

A modification of polystyrene supported palladium(II) complex as effective catalyst for Mizoroki-Heck reaction

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Abstract: Chloromethylated polystyrene cross-linked with 5% divinylbenzene (PS5) has been successfully functionalized with phenyldithiocarbazate ligand (PS5-PDC). The polymer was used as solid support for anchoring the palladium metal (PS5-PDC-Pd). The properties of dark colored polymer, impregnated with palladium complex was then characterized by various spectroscopic and analytical techniques namely Fourier Transform Infrared (FTIR), elemental chemical analysis CHNS, Thermogravimetric analysis (TGA), BET surface area, powder X-ray Diffraction (XRD), Inductively Coupled Plasma-Optical Emission Spectrometer (ICP-OES) and Scanning Electron Microscopy/Energy Dispersive X-ray (SEM-EDX). Supported catalyst of PS5-PDC-Pd was then tested in the Mizoroki-Heck reaction of 4-bromoacetophenone with methyl acrylate. The reaction was monitored by GC-FID. Preliminary results showed that supported catalyst could be used in at least three consecutive Mizoroki-Heck reactions with the same catalytic activity.

Key words: Polystyrene; Supported catalyst; Mizoroki-Heck reaction

1. Introduction

Palladium catalyzed carbon-carbon bond formations have been recognized as powerful synthetic tools in organic transformations for fine chemical production (Keles et al., 2008). Currently, the designing of environmentally, simple and efficient supported catalyst has become a goal for many researchers due to its great potential in catalyzing of organic transformations (Demel et al., 2010). Ideally, the preparation of supported catalyst is to enhance the thermal and chemical stabilities and most significantly, the supported catalyst can be reused for several times without any appreciable loss of catalytic activity (Soh et al., 2014). Therefore, the synthesizing of supported catalyst can give an alternative solution to overcome the homogeneous system (Bakherad et al., 2012a).

Clearly, most of homogeneous catalysts suffer from a number of drawbacks which lie in the removal, difficult regeneration to original catalytic activity and contamination of product reaction (Islam et al., 2011; He and Cai, 2011). As there is no recovery of the catalyst, reusing it is out of consideration. Palladium catalysts such as Pd₂(dba)₃, Pd(PPh₃)₄ or Pd(PPh₃)₂Cl₂ are expensive and sometimes difficult to handle and recover (Feuerstein et al., 2005; Hajipour et al., 2012). Besides, the use of phosphine types ligand tend to be moisture and air sensitive thus required an inert atmosphere conditions to perform as an efficient catalyst, and less useful for industrial applications

(Li et al., 2007; Ojwach et al., 2007). So, due to the high cost of catalysts preparation and the toxicity of the reaction residues make it necessary to develop palladium catalysts which are eco-friendly recover and that cycle without losing their catalytic performance and activity (Rouhi, 2004).

In this regard, stable and reusable active polystyrene supported palladium(II) complex has been designed for Mizoroki-Heck reaction. Polymers widely used as solid support due to ease of handling and easy availability. Polystyrene is a popular polymer support because having special properties such as inert material, non-toxic, non-volatile, mechanical robustness as well as facile functionalization (Patel et al., 2010; Handa et al., 2009). The characteristics of polystyrene may be altered by varying the degrees of cross-linking (Dalal, 2012) Bakherad and co-workers (2012b) reported that polystyrene also can offer assorted routes of interaction through covalent bonding, hydrogen bonding or donor-acceptor interaction.

Inspired by the unique properties of supported catalyst in numerous reports applications, thus, this report we focus on the design and synthesis of functionalized polystyrene with phenyldithiocarbazate ligand and palladium metal acting as heterogeneous catalyst for Mizoroki-Heck reaction. As we expected, the catalyst exhibited excellent performance in catalytic activity. Furthermore, the catalyst can be easily recovered by simple filtration and reused at least three consecutive cycles in catalytic reaction.

