

**SYNTHESIS, CHARACTERIZATION AND
CATALYTIC APPLICATION OF
PHENYLDITHIOCARBAZATE-
FUNCTIONALIZED POLYSTYRENE
SUPPORTED PALLADIUM(II) COMPLEXES IN
THE MIZOROKI-HECK REACTION**

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MASTER OF SCIENCE

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**Thesis submitted in Fulfillment of the Requirement for the Degree of Master of
Science in the School of Marine and Environmental Sciences
Universiti Malaysia Terengganu**

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DEDICATION

*For my super patience supervisor,
&
To my beloved parents,
Thanks for your great support and continuous care.*

Abstract of thesis presented to the Senate of Universiti Malaysia Terengganu in fulfilment of the requirement for the degree of Master of Sciences

SYNTHESIS, CHARACTERIZATION AND CATALYTIC APPLICATION OF PHENYLDITHIOCARBAZATE-FUNCTIONALIZED POLYSTYRENE SUPPORTED PALLADIUM(II) COMPLEXES IN THE MIZOROKI-HECK REACTION

SITI AMINAH BINTI JUSOH

APRIL 2016

Main Supervisor : Siti Kamilah Che Soh, Ph.D
Co-supervisor : Assoc. Prof. Mohd Sukeri Mohd Yusof, Ph.D
School : School of Marine and Environmental Sciences

The development of supported catalyst for chemical transformation has met the highest demand for stringent environmental due to its significance advantages in numerous applications. Due to these interest, this research has been focused on the synthesis, characterization and catalytic activity of phenyldithiocarbazate-functionalized polystyrene supported palladium(II) complexes as a potential catalyst in the Mizoroki-Heck coupling reaction. Two palladium supported catalyst were prepared using 2% cross-linked polystyrene (PS2-PDC-Pd) and 5% cross-linked polystyrene (PS5-PDC-Pd). The supported catalysts were synthesized by heating a mixture of chloromethyl polystyrene with phenylhydrazine and carbon disulfide (CS₂) in the presence of potassium hydroxide (KOH) in dimethylformamide (DMF) and were treated with bis(benzonitrile)palladium(II) chloride. All synthesized compounds were characterized using Fourier Transform Infra Red (FTIR), CHNS elemental analysis, Scanning Electron Microscopy/Energy Dispersive X-Ray (SEM/EDX), Thermogravimetric Analysis (TGA), X-Ray Diffraction (XRD), BET surface area and Inductively Coupling Plasma-Optical Emission Spectroscopy (ICP-OES). FTIR spectrum data showed that the palladium(II) metal ion is coordinated to the ligand through nitrogen and sulphur atom. ICP-OES analysis reveals the amounts of palladium loading are 0.285 mmol/g (PS2-PDC-Pd) and 0.4928 mmol/g (PS5-PDC-Pd), respectively. The performance of PS2-PDC-Pd and PS5-PDC-Pd were tested in the reaction of 4-bromoacetophenone with methyl acrylate. The conditions for the Mizoroki-Heck coupling were optimized using different type of bases, catalyst loading and temperature. The results gave an excellent conversion of product when sodium acetate (NaOAc) was used as a base, dimethylformamide (DMA) as solvent with catalyst loading of 0.25 mmol % and at reaction temperature of 120 °C in 3 hours. From the optimized condition, the catalyst can be readily recovered by simple filtration and reused for several times without loss it activity.

Abstrak tesis yang dikemukakan kepada Senat Universiti Malaysia Terengganu
sebagai memenuhi keperluan untuk Ijazah Sarjana Sains

**SINTESIS, PENCIRIAN DAN APLIKASI PEMANGKINAN BAGI
KOMPLEKS PALADIUM(II) BERPENYOKONG POLISTIRENA YANG
DIFUNGSIKAN OLEH FENILDITIOKARBAZAT DALAM TINDAKBALAS
MIZOROKI-HECK**

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APRIL 2016

Penyelia Utama : Siti Kamilah Che Soh, Ph.D
Penyelia Bersama : Prof Madya Mohd Sukeri Mohd Yusof, Ph.D
Pusat Pengajian : Pusat Pengajian Sains Marin dan Sekitaran

Pembangunan mangkin penyokong dalam tindakbalas transformasi kimia telah memenuhi permintaan yang paling tinggi dalam kepentingan alam sekitar kerana kelebihannya dalam pelbagai aplikasi. Oleh kerana kepentingan ini, kajian penyelidikan ini tertumpu kepada sintesis, pencirian dan aktiviti pemangkinan bagi kompleks paladium(II) berpenyokong polistirena yang difungsikan oleh fenilditiokarbamat dan berpotensi sebagai mangkin dalam tindak balas pergandingan Mizoroki-Heck. Dua mangkin paladium berpenyokong telah disediakan dengan menggunakan 2% polistirena berangkai silang (PS2-PDC-Pd) dan 5% polistirena berangkai silang (PS5-PDC-Pd). Mangkin berpenyokong telah disintesis dengan memanaskan campuran polistirena klorometil dengan fenilhidrazina dan karbon disulfida (CS_2) dengan kehadiran kalium hidroksida (KOH) dalam pelarut dimetilformamida (DMF) dan telah bertindakbalas dengan bis(benzonitril)paladium(II) klorida. Semua sebatian yang disintesis dicirikan oleh beberapa analisis fizikokimia iaitu Transformasi Fourier Inframerah (FTIR), analisis unsur CHNS, Mikroskopi Elektron Imbasan Pancaran Medan/Sinar-X Tenaga Tersebar (SEM/EDX), analisis Termogravimetri (TGA), Pembelauan X-Ray (XRD), Luas Permukaan BET dan Gandingan Plasma Induktif-Optical Pelepasan Spektroskopi (ICP-OES). Data spektrum FTIR menunjukkan bahawa ion logam paladium(II) terkoordinat kepada ligan melalui atom nitrogen dan sulfur. Analisis ICP-OES menunjukkan jumlah muatan paladium adalah 0.285 mmol/g (PS2-PDC-Pd) dan 0.4928 mmol/g (PS5-PDC-Pd). Prestasi PS2-PDC-Pd dan PS5-PDC-Pd telah dikaji dalam tindakbalas antara 4-bromoasetofenon dengan metil akrilat. Parameter untuk gandingan Mizoroki-Heck kemudiannya dioptimumkan menggunakan beberapa jenis bes, muatan mangkin dan suhu yang berbeza. Hasil yang didapati memberikan penukaran produk yang baik apabila natrium asetat (NaOAc) telah digunakan sebagai bes, dimetilformamida (DMA) sebagai pelarut dengan muatan mangkin iaitu 0.25 mmol% pada suhu 120 °C dalam masa 3 jam. Disamping itu, mangkin ini boleh dikitar semula untuk beberapa kali tanpa kehilangan sebarang aktiviti.