POLYMER-IMMOBILISED IONIC LIQUID PHASE (PIILP) CATALYSIS: SUPPORTS FOR MOLECULAR AND NANOPARTICLES CATALYSTS

A Thesis Submitted to

The School of Natural and Environmental Sciences: Chemistry

of

Newcastle University

By

Einas Abdulaziz Abood

In Partial Fulfillment of the
Requirements for the Degree

of

Doctor of Philosophy in Chemistry

June 2018

Newcastle University

Newcastle upon Tyne, UK

PREFACE

DECLARATION

This thesis is submitted to Newcastle University for the degree requirements of Doctor of Philosophy in Chemistry. The research detailed within was performed during the period of 2014-2018 and was conducted in Newcastle University laboratories under the supervision of Dr. Simon Doherty and Dr. Julian Knight. I certify that all material is original except where acknowledged by reference and that none of the material offered in this thesis has been previously submitted by me for a degree or any other qualification at this or any other university.

ABSTRACT OF THE THESIS

Polymer-Immobilised Ionic Liquid Phase (PIILP) Catalysis: Supports for Molecular and Nanoparticles Catalysts

by

Einas Abdulaziz Abood

The Polymer Immobilised Ionic Liquids (PIILs) has been an area of interest recently, particularly, Doherty-Knight group has recently explored and developed this concept, with the aim of designing novel functionalised PIILPs and utilising them as supports to immobilise transition metals catalysts and nanoparticles and then exploring their applications.

The second chapter describes the synthesis of tungstate and polyoxotungstate based catalysts for the selective oxidation of sulfides. The polymer immobilised ionic liquids were based on linear pyrrolidinium-modified norbornene-cyclooctene co-polymers prepared by ring opening metathesis polymerisation and the corresponding catalysts were prepared by exchange of the polymer anions with either tungstate or polyoxotungstate. High selectivity for sulfoxide was obtained across a range of aryl-alkyl sulfides using either (WO_4@$ROMP_x$ or $PW_{12}O_{40}$@$ROMP_1$) in either acetonitrile or methanol with 2.5 equivalents of hydrogen peroxide for 15 minutes at room temperature. Different catalytic activity was observed based on the nature of the cross-linker whether it is linear ($ROMP_1$) or cyclic ($ROMP_2$).

The third chapter describes the synthesis and characterisation of a range heteroatom donor modified polymer immobilised palladium nanoparticles. Three types of polystyrene-based PIILP (amino-, phosphino-, and pyrrolidino-) were prepared via free radical polymerisation and used to support platinum group metal nanoparticles (MNP@R-PIILP; R = CH_2NH_2, PPh_2, CH_2Pyrr). All the prepared catalysts have been characterised by a range of techniques including solid-state NMR spectroscopy, SEM, TEM, XRD, XPS, EDX, ICP, TGA and BET analysis.

Chapter 4 presents the results of our systematic evaluation of the efficacy of the newly prepared MNP@PIILP (M = Pd, Pt) systems as catalysts for the selective hydrogenation of α, β-unsaturated aldehydes. Our studies have shown that PdNP@PPh_2-PIILP catalyses

the hydrogenation of trans-cinnamaldehyde in water with high selectivity for reduction of the C=C double bond to afford dihydrocinnamaldehyde in 76 % selectivity at 96 % conversion under mild conditions and in short reaction times. Notably, the addition of base (K_2CO_3) to the reaction allows higher selectivities to be obtained (up to 95 % for C=C reduction), however, this results in a decrease in reaction rate (96 to 67.5 %).

Chapter 5 explores the use of PdNP@R-PIILP (R = NH_2, PPh_2) as catalysts for the Suzuki-Miyaura cross-coupling. Interestingly, palladium NPs stabilised by amino-decorated polymer immobilised ionic liquids (PdNP@NH_2-PIILP) were shown to be inactive for the Suzuki-Miyaura cross-coupling of aryl bromides with phenyl boronic acid. However, the corresponding PdNP@NH_2-PIILP generated by *in-situ* by reduction of $PdCl_4$@NH_2-PIILP was highly active for the Suzuki-Miyaura cross-coupling. Kinetic studies, reaction dilution experiments, mercury poisoning and catalyst loading studies have been employed to investigate the difference between the performance of *pre-reduced* PdNPs and those generated *in-situ*.