



## Polyaniline-Supported Palladium(II)-Schiff Base Complex as Efficient Catalyst for Mizoroki-Heck Cross-Coupling Reaction

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### ABSTRACT

Mizoroki-Heck cross-coupling reaction of 4-bromoacetophenone with methyl acrylate were investigated as a model system of heterogeneous reaction in order to evaluate the performance of polyaniline supported  $N,N'$ -bis(3,5-di-tert-butylsalicylidene)propane-1,3-diaminepalladium(II) complex as catalyst. The reactions were carried out in both  $N,N$ -dimethylacetamide (DMAc) and water-DMAc mixed solvent. The performances of the catalyst in both media are comparable, giving more than 90 % conversion after 24 hours of reaction with 100 % selectivity and high isolated product yields of cinnamic esters were obtained. The used of mixed solvent gave more advantages such as less organic solvent was required and an enhanced recyclability in which the supported catalyst could be reusable at least four times without noticeable decrease in the product conversion. The properties of the catalyst was characterized by various techniques such as FTIR spectroscopy, TG-DTA, AAS, BET surface area, XRD and FESEM.

| Mizoroki-Heck cross-coupling reaction | Palladium | Schiff base | Polyaniline | Catalyst |

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### 1. INTRODUCTION

The Heck reaction is referred to the palladium catalysed arylation or vinylation of olefins has gained prominence over past decade, as it is a selective single operational step for C-C bonds formation and has established to be an exceedingly effective and powerful tool for the carbon-carbon construction [1-4]. It has been utilised for synthesis of fine chemicals and producing several intermediates in pharmaceuticals such as one of active anticancer drugs, taxol which involves an intramolecular Heck reaction. While, the substituted cinnamic acids and corresponding esters are also synthesized via Heck reactions have found to be an extensive applications as ultraviolet absorbers as well as antioxidants [5-7].

The numerous palladium complexes have been investigated as homogeneous catalysts and the supported palladium complexes as heterogeneous catalysts because palladium is arguably the most versatile and the most widely applied catalytic metal in Heck reaction [8-9].

Traditionally, soluble phosphine palladium complex employed as catalysts for Heck reaction. Despite its remarkable usefulness, phosphine ligand is expensive, toxic, unrecoverable and sensitive towards air and moisture and therefore environmentally unfavourable [10]

Much effort has been made to design the new phosphine-free catalysts which also allowed of using other aryl derivatives [11]. In our attempts to evaluate the phosphine-free system in the Heck reaction,  $N_2O_2$ -tetradentate Schiff base ligands have been chosen for this purpose.  $N_2O_2$ -tetradentate ligands possess many advantages such as facile approach, readily adjusted ancillary ligand and electronic environments on the metal centre [12]. Active and well defined Schiff base metals complexes have been widely studied due to the versatility of their steric and electronic properties, which can be fine-tuned by choosing the amine precursors and ring substituents [13]. Due to these properties, tetradentate  $N_2O_2$  ligands and their transition metal complexes often act as catalyst.

Mostly palladium-containing homogeneous catalyst is suffers from a number of drawbacks which lie in the removal, difficult regeneration to original activity and palladium contamination in the products [14-16]. Considerable efforts have been made for this reaction in order to achieve a high degree of efficiency under mild conditions [17]. In this study, heterogeneous Pd-catalysis is developed as an alternative to overcome the homogeneous one. Heterogeneous system possesses significant advantages from the viewpoint of heat and air-stability recoverability, reusability and non-residual property [4, 18].

Currently, the discoveries of polyaniline supported palladium(II)-Schiff base catalyst offers a great potential and opportunity to develop the phosphine-free

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heterogeneous catalysis. Polyaniline (PANI) has attracted great attention in recent years as catalyst support due to its environmental stability and interesting redox properties but only a few reports are available using PANI supported metal catalyst in carbon-carbon bonds formation. This organic polymer offers assorted routes of metal attachment to the polymer matrix via covalent or non-covalent bonding, through hydrogen bonding, as well as through ionic, hydrophobic or fluorine interactions [19]. Kantam and co-workers reported polyaniline supported palladium is excellent catalyst for Suzuki-Miyaura cross-coupling of bromo- and chloroarenes in water [20].

