Palladium Nanoparticles Immobilized with Polymer Containing Nitrogen-Based Ligand: A Highly Efficient Catalyst for Suzuki–Miyaura and Mizoroki–Heck Coupling Reactions

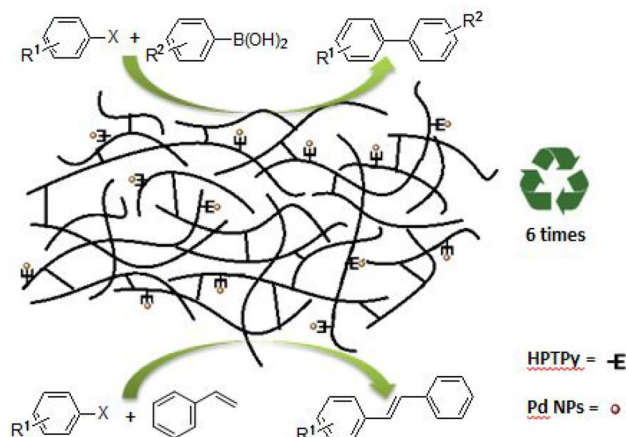Homa Targhan[1] · Alireza Hassanpour[2] · Samira Sohrabnezhad[3] · Kiumars Bahrami[1,4]

Abstract

An outstanding heterogeneous catalyst was successfully prepared by immobilization of palladium nanoparticles (Pd NPs) with polymer containing 4′-(4-hydroxyphenyl)-2,2′:6′,2″-terpyridine (HPTPy) ligand. The polymer cross-linked with trimethylolpropane triacrylate (TMPTA) units was synthesized by polymerization of itaconic acid-HPTPy (ITC-HPTPy) monomer (so-called cross-linked poly (ITC- HPTPy)). The cross-linked poly (ITC-HPTPy) can stabilize the Pd NPs effectively against aggregation, thereby improving the catalytic efficiency of Pd NPs. The presence of Pd NPs on the polymer was confirmed by various physicochemical techniques. The resulting cross-linked poly (ITC-HPTPY)-Pd was applied as a highly effective recyclable catalyst in Suzuki–Miyaura and Mizoroki–Heck coupling reactions under low Pd-loading conditions and straightforward methods, and provided the corresponding products with excellent yields (up to 98%), high catalytic activities (TOF up to 213 h^{-1}). The catalyst can be separated from the reaction mixture by centrifugation and can be reused consecutive six times with slight reduction in catalytic activity.

Graphic Abstract

Pd NPs immobilized with polymer containing terpyridine ligand are highly active heterogeneous catalysts for Suzuki–Miyaura and Mizoroki–Heck coupling reactions.

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1 Introduction

Cross-coupling reactions have been identified as outstanding tools to available to synthetic chemists to create or manipulate intricate organic molecules. Interestingly, the cross-coupling reactions provide straightforward possibilities for joining two organic fragments via carbon–carbon bond-forming reactions [1]. The cross-coupling reactions have been used as key steps in the synthesis of many medicines, natural products and valuable starting materials [2, 3]. Therefore, development of these reactions provides access to a diverse range of intricate organic scaffolds.

Since the heterogeneous nanocatalysts have the potential to develop more environmentally-friendly and economical catalytic processes, one of the most significant aspects of chemistry investigation has been the development of efficient, selective, stable and recyclable nanocatalysts. Palladium (Pd)-based nanocatalysts have found widespread use for catalytic applications, especially in carbon–carbon coupling reactions due to their superior catalytic performance [1]. As are well known, small metal nanoparticles (MNPs) have high surface energies and large surface area, which these properties could often lead to aggregation of the naked MNPs and decreasing of catalytic activity [4]. In particular, highly active palladium nanoparticles are prone to aggregate easily to form larger particles [5]. Recently, many stabilizing methods have been developed to make Pd-based nanocatalysts with small size, high thermodynamically stability and catalytic efficiency. In the case of noble metals such as palladium, the common stabilizing methods to prevent nanoparticles aggregation are to use polymers or ligands [6]. The use of various organic-ligand stabilizers such as amines, phosphines, and thiols has been extensively developed [7]. It is interesting to note that dispersion and stability of the MNPs can be obtained employing tridentate nitrogen ligands due to the strong interaction metal-nitrogen and the formation of two five-membered metallacycles [8–10].

Since the early 1970s, functionalized polymers offer a broad range of applications in areas such as catalysis, ultrafiltration, separation methods, membrane technologies, medicine, pharmacy and others [11]. Use of polymer-immobilized MNPs as catalyst provides essential technique whereby classical organic synthetic process can shift towards green chemistry. In addition to the aspect of simplicity of catalyst recovery and recycling, it is even possible to apply the polymeric catalysts to the continuous flow system which can lead to an economical automation system [12–14].

Various methods, including chemical methods and electrochemical methods, have been developed to prepare the polymers containing MNPs. In most of the chemical techniques, monomer or polymer plays the role of reducing agent for the metal species. The chemical techniques include the following methods: polymerization of the monomer in the presence of the MNPs, in situ reduction of metal ions from their salt solution in the presence of the polymer, simultaneous formation of MNPs and polymerization of the monomer [15].

Our early interest in the use of noble metal nanoparticles as catalyst for organic transformations prompted us to examine various methods for the immobilization these nanoparticles [10, 17]. As part of our continuing investigations and considering potential advantages of using polymers to immobilize MNPs, herein, we report the synthesis of a new polymer containing HPTPy ligand for the stabilization of Pd NPs (cross-linked poly (ITC-HPTPy)-Pd). The catalytic activity of the cross-linked poly (ITC-HPTPy)-Pd was evaluated in the Suzuki–Miyaura and Mizoroki-Heck coupling reactions (Scheme 1).

2 Experimental

2.1 Materials and Methods

The materials were purchased from Merck and Fluka and were used without any additional purification. Melting
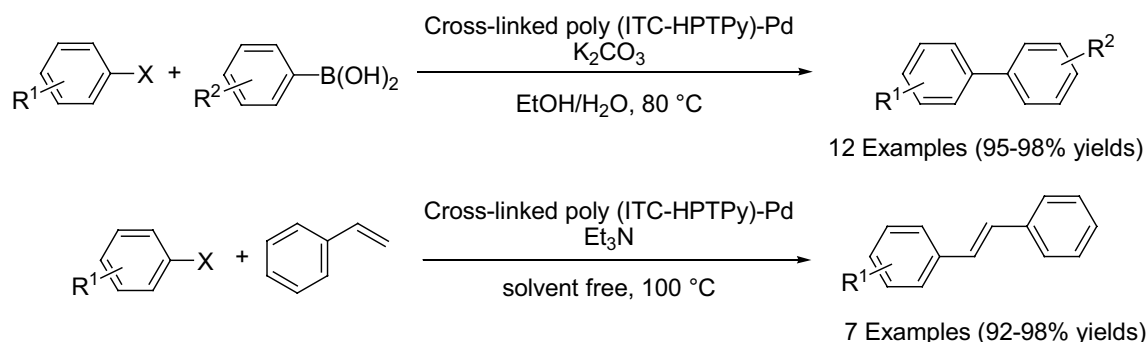
Scheme 1 The cross-linked poly (ITC-HPTPy)-Pd catalyzed Suzuki–Miyaura and Mizoroki-Heck coupling reactions

points were determined using a Stuart Scientific SMP2 apparatus. FT-IR spectra were determined with a Perkin Elmer 683 instrument. Thermogravimetric analysis (TGA) was carried out with a STA PT- 1000 Linseis instrument (Germany) under air atmosphere at a heating rate of 10 °C min^{-1}. SEM and energy-dispersive X-ray (EDX) measurements were performed using a TESCAN- MIRA3 operated at 26 kV with the electron gun filament: tungsten. TEM observations were carried out with a Zeiss-EM10C (Germany) operating at 100 kV with samples on formvar carbon-coated Cu grid (mesh 300). The elemental palladium content of nanocatalyst was determined by Perkin Elmer Optima 7300D inductively coupled plasma (ICP). X-rays diffraction (XRD) patterns were obtained using STOE STADI-P diffractometer (Cu K-α radiation λ = 1.54060 Å). N_2 adsorption study of nanocatalyst was done using BET (BELSORP Mini, Microtrac Bel Corp). The chemical compositions of the catalysts were performed using XPS a Kratos Axis Ultra DLS spectrometer with an Al Kα as a source.

