). The combined organic phases were dried over Na_2SO_4, filtered and evaporated under vacuum. The pure product was isolated by flash chromatography using petroleum ether or EtOAc or their mixture as eluents. Characterization of the products was performed by comparison of their FT-IR, ^{1}H-NMR, ^{13}C-NMR and physical data with those of the authentic samples.

Conclusion

In summary, we have developed a protocol for the cyanation of aryl iodides *via* a new recyclable PCP-pincer palladium catalyst supported on Merrifield resin in the presence of $K_4[Fe(CN)_6]$ as cyanide source. The catalyst was easily separated from the reaction mixture by filtration and re-used without appreciable loss in its activity. Characterization of the catalyst showed high Pd dispersion and small particle size in nanoscale. This polymeric catalyst is attractive due to easy recyclability, low Pd leaching and high efficiency in the cyanation reaction such as acceptable reaction times and moderate to high yields. This supported catalyst is air-stable and reactions can be conducted in air.

Acknowledgements

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42. Iodobenzene (1.0 mmol), $K_4[Fe(CN)_6].3H_2O$ (1.0 mmol), K_2CO_3 (1.0 mmol), Pd complex (0.5 mol%) and DMAc (5 mL) were taken in a round-bottomed flask and stirred at 120 ^oC. The reaction stopped at 25% conversion. After that, the catalyst was filtered off and the experiment was continued with the filtrate for another 24 h. There was no detectable increase in the product concentration, as was evident from the GC analysis.

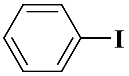
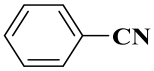
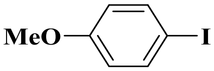
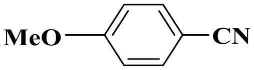
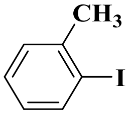
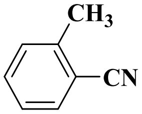
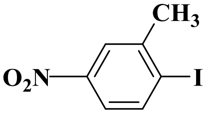
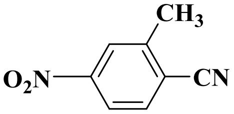
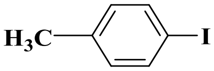
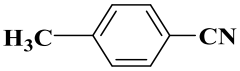
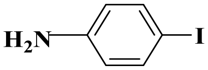
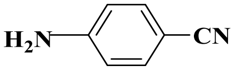
Table 1. Optimization of base and solvent for catalyzed cyanation reaction of iodobenzene with $K_4[Fe(CN)_6]$ [a]

Entry	Base	Solvent	Time (h)	Conversion (%) [b]
1	K_2CO_3	NMP	4	90
2	K_2CO_3	$C_6H_5CH_3$	4	50
3	K_2CO_3	DMAc	2.15	100
4	K_2CO_3	H_2O	4	30
5	K_2CO_3	DMF	4	80
6	Et_3N	DMAc	4	80
7	NaOAC	DMAc	4	50
8	KF	DMAc	4	30
9	-	DMAc	4	10

[a] Reaction conditions: iodobenzene (1.0 mmol), $K_4[Fe(CN)_6]$ (1.0 mmol), base (1 mmol), Pd catalyst (0.5 mol%) and solvent (5 mL) at 120 ^oC

[b] Conversions based on iodobenzene

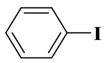
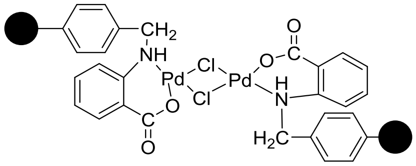
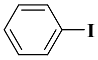
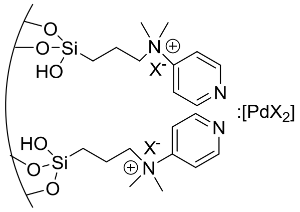
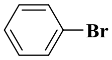
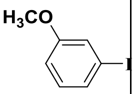
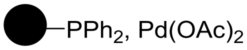
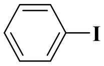
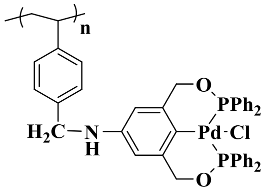
Table 2. Catalyzed cyanation reaction of aryl iodides with $K_4[Fe(CN)_6]$ [a]

Entry	Aryl halides	Product	Time (h)	Isolated Yield [b]	Ref.
1			2	87	11, 13, 39
2			3	85	11, 13, 14, 39
3			4	75	13, 39
4			4	75	-
5			3	90	11, 13, 14, 39
6			5	65	14, 29, 39

[a] Molar ratio of the reagents ArI: $K_4[Fe(CN)_6]$: K_2CO_3: palladium catalyst = 1.0:1.0:1.0:0.005. Reaction conditions: DMAc, 120 ^{o}C