In continuation of our research on the development of heterogeneous palladium catalyst for carbon-carbon bond formation, we have investigated whether a PANI supported palladium(II)-Schiff base complex could catalyze the Mizoroki-Heck cross-coupling reaction efficiently. In this paper, we reported on the performance of this catalyst for the Heck cross-coupling reaction (Scheme 1). As we expected, the catalyst showed high stability and excellent in catalytic activity. Furthermore, the catalyst can be readily recovered by simple filtration and reused for several times.

## 2. EXPERIMENTAL

### 2.1 Materials, method and instruments

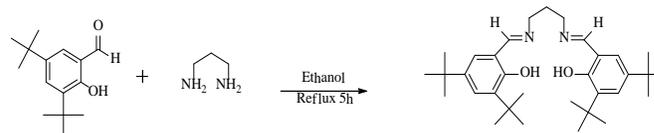
All of the reagents were analytical grade. Polyaniline, emeraldine base, Mw ca. 20 000 (Aldrich), Palladium(II) acetate (Aldrich), 3,5-di-*tert*-butylbenzaldehyde (Aldrich), 1,3-diaminopropane (Aldrich), 4-bromoacetophenone (Aldrich) and methyl acrylate (Fluka) were used without further purification and others chemical were purchased from local suppliers. Commercial grade solvents were distilled according to normal procedures and dried over molecular sieves (4 Å) before used. All reactions were carried out in an inert atmosphere of dry nitrogen.

Fourier transform infrared (FTIR) spectra for solid samples were recorded as potassium bromide (KBr) discs with a Perkin-Elmer Spectrum One FTIR over the wave number range from 400 to 4000  $\text{cm}^{-1}$ . Liquid  $^1\text{H}$  and  $^{13}\text{C}$  spectra were recorded on a Bruker Avance 400 MHz spectrometer with TMS as an internal standard in  $\text{CDCl}_3$  as solvent. The CHN elemental analyses were determined using a Thermo Finnigan CE 125 CHN analyzer. XRD patterns of the samples were carried out by using a Siemens D5000 powder diffractometer using  $\text{Cu K}_\alpha$  radiation ( $\lambda = 1.5418\text{\AA}$ ,  $kV = 40$ ,  $mA = 40$ ) and was measured in the  $2\theta$  scale of  $1.5\text{-}10^\circ$  with step interval at  $0.0025^\circ$   $2\theta$  with counting time of 1 sec/step. The BET surface area was calculated by using Thermo Finnigan Qsurf surface analyzer. Palladium loading on the supported catalyst was measured by Atomic Absorption Spectrometer (AAS-Perkin Elmer). A Mettler Toledo TGA/DTA 851 instrument was used to determine the thermal stability of the supported catalyst while, the surface morphology of polyaniline and polyaniline supported palladium-Schiff base complexes were analyzed using a JOEL JSM 67017 field emission

scanning electron microscopy (FESEM) equipped with EDAX facility. Powder materials were deposited on adhesive tape fixed to specimen tabs and then coated with gold.