2.2 Preparation of HPTPy- ITC

First, HPTPy was prepared according to recipes investigated in the literature [16, 17], then a mixture of HPTPy (0.325 g, 1 mmol) and ITC (0.065 g, 0.5 mmol) in DMSO (4 mL) was stirred at 100 °C for 48 h. After this time, EtOH (10 mL) and H_2O (5 mL) were added into the reaction mixture, and the precipitate collected by filtration and dried at 70 °C.

2.3 Preparation of Cross-Linked Poly (ITC-HPTPy)

Briefly, HPTPy- ITC (0.033 g) and TMPTA (0.9 mL) were added to a 40:60 mixture of MeOH/CH$_3$CN (5 mL) and the mixture was sonicated for 2 min then 0.06 g of 2,2-azobisisobutyronitrile (AIBN) was added. The final volume is adjusted with MeOH/CH$_3$CN (40:60) to 35 mL. The mixture was sonicated for 2 min and then purged with nitrogen to remove dissolved oxygen. The resulting mixture was refluxed at 60–70 °C for 24 h. Finally, after air cooling, the mixture was centrifuged and the solid obtained was dried in vacuum at 50 °C.

2.4 Preparation of Cross-Linked Poly (ITC-HPTPy)-Pd

0.1 g of the cross-linked poly (ITC-HPTPy) was sonicated in 5 mL EtOH for 10 min. To the resulting mixture PdCl$_2$ (0.005 g, 0.028 mmol) was added and refluxed for 24 h. Then, the mixture was filtered and the solid catalyst was washed with EtOH to remove the excess of PdCl$_2$ and dried under vacuum for 24 h. ICP showed 0.023 mmol of

palladium loaded on the 0.1 g of cross-linked poly (ITC-HPTPy)-Pd (2.48 wt%).

2.5 General Procedure for the Suzuki–Miyaura Cross-Coupling Reactions

ArX (1.2 mmol), ArB(OH)$_2$ (1 mmol) and K_2CO_3 (1.5 mmol) were added into a flask containing cross-linked poly (ITC-HPTPy)-Pd (0.01 g, 0.23 mol%) and EtOH/H$_2$O (2/1). The mixture was then stirred in an 80 °C oil bath for an appropriate reaction time (Table 2). The progress of the reaction was monitored by TLC. After completion of the reaction, ethyl acetate (10 mL) was added into the reaction mixture, the catalyst was separated by using centrifugation and the organic solvent was evaporated to obtain biaryl products in excellent yields.

2.6 General Procedure for the Mizoroki–Heck Cross-Coupling Reactions

A mixture of aryl halide (1 mmol), styrene (1.2 mmol), Et$_3$N (3 mmol) and the cross-linked poly (ITC-HPTPy)-Pd (0.012 g, 0.27 mol%) was stirred at 100 °C (oil bath temperature) under solvent-free conditions. After completion of the reaction, which was monitored by TLC, ethylacetate (10 mL) was added to the reaction mixture. The catalyst was separated using centrifugation. Water (3 × 15 mL) was added to the ethylacetate phase and decanted. After evaporation of the solvent, the resulting crude products were purified from *n*-hexane/ethylacetate giving the pure products in high to excellent yields (Table 4).

3 Results and Discussion

3.1 Synthesis and Characterization of Cross-linked poly (ITC-HPTPy)-Pd

The steps of synthesis of cross-linked poly (ITC-HPTPy)-Pd are summarized in Scheme 2. HPTPy-ITC was initially prepared via esterification reaction of ITC and HPTPy. Then, polymerization of HPTPy-ITC as a monomer and TMPTA as a cross-linker was achieved in the presence of AIBN as an initiator in a mixture of MeOH/CH$_3$CN affording the final polymer. The cross-linked poly (ITC-HPTPy)-Pd was obtained by interaction of PdCl$_2$ with cross-linked poly (ITC-HPTPy) in EtOH as a solvent and green reducing agent (Scheme 2). Moreover, Pd NPs can be successfully prepared and stabilized on Polymer-TPy
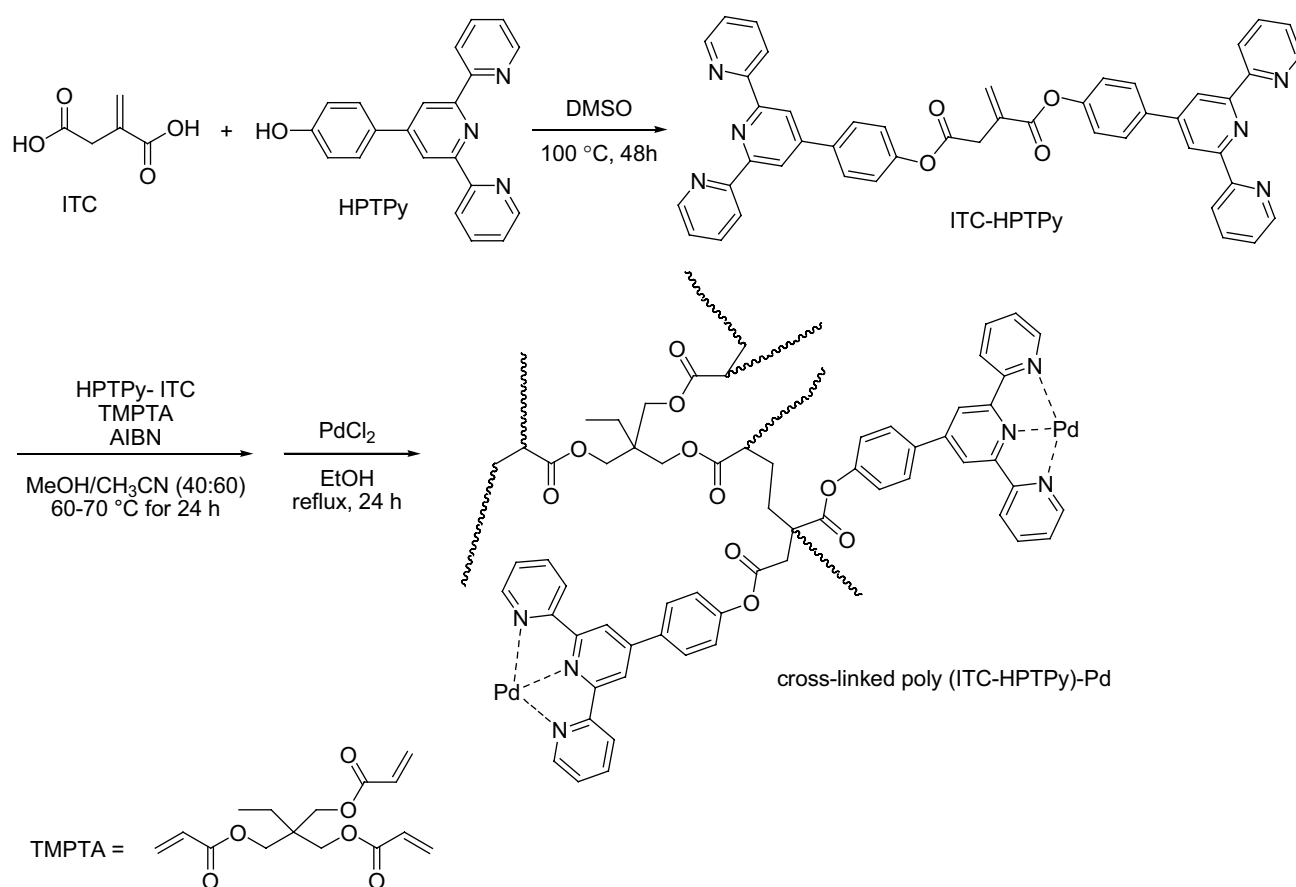
Scheme 2 Synthetic steps for the preparation of cross-linked poly (ITC-HPTPy)-Pd

