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OPTIMISATION, HETEROGENEITY AND RECYCLABILITY STUDIES OF PS-Pd(CH_3) CATALYST IN THE HECK REACTION

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Abstract— Polystyrene-supported palladium catalysts have gained significant attention in heterogeneous cross-coupling reactions due to their structural robustness and ease of separation. The present study evaluated the catalytic performance of a polystyrene-supported palladium(II)-hydrazone complex incorporating a methyl substituent (PS-Pd(CH_3)) in the Heck reaction. The optimisation of key reaction parameters including different starting materials (aryl bromide), solvent, catalyst loading, and

Ligand, Polystyrene Polymer Support, Palladium (II) Catalyst, Heterogeneous Catalysis

reaction time was carried out using 1-bromo-4-nitrobenzene and methyl acrylate. Optimal conditions were identified as DMA solvent, 1.0 mmol% catalyst loading, K_2CO_3 base, and 165 °C for 60 minutes, yielding a conversion of 99.8% (TON = 99.8). Hot-filtration and leaching analyses confirmed that the catalytic process predominantly proceeds via a heterogeneous pathway. The catalyst maintained appreciable activity over three consecutive cycles before a decline in performance was observed.

I. Introduction

The Heck reaction is a well-established palladium catalysed for forming carbon-carbon bonds between aryl halides and alkenes, producing substituted olefins that are widely used in pharmaceuticals, agrochemicals, and advanced materials [1-4]. Despite its efficiency, conventional homogeneous palladium catalysts suffer from limitations such as difficult separation, poor recyclability, and metal contamination in products.

To address these challenges, heterogeneous catalytic systems based on polymer supports have been extensively explored. Polymer support including polyvinyl alcohol-sodium alginate (PVA-SA), polyaniline (PANI), chloromethylated polystyrene (PS), and polypyrrole (PPy) have been successfully employed in catalyst applications. Among these, polystyrene-supported palladium catalysts offer distinct advantages, including enhanced thermal stability, ease of recovery, and improved catalyst lifetime. The structure of polystyrene, combined with its resistance to chemical degradation, makes it a suitable platform for anchoring catalytically active metal centres [5-8]. Figure 1 shows the example of polystyrene being used as a support namely

chloromethylated polystyrene-co-divinylbenzene.

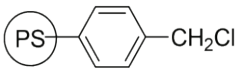


Figure 1: Structure of Chloromethylated Polystyrene-Co-Divinylbenzene

Despite these benefits, the practical utility of polymer-supported palladium catalysts is often hampered by metal leaching and subsequent loss of recyclability [9, 10]. Previous studies have shown that polystyrene-supported catalysts often achieve moderate reaction conversions and experience significant leaching issues, which diminish their overall viability [11]. Efforts to enhance the stability of palladium catalysts in the Heck reaction through ligand modification have gained significant traction in recent literature. One notable approach involves the enhancement of the electron-donating capabilities of ligands, which has been proven to be effective in improving metal coordination and minimising leaching [6, 12, 13]. Various studies have provided evidence for the beneficial impacts of such modifications within palladium-catalysed systems, particularly in the context of cross-coupling reactions like Heck reactions. Specifically, increasing electron density at the palladium center can enhance the oxidative addition step, a crucial phase for catalytic effectiveness [14, 15].

In this work, previously synthesised polystyrene-supported Pd(II)-hydrazone with methyl group substituted (PS-Pd(CH_3)) catalyst have been used to study unexplored optimal conditions for Heck reaction [9]. The study systematically investigated the influence of aryl bromide, solvent polarity, reaction time, and catalyst loading on yield. The catalyst's heterogeneity and recyclability were also assessed to observe the impact of the methyl-substituted ligand on catalyst stability.

II. Materials and Methods

A. Materials

All reagents and solvents, including 1-bromo-4-nitrobenzene, 4-bromoanisole,

4-bromoacetophenone, bromobenzene, methyl acrylate, potassium carbonate (K_2CO_3), acetonitrile, methanol (MeOH), nitric acid (HNO_3), hydrogen peroxide (H_2O_2), dimethylacetamide (DMA), dimethyl sulfoxide (DMSO), and toluene were purchased from Sigma-Aldrich and used without further purification unless otherwise specified. Analytical grade solvents were used throughout the study.

B. Instruments for Analysis

The palladium content and leaching studies were carried out using an Atomic Absorption Spectrometer (PerkinElmer AAnalyst 400) operated using a flame atomisation technique.

