SUMMARY AND CONCLUSIONS

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The present investigation deals with the studies on the preparation, characterization and catalytic activity of polymer anchored metal complex catalysts. The catalytic activity of the prepared catalysts has been investigated for two model reactions (viz., hydrogenation and oxidation) giving emphasis on the stability of the metal chelates on the polymer matrix and role of polymer support. Commercially available polymer beads were also used as support to synthesize catalysts and comparison of catalytic activity of polymer bound and unbound metal chelates has been made.

The thesis is summarized in five parts. Chapter - I contains a brief literature survey on homogeneous as well as supported metal complex catalysts, advantages and disadvantages of both homogeneous and heterogeneous catalysts, progress in the studies on immobilization of complexes for catalysis, general type of anchoring and supports for loading metal complexes and the classification of immobilized complex catalysts.

Chapter - II includes the experimental details of the synthesis of crosslinked macroporous polymer (i.e. styrene divinylbenzene), ligand introduction and the anchoring of the metal ions on the surface. The various physical properties such as bulk density, moisture content, swelling studies and surface area measurement for the anchored catalysts have been described. The modern techniques viz UV-Vis, IR, FTIR, NMR, SEM, EPR and ESCA have also been included in order to characterize the catalysts. The experimental procedures as well as the reactor employed for the kinetics of the hydrogenation as well as oxidation reactions have been discussed in detail.

Chapter - III describes physico-chemical characterization of the polymer support and anchored metal complex catalysts. A sincere attempt has been made to understand the texture of the support and catalyst by measuring the BET surface area, pore volume and morphology by scanning electron microscope. The mode of anchoring of metal chelates onto polymer support has been arrived at by elemental analysis, UV-Vis reflectance, IR, FTIR, and ESCA. EPR measurements are also described. Selection of a solvent for catalytic study has been made on the basis of swelling studies. The thermal stability of the polymer bound catalysts has been seen by the comparative study of polymer support, polymer bound catalysts and unbound catalysts. On the basis of available evidences, probable structures for the polymer anchored metal chelates have been proposed.

The kinetics of the hydrogenation of cyclohexene catalysed by these metal complex catalysts are included in chapter - IV. The influence of various factors such as substrate and catalyst concentration, temperature of the system, hydrogen concentration in methanol and the effect of different solvents on the reaction system has been investigated. Experiments were carried out with metal complex catalysts in homogeneous system and the results have been compared with heterogenised homogeneous system. On the basis of the kinetic studies a probable reaction mechanism has been proposed. Recycling efficiency of the catalysts is also included.

Chapter - V describes the kinetics of oxidation of cyclohexane by the use of the synthesised catalysts. The influence of factors such as substrate and catalyst concentration, temperature, amount of solvent and effect of different solvents on the kinetics of oxidation has been seen. The results are compared with metal complexes in homogeneous system. A probable reaction mechanism has been proposed.

Conclusions :

Styrene divinyl benzene copolymer offers the advantage of high purity catalyst supports which can be easily synthesized and funtionalized.

This polymer is thermally stable upto - 150°C. Controlled synthesis permits systematic variation of physical form, crosslinking and the nature of the functional groups. Incorporation of the catalytically active component is possible by the treatment of metal salt with functionalized 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. crosslinked with 5 - 15 % DVB), choosing a good swelling-agent, incorporating efficient chelating ligands and allowing sufficient time for the complexation.

Characterization of supports as well as the polymer bound catalysts is possible by utilizing the conventional techniques such as elemental analysis, moisture content determination, bulk density measurement and swelling studies The mode of anchoring of metal complexes onto the polymer matrix is well understood by the detailed spectroscopic studies of polymer supports, functionalized polymer supports, polymer bound metal complexes and comparing them with the similar unbound metal complex. The change in morphology of the support after complexation is revealed by SEM and surface area measurements.

Following conclusions could be drawn from this study :

1. Heterogenized homogeneous catalysts have higher activity than that of homogeneous counterparts. Polymer bound catalysts (i.e., 15PRu(III)DAP, 15PPd(II)DAP, 8XPd(II)DAP are noted to be good catalysts for hydrogenation of cyclohexene as well as for the oxidation of cyclohexane in comparison to unbound complex catalysts. i.e.$[RuDAPCl_2]Cl$ and $[PdDAP]Cl_2$.

2. Polymer bound catalysts are active for both hydrogenation as well as for oxidation reactions.

3. Polymer bound palladium complexes have shown better catalytic activity towards the hydrogenation of cyclohexene than the anchored ruthenium catalysts.

4. Palladium catalysts are found to be selective towards cyclohexanone in the oxidation reaction, whereas ruthenium catalysts give both cyclohexanol and cyclohexanone.

5. On the basis of catalytic activity, the synthesised supports are found to be better than that of commercially available supports. An enhanced catalytic activity is observed with an increase in crosslinking of the synthesized as well as commercially available polymers. This is propably due to more dispersion of the metal ions on the surface.

6. Better catalytic activity could be achieved using good swelling agent and with proper selection of the polymer support.

Thus, by proper selection of the polymer support, chelating ligand and swelling agent, a higher catalytic activity could be achieved while using polymer anchored metal complex catalysts. This was the primary objective of the thesis.