

The present work gives an account of polymer supported transition metal complexes and their use as catalysts. The study describes the detailed synthesis, characterisation and catalytic activity of polymer supported metal complexes in the epoxidation and hydrogenation of olefins under mild reaction conditions. The influence of various reaction parameters on conversion and selectivity of products of epoxidation and the kinetics of hydrogenation of olefins has been studied.

The thesis is divided in to three chapters.

## **Chapter I**

In this chapter an introduction to catalysts and catalysis has been provided. A brief survey of homogeneous, heterogeneous, heterogeneous homogeneous catalysts and the advantages and disadvantages of using different types of support is made. Relevant literature on polystyrene supported catalysts and their applications is also highlighted.

## **Chapter II**

In Chapter-II the experimental details on the synthesis of poly(styrenedivinylbenzene) supported Schiff base liganded complexes of Ru(III), Fe(III) and Pd(II) is compiled. The strategy adopted to synthesize a Schiff base bearing liganded polymer support using ethylenediamine and 2-aminopyridine has been presented. These liganded polymer supports were complexed with metal salts of Ru, Fe and Pd to form the polymer supported metal complexes. The physico-chemical properties such as surface area, bulk density, moisture content and swelling behaviour in polar and non polar solvents were studied. In order to understand the mode of attachment of the ligand to the polymeric support and also the nature of complexation of the metal, different spectroscopic techniques such as FT-IR, UV-Visible, Scanning Electron Microscopy (SEM), Electron Spin Resonance spectroscopy (ESR) and Electron Spectroscopy for Chemical Analysis (ESCA) were employed. In addition, the Thermogravimetric Analysis (TGA) of the supports and complexes is given. The experimental procedure involved in carrying out the epoxidation and hydrogenation reactions is described including pictorial representation of the experimental set-up.

## Chapter III

The results and discussions on the characterisation and catalytic activity of polymer supported metal complexes is provided in this chapter.

The first part deals with the results of poly(styrene-divinylbenzene) supported Ruthenium(III)-Schiff base complexes. From the observed data it can be inferred that Ru(III) immobilised on functionalised poly(styrene- divinylbenzene) was shown to affect the oxidation of *cis*-cyclooctene and styrene in a catalytic manner in the presence of alkyl hydroperoxide(TBHP) as oxidant. The degree of cross linking in the polymer support and the nature of Schiff base bound to the metal have a bearing on epoxide formation. Kinetic experiments reveal that temperature influences the catalytic activity significantly.

In the second part the results of Iron(III) anchored to Schiff base bound poly(styrene-divinylbenzene) supports are discussed. These complexes catalyse the epoxidation of styrene and *cis*-cyclooctene in presence of alkyl hydroperoxide under mild reaction conditions.

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In the third part, using a simple methodology Ruthenium was anchored to a functionalised polystyrene matrix. The new polymer supported Ruthenium catalysts were shown to be effective in the epoxidation of cyclic olefins and styrene. The ease of preparation of these catalysts provides a useful strategy for oxidation of organic compounds under mild conditions.

In the fourth part the mechanistic aspects of epoxidation are described. A simplified dual mechanistic pathway for the catalytic epoxidation of olefins in presence of TBHP has been be proposed based on experimental data

The discussion on the recyclability of the newly synthesized polymer supported catalysts in the epoxidation of olefins is presented in the fifth part. Based on the findings, it can be inferred that the catalysts can be recycled several times without any loss in selectivity. Slow deactivation of the catalysts however, was observed over extended use.

In the sixth part the results of hydrogenation of olefins by Palladium(II)-Schiff base complexes are compiled. Influence of various parameters such as temperature, pressure, substrate and catalyst concentrations was investigated. The study reveals a near linear relationship with respect to above parameters.

In conclusion, the objective to successfully synthesise Schiff base functionalised polymer supports by adopting a new strategy and anchoring of metal on the polymer matrix was achieved. Moreover, the newly synthesized polymer supported metal complexes were shown to act as catalysts in the epoxidation and hydrogenation of olefins which was the major objective of this study.

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