without the addition of external reducing agents because HPTPy ligands serve also as a reducing agent due to its nitrogen atoms [18, 19].

The cross-linked poly (ITC-HPTPy)-Pd was extensively analyzed by several characterization techniques including, FT-IR, TEM, SEM, BET, TGA, EDX, XRD, XPS, UV–Vis and ICP.

At outset, influence of cross-linker concentration, on the resulting polymer porosity was investigated. For this purpose, two of polymeric samples using different TMPTA concentrations and the same degree of ITC-HPTPy dilution have been prepared under the same conditions. Porous properties of the polymeric samples were investigated by BET. The N_2 adsorption/desorption isotherms of the polymers declare typical type IV isotherms (Fig. 1a and c). Furthermore, it is found that porosity, pore volume, surface area and mean pore diameter are greatly influenced by varying the concentration of cross-linker (Table 1) and using higher concentration of cross-linker (0.9 mL of TMPTA) has provided a better result (Table 1, entry 1). These findings are consistent with the literature results which confirm increasing amount of

cross-linker in the polymer structure leads to increase of the pores number and decrease of their size [20].

In previous studies, EtOH has been suggested as a green reducing agent in the synthesis of Pd NPs [18]. Moreover, the nitrogen-based ligands have been employed to work as both reducing and stabilizing reagent in the reaction for preparation of Pd NPs [19]. UV–Visible spectroscopic technique is used to investigate the reduction of Pd(II) ions to Pd NPs (Fig. 2). The UV–visible spectrum of a solution of $PdCl_2$ in EtOH at room temperature showed a distinct peak approximately at 425 nm, which is related to the existence of Pd(II) ion [21]. During the formation of Pd NPs on the polymer containing HPTPy ligand, the peak was removed indicating reduction of Pd(II) ions to Pd NPs.

The immobilization of Pd NPs on cross-linked poly (ITC-HPTPy) was also confirmed by the color changes of the polymer from white into dark grey during the preparation of the catalyst in EtOH within 24 h (Fig. 3). The color changes are due to reduction of Pd(II) to Pd(0) [22] and immobilization of Pd NPs on cross-linked poly (ITC-HPTPy).
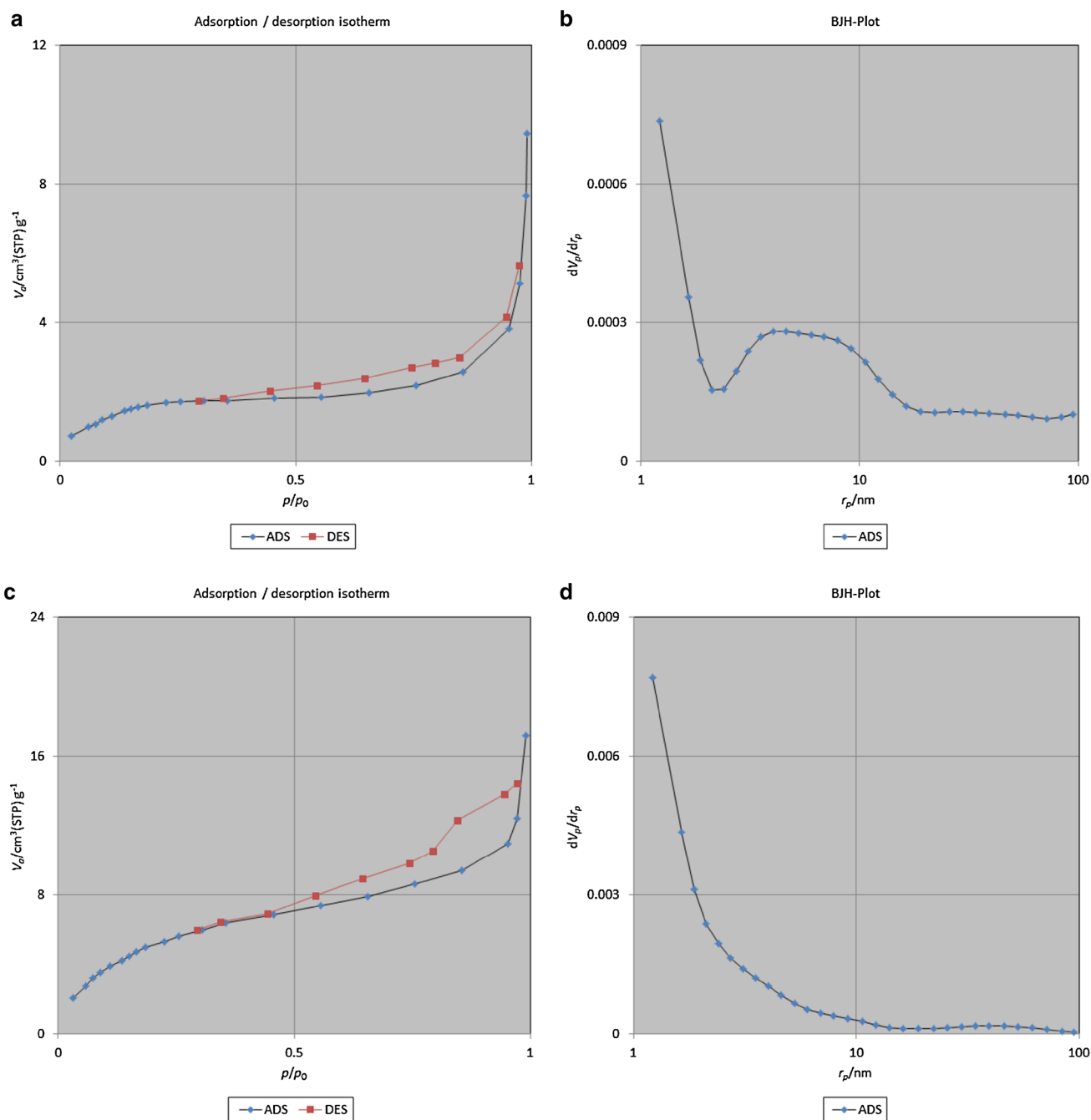
Fig. 1 BET adsorption/desorption isotherms of the polymeric samples using 0.6 and 0.9 mL TMPTA (**a** and **c** respectively), BJH pore size distributions for the polymeric samples using 0.6 and 0.9 mL TMPTA (**b** and **d** respectively)