### 2.2 Preparation of *N,N'*-bis(3,5-di-*tert*-butylsalicylidene)propane-1,3-diamine

Stoichiometric amount of 1,3-diaminopropane (2.15 mmol) with two equivalents of 3,5-di-*tert*-butyl-2-hydroxybenzaldehyde were mixed together in 10 mL anhydrous ethanol (Scheme 1.0). The resulting mixture was refluxed under  $\text{N}_2$  atmosphere for 5 h after which a yellow solid had precipitated out. This was separated by vacuum filtration, washed with cold ethanol and dried in vacuum. Yield 82.48%. m.p. = 132-133  $^\circ\text{C}$ . Experimental: C, 79.02; H, 9.98; N, 5.89. Calculated for  $\text{C}_{33}\text{H}_{50}\text{N}_2\text{O}_2$  requires: C, 78.21; H, 9.94; N, 5.53. IR (KBr)  $\nu_{\text{max}}$   $\text{cm}^{-1}$ : 3426 (OH), 1633 (C=N), 1173 (C-O).  $^1\text{H-NMR}$  ( $\text{CDCl}_3$ ),  $\delta_{\text{H}}$ : 13.81 (s, 2H, OH), 8.37 (s, 2H, N=C-H), 7.37-7.36 (d, 2H, Ar-H), 7.07-7.06 (d, 2H, Ar-H), 3.70-3.67 (t, 4H, N-CH<sub>2</sub>), 2.15-2.09 (m, 2H, C-CH<sub>2</sub>-C), 1.44 (s, 18H, Ar-*tert*-butyl-C<sub>4</sub>H<sub>9</sub>) and 1.29 (s, 18H, Ar-*tert*-butyl-C<sub>4</sub>H<sub>9</sub>).  $^{13}\text{C-NMR}$  ( $\text{CDCl}_3$ ),  $\delta_{\text{C}}$ : 166.48 (C=N), 158.11 (C-OH), 140.04, 136.68, 126.88, 125.83, 117.84 (arom. C), 56.74 (N-CH<sub>2</sub>), 35.04 (C-(CH<sub>3</sub>)<sub>3</sub>-{b}), 34.13 (C-(CH<sub>3</sub>)<sub>3</sub>{a}), 31.72 (C-CH<sub>2</sub>-C) 31.50 (*tert*-butyl-C<sub>4</sub>H<sub>9</sub>) and 29.44 (*tert*-butyl-C<sub>4</sub>H<sub>9</sub>).

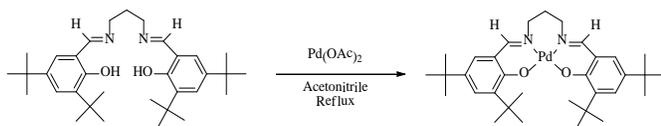


Scheme 1 Synthesis of Schiff base ligand

### 2.3 Preparation of *N,N'*-bis(3,5-di-*tert*-butylsalicylidene)propane-1,3-diaminepalladium(II)

A solution of ligand (0.5 mmol) in acetonitrile (10 mL) was added to a solution of palladium(II) acetate (0.5 mmol) in acetonitrile (10 mL) in a three necked round bottom flask (Scheme 2.0). The resulting mixture was refluxed under  $\text{N}_2$  atmosphere for 5 h after which it was allowed to cool, filtered and evaporated to low volume. The required palladium complex was obtained as gold solid. These was filtered off and dried in vacuum. Yield 78.02%. m.p. = 375-376  $^\circ\text{C}$ . Calc. for  $\text{C}_{33}\text{H}_{48}\text{N}_2\text{O}_2\text{Pd}$ : C, 64.85; H, 7.92; N, 4.58%. Found: C, 61.37; H, 6.08; N, 4.50%. IR (KBr)  $\nu_{\text{max}}$   $\text{cm}^{-1}$ : 1613 (C=N), 1175 (C-O).  $^1\text{H-NMR}$  ( $\text{CDCl}_3$ ),  $\delta_{\text{H}}$ : 7.64 (s, 2H, N=C-H), 7.41-7.40 (d, 2H, Ar-H), 7.92-6.91 (d, 2H, Ar-H), 3.70-3.68 (t, 4H, N-CH<sub>2</sub>), 2.08-2.07 (m, 2H, C-CH<sub>2</sub>-C), 1.50 (s, 18H, Ar-*tert*-butyl-C<sub>4</sub>H<sub>9</sub>{b}) and 1.28 (s, 18H, Ar-*tert*-butyl-C<sub>4</sub>H<sub>9</sub>{a}).  $^{13}\text{C-NMR}$  ( $\text{CDCl}_3$ ),  $\delta_{\text{C}}$ : 163.79 (C=N), 157.18 (C-OH), 139.69, 135.81, 130.29, 127.61, 118.61 (arom. C), 60.06 (N-CH<sub>2</sub>), 35.97 (C-(CH<sub>3</sub>)<sub>3</sub>-{b}), 33.72 (C-(CH<sub>3</sub>)<sub>3</sub>{a}), 32.18 (C-CH<sub>2</sub>-