2. Experimental

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2.1. Materials, method and instruments

All reagents were obtained commercially and directly used without further purification. Merrifield's polymer, chloromethyl poly(styrene-divinyl benzol) 5% (PS5) was supplied by Sigma-Aldrich. Bis(benzonitrile)dichloropalladium(II) and other reagents were purchased from Merck. FTIR spectra were recorded as potassium bromide (KBr) disc on a Perkin Elmer Spectrum 100 FTIR spectrometer in the range of 400 to 4000 cm^{-1} . Microanalytical data (C, H and N) were analysed using a Flash EA1112. The thermal stability of sample was carried out using a Perkin Elmer Pyris 1 DSC. Surface morphology of the PS and PS5-Pd were analyzed using a scanning electron microscope JOEL JSM 6360 equipped with Energy Dispersive X-Ray facility (SEM-EDX). X-ray powder diffraction (XRD) patterns were measured using a Rigaku Miniflex II X-ray Diffractometer and was obtained in the range 3-70°, with 2θ scale and counting time of 1 sec/step. BET surface area was calculated by using Thermo Finnigan Qsurf Surface Analyzer. Inductively coupled plasma-optical emission spectroscopy (ICP-OES) was performed using Vista-Pro Varian ICP-OES. Gas chromatography (GC) analysis were carried out on a 2010 Shimadzu gas chromatograph equipped with a 30 m \times 250 μm \times 0.25 μm nominal capillary column (BP-1, 100% dimethylpolysiloxane) and Flame Ionization Detector (FID). The microliter samples are injected at 50 °C. The temperature increment is at 15 °C per minute and the final temperature was 300 °C.

2.2. Preparation of polystyrene supported phenyldithiocarbazate ligand (PS5-PDC)

The preparation of such catalyst is simple and visual observation at each stage can confirm the successful synthesis. Firstly, the polymer was functionalized using a carousel tube that equipped with magnetic stirrer bar. Chloromethylated polystyrene (1.5 g) was swelled in 15 mL *N,N*-dimethylformamide (DMF) for 30 minutes while stirring. Then, 2.5 mL of phenylhydrazine (PhNHNH_2), 2.5 mmol of potassium hydroxide (KOH), and 2.5 mmol of carbon disulphide (CS_2) were added and heated at 90 °C for 36 hours under nitrogen atmosphere. The color of the beads changed from white to light yellow. The beads were filtered off, washed with DMF and air-dried. Then the completed incorporation of the ligand to the polystyrene was determined by elemental analyses.

2.3. Preparation of polystyrene supported phenyldithiocarbazate ligand (PS5-PDC-Pd)

The functionalized polymer (PS5-PDC) was then treated with palladium metal. The synthetic procedure of polymer supported palladium complex is illustrated in Fig. 1. The resulting bright yellow PS5-PDC (1.0 g) subsequently reacted with bis(benzonitrile)dichloro palladium(II) (1.0 g) in 15

mL *N,N*-dimethylformamide (DMF) to form supported catalyst PS5-PDC-Pd. The mixture was stirred at 80 °C for 20 hours to generate the corresponding polymer supported palladium(II) complex. The catalyst obtained was filter off, washed with acetonitrile and distilled water, then dried for 24 hours to afford the black supported catalyst.

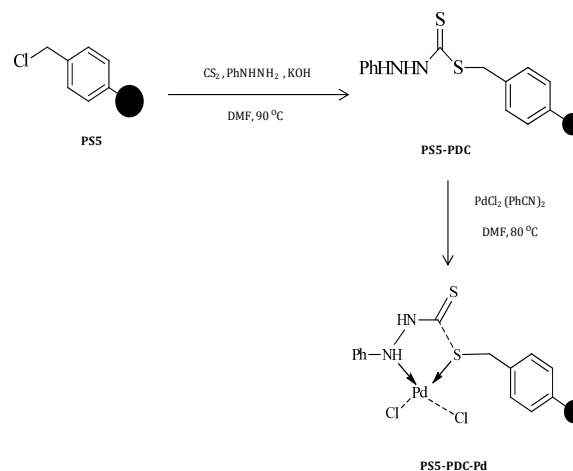


Fig. 1: Synthesis of the PS supported Pd(II) complex

2.4. General experimental procedure for Mizoroki-Heck reaction

In a typical experiment, a reaction mixture of aryl bromide (1.0 mmol), methyl acrylate (1.5 mmol), base (2.0 mmol), *N,N*-dimethylacetamide (5 mL) and the catalyst (1 mmol %) were introduced into a Radley's carousel tube whilst purging with nitrogen (Fig. 2). The reaction carousel was then heated to 120 °C with temperature carefully control by a contact thermometer (± 1 °C) for 15, 30, 60 and 180 minutes. The percentage conversion of reactants was monitored by GC-FID. At the end of the reaction the catalyst was separated by simple filtration. The filtrate was acidified with 2% hydrochloric acid solution and cooled at 0°C (Zhao et al., 2004). The purified product was confirmed by NMR and FTIR spectroscopies.