[b] Isolated yields

Table 3. A comparison of the catalyst with some previous heterogeneous catalysts reported in the literature for cyanation of aryl halides

substrate	Catalyst	Reaction conditions	Yield%	Ref.
	 PS-Pd(II)-anthra complex	Et$_3$N, DMF, K$_4$Fe(CN)$_6$, 1.0 mol% catalyst, 100 ^{o}C, 24 h	98	26
	 Pd containing nanostructured silica functionalized with pyridine sites	Et$_3$N, DMF, K$_4$Fe(CN)$_6$, 500 mg catalyst, reflux, 24 h	78	27
	ZnO- Pd NPs	DMF, K$_4$Fe(CN)$_6$, 0.2 mol% catalyst, 130 ^{o}C, 13 h	81	28
	 polymer-supported triphenyl phosphine (ligand), Pd(OAc)$_2$	DMF, Zn(CN)$_2$,0.15 mmol ligand + 0.07 mmol Pd(OAc)$_2$, 140 ^{o}C, microwave, 30 min	92	29
		K$_2$CO$_3$, DMAc, K$_4$Fe(CN)$_6$, 0.5 mol% catalyst, 120 ^{o}C, 2 h	87	present

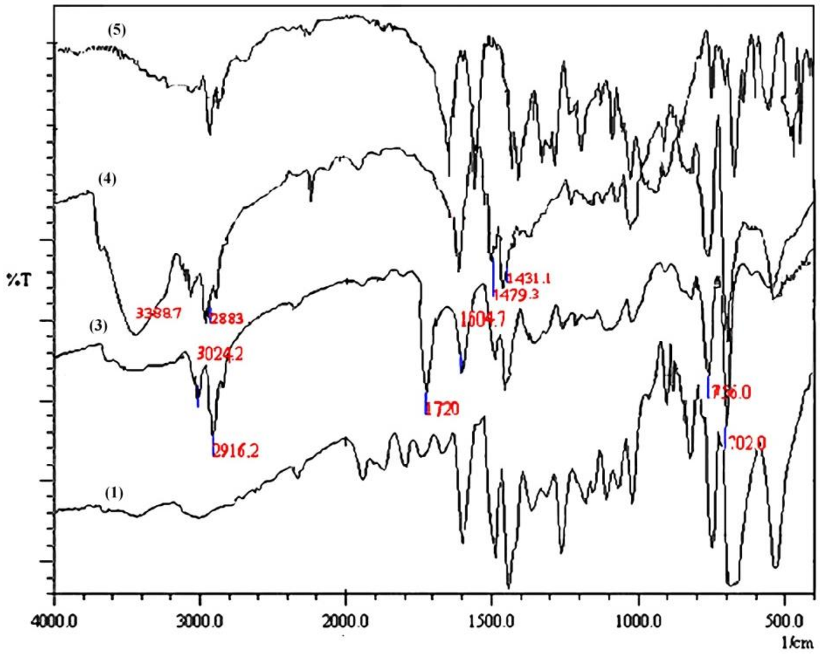


Figure 1. FT-IR spectrum of chloromethylated polystyrene (1), ester modified polymer (3), hydroxyl modified polymer (4) and polymeric phosphinite ligand (5)

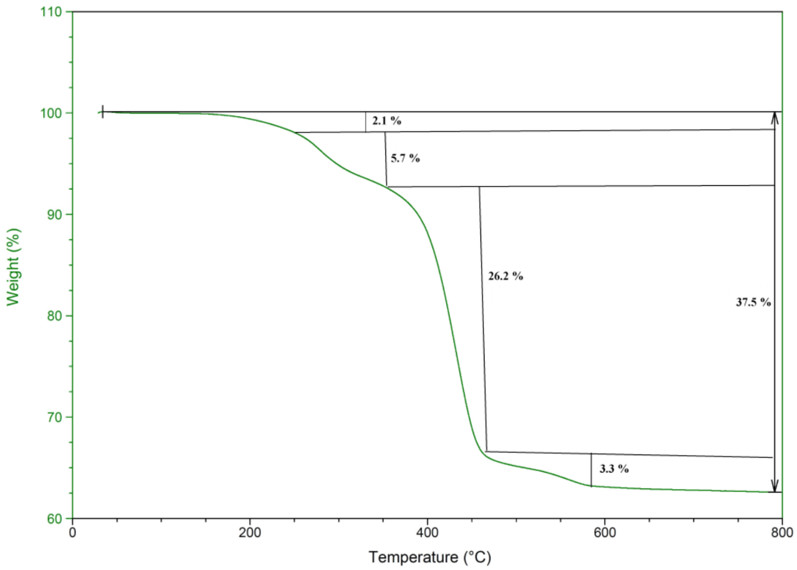


Figure 2. A typical TGA curve of the polymeric Pd catalyst

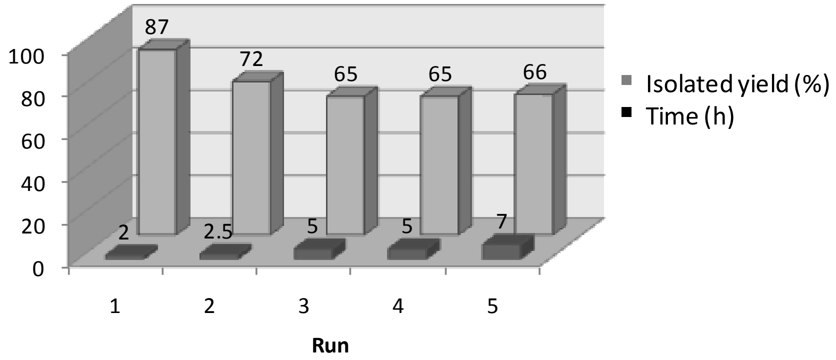


Figure 3. Recyclability of polymer supported Pd(0) catalyst in the cyanation reaction. *Reaction condition:* iodobenzene (1.0 mmol), $K_4[Fe(CN)_6]$ (1.0 mmol), K_2CO_3 (1.0 mmol), Pd cat. (0.5 mol%) in DMAc (5 mL) at 120 ^{o}C

