

SUMMARY AND CONCLUSION

The present investigation deals with the studies on the synthesis, characterization and catalytic activity of polymer supported transition metal complex catalysts. The catalytic activity of the synthesized catalysts has been investigated for oxidation of toluene 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 four parts Chapter-I contains a brief literature survey on homogeneous, heterogeneous and heterogenised homogeneous catalyst, advantages and disadvantages of homogeneous and heterogeneous catalysts, classification of supported catalysts and emergence, advantages and application of polymer supported catalysts.

Chapter-II includes experimental details of modification of polymer support (i.e. styrene-divinyl benzene co-polymer) with ligands o-phenylene diamine and ions to synthesise polymer supported metal complex catalysts. Various physico-chemical properties such as bulk density, moisture content, swelling and surface area for the supported catalysts have been studied. Use of modern techniques for characterization of catalysts i.e. IR : FTIR, UV-Vis, SEM, ESR and TGA have been described. Experimental procedure, to study kinetics of oxidation reactions have been discussed in details.

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. It was observed that the beads are porous and texture changes with the change in degree of cross-linking. A change in the shape of polymer beads has been

observed after anchoring the metal complexes. The mode of anchoring metal chelates on the polymer support has been studied by elemental analysis, reflectance UV-Vis., IR, FTIR and ESR spectroscopy.

Selection of proper solvent of 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. The 6% cross-linked polymer were found to be thermally stable upto $\sim 140^{\circ}\text{C}$ and 14% cross-linked polymer were found to be thermally stable upto $\sim 350^{\circ}\text{C}$. On the basis of the available characterization data, probable structures for the polymer supported metal complexes have been suggested.

The kinetics of oxidation of toluene is discussed in chapter-IV. The influence of various parameters such as concentration of substrate, temperature of the system, concentration of catalysts, as well as the nature of solvent used on the rate of reaction has been investigated. It was observed that as the temperature increases, the rate of reaction increases. The rate increases with the increase in the concentration of substrate and catalysts. The change in temperature was in the range of 30°C to 45°C . The change in substrate concentration was from 10umol to 40umol and the catalyst concentration was changed from 750 mg and 150 mg.

Experiments were carried out with metal complex catalysts in homogeneous medium and results have been compared with polymer supported catalysts. Both Energy of activation and entropy of activation have been evaluated using the kinetic data. The recycling efficiency of catalysts has been studied to investigate the stability of the catalysts. The catalysts were found to be active upto four cycle. After four cycles the activity decreases due to leaching of metal. On the basis of experimental evidences as well as literature survey, a probable reaction mechanism has been suggested.

Styrene-divinyl benzyne copolymer offers the advantage. It can be easily functionalized and physical properties, cross-linking as well as nature of the functional groups can be varied. The 6% and 8% cross-linked polymer was thermally stable up to $\sim 350^{\circ}\text{C}$. Incorporation of the catalytically active component is possible by the treatment of solution of metal salt with functionalized polymer under stable conditions. Chelation of the metal complexes on the polymer matrix is ensured by functionalizing the macroporous beads using suitable functional groups, 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 on to the polymer matrix is well understood by spectroscopic studies of polymer supports, functionalized polymer, polymer bound analysts and unbound metal complexes. The change in morphology of the support after complex formation is revealed by SEM.

The synthesized catalysts were tested to investigate the catalytic behavior for the oxidation of toluene to benzaldehyde by varying the parameters such as solvent used. By varying the concentration of catalyst, it was observed that higher catalytic activity was possible with the higher concentration of catalyst. In case of substrate concentration change, the higher the concentration of substrate, the better is the activity. Temperature plays a vital role to increase the activity of the catalyst. By increasing the temperature, the catalytic activity increases.

An interesting observation was that a higher activity was observed with polymer supported catalysts compared to the activity of the homogeneous analogue which might be due to the formation of oxo and peroxy complexes on the surface of the support.

The probable reaction mechanism was proposed on the basis of experimental evidences and literature survey for oxidation processes.

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