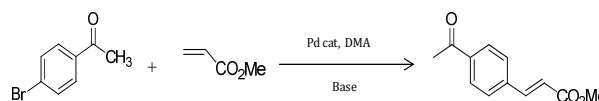


Fig. 2: Synthetic approach for the Mizoroki-Heck reaction

2.4. Recovery and reuse of the catalyst

The recyclability of PS5-PDC-Pd was further investigated because the recyclability of the heterogeneous catalyst is important issues in the coupling reactions. The reusability of the catalyst was tested using 4-bromoacetophenone and methyl acrylate as model reaction. After the completion the reaction, the catalyst was recovered by simple filtration, followed by washing with acetonitrile and distilled water. The recovered catalyst was dried under vacuum. Then, the catalyst was reused directly

for the next reaction. The conversion of products remains almost identical to the fresh catalyst.

3. Results and discussion

3.1. Synthesis and characterization of the polystyrene supported palladium(II) complex (PS5-PDC-Pd)

Polystyrene supported palladium(II) complex was successfully synthesized by heating a mixture of polystyrene with carbon disulphide and phenylhydrazine to produce PS5-PDC which was then reacted with bis (benzotriple) dichloro palladium(II) to yield corresponding supported catalyst PS5-PDC-Pd. The catalyst was well characterized using analytical and spectroscopic techniques.

Polystyrene functionalized ligand was characterized by CHNS elemental analysis. The nitrogen and sulfur contents are 8.38% and 4.65%, respectively. According to these values, the degree of phenyldithiocarbamate introduced to the polystyrene were 2.99 mmol/g and 0.73 mmol/g of the support. These confirmed that the complete incorporation of both species in PS5-PDC. The reaction of polystyrene-bound phenyldithiocarbamate with $\text{PdCl}_2(\text{PhCN})_2$ in DMF under reflux conditions resulted in the covalent attachment of palladium onto functionalized polymer.

The surface area observed for PS5 and PS5-PDC-Pd were $10.41 \text{ m}^2/\text{g}$ and $9.85 \text{ m}^2/\text{g}$, respectively. PS5-PDC-Pd slightly decreased of specific surface area than parent polystyrene (PS5) due to the blocking pores and steric hindrance effect during complexation reaction (Dalal, 2012; Bakherad et al., 2010; Antony et al., 2003). The amount of palladium incorporated into the polystyrene was also determined by ICP-OES which showed a value of 0.49 mmol/g of the heterogeneous catalyst.

The FTIR spectrum of PS5-PDC-Pd has been analyzed in the expected frequency region of the $\nu(\text{N-H})$, $\nu(\text{C-N})$, $\nu(\text{C=C})$ and $\nu(\text{C=S})$. According to IR spectrum for PS5, the vibration for $\nu(\text{N-H})$ is assigned 3425 cm^{-1} . However for PS5-PDC-Pd, the vibration signal has shifted for $\nu(\text{N-H})$, 3430 cm^{-1} suggesting formation of bonding between the ligand and the metal (Gupta et al., 2009). Meanwhile, the presence of strong band at 1384 cm^{-1} is assigned to the stretching vibration $\nu(\text{C-N})$ and the absorption band at 1598 cm^{-1} , attributed to the C=C bond of phenyldithiocarbamate-functionalized polystyrene. The $\nu(\text{C=S})$ stretching absorption band showed a decrease in peak intensity and shifted to the lower frequency at 1065 cm^{-1} . This indicated that the sulfur atom is probably involved in the attachment of functionalize ligand to the central palladium (II) ion (Ameram and Othman, 2013).

XRD analysis was performed in order to identify the different phases present in the PS5 and PS5-PDC-Pd. As shown in Fig. 3, the diffractogram of PS5-PDC-Pd showed dramatic changes compare to PS5 structure. XRD pattern of PS5 suggested its non-

crystalline nature. It has been reported that the broad peaks at 2θ values between 10° and 30° are classically attributed to the periodicity parallel to the amorphous polymer chain (Tamami and Ghasemi, 2011). Meanwhile, the functionalize ligands remain virtually unchanged and represent the same patterns. A sharp peak at the range of 40° - 42° in PS5-PDC-Pd indicated the presence of palladium metal in the supported catalyst (Ohtaka et al., 2011; Fei et al., 2012; Zhou et al., 2013). This propose that the macroporous structure is not largely unaffected by the surface modifications (Demel et al., 2010).