Table 1 The influence of the cross-linker concentration on the total pore volume, mean pore diameter and surface area of the polymers

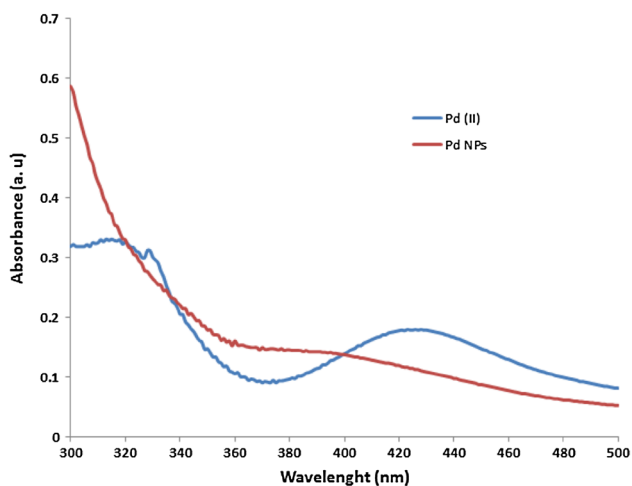| Entry	ITC-HPTPy (g)	TMPTA (mL)	Total pore volume ($cm^3\ g^{-1}$)	Mean pore diameter (nm)	Surface area ($m^2\ g^{-1}$)	
					BET	Langmuir
1	0.033	0.6	0.012	7.92	6.34	9.23
2	0.033	0.9	0.026	4.94	21.14	31.10

Fig. 2 UV-Vis spectrum of the Pd NPs and PdCl$_2$ solution in EtOH
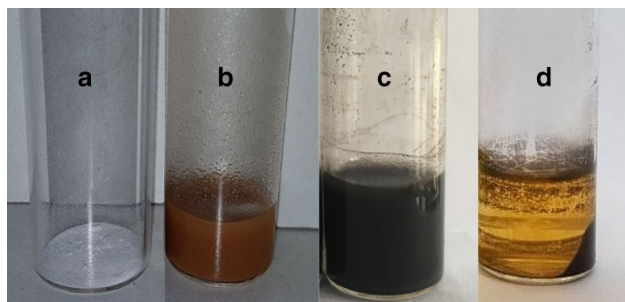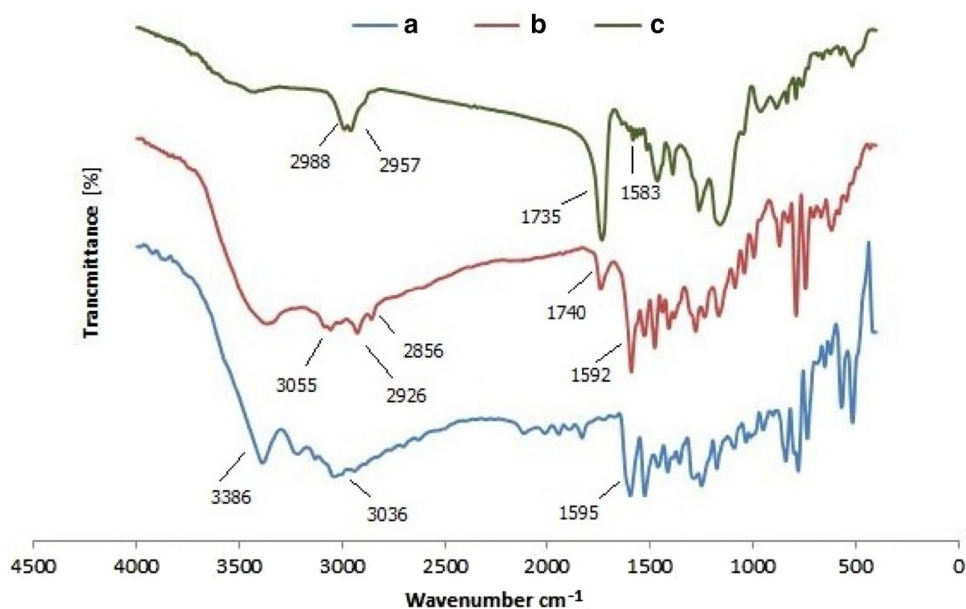

Fig. 3 The color change of the polymer, cross-linked poly (ITC-HPTPy) (**a**), preparation of Pd catalyst after 1 min (**b**), after 2 h (**c**) and after separating using centrifugation (**d**)

Grafting of the HPTPy ligand to the ITC monomer and the synthesis of cross-linked poly (ITC-HPTPy)-Pd was further confirmed through FT-IR spectra (Fig. 4). In the FT-IR spectrum of HPTPy (Fig. 4a), the following functional groups were identified: OH stretching vibration (3386 cm^{-1}), sp^2 C–H stretching vibration (3036 cm^{-1}), and C=N stretching frequency (1595 cm^{-1}). In the case of HPTPy-ITC (Fig. 4b), the band at 1740 cm^{-1} corresponds to C=O stretching of ester groups. The weak absorption peak at 2856 cm^{-1} and 2926 cm^{-1} are attributed to the sp^3 C–H stretching vibrations. The bands observed at 1592 cm^{-1} and 3055 cm^{-1} can be attributed to the C=N stretching frequency and C–H aromatic (pyridine rings) stretching vibration, respectively. The C=N bands of complex TPy-Pd in cross-linked poly (ITC-HPTPy)-Pd is shifted to a lower frequency (1583 cm^{-1}) in the FT-IR spectrum compared to that of TPy (1595 cm^{-1}). The lowering in frequency of the C=N peak is indicative of the interaction of TPy with Pd (Fig. 4c).

Figure 5a and b display SEM images of cross-linked poly (ITC-HPTPy)-Pd with different magnifications. The size of the Pd NPs produced on the polymer was analysed by TEM. The image in Fig. 5c indicates the presence of uniform and small sized Pd NPs on the cross-linked poly (ITC-HPTPy)-Pd. The particle size distribution of Pd NPs on the polymer was evaluated using TEM and showed that the maximum numbers of Pd NPs were around 9 nm in diameter (Fig. 5d).