C) 31.28 (*tert*-butyl-C<sub>4</sub>H<sub>9</sub> {b}) and 29.89 (*tert*-butyl-C<sub>4</sub>H<sub>9</sub> {a}).



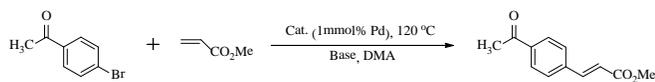
**Scheme 2** Synthesis of palladium(II)-Schiff base complex

## 2.4 Preparation of polyaniline-supported palladium(II)-complex

A mixture of polyaniline (0.2 g) and the palladium(II)-Schiff base complex (0.2 g) was stirred in acetonitrile (20 mL) for 72 hours at room temperature (Scheme 3.0). The resultant solid was filtered off and washed with acetonitrile (2 x 5 mL) followed by acetone. The residue was dried in an oven for 24 hours. The content of palladium was 0.10 mmol/g as determined by AAS.

## 2.5 General procedure for Heck reaction

The Heck reactions of aryl halide with methyl acrylate (Scheme 4.0) were carried out in a Radley's 12-placed reaction carousel with magnetic stirring. A mixture of 4'-bromoacetophenone (1 mmol; 0.20 g), methyl acrylate (3 mmol; 0.3 mL), base (2.4 molar equiv.), polyaniline-supported palladium(II) complex (1 mmol% with respect to Pd) and *N,N*-dimethylacetamide (5.0 mL) were stirred at 120 °C whilst purging with nitrogen for 24 h. After reaction completed, the catalyst was separated by filtration, wash with water to remove base and salt and finally dried under vacuum for next cycle. The organic product (filtrate) was then separated by extraction with diethyl ether (twice with 10 cm<sup>3</sup>), dried over Na<sub>2</sub>SO<sub>4</sub> and filtered. The product was analyzed by FTIR and NMR spectroscopy.



**Scheme 3** Heck reaction of 4-bromoacetophenone with methyl acrylate

## 2.6 Isolation Isolation of 3-(4-acetylphenyl) acrylic acid methyl ester

The product obtained from Mizoroki-Heck reaction had yielded 78% as pale yellow solid with its melting point (66-67 °C). IR (KBr)  $\nu_{\max}$  cm<sup>-1</sup>: 1712 (O-C=O), 1683 (C=C=O). <sup>1</sup>H-NMR (CDCl<sub>3</sub>),  $\delta_{\text{H}}$ : 7.99-7.97 (d, H, J=8.0 Hz, Ar-H), 7.74-7.70 (d, H, C=CH), 7.63-7.61 (d, H, J=8.0 Hz, Ar-H), 6.56-6.52 (d, H, C=CH), 3.84 (s, 3H, O-CH<sub>3</sub>) and 2.63 (s, 3H, C-CH<sub>3</sub>). <sup>13</sup>C-NMR (CDCl<sub>3</sub>),  $\delta_{\text{C}}$ : 197.26 (C-C=O), 166.90 (O-C=O), 143.28 (C=CH), 138.72, 138.07, 128.84,

128.13 (arom. C), 120.35 (C=CH), 51.86 (O-CH<sub>3</sub>) and 26.63 (C-CH<sub>3</sub>).

