Coordination-polymer anchored single-site 'Pd-NHC' catalyst for Suzuki-Miyaura coupling in water

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Abstract. A single-site, heterogeneous Pd-NHC-based catalyst was designed on a coordination polymer platform *via* metal-terpyridine interaction. The catalyst was successfully applied in Suzuki-Miyaura coupling in water showing good activity and reusability.

Keywords. Palladium-NHC complex; coordination polymer; heterogeneous catalysis; Suzuki-Miyaura coupling; water.

1. Introduction

For high reactivity and ease of tunability molecular catalysts are used in homogeneous manner. But practical issues such as stability/recyclability hinder its industrial application. Robust, active heterogeneous catalysts are required to be designed which will afford easy product separation with excellent turnover.^{1–6} Molecular catalyst is heterogenized by attaching it to a heterogeneous support, e.g., silica, activated carbon, zeolites, resins, molecular sieves, metal oxides, metal-organic framework (MOFs), coordination polymers (CPs), porous organic polymers (POPs), etc.^{7–9} Physical and chemical properties of heterogeneous support not only enhance the lifetime of the catalyst but also its reactivity and selectivity towards substrate. Coordination polymers (CPs) have been used as heterogeneous support because of its easily tunable electronic and structural properties.^{10–14} CPs are constituted by linking metal centres with well-defined organic ligands. These materials have been widely used in sorption, separation, sensing, ion-exchange and transport, proton conduction, optics, magnetic materials, and catalysis. Literature reports showed fabrication of CP further with another

metal and the use of hetero-metallic catalyst in heterogeneous reactions. Pd was successfully incorporated by Ebitani *et al.*, in amino functionalized organo-Zn coordination polymer,⁹ and utilized in various coupling reactions as well as in hydrogenation of nitro and unsaturated C–C bond in organic solvents, e.g., ethanol, and N-methyl-2-pyrrolidone. Incorporation of Pd in various types of heterogeneous support including CPs has been done since long in order to get efficient heterogeneous catalysts, as Pd is known to catalyse many reactions, specially coupling reactions. Suzuki-Miyaura coupling (SMC) is a versatile and greatly explored Pd catalyzed coupling reaction of aryl halides with aryl boronic acids. This reaction offers a very important route to constructing biaryl units in organic synthesis under mild conditions. SMC has important applications in industry also. Pd complexes with a variety of ligands are reported in literature to perform this reaction efficiently in heterogeneous condition.^{15–20} In this regard, it is well-known that N-heterocyclic carbene (NHC) ligands form robust bond with Pd center due to their strong sigma donor capacity. Such Pd-NHC complexes, if incorporated onto heterogeneous support, are expected to survive in harsh conditions even in water.

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Figure 1. Ru(terpy)₂-based coordination polymer-supported (NHC)Pd^{II}-catalyst for, (A) oxidative arene C-H functionalization (previously reported work²¹), and (B) Suzuki-Miyaura coupling in water (this work).

Recently, we reported the incorporation of Pd-NHC catalytic struts onto Ru- and Zn-bis(terpyridine)-based coordination polymers for their application in arene C-H activation-halogenation catalysis under oxidative conditions (**Ru-CP-Pd** and **Zn-CP-Pd**, Figure 1).²¹ The polymeric heterogeneous platform was prepared by coordination of Ru and Zn centers with a bis-terpyridine ligand as linker, consisting of imidazolium motifs as NHC precursor. Palladation of the heterogenized NHC precursors was achieved with Pd(OAc)₂. Herein, we demonstrate the extension of the application of this single-site heterogenized Pd-NHC-based catalyst, **Ru-CP-Pd**, towards Suzuki-Miyaura reaction in water medium.^{22–25}

2. Experimental

2.1 Methods and materials

Thin layer chromatography was performed using Merck Silica gel 60F-254 precoated plates. ¹H and ¹³C{¹H} NMR spectra were recorded on Bruker AVANCE III 400 MHz,

500 MHz and 700 MHz NMR spectrometers. For the NMR spectra, chemical shifts (δ) are expressed in ppm using the residual proton resonance of the solvents as an internal standard (CHCl₃: δ = 7.26 ppm for ¹H spectra, 77.36 ppm for ¹³C{¹H} spectra; DMSO: δ = 2.50 ppm for ¹H spectra, 39.52 ppm for ¹³C{¹H} spectra; CD₃CN: δ = 2.13 ppm for ¹H spectra, 118.26 ppm for ¹³C{¹H} spectra). All coupling constants (*J*) are expressed in hertz (Hz) and only given for ¹H–¹H couplings unless mentioned otherwise. The following abbreviations were used to indicate multiplicity: s (singlet), d (doublet), t (triplet), dd (doublet of doublets), dt (doublet of triplets) bs (broad singlet) and m (multiplet). ESI mass spectrometry was performed on a Bruker microTOF QII spectrometer. UV-Vis spectra were recorded on Agilent Technology Cary 100 UV-Vis spectrophotometer. Electrochemical experiments were done using CHI 620E Electrochemical Analyzer. Thermo Gravimetric Analysis (TGA) was carried out using Perkin Elmer TGA-6000 instrument. The morphology of coordination polymers was examined using a Carl Zeiss (Ultra Plus) field emission scanning electron microscope (FESEM). Energy dispersive X-ray spectroscopy was performed using Oxford Instruments X-MaxN. The polymers **Ru-CP-Pd** and **Zn-CP-Pd** were synthesized and characterized fully according to our previously published report.²¹

Table 1. Comparison of catalytic activities in SMC and control studies^a.