The thermal behaviour of the prepared polymer was investigated by TGA in oxidative environment (air). TGA thermogram for the cross-linked poly (ITC-HPTPy) is shown in Fig. 6. The TGA result can prove that the polymer has excellent thermal stabilities up to 320 °C in air.
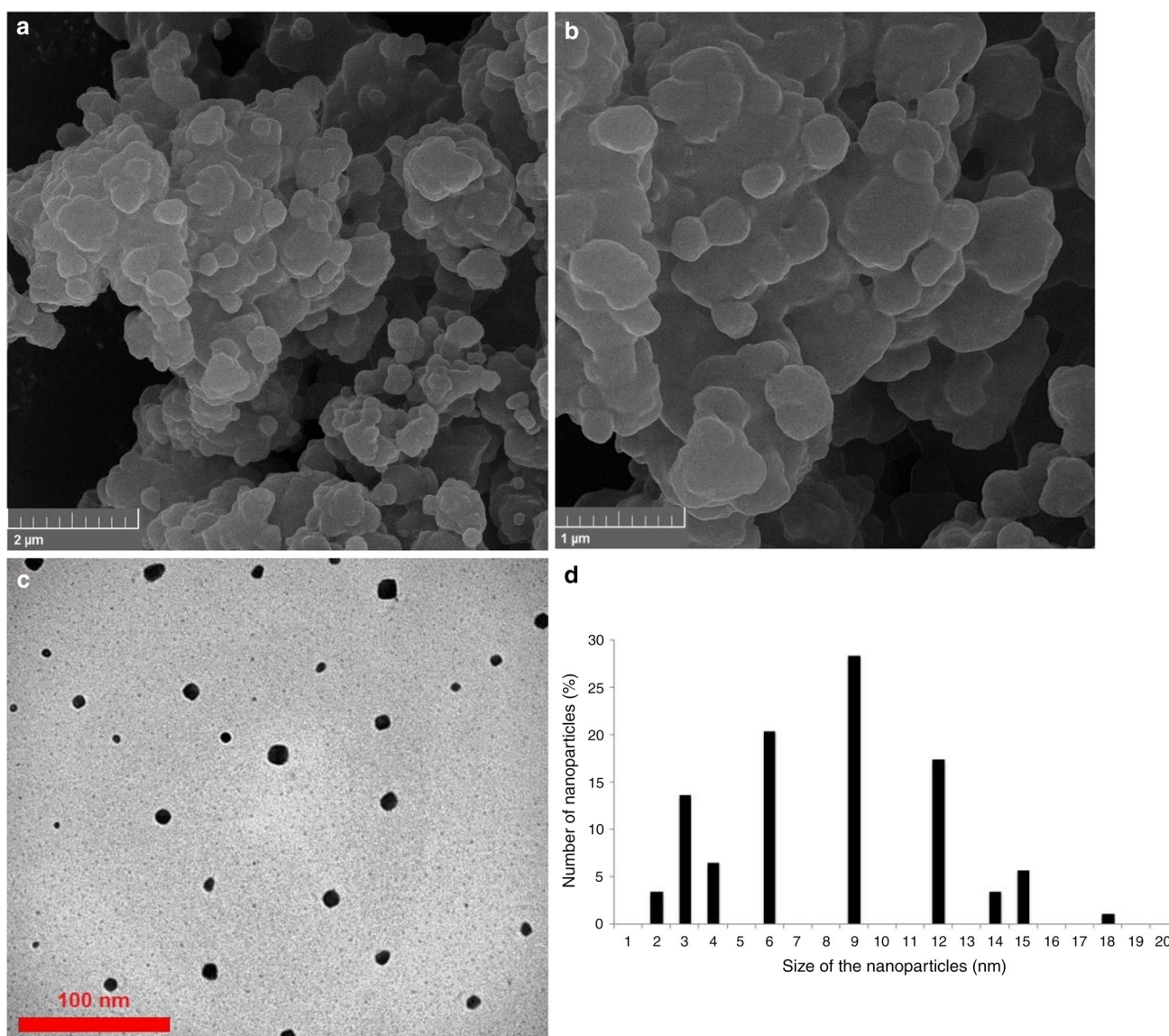
Fig. 4 FT-IR spectra of HPTPy (a), HPTPy-ITC (b) and cross-linked poly (ITC-HPTPy)-Pd (c)

Fig. 5 **a** and **b** SEM images and **c** TEM image of cross-linked poly (ITC-HPTPy)-Pd, **d** particle size distribution histogram of Pd NPs on the polymer from TEM images

Maximum weight loss occurred between 350 and 470 °C and above 600 °C, virtually no mass remains.

Figure 7 presents XRD pattern of the MP-TPy/Pd. The diffraction peaks at the Bragg angles of 40.10°, 46.66°, and 68.14° correspond to the 111, 200, and 220 facets of elemental palladium in the cross-linked poly (ITC-HPTPy)-Pd [23, 24].

A sample of the cross-linked poly (ITC-HPTPy)-Pd was studied using EDX technique for precise elemental analysis, and successful synthesis of the cross-linked poly (ITC-HPTPy)-Pd was inferred from this technique. EDX spectra show the presence of C, O, N and Pd in the cross-linked poly (ITC-HPTPy)-Pd (Fig. 8).

The cross-linked poly (ITC-HPTPy)-Pd was also studied by XPS, the observed characteristic peaks in XPS are attributed to C 1 s, O 1 s and Pd 3d (Fig. 9a). Furthermore, high resolution XPS results confirmed the presence of Pd (0) and Pd (II) on the catalyst (Fig. 9b). The peaks at 335.5 eV (Pd $3d_{5/2}$) and 340.5 eV (Pd $3d_{3/2}$) regard to Pd (0), whereas peaks at 336.5 eV (Pd $3d_{5/2}$) and 341.5 eV (Pd $3d_{3/2}$) are assigned for Pd (II) species present on the polymer [25, 26]. The XPS results also allow us to determine the percentage of the respective oxidation states of Pd by measuring the area under the peaks: 41% as Pd(0) and 59% as Pd(II) in the sample.

