UNIVERSITI TEKNOLOGI MARA

SYNTHESIS, CHARACTERIZATION AND CATALYTIC APPLICATIONS OF NITROGEN BASED METAL ORGANIC FRAMEWORKS (MOFS)

SITI NURHAZLIN BINTI JALUDDIN

Thesis submitted in fulfillment
of the requirements for the degree of
Master of Science

Faculty of Applied Sciences

December 2016

ABSTRACT

Three different group of nitrogen based Metal Organic Frameworks (MOFs) derived from amine, nitro and nitrile group were successfully synthesized using solvothemal of mixed linker method, which are also known as MIXMOF. MIXMOF is formation of "mixed-linker" metal frameworks which consists of two isoreticular ligands (terepthalic acid and nitrogen based carboxylic acid) that randomly combined with metal such as zinc(II) acetate. The ligands syntheses of MOFs were characterized by NMR spectroscopy. The NMR results shows that the methyl group (-CH_3) was successfully removed from the compounds. In addition, the MOF-NH_2, MOF-NO_2 and MOF-N_2 and their palladium(II) complexes were characterized by fourier transform infrared (FTIR), Xray-diffraction (XRD), thermal gravimetric analysis (TGA), and field emission scanning electron microscopy (FESEM). The disappearance of C=O absorption peaks in FTIR spectrum shows the complexation of nitrogen based ligands with metal linker of zinc metal was successful in forming MOFs. Besides that, XRD pattern also shows an attachment of zinc and palladium to the MOFs compounds. Despite of that, the thermal gravimetric analysis revealed that all the MOFs compounds exhibits thermal stability up to 500°C. Instead of characterization, the synthesized MOFs supported palladium complexes were subjected to the carbon-carbon cross coupling reaction, Suzuki and Heck reaction. The results show the Pd/MOF-NH_2 catalyst gave conversion of bromobenzene up to 100% at 100°C using K_2CO_3 for Suzuki reaction and Na_2CO_3 for Heck reaction as a base. These higher activities of Pd/MOF-NH_2 may be explained in terms of functional group of MOFs. The cross coupling Suzuki and Heck reaction using Pd/MOF-NH_2 catalyst shows excellent recyclability of catalyst as well in leaching testing. The catalyst was reused up to five times with little loss of activity. Thus, nitrogen based MOFs had been successfully synthesized and can be applied as an effective supported palladium catalyst for carbon-carbon cross coupling reaction.

ACKNOWLEDGEMENT

Assalammualaikum w.b.t

Alhamdulillah and praise to Allah, the Almighty God for His mercy has given me strength, patience and blessings to complete this study. Here, I would like to express my sincere to every single person for their effort and support that contributed to help me in completing all the process of the research and development activities.

First and foremost, I would like to express my sincere thanks to my supervisors; Dr Karimah Kassim and Pn. Wan Nazihah Wan Ibrahim for their patience, supervision, encouragements and thoughtful guidance towards the completion of this thesis.

I am also indebted to the Ministry of High Education, Ministry of Education Malaysia and Universiti Teknologi MARA (UiTM) for funding my MSc study and providing the instrument facilities. I take this opportunity to express my special appreciation to all laboratory assistants and staff from the Department of Chemistry, Research Department of IPSIS and Faculty of Applied Sciences Universiti Teknologi MARA for assistance in handling instrument and also supplying relevant literature and information.

Last but not least, heartfelt appreciation is given to my beloved family especially to my parents Mr. Jaluddin bin Mohd Ali and Mrs for their support, endless love, prayers and most precious care. I also place on record, a very warm thank you to my friends who directly or indirectly have lent their helping hand in this venture. I also wish to express my special appreciation and gratitude to 'csi' team for sincere and valuable guidance and encouragement extended to me.
Thank you.

Siti Nurhazlin Jaluddin

TABLE OF CONTENTS

CHAPTER ONE
INTRODUCTION

1.1 RESEARCH BACKGROUND

The first catalyst used in chemical industry was in 1746. However, only pure components were used as catalyst during that time. In year 1900, variations of catalyst were introduced in industry. Since then, catalysis started to impact on the chemical industries and plays a key role in the manufacture of majority of chemicals and materials until now. According to Department of Statistic Malaysia (2015), manufacturing industries profit growth every year. This includes the production of catalyst in chemical industry. In May 2015, the industrial production index (IPI) increased by 4.5% compared in the previous year. Subsequently, the value of product will increase depending on process catalyst such as petroleum products, chemicals, pharmaceuticals, synthetic rubber, plastics and many more. Thus, new catalyst that provides special feature such as higher porosity and reusability is expected to be useful in industry. As a concern to environmental issues, more catalysis activities are relevant to many aspect of environmental science.

Catalyst is defined as a substance that is added to the reaction in order to speed up the rate of the reaction without being consumed or produced in the process. Catalytic reactions have lower activation energy which resulting in higher reaction rate at the same temperature and for the same reactant concentration compare to the uncatalyzed reaction (Davis *et al.,* 2012).According to Haveling (2012), catalyst can be divided into homogeneous and heterogeneous catalyst. Homogeneous catalyst is catalyst that present in same phase as reactants while the heterogeneous catalyst present in different phase as reactants.The biggest problem of homogeneous catalyst is difficulty in catalyst recovery, which led to increasing of production cost. Thus, heterogenization of the catalyst could overcome the recovery problem, lowering the cost and increase their thermal stability (Farnetti *et al.*, 2009).

Since 1994, metal-organic frameworks (MOFs) have emerged as an interesting class of materials for applications in catalysis. Metal organic frameworks are crystalline porous solids which composed of three-dimensional (3D) network of metal