SOME STUDIES ON SYNTHESIS OF CATALYSTS AND THEIR APPLICATION IN ORGANIC SYNTHESIS

SUMMARY OF THE
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SUMMARY AND CONCLUSION

The present investigation deals with the studies on the synthesis of polymer anchored optically active α-amino acid metal complexes and their use as catalysts. The study describes the detailed synthesis, characterization and catalytic activity of polymer supported metal complexes in the epoxidation/oxidation of alkenes/alkanes, hydrogenation of alkenes, carbonyl & nitro compound, asymmetric epoxidation of olefins and asymmetric hydrogenation of acetophenone. The influence of various reaction parameters on conversion & selectivity has been studied. In addition, kinetics of high pressure hydrogenation of 1-octene has been discussed.

The thesis is divided in to four chapters:

Chapter I

In this chapter an introduction to catalysts and catalysis has been provided. A brief survey of supported catalysts, the advantages of polymer supported catalysts and the importance of asymmetric synthesis in chemical and pharmaceutical industries is outlined. Relevant literature on polystyrene supported catalysts and their applications is also highlighted.

Chapter II

The experimental details of the synthetic strategy employed for anchoring optically active α-amino acids to chloromethylated poly(styrene-divinyl benzene) resin and subsequent complexation with metal ions such as Mn(II), Cu(II), Ru(III) and Pd(II) to obtain the polymer supported catalysts are described in this chapter. The physico-chemical properties such as surface area, bulk density, pore volume 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) and Diffuse Reflectance Spectroscopy were employed. In addition, the stability of the supports and supported catalysts were studied by Thermo Gravimetric Analysis (TGA). The procedure involved in carrying out the epoxidation and hydrogenation reactions is described along with the details of the experimental set-up. Oxidation and hydrogenation reactions were monitored by Gas Chromatography and a few representative chromatograms displayed.

Chapter III

The *first* part of the results and discussions on the characterization and catalytic activity of polymer supported metal complexes of Mn(II), Ru(III) and Cu(II) is provided in this chapter.

First section deals with the results of poly(styrene-divinylbenzene) supported Manganese (II) amino acid complexes. From the observed data it was inferred that the Mn(II) immobilized on amino acid liganded poly(styrene-divinylbenzene)resin are able to catalyze the epoxidation of styrene, norbornylene, *cis*-cyclooctene and cyclohexene in the presence of alkyl hydroperoxide (TBHP) as oxidant. Kinetic experiments reveal that temperature influences the catalytic activity significantly.

In the second section the results of Ruthenium(III) anchored to amino acid liganded poly(styrene-divinylbenzene) supports are discussed. These complexes catalyze the epoxidation of styrene, norbornylene, *cis*-cyclooctene , cyclohexene as well as the the oxidation of toluene & cyclohexane in presence of alkyl hydroperoxide under mild conditions. The catalysts could be used in multiple cycles.

The third section deals with the results of poly(styrene-divinylbenzene) supported Copper (II) amino acid complexes. The results indicate that polymer supported Cu(II) complex shows excellent selectivity with good activity for oxidation of benzyl alcohol and cyclohexanol in presence of TBHP under mild condition. Kinetic experiments reveal that temperature influences the catalytic activity significantly. The recycling efficiency of the supported catalysts has been discussed.

In the fourth section the mechanistic aspects of epoxidation/oxidation are described for all the three types of polymer supported metal complexes. Generally the existence of a dual mechanistic pathway has been observed . Interestingly in case of supported Mn(II) catalysts, *free radical* pathway is the major one where as in case of polymer supported Ru(III) & Cu(II) catalysts, the possibility of involvement of *high valent metal oxo species* has been be proposed based on experimental data.

The fifth section deals with the results of asymmetric epoxidation of unfunctionalized straight chain olefins like 1-octene, 1-hexene etc. using Mn, Cu and Ru supported catalysts in presence of *m*-chloro perbenzoic acid as the terminal oxidant. Excellent conversion and good enantioselectivity were observed for Mn and Cu catalysts, whereas they were slightly lower in case of Ru catalysts. Mechanistic aspect of the asymmetric epoxidation has been briefly discussed.

Chapter IV

The *second* part of the results and discussions on the characterization and catalytic activity of polymer supported metal complexes of Pd(II) is provided in this chapter.

It was shown in the first section that all the Pd-catalysts affect the hydrogenation of 1-octene, cyclohexene, nitro benzene and acetophenone in the presence of high pressure hydrogen. Experimental data suggest that the reaction is sensitive to both temperature and pressure. Supported Pd catalysts show excellent recycling efficiency.

In the second section the mechanistic aspects of hydrogenation reaction are described. A simplified mechanistic pathway of hydrogenation by polymer supported Pd complex has been discussed.

In the third section the catalytic asymmetric hydrogenation of *pro* chiral substrate like acetophenone has been described . In this case too good conversions were observed, though the optical yields were moderate..

On the basis of the above studies, the following conclusions can be drawn :

1. Manganese, Copper & Ruthenium anchored to optically active amino acid bound styrene-divinylbenzene copolymer catalyze the epoxidation/oxidation of alkenes/alkanes in presence of alkylhydroperoxide under mild conditions. The Pd analogues catalyze the reduction of alkenes, ketones and nitro compounds under high pressure of hydrogen.

2. Mn, Cu & Ru catalysts induce enantioselectivity in the asymmetric epoxidation of unfunctionalized straight chain olefins and the Pd catalysts induce enantioselectivity in the asymmetric reduction of acetophenone.

3. All the catalysts could be recycled without any loss in selectivity with the Pd catalysts exhibiting excellent recycling efficiency. Slow deactivation of the catalysts was observed over extended reuse.

4. Apart from the reaction conditions, the nature of amino acid and the stability of its metal complex on the surface of polymer support influence the formation of active species responsible for product selectivity in oxidation and hydrogenation reactions.