Fig. 6 TGA thermogram of the polymer
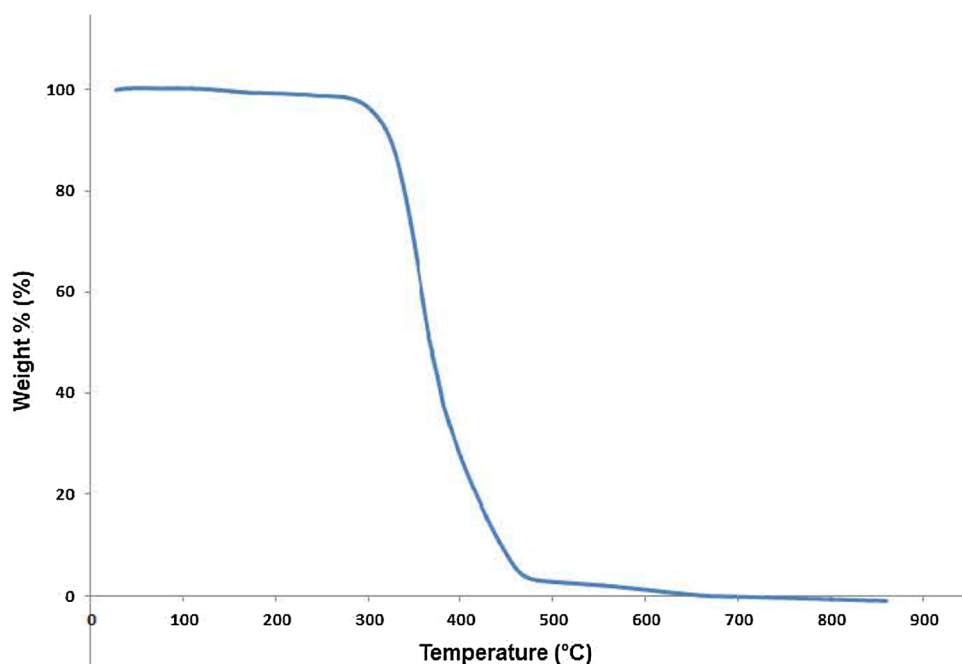
Fig. 7 XRD pattern of the cross-linked poly (ITC-HPTPy)-Pd
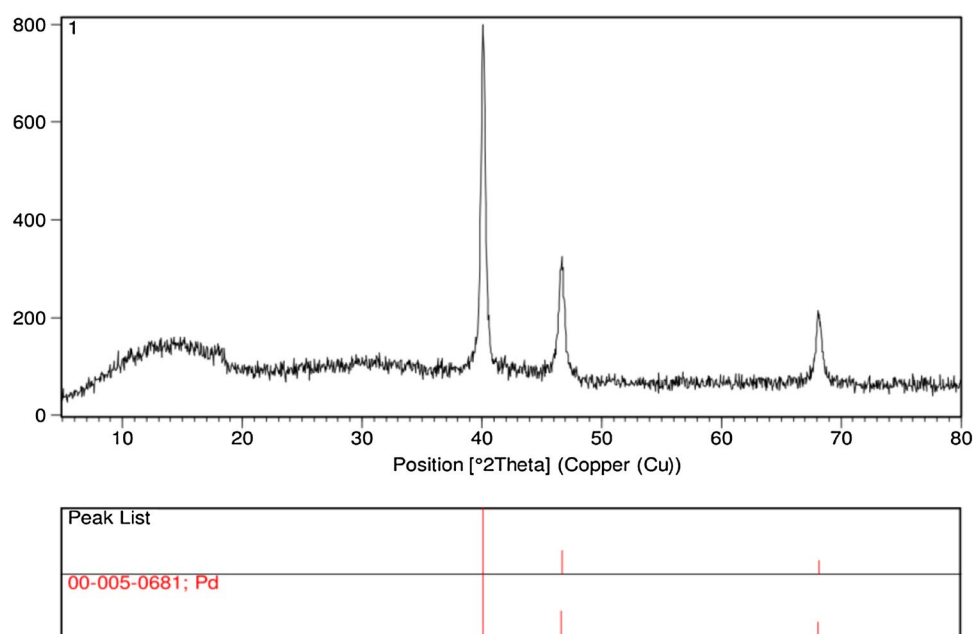
3.2 Catalytic Studies

The performance of cross-linked poly (ITC-HPTPy)-Pd catalyst was initially tested for the Suzuki–Miyaura coupling reaction. Phenyl boronic acid and iodobenzene were selected as a model substrate for optimization of the Suzuki C-C coupling reaction (Table 2). As shown in the Table, the catalytic activity of cross-linked poly (ITC-HPTPy)-Pd catalyst was studied in different temperatures, solvents, bases, and in the presence of various mol% of the cross-linked poly (ITC-HPTPy)-Pd for 2 h. As the first parameter of these set, the role of cross-linked poly (ITC-HPTPy)-Pd as a catalyst was investigated. In the absence of any catalyst and only in the presence of K_2CO_3 (1.5 mmol) at 80 °C, the product was not formed (Table 2, entry 1). However, the use of a
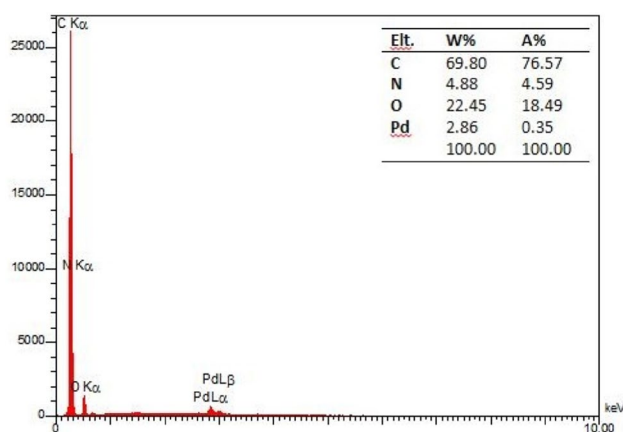
Fig. 8 EDX pattern of the cross-linked poly (ITC-HPTPy)-Pd

small amount (0.12, 0.16 and 0.23 mol%) of cross-linked poly (ITC-HPTPy)-Pd gave the desired product in good (65%) to excellent (98%) yields (Table 2, entries 2-4). It was found that applying 0.01 g of cross-linked poly (ITC-HPTPy)-Pd (0.23 mol%) and 1.5 mmol of K_2CO_3 as base at 80 °C for 2 h in a mixture of EtOH/H_2O (2/1) as solvent, is the best conditions for the reaction of iodobenzene (1 mmol) with phenylboronic acid (1.2 mmol) (Table 2, entry 4).

The generality and scope of this approach were illustrated in the reaction of commercially available aryl halides with arylboronic acids (Table 3). The cross-linked poly (ITC-HPTPy)-Pd effectively catalyzed the coupling reaction between aryl halides with arylboronic acids to

afford the corresponding biaryl products in excellent yields. The aryl iodides, bromides and chlorides are effectively treated as substrates with this procedure, though, the reaction of aryl chlorides required longer reaction times.

As an extension to use of the catalyst, we also investigated the catalytic activities of the cross-linked poly (ITC-HPTPy)-Pd for the Mizoroki–Heck coupling reaction. The iodobenzene and styrene were selected as substrates to optimization of condition in the presence of different mol% of the cross-linked poly (ITC-HPTPy)-Pd and various bases and solvents at 100 °C (Table 4). As can be seen from the Table 4, the best result was obtained in 98% yield by carrying out the reaction with aryl iodide (1 mmol), styrene (1.2 mmol) in the presence of 0.27 mol% of cross-linked poly (ITC-HPTPy)-Pd and Et_3N (3 mmol) as base, under solvent-free condition at 100 °C (Table 4, entry 4).

Using the optimized reaction conditions, in a simple experimental procedure, several *trans*-stilbene compounds were prepared and the results are presented in Table 5. As the table shows electronic effect of the substituents was not generally observed and donor- and acceptor substituted aryl iodides have been reacted with styrene in excellent yields. However, when iodobenzene was replaced by bromobenzene, the reactions require longer reaction times. However, the scope of this methodology was found not to be effective to chlorobenzene (Table 5, entry 7).

