SOME STUDIES ON SUPPORTED METAL COMPLEXES AS CATALYSTS

A SUMMARY OF THE THESIS SUBMITTED
TO
M. S. UNIVERSITY OF BARODA
FOR THE DEGREE OF
DOCTOR OF PHILOSOPHY
IN
CHEMISTRY

BY
SHAILESH A PATEL

DEPARTMENT OF CHEMISTRY
FACULTY OF SCIENCE
M. S. UNIVERSITY OF BARODA
VADODARA - 390 002, INDIA
JANUARY 2004

The present work gives an account of polymer supported transition metal complexes and their use as catalysts. The study describes the detailed synthesis, characterization and catalyst activity of polymer bound and unbound 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 into five chapters.

Chapter I

In this chapter an introduction to catalysts and catalysis has been provided. A brief survey of homogeneous, heterogeneous, heterogenized 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(styrene-divinylbenzene) supported Schiff base liganded complexes of Ru(III), Mn(II) and Pd(II) is complied. The strategy adopted to synthesize a Schiff base bearing liganded polymer support using 1,3-diaminopropane and 4,4'-diaminobiphenyl has been presented. The liganded polymer supports were complexed with metal salts of Ru, Mn 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) 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

Chapter-III describes physico-chemical characterization of the polymer support and polymer supported transition metal complex catalysts. Surface area and pore volume of the supports and the catalysts have been measured using BET method at liquid nitrogen temperature. The morphology of the catalysts has been seen by scanning electron microscope. The mode of anchoring of the metal chelates onto polymer support has been arrived at by elemental analysis, UV-visible reflectance spectroscopy, FT-IR and ESR. Selection of the solvent for catalytic study has been made on the basis of swelling studies. The thermal stability of the catalysts and the supports has been investigated using DTA and

TG analysis. On the basis of available evidences, probable structures for the polymer anchored catalysts have been proposed.

Chapter IV

In this chapter, a catalytic activity of polymer supported metal complexes is provided. The first part gives the results of poly(styrene-divinylbenzene) supported Ruthenium(III)-Schiff base complexes. The epoxidation of norbornene and *cis*-cyclooctene was investigated using Ruthenium(III)-Schiff base complexes in the presence of alkyl hydroperoxide (TBHP) as oxidant.

The influence of various reaction parameters such as substrate and catalyst concentration, temperature on conversion to product (epoxidation) has been discussed. Experiments were also carried out with metal complex catalysts in homogeneous system and the results have been compared with respective heterogenized-homogeneous system.

In the second part the results of manganese(II) anchored to Schiff base bound poly(styrene-divinylbenzene) support are discussed. These complexes catalyze the epoxidation of norbornene and *cis*-cyclooctene in presence of alkyl hydroperoxide under mild conditions.

A simplified dual mechanistic pathway for the catalytic epoxidation of olefins in the presence of alkyl hydroperoxide (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 this chapter. Based on 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.

Chapter V

Chapter-V, includes the hydrogenation of 1-decene catalyzed by Palladium (II)-Schiff base complexes. The influence on the rate of reaction of various factors such as substrate and catalyst concentration, temperature and the effect of different solvents has been investigated. Experiments were also carried out with metal complex catalysts in homogeneous system and the results have been compared with respective heterogenized-homogeneous systems. On the basis of the kinetic data, the values for energy of activation have been calculated. A probable reaction mechanism has been proposed on the basis of the literature survey as well as experimental evidences. Recycling efficiency of the catalysts is also included.

The following conclusions have been drawn:

1. Crosslinked styrene-divinylbenzene copolymer could be functionalized to the Schiff base containing polymeric support. Metals such as Ruthenium, Manganese and Palladium can be loaded on this matrix to give supported complexes having useful catalytic properties.

2. Polymer bound metal complexes were found to be stable upto 100° C.

3. Polymer bound metal complexes exibit higher catalytic activity than their homogeneous counterparts.

4. The nature of the ligand and the degree of crosslinking of the polymer support can significantly affect the conversion and selectivity.

5. The newly synthesized catalysts were found to be active for the epoxidation and hydrogenation of olefins.

6. Optimisation of conditions showed that methylene chloride is the most suitable solvent for epoxidation reaction and methanol for hydrogenation reaction which may be ascribed to better swellability of the catalysts in these solvents.

7. The study of recycling efficiency of the catalysts showed that the catalyst retain their activity for three to four cycles. Thereafter, activity was found to decrease which may be attributed to slow leaching of the metal ions.