Catalytic performance (% conversion) was evaluated using a Gas Chromatograph (Hewlett Packard 5890 Series II) fitted with an HP-5 capillary column (15 m × 0.25 mm × 0.25 µm) and a Flame Ionisation Detector (FID). A 1 µL aliquot of the reaction mixture was injected, and the oven temperature was programmed as follows: an initial temperature of 50°C (held for 1min), followed by a ramp of 15°C min^{-1} to a final temperature of 250°C (held for 30s). The carrier gas flow rate was maintained at 1.92mL min^{-1}. The Equation (1) was used to calculate catalytic performance, expressed as the percentage of product conversion.

$$\%\ conversion = \left[\left(A_i - A_f\right)/A_i\right] \times 100 \quad (1)$$

where:

A_i = peak area of reactant before reaction

A_f = peak area of reactant after reaction

C. Catalyst PS-Pd(CH_3)

Chloromethylated polystyrene -co-divinylbenzene (2% crosslinking) was employed as the support, with p-toluic hydrazide containing a methyl substituent serving as the ligand, and $PdCl_2$ as the metal precursor for catalyst synthesis. The methyl-substituted catalyst (PS-Pd(CH_3)) was prepared via a three-step procedure, as previously described in [9]. The same batch of catalyst synthesised in [9] as shown in Figure 2 was used in all catalytic

experiments reported in this study.

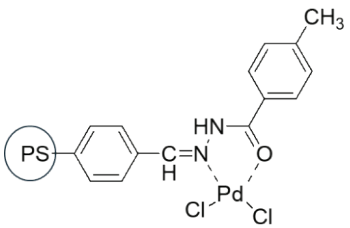


Figure 2: The Structure of PS-Pd(CH_3) Catalyst

D. Optimisation of Reaction Condition

PS-Pd(CH_3) (1.0mmol%) was tested as a catalyst in the Heck reaction between 1-bromo-4-nitrobenzene and methyl acrylate, as illustrated in Figure 3, where R represents $–NO_2$, –H, $–OCH_3$, and $–COCH_3$. In a typical procedure, 1-bromo-4-nitrobenzene (0.20g, 1mmol), methyl acrylate (0.17g, 2mmol), potassium carbonate (K_2CO_3, 0.25g, 2.4mmol), and N,N-dimethylacetamide (DMA, 5mL) were mixed and refluxed under a nitrogen atmosphere. The reaction was conducted at 165°C for 60minutes. At the end of the reaction, the mixture was cooled to room temperature, diluted with ethyl acetate, and filtered to separate the solid catalyst. The filtrate was analysed directly by GC-FID to determine the conversion rate. The procedure was repeated using different aryl bromides, namely 4-bromoanisole, bromobenzene, and 4-bromoacetophenone.

Additional experiments were carried out to evaluate the effect of the solvent. Reactions were performed using DMA, DMSO, toluene, and a DMA:H_2O mixture (60:40) as solvents, while maintaining 1.0mmol% catalyst loading, K_2CO_3 as the base, reflux conditions (boiling point for each solvent), and a 60 minutes reaction time.

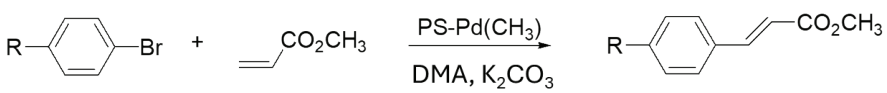


Figure 3: Catalytic Reaction of Aryl Bromide and Methyl Acrylate

Finally, the influence of catalyst loading and reaction time was studied by varying the palladium catalyst concentration (0.5 and 1.0 mmol%) and reaction durations (0, 15, 30, 45,

and 60 minutes). In these experiments, K_2CO_3 was used as the base, DMA as the solvent, and the reaction was maintained at 165°C.

E. Heterogeneity Studies

To confirm whether the reaction occurred on the surface of the solid Pd catalyst or via palladium species leached from the support, two test experiments were conducted for PS-Pd(CH_3).

Test (i): A hot-filtration test was performed following the general procedure for the Heck reaction, except that the catalyst was removed by filtration after 15 minutes of reaction time. The hot filtrate was then allowed to react further for an additional 30, 45, and 60 minutes. At each time point, a 2mL sample of the reaction mixture was collected, and the product conversion was determined by GC-FID analysis.

Test (ii): Heterogeneity tests were conducted to quantify the amount of palladium leached from the solid support. For this analysis, the catalyst recovered after 15 minutes of reaction in Test (i). The solid PS-Pd(CH_3) catalyst was dissolved in 5 mL of nitric acid (HNO_3) and 1 mL of hydrogen peroxide (H_2O_2), then diluted to volume in a 25 mL volumetric flask. The palladium content was measured by AAS.