## 3. RESULTS & DISCUSSION

### 3.1 Synthesis of polyaniline-supported palladium (II)-complex

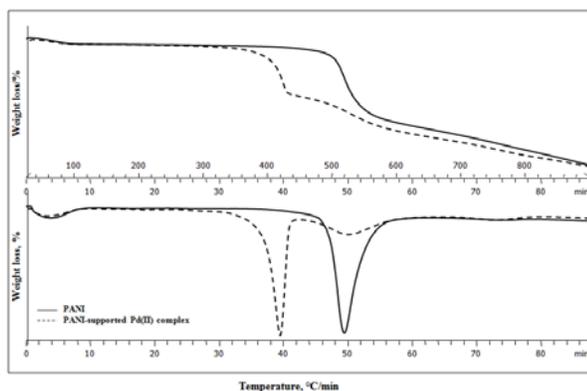
The outline for synthesizing of polyaniline-supported palladium(II)-complex was presented in Scheme 3.0. It was readily prepared by physical mixing procedure according to previous report [20, 21-22]. The catalyst prepared was well characterized by FTIR, FESEM-EDAX, TGA-DTA, BET surface area, XRD and AAS. The metal content of polyaniline-supported palladium(II) complex determined by AAS suggested 0.1015 mmol/g palladium loading onto supported palladium complex. The characteristic parameter of PANI and PANI-supported Pd(II) complex textures determined by BET surface area are 73.81 m<sup>2</sup>/g and 76.53 m<sup>2</sup>/g respectively.

In FTIR spectrum of polyaniline (PANI), the most important bands are located at 1590, 1496, 1379, 1299, 1164 and 828 cm<sup>-1</sup> which are due to the stretching vibrations of quinoid ( $\nu_{\text{C=N}} + \nu_{\text{C=C}}$ ), benzenoid ( $\nu_{\text{C=C}}$ ) units of the polyaniline, deformations of C-N bond, stretching vibrations of C-N bond, in plane deformations of C-H bonds present in the aromatic rings of the undoped polymer and the out of plane deformations of CH bonds in 1,4-substituted aromatic ring respectively [21, 23-24]. However, there is no significant shifted has been observed in the quinoid or benzenoid ring band position of polyaniline supported palladium(II) complex, which is in accord with earlier studies [25].

The thermal stability curves of PANI and PANI-supported palladium(II) complex are presented in Fig. 1.0. TGA-DTA of the catalyst was investigated at a heating rate of 10 °C/min in nitrogen over a temperature range of 25-600 °C. Thermogravimetric curves TGA and DTA of PANI show a decrease of mass (*ca.* 2%) within the temperature region 50-100 °C. The weight changes in this region are associated with release of solvent and water from the samples [26]. The mass of PANI became relatively constant in the temperature region 200-450 °C. The DTA curve shows the decomposition process of PANI backbone chains started *ca.* 500 °C and the minimum of exothermic DTA peak appear at 550 °C. While, PANI-supported palladium(II) complex is thermally stable up to 250 °C and above this temperature it decomposes. The decomposition of PANI-supported palladium(II) complex is lower than for PANI support (exothermic DTA peak at 410 °C). The thermogravimetric study suggested that PANI-supported palladium(II) complex degrades at considerably higher temperature.

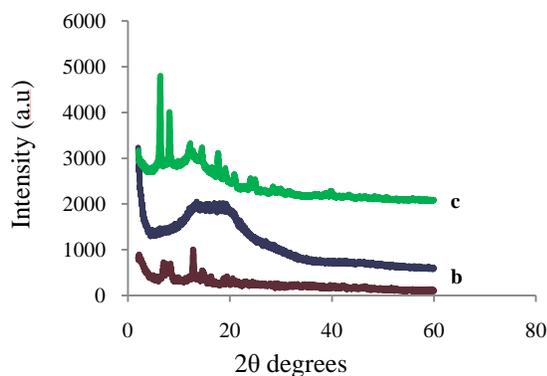
The FESEM images of PANI and its supported onto palladium(II) complex obviously showed the morphological difference which occurred on the surface of the PANI after palladium metal loading (Fig. 2.0). Flake like particles were observed throughout the specimen and the presence of the

Pd was also analyzed by energy dispersive of X-ray spectroscopy analysis (EDAX) (Fig. 3.0).