The performance of the present catalyst has been compared with some Pd-based nanocatalysts. Table 6 shows the comparison between cross-linked poly (ITC-HPTPy)-Pd as
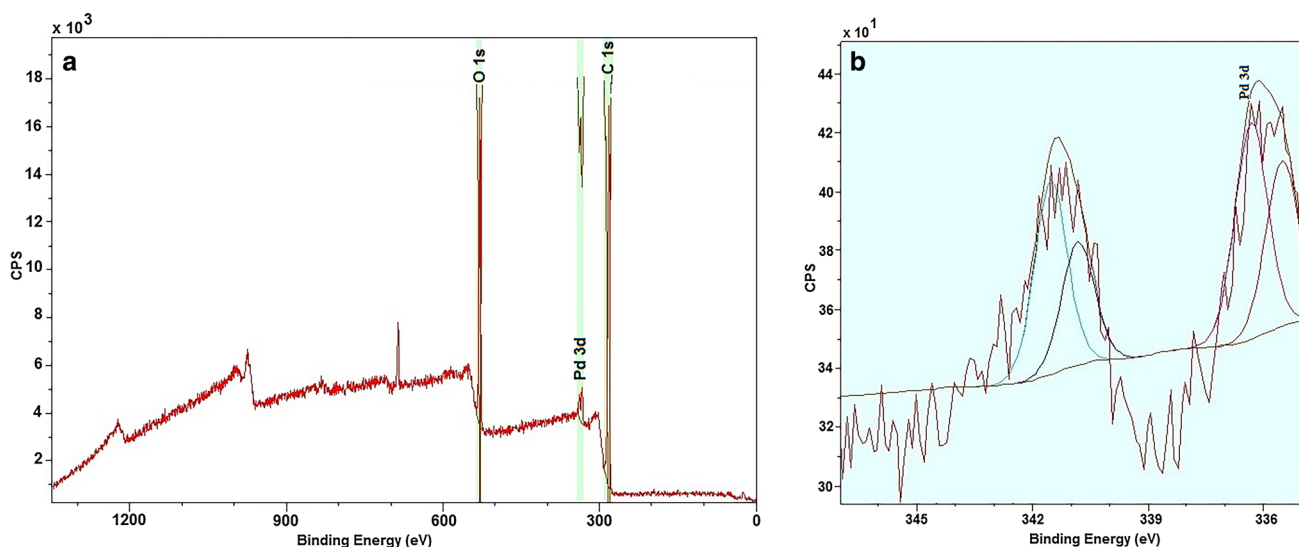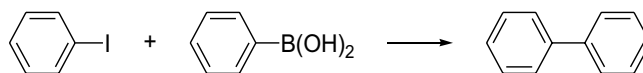

Fig. 9 XPS survey spectrum (**a**) and high-resolution XPS scan spectrum over Pd 3d peak of the cross-linked poly (ITC-HPTPy)-Pd

Table 2 Optimization of conditions in the Suzuki-Miyaura coupling reaction

Entry	Cat.(mol%)	Base	Solvent	T (°C)	Yield (%)[a]
1	0	K_2CO_3	EtOH/H_2O (2/1)	80	0
2	0.12	K_2CO_3	EtOH/H_2O (2/1)	80	65
3	0.16	K_2CO_3	EtOH/H_2O (2/1)	80	85
4	0.23	K_2CO_3	EtOH/H_2O (2/1)	80	98
5	0.23	Na_2CO_3	EtOH/H_2O (2/1)	80	87
6	0.23	Et_3N	EtOH/H_2O (2/1)	80	65
7	0.23	K_2CO_3	H_2O	80	23
8	0.23	KOH	H_2O	80	15
9	0.23	K_2CO_3	EtOH/H_2O (2/1)	r.t	46

Reaction conditions: Iodobenzene (1 mmol), phenylboronic acid (1.2 mmol), base (1.5 mmol), solvent (3 mL), under air atmosphere, 2 h

[a]Isolated yields

Table 3 Suzuki–Miyaura coupling reactions of aryl halides with phenylboronic acid
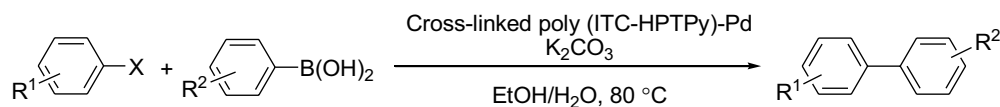
| Entry	X	R^1	R^2	Time (h)	Yield (%)[a]	TOF (h^{-1})	Mp [Refs.]
1	I	H	H	2	98	213	65-68 [27]
2	I	4-NO_2	H	2	97	210	110–116 [28]
3	I	H	4-Me	2	98	213	43–45 [28]
4	I	4-NO_2	3-NO_2	2	97	210	185–188 [29]
5	Br	H	H	4	98	106	65–67 [27]
6	Br	H	4-OMe	4	97	105	83–88 [27]
7	Br	H	4-F	4	96	104	75–78 [27]
8	Br	4-Me	H	4	96	104	46 [28]
9	Cl	H	H	10	96	41	63–68 [27]
10	Cl	H	4-Me	10	95	41	47 [28]
11	Cl	4-NO_2	H	10	95	41	112-116 [28]
12	Cl	H	4-F	10	95	41	75–79 [27]

Reaction conditions: Aryl halide (1 mmol), phenylboronic acid (1.2 mmol), catalyst (0.23 mol%), K_2CO_3 (1.5 mmol), EtOH/H_2O (3 mL), under air atmosphere

[a]Isolated yields

a catalyst for Suzuki coupling of iodobenzene and phenylboronic acid with some Pd-based nanocatalysts in terms of mol% of Pd, reaction time, and yields of the product. The results of comparison show that this catalyst is superior to some previously reported nanocatalysts in terms of mol% of Pd used, product yield and reaction time.

Reusability is important characteristic of the heterogeneous catalyst to be used for industrial applications, due to the

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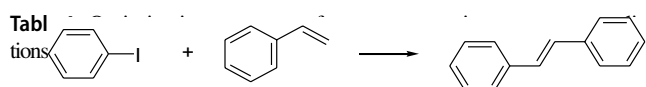
Entry	Cat. (mol%)	Base	Solvent	T (°C)	Yield (%)[a]
1	0	NEt$_3$	No solvent	100	0
2	0.16	NEt$_3$	No solvent	100	45
3	0.23	NEt$_3$	No solvent	100	87
4	0.27	NEt$_3$	No solvent	100	98
5	0.27	NEt$_3$	No solvent	r.t	18
6	0.27	K$_2$CO$_3$	DMF	100	96
7	0.27	K$_2$CO$_3$	H$_2$O	100	15

Reaction conditions: Iodobenzene (1 mmol), styrene (1.2 mmol), base (3 mmol), solvent (3 mL), under air atmosphere, 5 h

[a]Isolated yields

reducing production cost and environmental pollution substantially. We investigated recyclability of the cross-linked poly (ITC-HPTPy)-Pd by using the reaction of iodobenzene and phenylboronic acid. This heterogeneous catalyst easily separated from the reagents and products, and washed with ethanol and followed by water, dried for the next run. It is interesting to note that, recycling experiments confirmed the chemical stability and reusability of the catalyst and the recovered catalyst can be used during five runs (Fig. 10). To confirm this further, leaching of palladium during the course of the catalytic reactions was exactly evaluated by ICP analysis. ICP of the recovered catalyst after six catalytic cycles indicated that 26% of palladium was leached into the reaction medium (0.1 g of the manufactured catalyst and the

Table 5 Coupling reactions of aryl halides with styrene
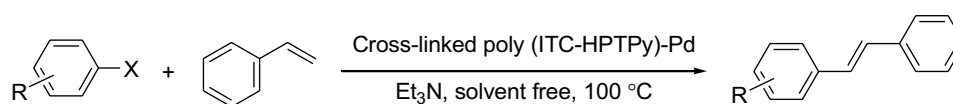
Entry	X	R	Time (h)	Yield (%)[a]	TOF (h^{-1})	Mp [Refs.]
1	I	H	5	98	72	117–121 [30]
2	I	4-NO$_2$	5	96	71	150–153 [30]
3	I	4-Me	5	97	71	113–117 [31]
4	Br	H	7	93	49	118–120 [30]
5	Br	4-NO$_2$	7	92	48	152–154 [30]
6	Br	4-Me	7	92	48	115–117 [31]
7	Cl	H	24	Trace	–	