Entry	Catalyst (mol%)	Time (h)	Yield (%) ^b
1	Ru-CP-Pd (0.1 mol%)	8	98
2	Zn-CP-Pd (0.1 mol%)	8	18
3	Model homogeneous Pd-catalyst (0.2 mol%)	2	98
4	Ru-CP (0.2 mol%) + Model homogeneous Pd-catalyst (0.2 mol%)	2	95
5	Zn-CP (0.2 mol%) + Model homogeneous Pd-catalyst (0.2 mol%)	2	19
6	Terpyridine(0.4 mol%) + Model homogeneous Pd-catalyst (0.2 mol%)	2	No conversion

^aReaction condition: aryl halide (1.0 mmol), phenylboronic acid (1.2 mmol) 90 °C, H₂O (5 mL). ^bIsolated yield after column chromatography.

2.2 Optimized catalytic condition for Suzuki-Miyaura Coupling (SMC) of phenylboronic acid and 4-bromo acetophenone

Phenylboronic acid (146.3 mg, 1.2 mmol), 4-bromo acetophenone (200 mg, 1 mmol), potassium carbonate (414 mg, 3 mmol) and 0.1 mol% of Pd (**Ru-CP-Pd**) were stirred in 4 mL of water for 8 h at 90 °C. After this time, the reaction mixture was extracted with 5 mL of diethyl ether for 4 times. The ether extract was evaporated under vacuum and the residue was subjected to a silica gel column chromatography. The corresponding product was eluted with 1:9 ethyl acetate/hexane eluent. The yield of product was found to be 98%. ¹H NMR (CDCl₃, 400 MHz): δ = 8.04 (d, *J* = 8.3 Hz, 2H), 7.66 (dd, *J* = 23.6, 7.8 Hz, 4H), 7.44 (dt, *J* = 29.0, 7.4 Hz, 3H), 2.64 (s, 3H).

2.3 General procedure for Suzuki-Miyaura Coupling reaction

Aryl boronic acid (1.2 mmol), haloarene (1 mmol), potassium carbonate (414 mg, 3 mmol) and 0.1 mol% of Pd (**Ru-CP-Pd**) were stirred in 4 mL of water for 8 h at 90 °C. After this time, the water layer was extracted with 5 mL of diethyl ether for 4 times. The ether layer was evaporated under vacuum and the residue was subjected to a silica gel column chromatography to afford the pure product.

3. Results and Discussion

The Ru(terpy)₂-based coordination-polymer-anchored single-site 'Pd-NHC' catalyst, **Ru-CP-Pd**, was obtained from its precursor **Ru-CP** polymer upon palladation with Pd(OAc)₂,²¹ and used for Suzuki-Miyaura coupling reaction in a water medium. Under optimized condition, 98% yield of the biaryl product was obtained with 0.1 mol% catalyst loading after 8 h at 90 °C for

coupling of phenylboronic acid and 4-bromo acetophenone (entry 1, Table 1). After extraction of the reaction mixture with diethyl ether, the product was purified by column chromatography. However, under same conditions, the product was obtained in only 18% yield (entry 2, Table 1), when the Zn(terpy)₂-based Pd-catalyst, **Zn-CP-Pd** (obtained from its precursor polymer **Zn-CP** upon reaction with Pd(OAc)₂) was used. To get insight into the observed dramatic difference in the activity of **Ru-CP-Pd** and **Zn-CP-Pd**, a few control studies were performed. A model molecular 'Pd-NHC'-based homogeneous catalyst [(PhImMe)PdI₂(pyridine)],²⁶ was used for Suzuki-Miyaura coupling reaction in water under similar reaction conditions. The coupling product was obtained in 98% yield in 2 h with 0.2% loading of Pd at 90 °C (entry 3, Table 1). The same model catalyst was

Table 2. SMC between various aryl boronic acids and aryl halides^a.

Entry	R ₁	R ₂	X	Yield (%) ^b
1	H	CH ₃ CO	Br	98
2	H	Me	I	97
3	H	OMe	I	95
4	Me	CH ₃ CO	Br	97
5	CN	CH ₃ CO	Br	95
6	OMe	CH ₃ CO	Br	65
7	H	CH ₃	Cl	23

^aReaction condition: aryl halide (1.0 mmol), boronic acid (1.2 mmol), 90 °C, H₂O (5 mL). ^bIsolated yield after column chromatography.