F. Reusability Studies

fter completion of the Heck reaction, the PS-Pd(CH_3) catalyst was separated from the liquid reaction mixture by simple filtration, followed by several washes with acetonitrile and methanol. The recovered catalyst was dried under vacuum and then reused in the Heck reaction with a fresh reaction mixture. The conversion rate and turnover number (TON) were determined using GC-FID analysis.

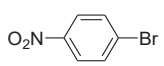
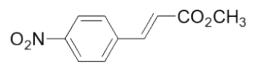
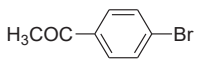
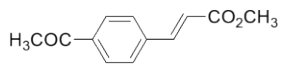
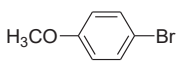
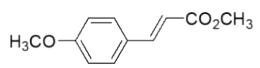
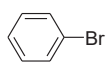
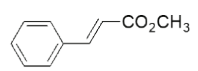
III. Results and Discussion

A. Optimisation of Reaction Condition

The results showed the Heck reaction of four different aryl bromide with methyl acrylate in the presence of PS-Pd(CH_3) catalyst (Table 1). The use of aryl bromide 1-bromo-4-nitrobenzene (entry 1) gave an

excellent conversion rate of 99.84%. In contrast, 4-bromoacetophenone (entry 2) yielded only 28.72% conversion. Meanwhile, 4-bromoanisole (entry 3) and bromobenzene (entry 4) showed no conversion at all.

Table 1: The Reaction of Difference Aryl Bromide with Methyl Acrylate

Entry	Aryl Bromide	Targeted Product	% Conversion (TON)
1			99.8 (99.4)
2			28.7 (28.7)
3			0
4			0

*Reaction conditions: K_2CO_3 as the base (2.4 mmol), PS-Pd(CH_3) catalyst loading (1 mmol %), DMA as the solvent (5 mL) under a N_2 gas at 165°C, within 60 min.

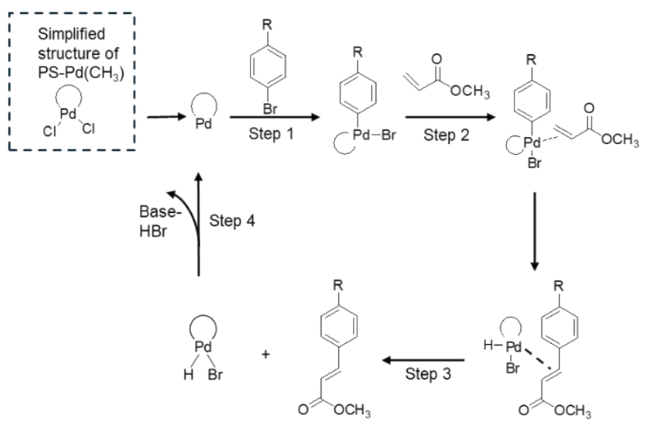


Figure 4: Mechanism of Heck Reaction with Difference Aryl Bromide

The Heck reaction generally proceeds through four fundamental steps (Figure 4). Step 1: Oxidative addition occurs, in which the aryl bromide reacts with Pd(0) to form an aryl–Pd(II) bromide complex. Step 2: The

coordination and migratory insertion step takes place, where the methyl acrylate coordinates to the Pd(II) centre and subsequently inserts into the Pd–aryl bond to form a new C–C bond. Step 3: The resulting intermediate undergoes β-hydride elimination, yielding the substituted alkene product and Pd(II)HBr species. Step 4: Reductive elimination regenerates the active Pd(0) catalyst, thereby completing the catalytic cycle [16].

In reactions involving aryl bromides bearing electron-withdrawing groups (EWGs), a significant amount of product formation was observed. The presence of an EWG increased the rate of oxidative addition in the Heck catalytic cycle, which explains the conversion rates observed for entry 1 and 2. Specifically, EWGs render the carbon–halogen bond more electrophilic, thereby facilitating its activation by the Pd(0) species [14]. Meanwhile, no conversion was observed in the presence of a methoxy group (entry 3) or unsubstituted hydrogen (entry 4), as these substituents had no effect on the olefin insertion step [15].