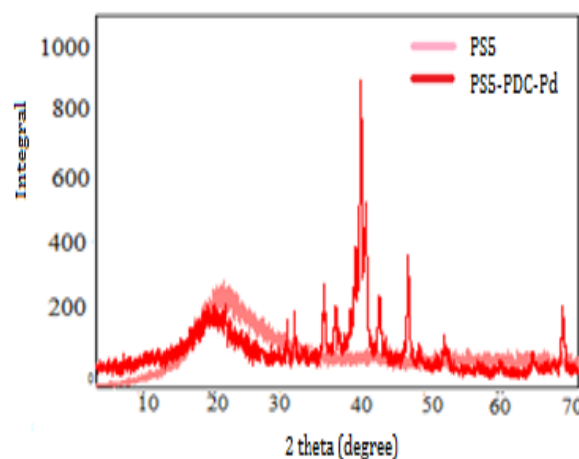


Fig. 3: XRD patterns of PS5 and PS5-PDC-Pd

The morphological changes and size of PS5-PDC-Pd were also performed by SEM-EDX analyses. A clear change in the morphology was observed with the spherical shape of the particles is more visible throughout the specimen (Fig. 4).

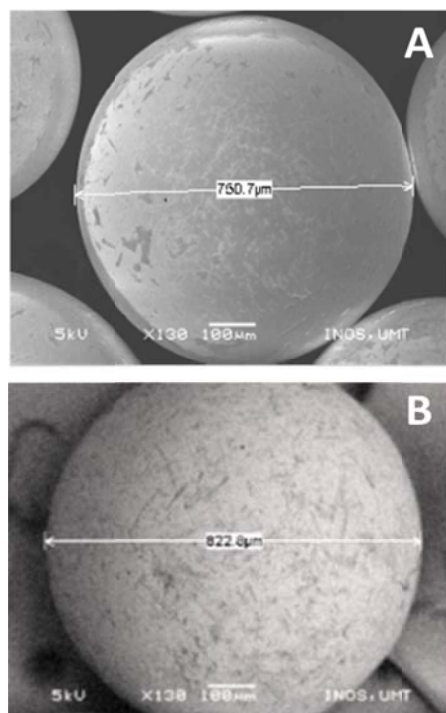


Fig. 4: SEM micrograph for PS5 (A) and PS5-PDC-Pd (B)

The surface of PS5-PDC-Pd is roughened suggested the loading of Pd metal on the surface of

polymer (Islam et al., 2010). EDX analysis was used to determine chemical composition of supported catalyst. In the EDX spectrum of catalyst (Fig. 5), peaks related to N, S and Pd were observed. EDX data also supports the metal attachment on the surface of polymer matrix.

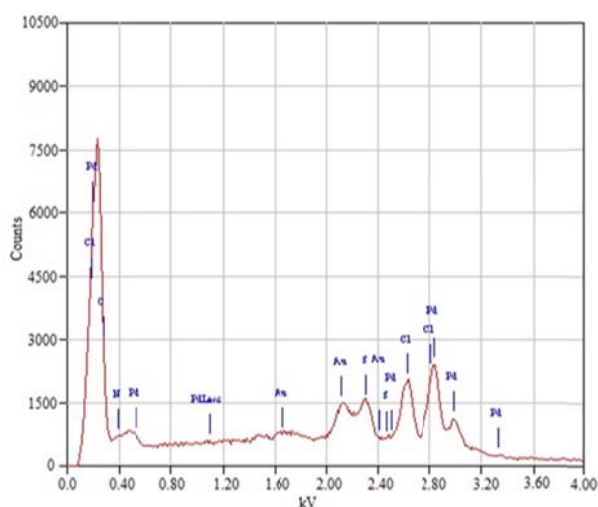


Fig. 5: EDX image of polystyrene supported Pd (II) catalyst

Thermo gravimetric analysis of supported catalyst reveals that its quiet stable up to 280 °C. The degradation occurred above 300 °C may be due to the dissociation of anchored ligand or breaking of polymeric chain (Patel et al., 2010). It can be concluded that the present analysis shows the supported catalyst can be safely used in standard Mizoroki-Heck with reaction temperature around 120 °C.

