SUMMARY AND CONCLUSIONS

SUMMARY AND CONCLUSIONS

The present investigation deals with the studies on the synthesis, characterization and catalytic activity of the polymer-supported transition metal complex catalysts. The catalytic activity of the synthesized catalysts has been investigated for hydrogenation of 1-hexene and styrene as well as oxidation of benzyl alcohol under mild operating conditions. Reaction kinetics has been studied and a comparison of catalytic activity of polymer-bound and unbound metal complexes has been made.

The thesis is divided into five parts. Chapter I contains a brief literature survey on homogeneous, heterogeneous and heterogenized homogeneous catalysts, advantages and disadvantages of homogeneous and heterogeneous catalysts, classification of supported catalysts and emergence, advantages and application of polymer supported catalysts.

Chapter II includes the experimental details of modification of polymer support (i.e. styrene-divinylbenzene copolymer) with ligands salicylaldehyde-ethylenediamine (Salen) and ethylenediamine tetraacetic acid (EDTA) and introduction of Ru(III) and Pd(II) metal ions to synthesise polymer supported metal complex catalysts. Various physico-chemical properties such as bulk density, moisture content, swelling studies and surface area measurement for the supported catalysts have been studied. Use of modern techniques for characterization of catalysts i.e. IR, FTIR, UV-vis, SEM, ESR, ESCA and TGA have been described. Experimental procedure to study kinetics of hydrogenation and oxidation reactions have been discussed in detail.

Chapter III describes physico-chemical characterization of the polymer support and polymer-supported transition metal complex catalysts. An attempt has been made to understand the texture of the support and catalyst by measuring the BET surface area and pore volume The morphology of the support and catalysts have been observed by scanning electron microscope. The mode of anchoring of metal chelates on to the polymer support has been studied by elemental analyses, reflectance UV-vis, IR, FTIR, ESR and ESCA. Selection of proper solvent for studying catalytic reaction kinetics has been made on the basis of swelling studies using different solvents. Thermal stability of polymer support and catalysts has been investigated using thermogravimetric analysis. On the basis of the evidence available from characterization data, probable structures for the polymer supported metal complexes have been suggested

The kinetics of hydrogenation of 1-hexene as well as styrene catalysed by these metal complex catalysts is included in Chapter IV. The influence of various parameters such as concentration of substrate and catalysts, temperature of the system as well as nature of solvent used on the rate of reaction has been investigated. Experiments were carried out with metal complex catalysts in homogeneous medium and results have been compared with polymer supported catalysts. Energy of activation and entropy of activation have been evaluated using the kinetic data. Recycling efficiency of the catalysts has been studied to investigate the stability of the catalysts. On the basis of experimental evidences as well as literature survey, a probable reaction mechanism has been suggested

Chapter V describes kinetics of oxidation of benzyl alcohol to benzaldehyde using some of the synthesised catalysts. Influence of various factors such as concentration of substrate and catalysts, temperature of the system and nature of solvent used on the rate of reaction has been studied. The results are compared with metal complexes in homogeneous system. A probable reaction mechanism has also been proposed in case of the oxidation reaction. Recycling efficiency of the catalysts has also been studied to investigate stability of the catalysts. On the basis of the above results the following conclusions have been made.

Styrene-divinylbenzene copolymer offers the advantage of high purity catalyst support. It can be easily functionalized and physical properties, cross-linking as well as nature of the functional groups can be varied. Thermal stability of 2% and 8% cross-linked polymer was found upto ~140°C, however 14% cross-linked polymer was stable upto 350°C. Incorporation of the catalytically active component is possible by the treatment of solution of metal salt with functionalized polymer under suitable conditions. Chelation of the metal complexes on the polymer matrix is ensured by functionalising the macroporous beads using suitable functional group, by choosing a good swelling agent, incorporating efficient chelating ligands and allowing sufficient time for the complexation.

Characterization of the support as well as polymer supported catalysts is possible by utilizing the conventional techniques such as elemental analysis, moisture content, bulk density measurement and swelling studies. The mode of anchoring of metal complexes onto the polymer matrix is well understood by spectroscopic studies of polymer supports, functionalized polymer, polymer-bound catalysts and unbound metal complexes. The change in morphology of the support after complex formation is revealed by SEM. 14% cross-linked polymer-supported catalysts were found to be more thermally stable.

Polymer supported Ru(III) and Pd(II) complexes were found to be effective catalysts for hydrogenation of 1-hexene to n-hexane and styrene to ethylbenzene. An enhanced rate of hydrogenation was observed in the case of polymer-bound complexes as compared to unbound complexes probably due to the formation of an intermediate surface active hydrido complex. The order of reaction was found to be fractional with respect to the substrate as well as the catalyst concentration which might be due to non-accessibility of the catalytic sites and the steric hinderance due to the chelating ligand molecules. The values of energy of activation and entropy of activation have been calculated using kinetic data. The negative values of entropy of activation indicate considerable loss of freedom due to fixation of the catalyst molecules on the surface of the polymer.

Study was made using polar as well as non-polar solvents and an enhanced rate was observed as the nature of the solvent changes from non-polar to polar This may be due to higher swelling and therefore, availability of more catalytic sites in polar solvents Stability of the catalysts under repeated catalytic cycles was studied and most of the catalysts were found to be stable upto four cycles

Some of the synthesised catalysts were also tested to investigate the catalytic behaviour for the oxidation of benzyl alcohol to benzaldehyde by varying the parameters such as concentration of catalyst and substrate, temperature of the system and nature of the solvent used A higher activity was observed with polymer-supported catalysts compared to homogeneous analogue which might be due to formation of oxo and peroxo complexes on the surface of the support. The probable reaction mechanism was proposed on the basis of experimental evidences and literature survey for hydrogenation/oxidation

The study thus shows that better catalytic activity could be achieved by proper selection of polymer support, chelating ligand, swelling agent and the active component to synthesise heterogenized homogeneous catalysts for a given reaction with several advantages over their homogeneous counterparts. This was the primary objective of the thesis