# SUMMARY AND CONCLUSIONS

## Summary

The present investigation deals with the studies on the preparation, characterization and catalytic activity of polymer-supported metal complex catalysts. Catalytic activity has been investigated for two model reactions giving emphasis on the stability of metal chelates on the polymer matrix, role of polymer supports and comparison of catalytic activity of polymer bound and unbound metal chelates.

The thesis is summarised in four parts. Chapter-1 of the thesis includes a brief literature survey on supported metal complex catalysts, advantages and disadvantages of both heterogeneous and homogeneous catalysis, progress in the studies on immobilization of complexes for catalysis, classification of immobilized complex catalysts, general type of immobilization and supports for anchoring metal complexes.

Chapter-2 describes the experimental details of the synthesis of macroporous polymer supports and the catalysts. Experimental techniques/instruments used for the characterization of the catalysts are the chemical analysis, measurement of surface area by the use of BET apparatus, bulk density, moisture content,. swelling, UV-Vis, IR, X-ray, SEM, EPR, ESCA and TGA/DTA. It also deals with the experimental procedures used for the measurement of solubility of dyhydrogen in methanol,kinetics of hydrogenation of cyclohexene as well as nitrobenzene at atmospheric pressure and at various temperatures.

Physico-chemical characterization of the polymer support and ancho-

red metal complex catalysts form the subject matter of Chapter-3. Investigation has been made to understand the texture of the support and the catalyst by measuring the surface area, pore volume and morphology of the catalysts using scanning electron micrograph. The mode of anchoring of metal chelates have been arrived at by elemental analysis, UV-Vis, IR, far-IR, X-ray and in some cases by ESCA. Selection of the solvent for catalytic study has been made on the basis of swelling studies. Thermal stability of the polymer bound catalysts have been noted by comparative study of polymer support, polymer-bound catalysts and unbound catalysts. On the basis of physico-chemical properties and spectroscopic evidences, probable structures for the polymer anchored metal chelates have been proposed.

Chapter-4 includes the study of the kinetics of hydrogenation of cyclohexene and nitrobenzene catalysed by the catalysts synthesised here. The influence of the factors on the rate of hydrogenation, such as substrate and catalyst concentration, temperature of the system, hydrogen concentration in methanol and effect of different solvent has been seen. Investigation has also been made by the use of the metal complex catalyst in the homogeneous and the results have been compared with the heterogenised-homogeneous catalysts. On the basis of kinetic studies a probable reaction mechanism has been proposed.

**Conclusions :**

Poly(Styrene-DVB) offers the advantage of high purity catalyst supports which can be easily synthesised and functionalised. This polymer is thermally stable upto $\sim$ 150 °C. Controlled synthesis permits systematic variation of the physical form, cross-linking and the nature of the functional groups. Incorporation of catalytically active components is possible by the treatment of metal salt with functionalised polymer. Chelation of the metal complexes on the polymer matrix is ensured by synthesising the macroporous beads having macromolecular segments of higher mobility (i.e. cross-linked with 3-30% DVB), choosing a good swelling agent, incorporating efficient chelating ligands and allowing sufficient time for the complexation.

Characterisation of supports as well as the polymer-bound catalysts is possible by utilizing the conventional techniques such as elemental analysis, moisture content, bulk density, crushing strength and swelling studies. The mode of anchoring of metal complexes and type of coordination with the metal atom is understood by the detailed sprectroscopic studies of polymer supports, functionalised polymer supports, polymer-bound metal complexes and comparing them with the similar unbound metal complex. The change in the morphology of the supports after complexation is revealed by SEM and surface area measurements.

Following conclusion could be drawn from this study.

(1) Polymer-bound ruthenium catalysts (i.e. 3PRu(III)TMDA, 10PRu(III)TMDA, 30PRu(III)TMDA, 2.5ZKRu(III)TMDA and 20ZKRu(III)TMDA are noted to be good catalysts for the hydrogenation of cyclohexene and nitrobenzene reactions as compared to unbound complex catalyst (i.e. [RuTMDAC $L_2$]Cl).

(2) In case of cyclohexene hydrogenation the rate of the reaction is found to increase with an increase in the cross-linking of the polymer support. Similar results are found in the case of Zeo-Karb 226 when used as the support for Ru-TMDA catalyst. This is probably due to more disper-

sion of the catalyst on the surface. However, in the case of the hydrogenation of nitrobenzene the rate increases initially upto 10% cross-link of polymer and after that a decrease is observed, probably due to the steric hindrance of the larger molecules of nitrobenzene.

(3) Poly(Sty- DVB) supported ruthenium catalysts are more active catalysts for hydrogenation reactions than Zeo-Karb 226 -supported catalysts, and also poly(Sty-DVB) supports are thermally more stable than Zeo-Karb 226 supports. It shows that the nature of polymer support and swelling are important factors which contributes towards the activity of the catalyst.

(4) On the basis of the kinetic data a probable reaction mechanism is suggested. The rate followed a fractional order with respect to the catalyst concentration perhaps because of the non-accessibility of catalytic sites due to the lack of swelling and the steric hindrance of chelating ligand molecules. The formation of an intermediate complex (i.e. the hydrido complex) is proposed which is probably responsible for a higher catalytic activity.

(5) The successful catalysts showed considerable stability of the anchoring of metal chelates wherein they have been reused for hydrogenation of cyclohexene and nitrobenzene reactions.

The study shows that by proper selection of the polymer support, chelating ligand, swelling agent and the active component, it is possible to obtain heterogenised homogeneous catalysts for a given reaction which show considerable advantages over its homogeneous counterparts. This was the primary objective of the thesis.