3.2. Mizoroki-Heck reaction using polystyrene supported palladium(II) complex, PS5-PDC-Pd

The main aim to design supported metal complex on polystyrene is to enhance the life of resulting catalyst, ensure easy separation from reaction mixture, more feasible for recyclability of catalyst and hence increase its overall efficacy. The synthesized catalyst was screened for the standard reaction of Mizoroki-Heck. A preliminary test was carried out of 4-bromoacetophenone with methyl acrylate as a model reaction. The reaction was monitored for 15, 30, 60 and 180 minutes. Control experiments show that there is no effective reaction in the absence of catalyst.

The supported catalyst, PS5-PDC-Pd was quite effective and the percentage of conversion obtained in good yield with respectable turnover number (TON) for the reactions. Our initial exploration of reaction condition focused on the influence of different bases. Base plays a crucial role in the rate and product distribution of the Mizoroki-Heck reaction. Base is also needed to neutralize and remove hydrogen halide (HX) from the intermediate palladium complex (Nadri et al., 2009).

The results are shown in Table 1. Catalytic loading was kept to 1.0 mmol% so as to give an expected TON 100 if 100% conversion was achieved.

Table 1: Effect of different type of bases on the catalytic performance

Entry	Base	Time(min)	Conversion ^b (%)
1	NaOAc	15	100 (100)
2	NaOAc	30	100 (100)
3	NaOAc	60	100 (100)
4	NaOAc	180	100(100)
5	Na ₂ CO ₃	15	36 (36)
6	Na ₂ CO ₃	30	48 (48)
7	Na ₂ CO ₃	60	87 (87)
8	Na ₂ CO ₃	180	100 (100)
9	NaHCO ₃	15	56 (56)
10	NaHCO ₃	30	80 (80)
11	NaHCO ₃	60	87 (87)
12	NaHCO ₃	180	100 (100)

^a Reaction were performed at 120 °C with catalyst (1.0 mmol%), 4-bromoacetophenone (1.0 mmol), methyl acrylate (1.5 mmol), base (2.0 mmol), DMA (5.0 mL), in N₂ atmosphere.

^bDetermine by GC-FID.

Values in parenthesis is turnover number (TON): moles of substrate converted per mole of metal in the catalyst

Among the selected bases, sodium acetate (NaOAc) was found to be most effective one as highest products conversion was obtained after 15 minutes (entry 1). The result shows that NaOAc performed effectively giving 100% conversion of 4-bromoacetophenone with TON of 100 to produce 3-(4-acetyl-phenyl)-acrylic acid methyl ester. In contrast, the lowest conversion was obtained when Na₂CO₃ (entry 5) probably due to the insolubility of that base in organic solvent. It was noted that NaHCO₃ was less effective and affords moderate conversion of coupled product (entry 9).

3.3. Reusability of the catalyst

In heterogeneous catalytic system, the catalyst was recycled in order to test its activity as well as stability. The recovered catalyst was employed in the next run under the similar conditions (Fig. 4) giving 100, 100 and 95% conversion of the products (Fig. 6).

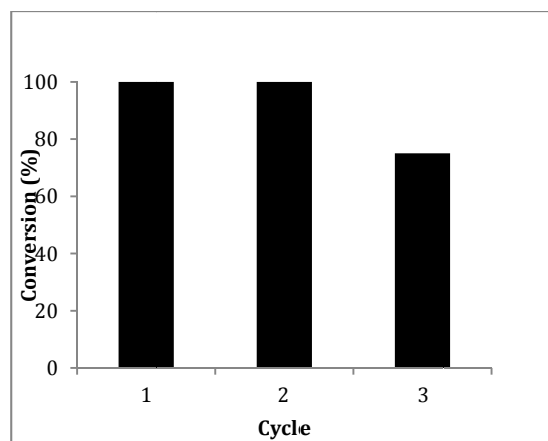


Fig. 6: Recycling study of the catalyst PS5-PDC-Pd

The results show the catalytic activity did not decrease considerably after three consecutive in the Mizoroki-Heck reaction, indicating that the synthesized supported catalyst is stable and can be regenerated for repeated use. The conversion of 4-bromoacetophenone can also be maintained. It was notable that PS5-PDC-Pd showed consistent catalytic activity without significant loss active species after being reused so many times.