**Fig. 1** TGA-DTA curves for PANI and PANI-supported Pd(II) complex

Powdered X-ray diffraction studies of PANI and PANI-supported palladium(II) complex were showed in Fig. 4.0. PANI support almost similar to amorphous nature and no characteristic of XRD pattern was observed. While, PANI-supported palladium(II) complex resulted in dramatic changes compared to PANI structure probably because the active phase exist as a crystalline form and highly dispersed as fine particles on PANI support matrix.



**Fig. 2** XRD patterns of (a) Pd(II) complex (b) PANI free(c) PANI-supported Pd(II) complex

### 3.2 Catalytic Study

The heterogeneous PANI-supported Pd(II) complex was investigated in Heck coupling reactions of 4-bromoacetophenone with methyl acrylate in the presence of sodium acetate as a base in DMAc and water-DMAc mixed solvent at reflux temperature 120 °C. Sodium acetate was chosen as a base due to the capability of this base to give highest conversion compared to the other bases [21]. Catalytic loading was kept to 1.0 mmol% so as to give an expected turnover number 100 if 100% conversion was achieved. The conversion of the starting was monitored by <sup>1</sup>H NMR spectroscopy. As shown in Table 1.0 the catalytic

data obtained indicate that these polyaniline supported Pd(II) complex efficiently catalysed the Heck reaction of 4-bromoacetophenone with methyl acrylate, giving more than 90% conversion after 24h. The effect of temperature, solvent, base and amount of catalyst on the catalytic properties of the palladium(II) complexes is currently in progress.

**Table 1** Heck reaction of 4-bromoacetophenone with methyl acrylate catalysed by PANI-Pd(II) complex

Catalyst	% Conversion	
	DMAc <sup>a</sup>	Water-DMAc <sup>b</sup>
PANI-Pd(II) complex	100	97

Reaction conditions: 4'-bromoacetophenone (1.0 mmol), methyl acrylate (3.0 mmol), NaOAc (2.40 mmol), catalyst (1.0 mmol% of Pd), solvent (5.0 mL); all reactions were carried out at 120 °C in N<sub>2</sub> atmosphere

<sup>a</sup>Conversion of reactant was determined by <sup>1</sup>H NMR

<sup>b</sup> Isolated yield

### 3.3 Heterogeneity Test

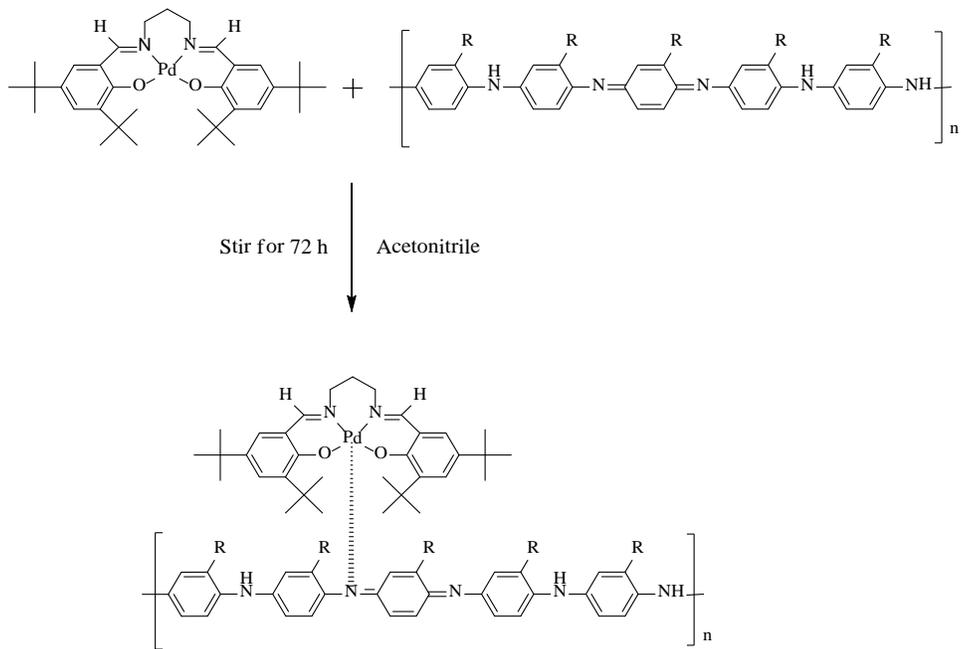
In order to confirm the reaction takes place on the surface of the solid Pd catalyst [22] or with palladium leached out from the support [23], two test experiments were undertaken:

(a) A hot filtration test was carried out in a similar manner as general procedure for Heck reaction with the exception that catalyst was separated after 14 h with approximately 21% conversion. Then, the hot filtrate was further reacted for 10 h. The conversion of the product was determined by <sup>1</sup>H NMR spectroscopy for every 1 h and it was found that no further reaction was noted after the catalyst removal (Fig. 5.0). This study performed that the Heck cross-coupling reaction followed a heterogeneous pathway.

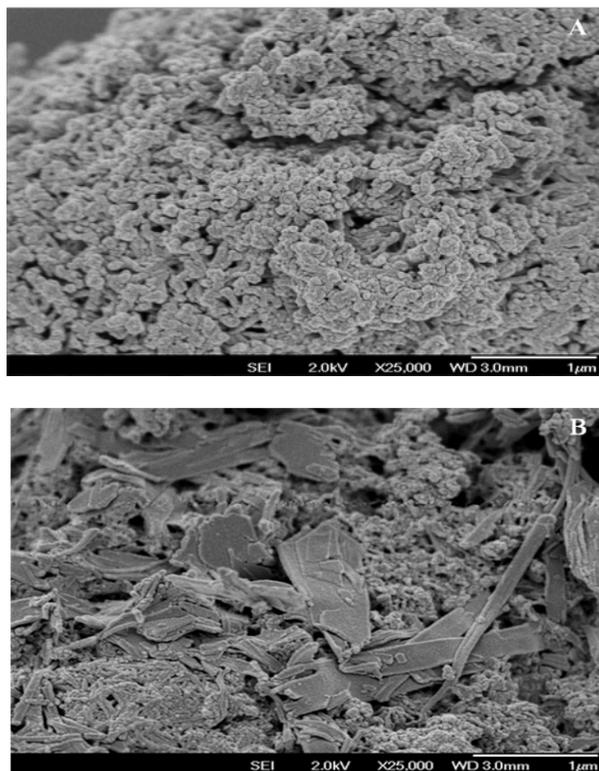
(b). Percent of palladium leached out from the solid surface also could be studied by atomic absorption spectroscopic analysis. The catalyst was subjected to the Heck reaction and filtered off the catalyst after 24 h of the reaction. The solid catalyst was dissolved in 5 mL aqua regia and diluted to 25 mL. The difference of palladium content between the fresh and first used catalyst was 0.01426 mmol/g which suggests the heterogeneous nature of the PANI-supported Pd(II) catalyst.

### 3.4 Recyclability of the catalyst

In heterogeneous catalytic system, the lifetime of the catalyst and its level of recyclability are very important theme. Reusability studies were investigated with the present catalyst using the reaction of 4'-bromoacetophenone with methyl acrylate. The PANI-supported Pd(II) catalyst can easily be recovered from the reaction mixture by simple filtration and was charged to the next run after washing with distilled water followed by acetone and air drying. The conversions of the final products were comparable to the first run (Table 2.0).