Furthermore, the electronic nature of the aryl bromide exerted a dominant influence on the reaction outcome. The catalytic performance followed the trend: NO_2> $COCH_3$> OCH_3 ≈ H. The catalyst was also unable to process deactivated or sterically hindered aryl bromides, even at high reaction temperatures [9, 17]. When unreactive aryl bromides such as 4-bromoanisole or bromobenzene were used as starting materials with methyl acrylate, the catalysts were completely inactive, resulting in no conversion in the Heck reaction [18]. Therefore, the presence of EWGs facilitates the crucial oxidative addition step, lowering the activation barrier for C–X bond cleavage and thereby accelerating the overall catalytic cycle. This mechanistic pathway explains the higher activity observed with aryl bromides bearing EWGs compared to their electron-donating counterparts [14].

Different solvent polarities were evaluated, including polar

solvents (DMA, DMSO, and a mixture of DMA:H_2O) and a non-polar solvent (toluene). As shown in Table 2, the Heck reaction carried out in DMA exhibited the highest activity, achieving a conversion rate of 99.84% (entry 1). In contrast, significantly lower activity was observed in DMSO, with only 15.16% conversion for PS-Pd(CH_3) (entry 2). A similar catalytic study using the non-polar solvent toluene (entry 3) and the cosolvent mixture DMA:H_2O (entry 4) showed no formation of the target product in either reaction. These results indicate a failure in C–C bond formation under those conditions.

Table 2: The Effect of Difference Solvent in Heck Reaction

Entry	Solvent	% Conversion (TON)
1	DMA	99.8 (99.8)
2	DMSO	15.2 (15.2)
3	Toluene	-
4	DMA:H_2O	-

*Reaction conditions: K_2CO_3 as the base (2.4 mmol), PS-Pd(CH_3) catalyst loading (1 mmol %), under a N_2 gas at 165°C within 60 min.

The results demonstrate that in the polar solvent DMA, in the presence of the inorganic base K_2CO_3, the solvent can coordinate to the palladium centre and promote a switch in the chemoselectivity of the oxidative addition step compared to other solvents [19, 20]. In contrast, when other solvents were used, palladium leaching likely occurred during the reaction. The loss of a large amount of palladium could have reduced the catalytic performance [5].

The amount of catalyst loading significantly affected the overall catalytic activity, including both the conversion rate and the turnover number (TON). Controlling the catalyst loading is crucial to achieving a high TON and maximising the percentage conversion of the desired product. This helps prevent the formation of inactive palladium black and avoids

deactivation of the catalytic cycle [21, 22]. The turnover number (TON) was determined by dividing the percentage conversion by the amount of catalyst loading.

To study the influence of palladium catalyst loading and reaction time, two different catalyst loadings (0.5 mmol% and 1.0 mmol%) were tested at various reaction times (0, 15, 30, 45, and 60 minutes). The substrate used was 1-bromo-4-nitrobenzene, under optimised conditions: 165 °C, PS-Pd(CH_3) as the catalyst, K_2CO_3 as the base, and DMA as the solvent. The corresponding results are shown in Table 3. The data indicates that the conversion rate increased with higher palladium loading. A loading of 1.0 mmol% was found to be optimal, giving the highest conversion rate of 99.84% (entry 1).

Table 3: The Effect of Difference Catalyst Loading and Reaction Time

Entry	PS-Pd(CH_3) loading (mmol%)	Reaction Time (min)	% Conversion (TON)
1	1.0	60	99.8 (99.8)
2	1.0	0	-
3	1.0	15	66.1 (66.1)
4	1.0	30	74.9 (74.9)
5	1.0	45	90.7 (90.7)
6	0.5	0	-
7	0.5	15	6.55 (13.1)
8	0.5	30	12.8 (25.6)
9	0.5	45	18.6 (37.2)
10	0.5	60	24.0 (48.1)

*Reaction conditions: K_2CO_3 as the base (2.4 mmol), under a N_2 gas at 165°C

Reaction time also plays a key role in the catalytic performance of the Heck reaction. The optimum reaction time is essential to identify the point at which a high yield of the desired product is obtained in the shortest time [23]. At 0 minutes, no product conversion was observed. As the reaction progressed to 15, 30, and 45 minutes, the conversion of the product gradually increased over time. Table 3 shows at 60

minutes, the conversion reached an excellent 99.8% for PS-Pd(CH_3) (entry 1). In conclusion, a catalyst loading of 1.00 mmol%, combined with a 60 minutes reaction time, was the most effective, giving the highest conversion rate and TON compared to 0.5 mmol% loading.

B. Heterogeneity Studies

The results from Test (i) showed that after 15 minutes of reaction, the conversion rate reached 66.14%. However, only a small increase in conversion was observed at 30, 45, or 60 minutes once the catalyst had been removed. This finding was compared with the Heck reaction conducted in the presence of the PS-Pd(CH_3) catalyst, as shown in Figure 5. These results demonstrate that the Heck cross-coupling reaction proceeds via a heterogeneous pathway.

