UNIVERSITI TEKNOLOGI MARA

SYNTHESIS, CHARACTERIZATION AND CATALYTIC STUDY OF FUNCTIONALIZED POLYMER SUPPORTED PALLADIUM(II) HYDRAZONE COMPLEXES CONTAINING ELECTRON DONATING GROUP AS CATALYSTS IN HECK REACTION

NAJWA ASILAH BINTI M SHAMSUDDIN

Thesis submitted in fulfillment
of the requirements for the degree of
Master of Science
(Chemistry)

Faculty of Applied Sciences

February 2023

ABSTRACT

Heck reaction was discovered as one of the cross-coupling reactions where the coupling occurs between aryl halides and alkenes that using palladium as catalyst. Immobilization of catalysts on insoluble supports which is chloromethylated polystyrene or Merrifield resin have been expected as best substitutes to soluble polymer supports due to inert, non-toxic, and non-volatile characteristics. Thus, this study reports on the synthesis and characterization of functionalized polystyrene-supported palladium(II)-hydrazone complexes containing electron donating group (-OH and -CH_3) and their catalytic behaviour for Heck reaction. The first step of synthesis began with aldehyde functionalization of chloromethylated polystyrene to form PS-CHO. This was then followed by the reaction of PS-CHO with 4-hydroxybenzhydrazide and *p*-toluic hydrazide to form a polystyrene-supported hydrazone ligand (PS-H(OH) and (PS-H(CH_3)), respectively. Further reaction of PS-H(OH) and PS-H(CH_3) with palladium(II) chloride form its corresponding polystyrene-supported palladium(II) hydrazone catalyst, PS-Pd(OH) and PS-Pd(CH_3). The synthesized compounds were characterized using Brunauer-Emmett-Teller (BET) surface area analysis, Atomic Absorption Spectroscopy (AAS), Carbon Hydrogen Nitrogen (CHN) elemental analysis, Fourier Transform Infrared (FTIR) spectroscopy, Field Emission Scanning Electron Microscope-Energy Dispersive X-Ray (FESEM-EDX), Powder X-Ray Diffraction (PXRD), and Thermogravimetric Analysis-Differential Thermal Analyser (TGA-DTA). The complexes were tested as catalysts for Heck reaction between 1-bromo-4-nitrobenzene and methyl acrylate. Performance of catalyst was determined by Gas Chromatography-Flame Ionization Detector (GC-FID). Several parameters have been selected, i.e., the effect of bases, temperatures, solvents, amount of loading, times and different of aryl bromides. The catalysts were then undergo heterogeneity and recyclability study. The Heck product was characterized using FTIR, Nuclear Magnetic Resonance (NMR) and Gas Chromatography-Mass Spectroscopy (GC-MS). The data revealed the functionalization of polymer to complexes where the palladium metal ion is coordinated to the ligand through imine nitrogen and oxygen state for PS-Pd(CH_3) and PS-Pd(OH) at 1618 cm^{-1} and 1668 cm^{1},respectively for C=O absorption whereas 1590 cm^{-1} and 1600 cm^{-1}, respectively for C=N absorption. The amount of Pd were confirmed using AAS where in PS-Pd(OH) is 33.44 % (3.142 mmol g^{-1}) which is more than in PS-Pd(CH_3) is 21.31 % (2.002 mmol g^{-1}). PXRD spectra confirms the functionalization of polymer to complexes from amorphous to semi crystalline stages. TGA-DTA confirms both complexes were thermally stable up to 800 °C and show endothermic peaks. Catalytic activity revealed that the best conversion rate (100 %) and turnover number (TON) was achieved at optimum reaction condition with the presence of 1.0 mmol % catalyst loading, potassium carbonate (K_2CO_3) as base, dimethylacetamide (DMA) as solvent at 165 °C for PS-Pd(CH_3) and 75 °C for PS-Pd(OH) in 60 minutes reaction time. Both complexes exhibited effective catalytic activity for different types of aryl bromides which have an electron withdrawing group in the order NO_2>$COCH_3$>OMe and H. It also showed that the catalyst can be recycled for 4 successive runs and metal leaching reduce which is 10.19 % for PS-Pd(OH) lower than PS-Pd(CH_3) which is 15.05 %. Thus, PS-Pd(OH) is the best catalyst due to OH group is more electronegative than CH_3 group that can activate the aromatic ring and improves the catalytic activity in Heck reaction.

ACKNOWLEDGEMENT

Bismillahirahmanirahim

In the name of Allah, the Most Gracious and the Most Merciful. All praise and thanks to Allah S.W.T for the blessing, wisdom, and guidance His bestow upon me, the strength and the opportunity for me to be able to complete my research work together with this thesis successfully. I would like to convey my earnest gratitude to all who has contributed to this research either directly or indirectly.

First, I would like to express the deepest appreciation to my advisor, Dr. Nur Rahimah binti Said and Prof. Yatimah binti Alias for their invaluable advice, constant encouragement, imparting their knowledge and the expertise toward the research during this 3 years hardship journey.

I warmly thanks and appreciate to Universiti Teknologi MARA (UiTM) as it provides the instruments, equipment, facilities, apparatus, and materials for me to complete my thesis work. I also would like to take this opportunity to express my sincere thanks to University of Malaya for the collaboration toward the completion of this project. Furthermore, I would like to thanks to laboratory assistant who helps me in handling equipment and instrument during this research project. Special thanks to my colleagues and friends for helping me with this project.

Finally, this thesis is dedicated to my beloved parents, Mr M Shamsuddin bin Mohamed Ismail and [redacted] for the vision and determination to educate me. Thank you again for being my backbone throughout this hardship. This piece of victory is dedicated to all of you.

Alhamdulilah.

TABLE OF CONTENTS