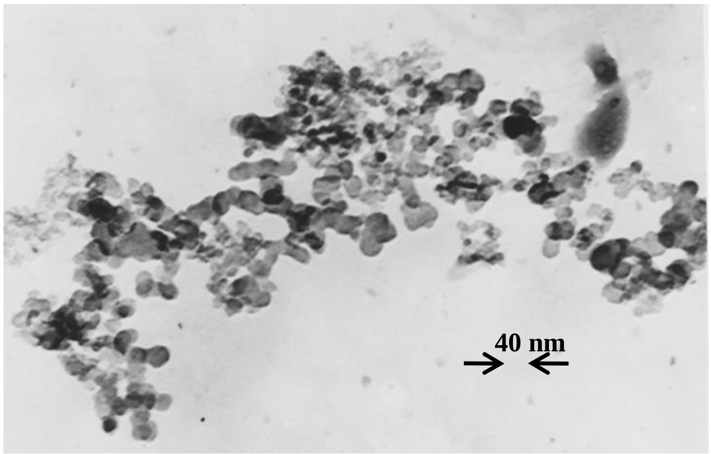
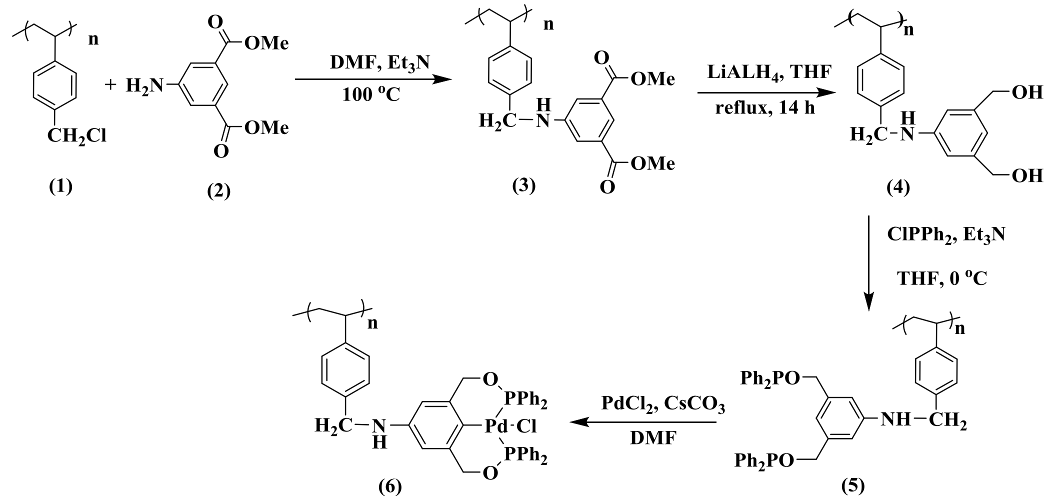
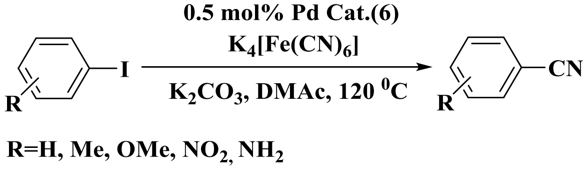


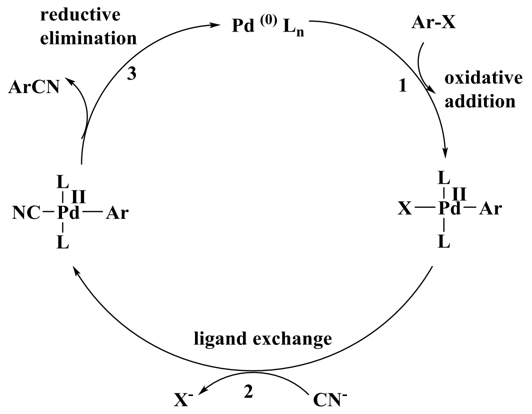
Figure 4. TEM image of the recycled PCP polymeric Pd catalyst



Scheme 1. Synthetic strategy for the preparation of modified Merrifield resin-supported PCP pincer palladium nanoparticles [34]



Scheme 2. Cyanation reaction of aryl iodides using $K_4[Fe(CN)_6]$ in the presence of polymeric Pd catalyst (6)



Scheme 3. Proposed mechanism for the heterogeneously Pd catalyzed cyanation reaction