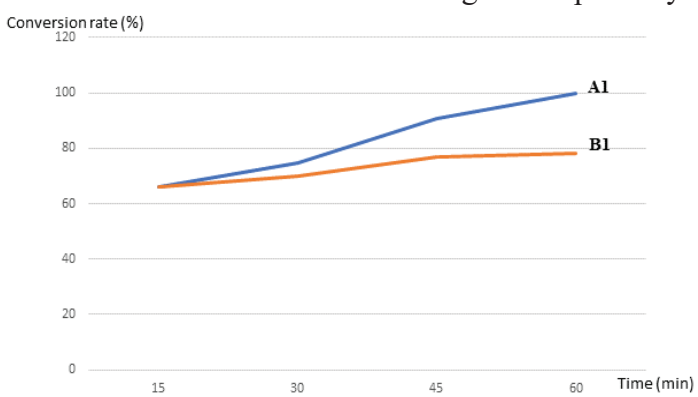


Figure 5: Plot of Conversion Rate (%) Versus Time (Min) for Heck Reaction with Catalyst (A1) and without Catalyst (B1) After 15 minutes

Additionally, AAS analysis in Test (ii) revealed that 15% of Pd was leached into the solution, indicating that approximately 85% of the Pd species were retained on the PS-Pd(CH_3) catalyst during the reaction. This suggests that incorporating electron-donating methyl group (–CH_3) in the ligand structure improved catalyst heterogeneity, resulting in lower Pd leaching [11, 24]. The improved stability of the catalyst is attributed to the nature of the methyl substituent, which increased the electron

density of the aromatic system through resonance effects, leading to stronger interactions between the ligand and metal ions. Consequently, this enhanced the catalytic performance [12, 13].

C. Reusability Studies

To perform the recyclability test, the reaction was monitored by GC-FID, and upon completion, the catalyst was removed from the reaction mixture by simple filtration. The recovered catalyst was washed several times with acetonitrile and methanol and subsequently dried in an oven at 70°C for 1 hour before reusing [25]. Notably, the PS-Pd(CH_3) catalyst exhibited a decrease of below 50% in product conversion after four cycles (Figure 6), likely due to palladium leaching from the support during the catalytic process [22, 26]. These results demonstrate that the presence of the electron-donating group in PS-Pd(CH_3) enhanced the catalyst's stability and activity in the Heck reaction, where satisfactory conversion was maintained only during the first three cycles [12, 13].

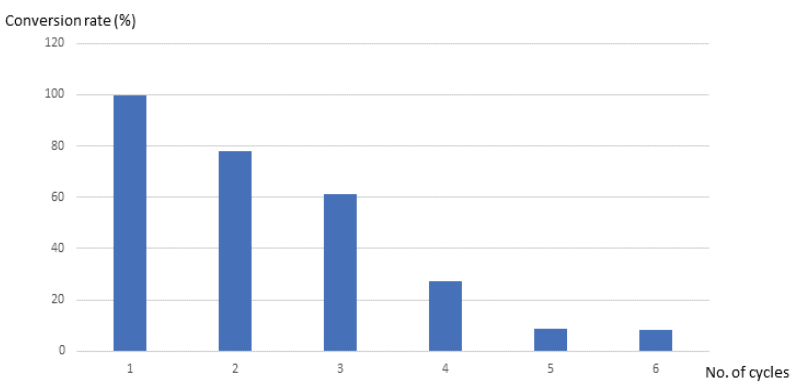


Figure 6: Plot of Conversion Rate (%) Versus Number of Cycles for Recyclability Test of PS-Pd(CH_3)

IV. Conclusion

The PS–Pd(CH_3) catalyst exhibited excellent catalytic performance in the Heck reaction, achieving up to 99.84% conversion under optimised conditions (DMA, 1.0 mmol% catalyst, K_2CO_3, 165°C, 60

minutes). Hot-filtration tests confirmed its heterogeneous nature, while reusability studies demonstrated that the catalyst retained activity above 50% over three cycles. The incorporation of methyl substituent plays a key role in improving catalyst stability through increased electron density at palladium centre, which strengthens metal-ligand interaction. As a result, the catalyst maintained satisfactory activity over three cycles. However, the observed decline in performance in subsequent cycles suggests that palladium leaching remains a limiting factor.

Future work should focus on the systematic modification of the hydrazone ligand with both electron-donating and electron-withdrawing groups to fine-tune the electronic environment around the palladium centre, with the aim of enhancing catalytic activity, selectivity, and long-term stability.

V. Acknowledgement

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