**Scheme 3** Synthesis of polyaniline-supported palladium(II) complex



**Fig. 2** FESEM images of the polyaniline (a) and polyaniline-supported Pd(II) complex (b)

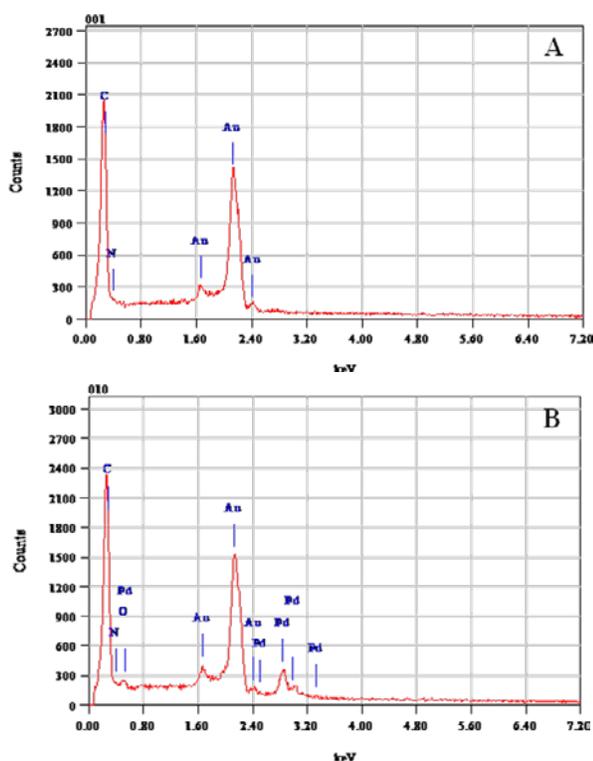


Fig. 3 EDAX spectrum of PANI (a) and PANI-supported Pd(II) complex (b)

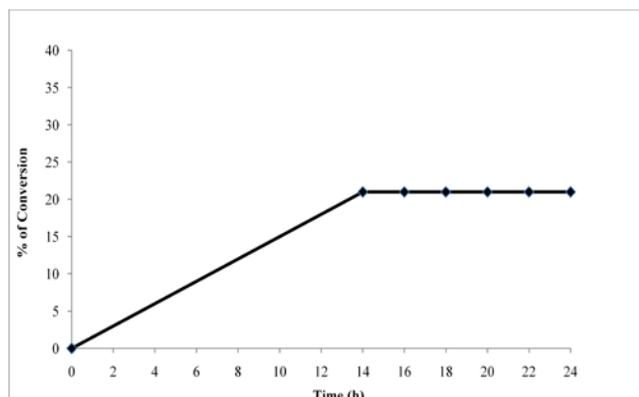


Fig. 5 Leaching test of PANI-supported Pd(II) complex towards the Heck cross-coupling reaction. Reaction condition: 4'-bromoacetophenone (1.0 mmol), methyl acrylate (3.0 mmol), NaOAc (2.40 mmol), catalyst (1.0 mmol% of Pd), DMAc (5.0 mL)

Table 2 Catalytic activity of the reusability PANI-supported Pd(II) complex

Catalyst	Conversion (%) <sup>a</sup>	
	DMAc	Water-DMAc
Run 1	100	97
Run 2	97	94
Run 3	27	85
Run 4	-	78

The conversions of the products obtained were comparable in both media. The results showed the reused

catalyst in water-DMAc is most effective compared to DMAc enhanced recyclability in which the supported catalyst could be recyclable up to four times without any appreciable loss of its catalytic activity. The presence of catalyst in mixed water-DMAc was fully recovered and less organic solvent was required in catalytic testing.

While, the amount of catalyst used in DMAc solvent was dramatically decreased to 70% and lower conversion was achieved after three runs. This is probably due to the solubility of polyaniline emeraldine powder in high polar solvents such as N,N-dimethylacetamide (DMAc), N,N-dimethyl formamide (DMF) and dimethyl sulfoxide (DMSO) [24].

#### 4. CONCLUSION

In summary, a heterogeneous PANI-supported Pd(II) complex has been successfully synthesized, characterized and applied in Heck coupling reaction of 4'-bromoacetophenone with methyl acrylate. The catalyst exhibits high activity and stable towards air. The heterogeneity test indicated that the reaction occurs at the heterogeneous pathway. The ease of recovery and availability make such supported catalyst an interesting alternative to the homogeneous catalysts.

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