Reaction conditions: Aryl halide (1 mmol), styrene (1.2 mmol), the catalyst (0.27 mol%), NEt$_3$ (3 mmol), under solvent-free, 100 °C

[a]Isolated yields

Table 6 Catalytic performances of some Pd-based nanocatalysts for Suzuki coupling of iodobenzene and phenylboronic acid

Entry	Conditions	Pd (mol%)	Time	Yield(%)	Refs.
1	GO/NHC-Pd, Na$_3$PO$_4$.12H$_2$O, H$_2$O, 100 °C	1	6 h	91.6	[32]
2	Pd–HoMOF, KOH, DMF, 100 °C	0.4	1 h	99	[33]
3	(Pd (II)–NHCs)$_n$@nSiO$_2$, K$_2$CO$_3$, DMF/H$_2$O (2:1), 60 °C	0.27	6 min	97	[34]
4	Pd NPs on polymer, K$_2$CO$_3$, H$_2$O, 25-100 °C	0.08	5 h	83	[22]
5	Pd(II)-NiFe$_2$O$_4$, K$_2$CO$_3$, EtOH/H$_2$O, 80 °C	0.5	3 h	96	[35]
6	GO-CPTMS@Pd-TKHPP, K$_2$CO$_3$, EtOH/H$_2$O, 80 °C	10	15 min	99	[36]
7	Pd–IPG, NaOH, EtOH/H$_2$O, 60 °C	0.1	1 h	99	[37]
8	(1,4-C$_6$H$_4$)(GO-CPTMS@HPTPy-Pd-TPy)$_2$, K$_2$CO$_3$, H$_2$O/EtOH, 80 °C	1.38	3 h	95	[17]
9	This work	0.23	2 h	98	
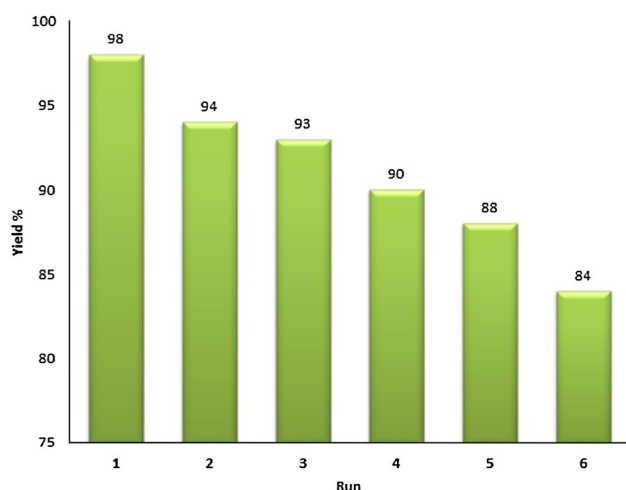
Fig. 10 Recycling of the catalyst for the reaction of iodobenzene and phenylboronic acid

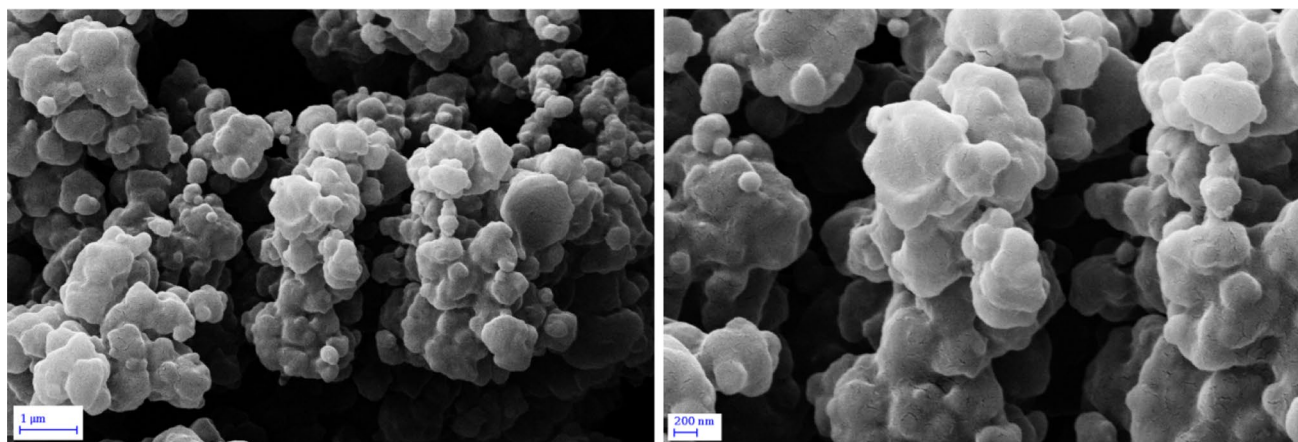| Elt	W%	A%
C	70.15	76.59
N	4.74	4.45
O	22.80	18.68
Pd	2.31	0.28
	100.00	100.00
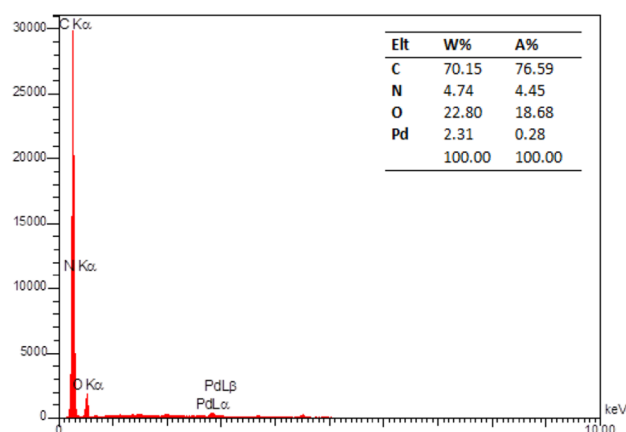
Fig. 11 EDX pattern of recovered catalyst after 6th run

catalyst after 6th run, contained 0.023 and 0.017 mmol of Pd, respectively).

The EDX spectrum of the recovered nanocatalyst is presented in Fig. 11, atoms such as C, O, N and Pd related to the catalyst structure, are seen in the spectrum. However the EDX spectra shows little leaching of Pd species into reaction solutions over multiple uses according to relative peak surfaces. Furthermore, The SEM images of the recovered catalyst after sixth run (Fig. 12) prove the stability of the nanocatalyst after several uses.

4 Conclusion

In summary, cross-linked poly (ITC-HPTPy)-Pd has been prepared and fully characterized. As expected, cross-linked poly (ITC-HPTPy)-Pd exhibited excellent activity in Suzuki–Miyaura and Mizoroki–Heck cross-coupling reactions under low palladium loading conditions, and provided the corresponding products with excellent yields (up to 98%) and high catalytic activities (TOF up to 213 h^{-1}). It is noteworthy that the Pd NPs were prepared by the in situ reduction of the $PdCl_2$ precursor in the presence of cross-linked poly (ITC-HPTPy) in ethanol as a green reducing agent. Furthermore the terpyridine-based ligands existing in the polymer structure can be considered as agent to stabilize Pd NPs. Ultimately we believe that this work offers several advantages including simplicity of product workup and separation of the catalyst. In addition, nanocatalyst was reused consecutive six times with small drop in catalytic activity, considering the high cost of palladium, reuse of the catalysts could lead to economical automation system.

Fig. 12 SEM images of recovered catalyst after 6th run

Compliance with Ethical Standards

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