3.4. Isolation of Mizoroki-Heck reaction product

The Mizoroki-Heck reaction of 4-bromoacetophenone with methyl acrylate using PS5-PDC-Pd gave 3-(4-acetyl-phenyl)-acrylic acid methyl ester as pale yellow powder. A structure of 3-(4-acetyl phenyl)-acrylic acid methyl ester is shown in Fig. 7. This product was isolated and spectroscopically characterized by FTIR and NMR spectroscopy. CHN elemental analysis: Experimental: C, 70.63%; H, 5.99%. Calculated for C₁₂H₁₂O₃ requires: C, 70.57%; H, 5.92%.

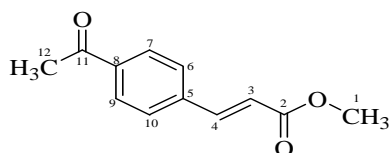


Fig. 7: Structure of acid methyl ester

The FTIR spectrum recorded as KBr disc showed two important sharp peaks at 1708 and 1682 cm⁻¹ which are assigned to the C=O ester and C=O ketone stretching modes, respectively. Meanwhile, the presence of the strong band at 1267 cm⁻¹ is assigned to the C-O ester stretching vibration. The C=C alkene stretching modes which are adjacent to the carbonyl group ester appeared at 1641 cm⁻¹. Two absorption bands of C=C aromatics stretching modes appeared at 1432 cm⁻¹ and 1361 cm⁻¹. These bands indicated the formation of 3-(4-acetyl phenyl)-acrylic acid methyl ester.

The ¹H and ¹³C NMR were used to resolve the chemical structure of the product. As observed in the ¹H NMR spectrum, the upfield chemical shift at δ_H 2.63 ppm is assigned to methyl -CH₃ protons resonance while at δ_H 3.84 ppm is due to methyl ester O-CH₃ group. The doublet resonance at δ_H 6.52-6.56 ppm (J_{HH} =16.0 Hz) is assigned to one alkene proton =CH₃ while the doublet resonance at δ_H 7.70-7.74 ppm (J_{HH} =16.0 Hz) appeared for another alkene proton. The signal from aromatic protons could be observed as two separated doublet resonances at δ_H 7.61-7.63 ppm and δ_H 7.97-7.99 ppm.

The ¹³C NMR spectrum for the catalytic product shows two different carbons with two quaternary carbons in agreement with the product structure (Fig. 7). The signal at δ_C 51.90 ppm is assigned to the O-CH₃ and -CH₃ signal observed at δ_C 26.67 ppm. Furthermore, the C=C alkenes carbon signals are observed at δ_C 120.3 ppm and 143.3 ppm. The signals from five aromatic carbons are observed in

the range of δ_C 128.1-138.7 ppm. The carbonyl(C=O) group ketone and ester clearly observed at downfield in δ_C 197.3 ppm and δ_C 166.9 ppm, respectively. Table 2 shows the ¹H and ¹³C NMR data for acid methyl ester product.

Table 2: The summary data for ¹H and ¹³C NMR for acid methyl ester product

¹ H NMR / δ_H (ppm)	
(s, 3H, CH ₃),	2.63
(s, 3H, O-CH ₃),	3.83
(d, 1H, C=CH),	6.52-6.56
(d, 1H, C ₆ H ₄),	7.61-7.63
(d, 1H, C=CH),	7.70-7.74
(d, 1H, C ₆ H ₄),	7.97-7.99
¹³ C NMR δ_C (ppm)	
(C-CH ₃),	26.67
(O-CH ₃),	51.90
(C=CH),	120.3, 143.3
(C ₆ H ₄),	128.1, 128.9, 138.1, 138.7
(O-C=O),	166.9
(C-C=O),	197.3

4. Conclusion

In the present work, polystyrene supported palladium(II) complex (PS5-PDC-Pd) was successfully synthesized and characterized. This supported catalyst was found to be very effective catalyst for Mizoroki-Heck reaction of 4-bromoacetophenone and methyl acrylate. The catalyst exhibits high activity and stable towards air. The ease of separation and recovery make such supported catalyst an interesting alternative to overcome the drawbacks of homogeneous system.

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