Figure 2. Recyclability (left) and hot filtration test (right) of **Ru-CP-Pd** for SMC reaction.

Figure 3. UV-Vis spectra of the original and recovered **Ru-CP-Pd** catalysts (left), and SEM image of the recovered catalyst (right).

used along with 0.2 mol% of **Ru-CP** and 0.2 mol% **Zn-CP** separately in two parallel catalytic reactions. The reaction performed in the presence of **Ru-CP** gave 95% yield of the product in 2 h (entry 4, Table 1), whereas the reaction performed in presence of **Zn-CP** gave only 19% yield (entry 5, Table 1). These results suggested that Zn^{2+} binds the terpyridine moiety loosely in comparison to Ru^{2+} , and therefore under catalytic condition the Zn^{2+} -terpy coordination bond breaks down releasing free terpyridine. This free terpyridine ligand blocks catalytically active Pd-species and thus inhibits it from taking part in catalysis. When 0.4 mol% of free terpyridine was used along with the model catalyst, no conversion was obtained (entry 6, Table 1), as expected due to the above reason.

Preliminary experiments showed that the model reaction between 4-bromo acetophenone (1 mmol) and phenylboronic acid (1.2 mmol) using 0.1 mmol% (based

on Pd) of **Ru-CP-Pd** as the catalyst and excess of K_2CO_3 (3.0 mmol) as the base proceeded smoothly in H_2O at 90°C affording the desired biaryl product within 8 h in excellent isolated yield (98%). Based on these optimized experimental conditions, we explored the substrate scope using chloro, iodo and bromoarenes and different arylboronic acids. The results are summarized in Table 2. In general, all the reactions were very clean and the corresponding biaryl products were isolated in good to excellent yields. As expected, iodobenzene was rapidly converted to the corresponding biaryl products with excellent yields (Table 2). The less reactive aryl chloride displayed a poor conversion. Next, to demonstrate the versatility of the catalytic system for the SMC reaction, we tested substituted boronic acids, bearing either electron-donating or electron withdrawing groups, such as $-\text{OMe}$, $-\text{CN}$, $-\text{Me}$, which also provided the corresponding products selectively

in good to excellent yields within 8 h. The activity of the **Ru-CP-Pd** catalyst was comparable to similar but non-CP-based heterogenized Pd–NHC catalysts reported in literature.^{27–31} The catalyst was not free of limitation. For example, with heteroaryl bromide, such as 2-bromopyridine, the yield of the coupling product was only 20%. Similarly, with alkyl iodide and arylboronic acid, only bis-aryl (homo-coupling) product was formed.

As an important aspect of heterogeneous catalysis, we further studied the recyclability of the **Ru-CP-Pd** for a model SMC reaction of 4-bromoacetophenone and phenylboronic acid. After each run, the product was separated by simple extraction of the aqueous layer with diethyl ether. The catalyst was separated from water by centrifugation and was washed with water and diethyl ether several times. Thus, with recovered **Ru-CP-Pd**, the catalysis was carried out further. The results showed a good recyclability furnishing 67% yield at the end of the 5th cycle (Figure 2). Another aspect was to test the heterogeneous nature of the system. Hot filtration test was performed for the reaction of 4-bromoacetophenone and phenylboronic acid to check the heterogeneity of the catalysis. The ongoing reaction mixture was filtered at hot condition after 4 h. With the filtrate solution, the reaction was carried out further. However, no further increment in product formation was observed (Figure 2). UV-Vis spectra of the filtrate does not show characteristic MLCT band for Ru-bis-terpyridine chromophoric group. On the other hand, when the recovered catalyst after the reaction was analyzed by UV-Vis spectroscopy, SEM and EDS techniques (Figure 3), it showed typically similar nature as the original catalyst, suggesting the robustness of the system under the reaction conditions. Hg-poisoning test provides an indication whether the catalysis is homogeneous or heterogeneous. Accordingly, when the reaction of 4-bromoacetophenone and phenylboronic acid was performed with the **Ru-CP-Pd** catalyst (0.1 mol%) in the presence of 1 drop of Hg, it was found that the yield of the coupling product was 84% (as compared to 98% without Hg). This good yield suggested that catalytically active Pd nanoparticles and/or soluble Pd-species were not formed during catalysis with the present **Ru-CP-Pd** catalyst, further suggesting the heterogeneity of the system (SI).

4. Conclusions

In summary, we demonstrated that simple Ru-terpyridine coordination chemistry can be applied to self-support Pd^{II}(NHC) moieties in a robust polymeric platform. The potential utility of the extended Ru^{II}(terpy)₂-based coordination polymer scaffold anchoring the

single-site Pd^{II}(NHC) catalytic sites for Suzuki–Miyaura reaction in water was explored. This new catalyst showed good efficiency and reusability. Mechanistic and control studies were performed to evaluate the heterogeneous nature of this system.

Supplementary Information (SI)

Additional experimental details and additional data and spectra for this article are available at www.ias.ac.in/chemsci.

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